Biological Thermodynamics

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Chapter 1

Energy transformation

A. Introduction

Beginning perhaps with Anaximenes of Miletus (fl. *c.* 2550 years before present), various ancient Greeks portrayed man as a microcosm of the universe. Each human being was made up of the same elements as the rest of the cosmos – earth, air, fire and water. Twenty-six centuries later, and several hundred years after the dawn of modern science, it is somewhat humbling to realize that our view of ourselves is fundamentally unchanged.

Our knowledge of the matter of which we are made, however, has become much more sophisticated. We now know that all living organisms are composed of hydrogen, the lightest element, and of heavier elements like carbon, nitrogen, oxygen, and phosphorus. Hydrogen was the first element to be formed after the Big Bang. Once the universe had cooled enough, hydrogen condensed to form stars. Then, still billions[1] of years ago, the heavier atoms were synthesized in the interiors of stars by nuclear fusion reactions. We are 'made of stardust,' to quote Allan Sandage (b. 1926), an American astronomer.

Our starry origin does not end there. For the Sun is the primary source of the energy used by organisms to satisfy the requirements of life (Fig. 1.1). (Recent discoveries have revealed exceptions to this generalization: see Chapter 9.) Some organisms acquire this energy (Greek, *en*, in + *ergon*, work) directly; most others, including humans, obtain it indirectly. Even the chemosynthetic bacteria that flourish a mile and a half beneath the surface of the sea require the energy of the Sun for life. They depend on plants and photosynthesis to produce oxygen needed for respiration, and they need the water of the sea to be in the liquid state in order for the plant-made oxygen to reach them by convection and diffusion. This is not necessarily true of bacteria *everywhere*. The recent discovery of blue-green algae beneath ice of frozen lakes in Antarctica has indicated that bacteria *can* thrive in such an environment. Blue-green algae, also known as cyanobacteria, are the most ancient photosynthetic, oxygen-producing organisms known. In order to thrive, however,

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[1] 1 billion = 10^9.

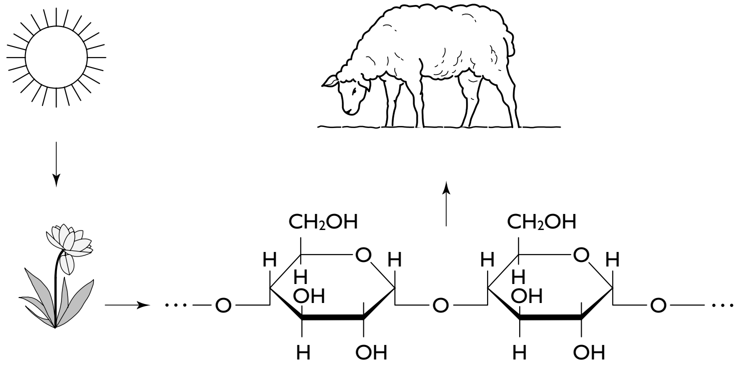

Fig. 1.1 A diagram of how mammals capture energy. The Sun generates radiant energy from nuclear fusion reactions. Only a tiny fraction of this energy actually reaches us, as we inhabit a relatively small planet and are far from the Sun. The energy that does reach us – *c.* 5×10^{18} MJ yr^{-1} (1.7×10^{17} J s^{-1}) – is captured by plants and photosynthetic bacteria, as well as the ocean. (J = joule. This unit of energy is named after British physicist James Prescott Joule (1818–1889)). The approximate intensity of direct sunlight at sea level is 5.4 J cm^{-2} min^{-1}. This energy input to the ocean plays an important role in determining its predominant phase (liquid and gas, not solid), while the energy captured by the photosynthetic organisms (only about 0.025% of the total; see Fig. 1.2) is used to convert carbon dioxide and water to glucose and oxygen. It is likely that all the oxygen in our atmosphere was generated by photosynthetic organisms. Glucose monomers are joined together in plants in a variety of polymers, including starch (shown), the plant analog of glycogen, and cellulose (not shown), the most abundant organic compound on Earth and the repository of over half of all the carbon in the biosphere. Animals, including grass eaters like sheep, do not metabolize cellulose, but they are able to utilize other plant-produced molecules. Although abstention from meat (muscle) has increased in popularity over the past few decades, in most cultures humans consume a wide variety of animal species. Muscle tissue is the primary site of conversion from chemical energy to mechanical energy in the animal world. There is a continual flow of energy and matter between microorganisms (not shown), plants (shown), and animals (shown) and their environment. The sum total of the organisms and the physical environment participating in these energy transformations is known as an **ecosystem**.

polar bacteria must be close to the surface of the ice and near dark, heat absorbing particles. Solar heating during summer months liquifies the ice in the immediate vicinity of the particles, so that liquid water, necessary to life as we know it, is present. During the winter months, when all the water is frozen, the bacteria are 'dormant.' **Irrespective of form, complexity, time or place, all known organisms are alike in that they must capture, transduce, store and use energy in order to live.** This is a profound statement, not least because **the concept of energy is the most basic one of all of science and engineering**.

How does human life in particular depend on the energy output of the Sun? Green plants flourish only where they have access to light. Considering how green our planet is, it is amazing that much less than 1% of the Sun's energy that penetrates the protective ozone layer, water vapor and carbon dioxide of the atmosphere, is actually absorbed by plants (Fig. 1.2). The chlorophyll and other pigment molecules of plants act as antennas that enable them to absorb photons of a relatively limited range of energies (Fig. 1.3). On a more detailed level, a pigment molecule, made of atomic nuclei and electrons, has a certain electronic *bound* state that can interact with a photon (a *free* particle) in the visible range of the electromagnetic spectrum (Fig. 1.4). When a photon is absorbed, the bound electron makes a transition to a higher energy but less stable 'excited' state. Energy captured in this way is then transformed by a very complex chain of events (Chapter 5). The mathematical relationship between wavelength of light, λ, photon frequency, ν, and photon energy, E, is

$$E = hc/\lambda = h\nu \tag{1.1}$$

where h is Planck's constant[2] (6.63×10^{-34} J s) and c is the speed of light *in vacuo* (2.998×10^{8} m s^{-1}). Both h and c are fundamental constants of nature. Plants combine trapped energy from sunlight with carbon dioxide and water to give $C_6H_{12}O_6$ (glucose), oxygen and heat. In this way solar energy is turned into chemical energy and stored in the form of chemical bonds, for instance the $\beta(1 \rightarrow 4)$ glycosidic bonds between the glucose monomers of cellulose and the chemical bonds of glucose itself (Fig. 1.1).

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[2] Named after the German physicist Max Karl Ernst Ludwig Planck (1858–1947). Planck was awarded the Nobel Prize in Physics in 1918.

Animals feed on plants, using the energy of digested and metabolized plant material to manufacture the biological macromolecules they need to maintain existing cells, the morphological units on which life is based, or to make new ones. The protein hemoglobin, which is found in red blood cells, plays a key role in this process in humans, transporting oxygen from the lungs to cells throughout the body and carbon dioxide from the cells to the lungs. Animals also use the energy of digested foodstuffs for locomotion, maintaining body heat, generating light (e.g. fireflies), fighting off infection by microbial organisms, growth, and reproduction (Fig. 1.5). These biological processes involve a huge number of exquisitely specific biochemical reactions, each of which requires energy in order to proceed.

To summarize in somewhat different terms. The excited electrons of photosynthetic reaction centers are reductants. The electrons are transferred to carbon dioxide and water, permitting (*via* a long chain of events) the synthesis of organic molecules like glucose and cellulose. The energy of organic molecules is released in animals in a series of reactions in which glucose, fats, and other organic compounds are oxidized (burned) to carbon dioxide and water (the starting materials) and heat. This chain of events is generally 'thermodynamically favorable' because we live in a highly oxidizing environment: 23% of our atmosphere is oxygen. Don't worry if talk of oxidation and reduction seems a bit mystifying at this stage: we shall return to it treat it in due depth in Chapter 4.

Two of the several **requirements for life** as we know it can be inferred from these energy transformations: ***mechanisms* to control *energy* flow**, for example the membrane-bound protein 'machines' involved in photosynthesis; and ***mechanisms* for the storage and transmission of biological *information***, namely polyribonucleic acids. The essential role of *mechanisms* in life processes implies that ***order* is a basic characteristic of living organisms**. A most remarkable and puzzling aspect of life is that the structures of the protein enzymes that regulate the flow of energy and information in a cell are encoded by nucleic acid within the cell. We can also see from the preceding discussion that energy flow in nature resembles the movement of currency in an

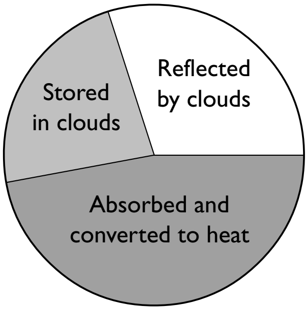


Fig. 1.2 Pie plot showing the destiny of the Sun's energy that reaches Earth. About one-fourth is reflected by clouds, another one-fourth is absorbed by clouds, and about half is absorbed and converted into heat. Only a very small amount ($\ll$1%) is fixed by photosynthesis (not shown).

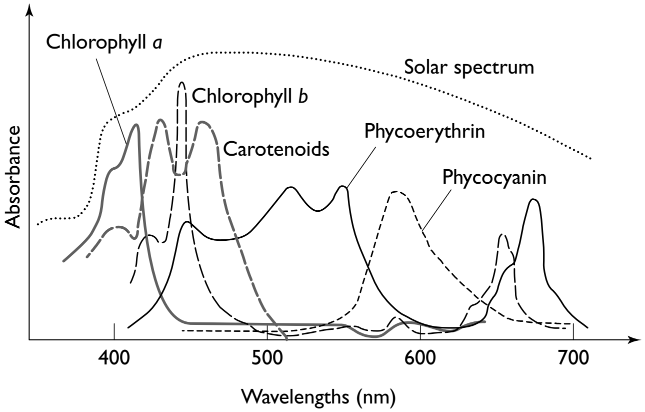


Fig. 1.3 Absorption spectra of various photosynthetic pigments. The chlorophylls absorb most strongly in the red and blue regions of the spectrum. Chlorophyll *a* is found in all photosynthetic organisms; chlorophyll *b* is produced in vascular plants. Plants and photosynthetic bacteria contain carotenoids, which absorb light at different wavelengths from the chlorophylls. The relationship between photon wavelength and energy is given by Eqn. 1.1 and illustrated in Fig. 1.4.

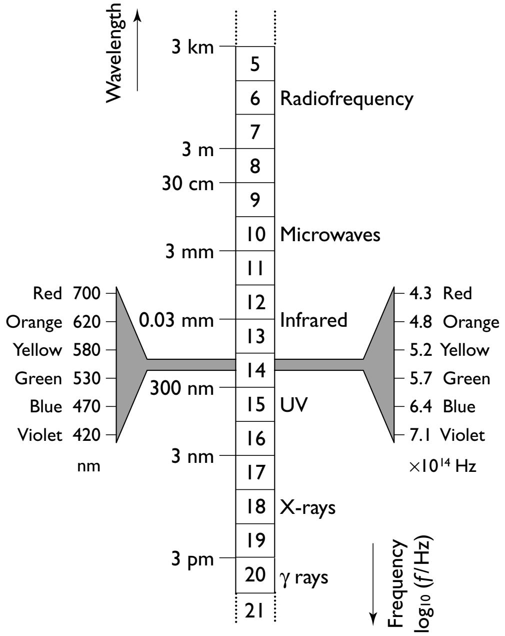


Fig. 1.4 The electromagnetic spectrum. The visible region, the range of the spectrum to which the unaided human eye is sensitive, is expanded. As photon wavelength increases (or frequency decreases), energy decreases. The precise relationship between photon energy and wavelength is given by Eqn. 1.1. Photon frequency is shown on a $\log_{10}$ scale. Redrawn from Fig. 2.15 in Lawrence *et al.* (1996).

economy: energy 'changes hands' (moves from the Sun to plants to animals . . .) and is 'converted into different kinds of currency' (stored as chemical energy, electrical energy, etc.).

A deeper sense of the nature of energy flow in biology can be gained from a bird's-eye view of the biochemical roles of adenosine triphosphate (ATP), a small organic compound. This molecule is synthesized from photonic energy in plants and chemical energy in animals. The mechanisms involved in this energy conversion are very complicated, and there is no need to discuss them in detail until Chapter 5. The important point here is that, once it has been synthesized, **ATP plays the role of the main energy 'currency' of biochemical processes in all known organisms**. For instance, ATP is a component of great importance in chemical communication between and within cells, and it is the source of a building block of deoxyribonucleic acid (DNA), the molecules of storage and transmission of genetic information from bacteria to humans (Fig. 1.6). We can see from

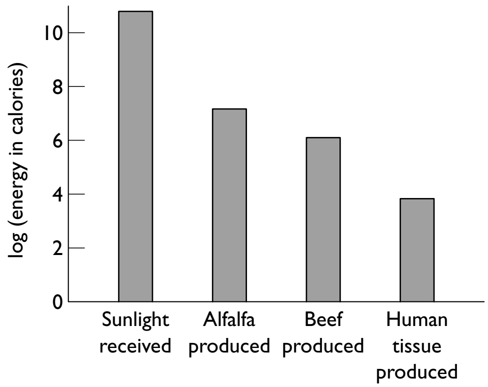


Fig. 1.5 Log plot of energy transformation on Earth. Only a small amount of the Sun's light that reaches Earth is used to make cereal. Only a fraction of this energy is transformed into livestock tissue. And only part of this energy is transformed into human tissue. (What happens to the rest of the energy?) A calorie is a unit of energy that one often encounters in older textbooks and scientific articles and in food science. A calorie is the heat required to increase the temperature of 1 g of pure water from 14.5 °C to 15.5 °C. 1 calorie = 1 cal = 4.184 J *exactly*. Based on Fig. 1-2 of Peusner (1974).

this that ATP is of very basic and central importance to life as we know it, and we shall have a good deal to say about it throughout the book.

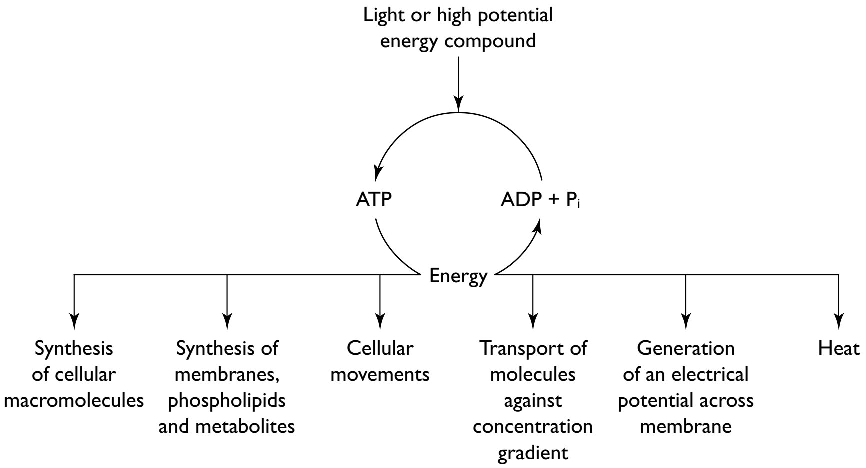
Let's return to the money analogy and develop it further. Just as there is neither an increase nor a decrease in the money supply when money changes hands: so in the course of its being transformed, energy is neither created nor destroyed. **The total energy is *always* constant**. As we shall see in the next chapter, this is a statement of the First Law of Thermodynamics. However, unlike the money analogy, energy transformations certainly can and do indeed affect the relative proportion of energy that is available in a form that is useful to living organisms. This situation arises not from defects inherent in the biomolecules involved in energy transformation, but from the structure of our universe itself. We shall cover this aspect of energy transformation in Chapter 3.

Thus far we have been talking about energy as though we knew what it was. After all, each of us has at least a vague sense of what energy transformation involves. For instance, we know that it takes energy to heat a house in winter (natural gas or combustion of wood); we know that energy is required to cool a refrigerator (electricity); we know that energy is used to start an automobile engine (electrochemistry) and to keep it running (gasoline). But we still have not given a precise definition of *energy*. What *is* energy? **Being able to say what energy is with regard to living organisms is what this book is about**.

B. Distribution of energy

Above we said that throughout its transformations energy is conserved. The idea that something can change and remain the same may seem strange, but we should be careful not to think that the idea is therefore untrue. We should be open to the possibility that some aspects of physical reality might differ from our day-to-day macroscopic experience of the world. In the present context, the something that stays the same is a quantity called the total **energy**, and the something that changes is

Fig. 1.6 ATP fuels an amazing variety of cellular processes. In the so-called ATP cycle, ATP is formed from adenosine diphosphate (ADP) and inorganic phosphate (P_i) by photosynthesis in plants and by metabolism of 'energy rich' compounds in most cells. Hydrolysis of ATP to ADP and P_i releases energy that is trapped as usable energy. This form of energy expenditure is integral to many key cellular functions and is a central theme of biochemistry. Redrawn from Fig. 2-23 of Lodish *et al.* (1995).



how that energy is *distributed* – where it is found and in which form and at which time. A crude analog of this would be a wad of chewing gum. Neglecting the change in flavor with time, the way in which the gum molecules are distributed in space depends, first of all, on whether the gum is in your mouth or still in the wrapper! Once you've begun to work your jaw and tongue, the gum changes shape a bit at a time, though it can change quite dramatically when you blow a bubble. Regardless of shape and the presence or absence of bubbles, however, the *total amount* of gum is *constant*. But one should not infer from this that energy is a material particle.

Elaboration of the money–energy analogy will help to illustrate several other important points. Consider the way a distrustful owner of a busy store might check on the honesty of a certain cashier. The owner knows that m_b dollars were in the till at the beginning of the day, and, from the cash register tape, that m_e dollars should be in the till at the end of trading. So, of course, the owner knows that the net change of money must be $m_e - m_b = \Delta m$, where 'Δ,' the upper case Greek letter *delta*, means 'difference.' This, however, says nothing at all about the way the cash is distributed. Some might be in rolls of coins, some loose in the till, and some in the form of dollar bills of different denomination. (*bill* = *banknote*.) Nevertheless, when all the accounting is done, the pennies, nickels, dimes and so on should add up to Δm, if the clerk is careful and honest. A simple formula can be used to do the accounting:

$$\Delta m = \$0.01 \times (\text{number of pennies}) + \$0.05 \times (\text{number of nickels}) + \ldots + \$10.00 \times (\text{number of ten dollar bills}) + \$20.00 \times (\text{number of twenty dollar bills}) + \ldots \tag{1.2}$$

This formula can be modified to include terms corresponding to coins in rolls:

$$\Delta m = \$0.01 \times (\text{number of pennies}) + \$0.50 \times (\text{number of rolls of pennies}) + \$0.05 \times (\text{number of nickels}) + \$2.00 \times (\text{number of rolls of nickels}) + \ldots + \$10.00 \times (\text{number of ten dollar bills}) + \$20.00 \times (\text{number of twenty dollar bills}) + \ldots \tag{1.3}$$

A time-saving approach to counting coins would be to weigh them. The formula might then look like this:

$$\Delta m = \$0.01 \times (\text{weight of unrolled pennies})/(\text{weight of one penny}) + \$0.50 \times (\text{number of rolls of pennies}) + \$0.05 \times (\text{weight of unrolled nickels})/(\text{weight of one nickel}) + \$2.00 \times (\text{number of rolls of nickels}) + \ldots + 10.00 \times (\text{number of ten dollar bills}) + 20.00 \times (\text{number of twenty dollar bills}) + \ldots \tag{1.4}$$

There are several points we can make by means of the money analogy. One, the number of each type of coin and bill is but one possible distribution of Δm dollars. A different distribution would be found if a wiseacre paid for a \$21.95 item with a box full of unrolled nickels instead of a twenty and two ones (Fig. 1.7)! One might even consider measuring the distribution of the Δm dollars in terms of the proportion in pennies, nickles, dimes, and so on. We shall find out more about this in Chapter

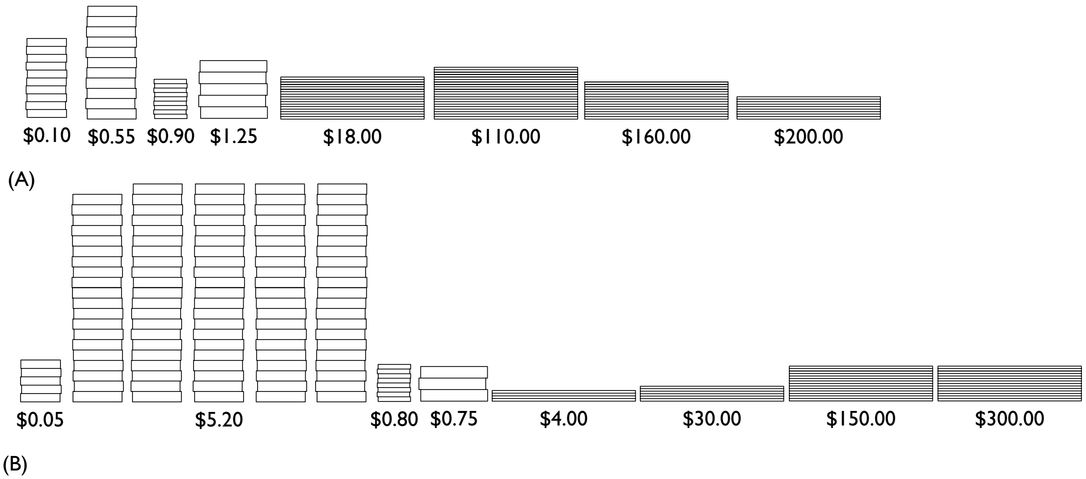


Fig. 1.7 Two different distributions of the same amount of money. The columns from left to right are: pennies ($0.01), nickels ($0.05), dimes ($0.10), quarters ($0.25), one dollar bills ($1.00), five dollar bills ($5.00), ten dollar bills ($10.00) and twenty dollar bills ($20.00). Panel (A) differs from panel (B) in that the latter distribution involves a relatively large number of nickels. Both distributions correspond to the same total amount of money. The world's most valuable commodity, oil, is the key energy source for the form of information flow known as domestic and international travel.

3. Two, given a distribution of Δm dollars into so many pennies, nickles, dimes, and so forth, there are many different ways of arranging the coins and bills. For example, there are many different possible orderings of the fifty pennies in a roll. The complexity of the situation would increase even further if we counted coins of the same type but different date as 'distinguishable' and ones of the same type and same date as 'indistinguishable.' Three, the more we remove ourselves from counting and examining individual coins, the more abstract and theoretical our formula becomes. (As Aristotle[3] recognized, the basic nature of scientific study is to proceed from observations to theories; theories are then used to explain observations and make predictions about what has not yet been observed. Theories can be more or less abstract, depending on how much they have been developed and how well they work.) And four, although measurement of an abstract quantity like Δm might not be very hard (the manager could just rely on the tape if the clerk were known to be perfectly honest and careful), determination of the contribution of each relevant component to the total energy could be a time-consuming and difficult business – if not impossible, given current technology and definitions of thermodynamic quantities. We shall have more to say about this in Chapter 2.

So, how does the money simile illustrate the nature of the physical world? **A given quantity of energy can be distributed in a multitude of ways**. Some of the different forms it might take are chemical energy, elastic energy, electrical energy, gravitational energy, heat energy, mass energy, nuclear energy, radiant energy, and the energy of intermolecular interactions. But **no matter what the form, the total amount of energy is constant.** All of the mentioned forms of energy are of interest to the biological scientist, though some clearly are more important to

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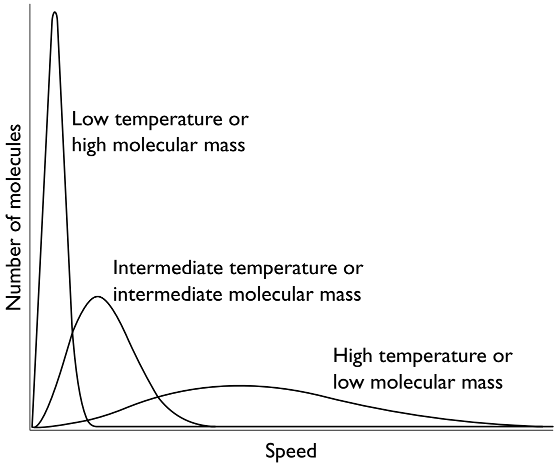
[3] Aristotle (384–322 BC) was born in northern Greece. He was Plato's most famous student at the Academy in Athens. Aristotle established the Peripatetic School in the Lyceum at Athens, where he lectured on logic, epistemology, physics, biology, ethics, politics, and aesthetics. According to Aristotle, minerals, plants and animals are three distinct categories of being. He was the first philosopher of science.

Fig. 1.8 The Maxwell distribution of molecular speeds. The distribution depends on particle mass and temperature. The distribution becomes broader as the speed at which the peak occurs increases. Low, intermediate, and high temperatures correspond to the solid, liquid, and gaseous states, respectively. James Clerk Maxwell, a Scot, lived 1831–1879. He is regarded as the nineteenth-century scientist who had the greatest influence on twentieth-century physics and is ranked with Isaac Newton and Albert Einstein for the fundamental nature of his contributions. He did important work in thermodynamics and the kinetic theory of gases. Based on Fig. 0.8 of Atkins (1998).



us than others; some are relevant only in somewhat specialized situations. The terms denoting the different types of energy will be defined below as we go along. In living organisms the main repositories of energy are macromolecules, which store energy in the form of covalent and non-covalent chemical bonds, and unequal concentrations of solutes, principally ions, on opposite sides of a cell membrane. In Fig. 1.3 we can see another type of energy distribution, the solar spectrum. For a given amount of solar energy that actually reaches the surface of our planet, more of the photons have a wavelength of 500 nm than 250 or 750 nm. According to the kinetic theory of gases, a subject we shall discuss at several points in this book, the speeds of gas molecules are distributed in a certain way, with some speeds being much more common than others (Fig. 1.8). In general, slow speeds and high speeds are rare, near-average speeds are common, and the average speed is directly related to the temperature. A summary of the chief forms of energy of interest to biological scientists is given in Table 1.1.

C. System, boundary, and surroundings

Before getting too far underway, we need to define some important terms. This is perhaps done most easily by way of example. Consider a biochemical reaction that is carried out in aqueous solution in a test tube (Fig. 1.9A). The **system** consists of the solvent, water, and all chemicals dissolved in it, including buffer salts, enzyme molecules, the substrate recognized by the enzyme and the product of the enzymatic reaction. The system is that part of the universe chosen for study. The **surroundings** are simply the entire universe excluding the system. The system and surroundings are separated by a **boundary**, in this case the test tube.

At any time, the system is in a given thermodynamic **state** or condition of existence (which types of molecule are present and the amount of each, the temperature, the pressure, etc.). The system is said to be closed if it can exchange *heat* with the surroundings but not *matter*. That is, the boundary of a **closed system** is *impermeable* to matter. A dialysis bag that is permeable

Table 1.1 Energy distribution in cells. Contributions to the total energy can be categorized in two ways: kinetic energy and potential energy. Each category can be subdivided in several ways

Kinetic energy (motion)	Potential energy (position)
Heat or thermal energy – energy of molecular motion in organisms. At 25 °C this is about 0.5 kcal mol^{-1}.	*Bond energy* – energy of covalent and non-covalent bonds, for example a σ bond between two carbon atoms or van der Waals interactions. These interactions range in energy from as much as 14 kcal mol^{-1} for ion–ion interactions to as little as 0.01 kcal mol^{-1} for dispersion interactions; they can also be negative, as in the case of ion–dipole interactions and dipole–dipole interactions.
Radiant energy – energy of photons, for example in photosynthesis. The energy of such photons is about 40 kJ mol^{-1}.	*Chemical energy* – energy of a difference in concentration across a permeable barrier, for instance the lipid bilayer membrane surrounding a cell of a substance which can pass through the membrane. The magnitude of this energy depends on the difference in concentration across the membrane. The greater the difference, the greater the energy.
Electrical energy – energy of moving charged particles, for instance electrons in reactions involving electron transfer. The magnitude of this energy depends on how quickly the charged particle is moving. The higher the speed, the greater the energy.	*Electrical energy* – energy of charge separation, for example the electric field across the two lipid bilayer membranes surrounding a mitochondrion. The electrical work required to transfer monovalent ions from one side of a membrane to the other is about 20 kJ mol^{-1}.

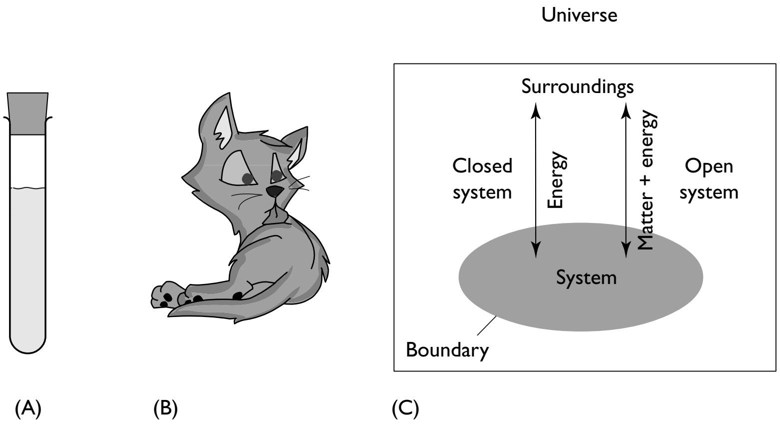


Fig. 1.9 Different types of system. (A) A closed system. The stopper inhibits evaporation of the solvent, so essentially no matter is exchanged between the test tube and its surroundings (the air surrounding the test tube). Energy, however, can be exchanged with the surroundings, through the glass. (B) An open system. All living organisms are open systems. A cat is a particularly complex open system. A simplified view of a cat as a system is given in Fig. 1.10. (C) A schematic diagram of a system.

to small molecules but not to large ones is not a closed system! As long as no matter is added to the test tube in Fig. 1.9A during the period of observation, and as long as evaporation of the solvent does not contribute significantly to any effects we might observe, the system can be considered closed. This is true even if the biochemical reaction we are studying results in the release or absorption of heat energy; as we have said, energy transfer between system and surroundings is possible in a closed system. Another example of a closed system is Earth itself: our planet continually receives radiant energy from the Sun and continually gives off heat, but because Earth is neither very heavy nor very light it exchanges practically no matter with its surroundings (Earth is not so massive that its gravitational field pulls nearby bodies like the Moon into itself, as a black hole would do, but there is enough of a gravitational pull on air to prevent it going off into space, which is why asteroids have no atmosphere).

If matter can be exchanged between system and surroundings, the system is open. An example of an **open system** is a cat (Fig. 1.9B). It breathes in and exhales matter (air) continually, and it eats, drinks, defecates and urinates periodically. In barely-sufferable technospeak, a cat is an open, self-regulating and self-reproducing heterogeneous system. The system takes in food from the environment and uses it to maintain body temperature, power all the biochemical pathways of its body, including those of its reproductive organs, and to run, jump and play. The system requires nothing more for reproduction than a suitable feline of the opposite sex. And the molecular composition of the brain of the system is certainly very different from that of its bone marrow. In the course of all the material changes of this open system, heat energy is exchanged between it and the surroundings, the amount depending on the system's size and the difference in temperature between its body and its environment. A schematic diagram of a cat is shown in Fig. 1.10. **Without exception, all living organisms that have ever existed are open systems**.

Finally, in an **isolated system**, the boundary permits neither matter nor energy to enter or exit. A schematic diagram of a system, surroundings and boundary are shown in Fig. 1.9C.

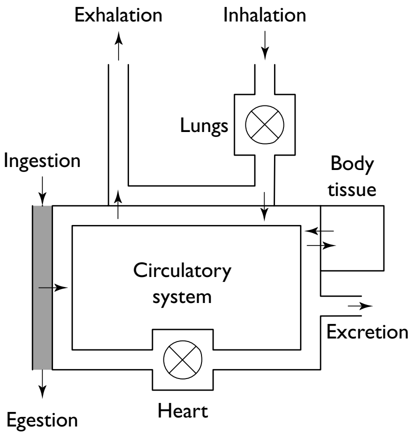


Fig. 1.10 The 'plumbing' of a higher animal. Once inside the body, energy gets moved around a lot (arrows). Following digestion, solid food particles are absorbed into the circulatory system (liquid), which delivers the particles to all cells of the body. The respiratory system enables an organism to acquire the oxygen gas it needs to burn the fuel it obtains from food. If the energy input is higher than the output (excretion + heat), there is a net increase in body weight. In humans, the ideal time rate of change of body weight, and therefore food intake and exercise, varies with age and physical condition. Based on Fig. 1–5 of Peusner (1974).

D. Animal energy consumption

Now let's turn briefly to a more in-depth view of the relationship between food, energy, and life than we have seen so far. We wish to form a clear idea of how the energy requirements of carrying out various activities, for instance walking or sitting, relate to the energy available from the food we eat. The comparison will be largely qualitative. The discussion will involve the concept of heat, and a formal definition of the term will be given.

Energy measurements can be made using a calorimeter. Calorimetry has made a huge contribution to our understanding of the energetics of chemical reactions, and there is a long tradition of using calorimeters in biological research. In the mid-seventeenth century, pioneering experiments by Robert Boyle (1627–1691) in Oxford demonstrated the necessary role of air in combustion and respiration. About 120 years later, in 1780, Antoine Laurent Lavoisier (1743–1794) and Pierre Simon de Laplace (1749–1827) extended this work by using a calorimeter to measure the *heat* given off by a live guinea pig. On comparing this heat with the amount of oxygen consumed, the Frenchmen correctly concluded that respiration is a form of combustion. Nowadays, a so-called bomb calorimeter (Fig. 1.11) is used to measure the heat given off in the oxidation of a combustible substance like food, and nutritionists refer to tables of combustion heats in planning a diet. There are many different kinds of calorimeter. For instance, the instrument used to measure the energy given off in an atom smasher is called a calorimeter. In this book we discuss three of them: bomb calorimeter, isothermal titration calorimeter and differential scanning calorimeter.

Thermodynamics is the study of energy transformations. It is a hierarchical science. This means that the more advanced concepts assume knowledge of the basics. To be ready to tackle the more difficult but more interesting topics in later chapters, we had better take time to develop a good understanding of *what* is being measured in a

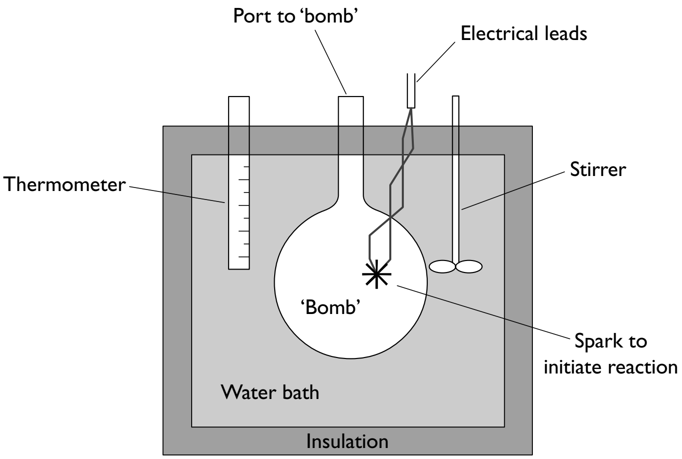


Fig. 1.11 Schematic diagram of a bomb calorimeter. A sample is placed in the reaction chamber. The chamber is then filled with oxygen at high pressure ($>$20 atm) to ensure that the reaction is fast and complete. Electrical heating of a wire initiates the reaction. The increase in the temperature of the water is recorded, and the temperature change is converted into an energy increase. The energy change is divided by the total amount of substance oxidized, giving units of $\mathrm{J\,g^{-1}}$ or $\mathrm{J\,mol^{-1}}$. Insulation helps to prevent the escape of the heat of combustion. Based on diagram on p. 36 of Lawrence *et al.* (1996).

Table 1.2 Heat released upon oxidation to CO_2 and H_2O

	Energy yield			
Substance	kJ (mol^{-1})	kJ (g^{-1})	kcal (g^{-1})	kcal (g^{-1} wet wt)
Glucose	2817	15.6	3.7	—
Lactate	1364	15.2	3.6	—
Palmitic acid	10040	39.2	9.4	—
Glycine	979	13.1	3.1	—
Carbohydrate	—	16	3.8	1.5
Fat	—	37	8.8	8.8
Protein	—	23	5.5	1.5
Protein to urea	—	19	4.6	—
Ethyl alcohol	—	29	6.9	—
Lignin	—	26	6.2	—
Coal	—	28	6.7	—
Oil	—	48	11	—

Note:
D-glucose is the principal source of energy for most cells in higher organisms. It is converted to lactate in anaerobic homolactic fermentation (e.g. in muscle), to ethyl alcohol in anaerobic alcoholic fermentation (e.g. in yeast), and to carbon dioxide and water in aerobic oxidation. Palmitic acid is a fatty acid. Glycine, a constituent of protein, is the smallest amino acid. Carbohydrate, fat and protein are different types of biological macromolecule and sources of energy in food. Metabolism in animals leaves a residue of nitrogenous excretory products, including urea in urine and methane produced in the gastrointestinal tract. Ethyl alcohol is a major component of alcoholic beverages. Lignin is a plasticlike phenolic polymer that is found in the cell walls of plants; it is not metabolized directly by higher eukaryotes. Coal and oil are fossil fuels that are produced from decaying organic matter, primarily plants, on a timescale of millions of years. The data are from Table 2.1 of Wrigglesworth (1997) or Table 3.1 of Burton (1998). See also Table A in Appendix C.

bomb calorimeter. We know from experience that the oxidation (burning) of wood gives off *heat*. Some types of wood are useful for building fires because they ignite easily (e.g. splinters of dry pine); others are useful because they burn slowly and give off a lot of heat (e.g. oak). The amount of heat transferred to the air per unit volume of burning wood depends on the density of the wood and its *structure*, and the same is true of food. Fine, but this does not tell us what heat is.

It is the nature of science to tend towards formality and defining terms as precisely as possible. With accepted definitions in hand, there will be relatively little ambiguity about what is meant. What we need now is a good definition of heat. **Heat**, q, or thermal energy, is a form of kinetic energy, energy arising from motion. Heat is the change in energy of a system that results from its temperature differing from that of the surroundings. For instance, when a warm can of Coke is placed in a refrigerator, it gives off heat continuously until it has reached the same temperature as all other objects inside, including the air. The heat *transferred* from the Coke can to the air is absorbed by the other items in the fridge. Heat is said to *flow* from a region of higher temperature (greater molecular motion) to one of lower temperature (lesser molecular motion). The flow of heat resembles a basic property of a liquid. But this does not mean that heat is a material particle.

Heat is rather a type of energy transfer. Heat makes use of *random* molecular motion. Particles that exhibit such motion (*all* particles!) do

Table 1.3 Energy expenditure in humans

Activity	Time (min)	Energy cost (kJ min^{-1})	Total energy expenditure (kJ)
Lying	540	5.0	2700
Sitting	600	5.9	3540
Standing	150	8.0	1200
Walking	150	13.4	2010
Total	1440	—	9450

Note:
The measurements were made by indirect calorimetry. Digestion increases the rate of metabolism by as much as 30% over the basal rate. During sleep the metabolic rate is about 10% lower than the basal rate. The data are from Table 2.2 of Wrigglesworth (1997).

so according to the laws of (quantum) mechanics. A familiar example of heat being transferred is the boiling of water in a saucepan. The more the water is heated, the faster the water molecules move around. The bubbles that form on the bottom of the pan give some indication of just how fast the water molecules are moving. This is about as close as we can get to 'see' heat being transferred, apart from watching something burn. But if you've ever been in the middle of a shower when the hot water has run out, you will know very well what it is to *feel* heat being transferred! By convention, $q > 0$ if energy is transferred *to* a system as heat. In the case of a cold shower, and considering the body to be the system, q is negative.

Now we are in a position to have a reasonably good quantitative grasp of the oxidation of materials in a bomb calorimeter and animal nutrition. The heat released or absorbed in a reaction is ordinarily measured as a change in temperature; calibration of an instrument using known quantities of heat can be used to relate heats of reaction to changes in temperature. One can plot a standard curve of temperature *versus* heat, and the heat of oxidation of an unknown material can then be determined experimentally. Table 1.2 shows the heats of oxidation of different foodstuffs. Importantly, different types of biological molecule give off more heat per unit mass than do others. Some idea of the extent to which the energy obtained from food is utilized in various human activities is given in Table 1.3.

It also seems fitting to mention here that animals, particularly humans, 'consume' energy in a variety of ways, not just by eating, digesting and metabolizing food. For instance, automobiles require gasoline to run, and in order to use electrical appliances we first have to generate electricity! The point is that we can think about energy transformation and consumption on many different levels. As our telescopic examining lens becomes more powerful, the considerations range from one person to a family, a neighborhood, city, county, state, country, continent, surface of the Earth, biosphere, solar system, galaxy . . .. As the length scale decreases, the considerations extend from a whole person to an organ, tissue, cell, organelle, macromolecular

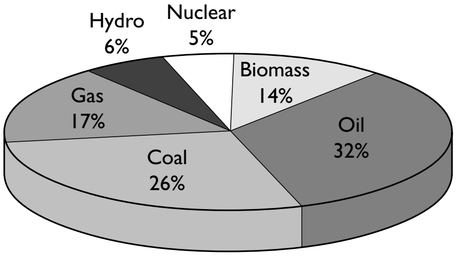


Fig. 1.12 Global human energy use. As of 1987, this totaled about 4×10^{20} J yr^{-1}. Energy production has increased substantially since then, but the distribution has remained about the same. Note that the rate of energy consumption is about four orders of magnitude smaller than the amount of radiant energy that is incident on Earth each year (cf. Fig. 1.1). Note also that *c*. 90% of energy consumption depends on the products of photosynthesis, assuming that fossil fuels are the remains of ancient organisms. Redrawn from Fig. 8.12 in Wrigglesworth (1997).

assembly, protein, atom, nucleus, proton or neutron . . .. Fig. 1.12 gives some idea of mankind's global energy use per sector. It will come as no surprise that a comprehensive treatment of all these levels of energy transformation is well beyond the scope of this undergraduate textbook. Instead, our focus here is on the basic principles of energy transformation and their application in the biological sciences.

E. Carbon, energy, and life

We close this chapter with a brief look at the *energetic* and *structural* role of carbon in living organisms. The elemental composition of the dry mass of the adult human body is roughly 3/5 carbon, 1/10 nitrogen, 1/10 oxygen, 1/20 hydrogen, 1/20 calcium, 1/40 phosphorus, 1/100 potassium, 1/100 sulfur, 1/100 chlorine and 1/100 sodium (Fig. 1.13). We shall see all of these elements at work in this book. The message here is that carbon is the biggest contributor to the weight of the body. Is there is an energetic 'explanation' for this?

Yes! Apart from its predominant structural feature – extraordinary chemical versatility and ability to form asymmetric molecules – carbon forms especially stable single bonds. N—N bonds and O—O bonds have an energy of about 160 kJ mol^{-1} and 140 kJ mol^{-1}, respectively, while the energy of a C—C bond is about twice as great (345 kJ mol^{-1}). The C—C bond energy is moreover nearly as great as that of a Si—O bond.

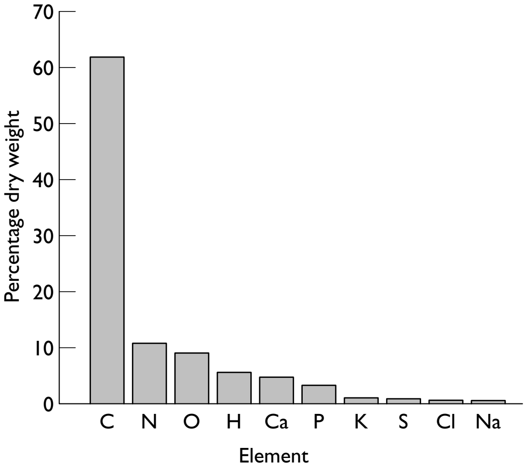


Fig. 1.13 Composition of the human body. Protein accounts for about half of the dry mass of the body. On the level of individual elements, carbon is by far the largest component, followed by nitrogen, oxygen, hydrogen and other elements. It is interesting that the elements contributing the most to the dry mass of the body are also the major components of air, earth, water, and carbon-based combustible matter. Based on data from Freiden (1972).

Chains of Si—O are found in tremendous abundance in the silicate minerals that form the crust of our planet, and one might guess therefore that silicates could support life in distant solar systems, if not elsewhere in our own. Although this possibility cannot be ruled out, Si—O is unlikely to be as useful for life as C—C because it is practically inert. The predominant importance of carbon in the molecules of life is likely to be the rule throughout the universe rather than the exception here on Earth.

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G. Exercises

1. What *is* energy? What is the etymology of *energy*? When did *energy* acquire its present scientific meaning? (Hint: consult the *Oxford English Dictionary* and any good encyclopedia of physics.)
2. Some primitive religions teach that the celestial bodies we call stars (or planets) are gods. This view was common in the ancient Greek world, and it was espoused by Thales of Miletus (fl. 6th century BC), one of the greatest thinkers of all time. Needless to say, the Greeks knew nothing about nuclear fusion in stars, though they were certainly aware that the Sun is much larger than it appears to the

unaided eye and that plants need light and water to grow. Explain briefly how the belief that stars are gods was remarkably insightful, even if polytheism and animism are rejected on other grounds.

3. According to Eqn. 1.1, E is a *continuous* and *linear* function of λ^{-1}; the energy spectrum of a *free* particle is *not* characterized by discrete, step-like energy levels. A continuous function is one that changes value smoothly; a linear function is a straight line. Consider Eqn. 1.1. Is there a fundamental limit to the magnitude of the energy of a photon? In contrast, the electronic *bound* state with which a photon interacts in photosynthesis is restricted to certain energy *levels*, and these are determined by the structure of the pigment molecule and its electronic environment; electromagnetic radiation interacts with *matter* as though it existed in small packets (photons) with *discrete* values. All of the energy levels are the bound electron are below a certain threshold, and when this energy level is exceeded, the electron becomes a free particle. What effect does exceeding the energy thershold have on the plant? What part of the biosphere prevents high-energy photons from the Sun from doing this to plants?
4. Chlorophylls absorb blue light and red light relatively well, but not green light (Fig. 1.3). Explain why tree leaves are green in summer and brown in late autumn.
5. The wavelength of blue light is about 4700 Å, and that of red light is about 7000 Å. (1 Å $= 10^{-10}$ m; the Ångström is named in honor of the Swedish physicist Anders Jonas Ångström (1814–1874).) Calculate the energy of a photon at these wavelengths. About 7 kcal mol^{-1} is released when ATP is hydrolyzed to ADP and inorganic phosphate (under ‘standard state conditions’). Compare the energy of the photons absorbed by plants to the energy of ATP hydrolysis (1 mole $= 6.02 \times 10^{23}$).
6. In the anabolic (biosynthetic) reduction–oxidation reactions of plant photosynthesis, 8 photons are required to reduce one molecule of CO_2. 1 mol of CO_2 gives 1 mol of carbohydrate (CH_2O). What is the maximum possible biomass (in g of carbohydrate) that can be produced in 1 hour by plants receiving 1000 μE s^{-1} of photons of a suitable wavelength for absorption? Assume that 40% of the photons are absorbed. (1 E = 1 einstein = 1 mol of photons. The einstein is named in honor of Albert Einstein.) The atomic masses of H, C and O are 1, 12 and 16, respectively.
7. The energy of oxidation of glucose to H_2O and CO_2 is -2870 kJ mol^{-1}. Therefore, at least 2870 kJ mol^{-1} are needed to synthesize glucose from H_2O and CO_2. How many 700 nm photons must be absorbed to fix one mole of CO_2? If the actual number needed is 3 to 4 times the minimum number, what is the efficiency of the process?
8. Devise your own analogy for energy conservation and distribution. Explain how the analog resembles nature and where the similarity begins to break down.
9. Give examples of a spatial distribution, a temporal distribution, and a spatio-temporal distribution.

10. Give three examples of a closed system. Give three examples of an open system.
11. Describe the preparation of a cup of tea with milk in terms of energy transformation.
12. Describe an astronaut in a spaceship in terms of open and closed systems.
13. The growth temperatures of almost all organisms are between the freezing and boiling points of water. Notable exceptions are marine organisms that live in seas a few degrees below 0 °C. Homeothermic (Greek, *homoios*, similar + *therme*, heat) organisms maintain an almost constant body temperature, independent of the temperature of the environment. Human beings are an example, as are horses and cats. Fluctuations about the average temperature of these organisms are generally less than 1 °C. All such organisms have an average temperature between 35 and 45 °C; a narrow range. Most birds strictly regulate their body temperatures at points between 39 and 44 °C. In some species, however, body temperature can vary by about 10 degrees centigrade. Poikilotherms, which include reptiles, plants, microorganisms, show much less temperature regulation. Eubacteria and archaebacteria exhibit the greatest range of growth temperatures of all known organisms. Suggest how a reptile might regulate its temperature. What about a plant?
14. Calculate the heat energy released by complete burning of an 11 g spoonful of sugar to carbon dioxide and water (Table 1.2).
15. Banana skins turn brown much more rapidly after the fruit has been peeled than before. Why?
16. Human daily energy requirement. A metabolic rate is a measure of energy consumption per unit time. Basal metabolic rate (BMR) is measured after a 12 h fast and corresponds to complete physical and mental rest. A 70 kg man might have a BMR of 80 W (1 W = 1 watt = 1 J s^{-1}. The watt is named after Scottish inventor James Watt (1736–1819)). A very active man might have a BMR three times as large. Calculate the minimal daily energy requirement of a man who has a BMR of 135 W.
17. The energy of protein catabolism (degradation) in living organisms is different from the energy of protein combustion in a calorimeter. Which energy is larger? Why?
18. Consider a 55 kg woman. Suppose she contains 8 kg of fat. How much heavier would she be if she stored the same amount of energy as carbohydrate?
19. Student A spends 15 hr day^{-1} sitting in the classroom, library, student cafeteria or dormitory. Another half-hour is spent walking between the dorm and lecture halls, and an hour is used for walking in the morning. Using Table 1.3, calculate Student A's daily energy requirement. Student B's routine is identical to Student A's except that his hour of exercise is spent watching television. Calculate the difference in energy requirements for these two students. Referring to Table 1.2, calculate the mass of fat, protein or carbohydrate Student A would have to ingest in order to satisfy her energy needs.

How much glucose does Student A need for daily exercise? List the underlying assumptions of your calculations.

20. In nuclear fusion, two deuterium atoms ^2H combine to form helium and a neutron

$$^2H + {}^2H \rightarrow {}^3He + n$$

The mass of ^2H is 2.0141 a.m.u. (atomic mass units), the mass of ^3He is 3.0160 a.m.u., and the mass of a neutron is 1.0087 a.m.u. 1 a.m.u. $= 1.6605 \times 10^{-27}$ kg. Perhaps the most famous mathematical formula in the history of civilization on Earth is $E = mc^2$, where m is mass in kg, c is the speed of light, and E is heat energy. Show that the heat released on formation of one mole of helium atoms and one mole of neutrons from two moles of deuterium atoms is about 3.14×10^8 J.

21. Worldwide energy production (WEP) of 320 quadrillion (320×10^{15}) Btu (British thermal units; 1 Btu = 1.055 kJ) in 1987 increased by 55 quadrillion Btu by 1996. Give the magnitude of energy production in 1996 in joules and the percentage increase ($[(WEP_{1996}-WEP_{1987})/WEP_{1987}] \times 100$). Calculate the average annual rate of increase in WEP between 1987 and 1996. In 1996, the U.S. produced 73 quadrillion Btu, more than any other country. Compute the contribution of the U.S. to WEP in 1996. Only about 0.025% of the Sun's energy that reaches Earth is captured by photosynthetic organisms. Using the data in the legend of Fig. 1.1, calculate the magnitude of this energy in kJ s^{-1}. Find the ratio of WEP_{1996} to the Sun's energy captured by photosynthetic organisms. Assuming that $173\,000 \times 10^{12}$ W of the Sun's energy reaches Earth and is then either reflected or absorbed, calculate the total energy output of the Sun. Diameter of Earth = 12 756 km; area of a circle $= \pi \times (\text{diameter}/2)^2$; surface area of a sphere $= 4 \times \pi \times \text{radius}^2$; mean distance of Earth from Sun $= 149.6 \times 10^6$ km.) Using your result from the previous problem, calculate the number of moles of ^2H consumed when a heat this large is released. Calculate the energy equivalent of the Earth (mass $= 5.976 \times 10^{27}$ g). Compare the mass energy of Earth to the energy of the Sun that reaches Earth in one year.

22. It is said that energy is to biology what money is to economics. Explain.

For solutions, see http://chem.nich.edu/homework