Energy Is a Capacity to Store and Move Work and Heat

In this chapter, we introduce energy, work, and heat. Energy and related quantities describe the capacity of a system to perform work. Energy is conserved, which means that it flows, so this capacity to perform work can be moved from one place to another. We introduce two fundamentally important ideas: the First and Second Laws of Thermodynamics. The First Law describes the conservation of energy and the interchangeability of heat and different types of work. The Second Law describes the tendencies of systems toward equilibrium.

Energy commonly has units of joules (J), calories (cal), watt-hours (Wh), or BTUs (British Thermal Units). The rate of energy transfer or conversion per unit time from one form to another is called power, and is typically measured in watts (W) or J s⁻¹.

Energy Is Ubiquitous and Important

Energy is important in commerce, technology, the environment, climate, and life. For example, a country’s standard of living, reflected approximately by its gross domestic product (GDP) per person, is correlated with its energy utilization per person. A person in one of the poorest countries adds $1000 to that country’s annual GDP and uses around 200 W [1]. A person in one of the
richest countries adds $35,000 dollars to its GDP and uses about 11 kW. The GDP, which is a measure of a nation’s income and output, depends on building, manufacturing, transportation, and services that rely on motors, pumps, engines, generators, batteries, heating, cooling, and energy interconversion of all types. In 2005, the worldwide human ‘consumption’ of energy was 487 exajoules (1 EJ = 10^18 J) or 139 petawatt-hours (1 PW h = 10^15 W h). Because energy is conserved, the term consumption or energy usage here just means that energy is converted from one form that can be readily captured and stored to another form that cannot. For example, car engines convert the chemical covalent bond energy in hydrocarbons to the work of moving the car and to heating its surroundings.

About 80% of the planet’s energy currently comes from the covalent bonds of hydrocarbons—oil, gas, and coal; see Figure 3.1. These are called nonrenewable sources because they are not readily replaceable. Because the world’s oil supplies are finite (estimated in 2008 to be about 1 yottajoule (1 YJ = 10^24 J), and being depleted at a substantial rate, there are efforts to find renewable sources of energy and to use nonrenewable sources wisely and efficiently. Systematic advances in thermodynamics have led to increases in efficiencies, from 1% in the steam engines of T Newcomen and J Watt 200 years ago to more than 50% in today’s fuel cells.

EXAMPLE 3.1 You are energetically equivalent to a light bulb. A typical adult eats about 2000 kcal per day (1 ‘food Calorie’ equals 1 kilocalorie). Converting units, you see that this would power a 100 W light bulb:

\[
\frac{2000 \text{ kcal}}{\text{day}} = \left( \frac{2 \times 10^6 \text{ cal}}{\text{day}} \right) \left( \frac{4.184 \text{ J}}{\text{cal}} \right) \left( \frac{1 \text{ W}}{1 \text{ J/s}^{-1}} \right) \left( \frac{1 \text{ day}}{3600 \times 24 \text{ s}} \right) = 97 \text{ W}
\]

This 100 W light bulb energy expenditure per person is a useful reference quantity. People in poor nations contribute about twice their body’s energy consumption to their country’s GDP, while people in richer nations contribute about 100 times their consumption.

Energy is also important for understanding the Earth’s environment and climate. The Earth has been approximately in thermal balance for most of its
history, neither cooling nor warming very much, on average. (Ice ages and warming periods are small fluctuations relative to the total energy flows.) So, the energy flow to the Earth equals the energy flow away from the Earth. A major source of energy influx to the Earth is electromagnetic radiation. The Earth receives almost all of its energy from sunlight, about 3.83 YJ per year, or 174 petawatts (PW).

**EXAMPLE 3.2 How much solar energy hits your backyard?** How much solar energy arrives on the Earth per unit time per square meter? Divide the total energy rate, $1.74 \times 10^{17}$ W, arriving on the Earth by the Earth’s surface area, $4\pi R^2 = 5.1 \times 10^{14}$ m$^2$ (the Earth’s radius is $R = 6.37 \times 10^6$ m), to get $341$ W m$^{-2}$, the solar energy per unit time arriving on an average patch of the Earth. A typical solar panel in 2009 is about 20% efficient, which means that 1 W of sunlight coming into the cell converts to 0.2 W of electricity out. So a solar panel of 1 m$^2$ in size could run a 70 W light bulb ($0.2 \times 341$ W m$^{-2} \times 1$ m$^2 \approx 70$ W).

**EXAMPLE 3.3 How much of the Earth’s solar energy budget do humans consume?** Divide the 487 EJ annual consumption rate above by the total energy from the Sun, 3.83 YJ per year, to get

$$\frac{487 \times 10^{18} \text{ J}}{3.83 \times 10^{24} \text{ J}} = 0.012\% \quad (3.2)$$

We consume only a small fraction of the Earth’s total solar energy.

Figure 3.2 shows a peculiar feature of the Earth’s electromagnetic radiation balance. Solar energy arrives on the Earth at high frequencies (i.e., short wavelengths, in the visible region of the spectrum, around 0.4–0.7 μm). That radiation is then converted to lower frequencies (i.e., longer wavelengths, in

![Figure 3.2](image-url)  
**Figure 3.2** The Sun’s energy is maximal in the visible part of the spectrum. This is what arrives on the Earth. The Earth radiates away electromagnetic energy too, mostly in the infrared part of the spectrum, called heat radiation.
Figure 3.3 Earth’s energy flows. (1) 342 W m\(^{-2}\) enters the Earth from sunlight (short wavelength). (2) 107 W m\(^{-2}\) of that energy is reflected away. (3) The Earth also radiates away 390 W m\(^{-2}\) of heat (longer wavelengths; see Problem 7). (4) 235 W m\(^{-2}\) of the radiation exits the Earth’s atmosphere back into space, and (5) 324 W m\(^{-2}\) of it is absorbed by greenhouse gases and returned to the Earth. Source: redrawn from JT Kiehl and KE Trenberth, Bull Am Meteor Soc 78, 197–208 (1997).

the infrared part of the spectrum, around 5–15 μm) by physical and biological processes on the Earth, and is then re-radiated away from the Earth as heat. This conversion to longer wavelengths comes mainly from geophysical water cycles of evaporation and, to a lesser extent, from driving winds, waves, ocean currents, and photosynthesis in plants.

Figure 3.3 shows the Earth’s energy balance. The main arrows on this diagram are constructed from a few facts and principles: (1) The incoming solar energy, as measured by satellites, is about 342 W m\(^{-2}\). (2) The energy transfer rate in, 342 W m\(^{-2}\), must equal the energy transfer rate out, 107 + 235 W m\(^{-2}\), where 107 is an estimate of sunlight reflected from the Earth and 235 is an estimate of the net heat radiating away from the planet. (3) The Earth’s core radiates away additional heat, about \(P = 390\) W m\(^{-2}\) (based on the Earth’s average temperature; see Problem 7 at the end of this chapter). Combining all these energy flows gives you one remaining large arrow on the diagram, indicating that a large amount (342 W m\(^{-2}\)) of the outgoing heat is reflected back to the Earth by greenhouse gases. What are greenhouse gases?

**EXAMPLE 3.4 What is the greenhouse effect?** The Earth’s atmosphere acts like the glass roof on a greenhouse; see Figure 3.4. A greenhouse roof allows sunlight freely into the greenhouse, but it does not let the heat (infrared) freely out of the greenhouse. So, greenhouses are warm inside. Similarly the
Figure 3.4 A greenhouse has a glass roof. Through glass, visible light passes freely, but infrared light (heat) is partially reflected. Sunlight enters a greenhouse and is converted to infrared radiation (heat) by evaporating water and photosynthesis by the plants. Because the infrared radiation cannot fully escape, it warms the inside of the greenhouse.

greenhouse effect warms up the earth. The Earth’s ‘glass roof’ is its atmosphere of greenhouse gases—mostly water vapor (which accounts for about 40–70% of the greenhouse effect), carbon dioxide (10–25%), and smaller contributors such as methane, nitrous oxide, and ozone. The Sun’s visible light reaches the Earth after passing freely through these atmospheric gases. But the heat that the Earth radiates outward is absorbed by vibrational motions of the greenhouse gases, and sent back down to Earth, as a greenhouse roof does, like a blanket warming the Earth. This greenhouse effect is responsible for the warming from $T = 255 \, \text{K}$ (the temperature that the Earth would have in the absence of greenhouse gases, due to the balance of energy fluxes) to $T = 288 \, \text{K}$. This greenhouse effect is natural and has been part of our planet’s energy balance ever since the Earth first had an atmosphere. However, more recently, man-made chemicals, such as chlorofluorocarbons, and carbon compounds from fossil fuels, are adding to the greenhouse gases, trapping additional heat. It is believed that this may contribute to global warming.

Energy also plays a key role in biology and evolution. Your intake of food energy must equal the work you perform plus the heat you generate plus the energy you store as fat. At the cellular level, energy utilization drives molecular motors, transporters, and biochemical reactions. On a grander scale, energy balance governs the sizes and lifespans of animals. You might first guess that the total amount of energy consumed by an organism at rest, per unit time, called the basal metabolic rate (BMR), would scale in linear proportion to an organism’s body mass $M$ ($\text{BMR} \propto M$). You might reason that each cell has about equal size and burns energy at about equal rates. But this argument would overestimate the energy usage in large organisms. (The BMR for humans is about 1200 kcal per day; the BMR is the minimal level measured after fasting and does not account for exertion or keeping warm in cold weather.) As a better approximation, you might reason that an organism’s energy utilization is governed by its surface area rather than its volume or mass, ($\text{BMR} \propto M^{2/3}$), because the surface area controls how much heat the organism can dissipate. Similar considerations are involved in designing computers.

But it is not clear that this argument is correct either. Figure 3.5 shows a different result, namely that $\text{BMR} \propto M^{3/4}$, over a wide range of sizes from single-celled mycoplasma to the largest mammals and whales [2]. Interestingly, many
Figure 3.5 Basal metabolic rate (BMR) versus sizes of animals and cells. Over 27 orders of magnitude, this measure of energy utilization in organisms increases with $M^{3/4}$, where $M$ is the body mass.

such allometric scaling laws are observed in biology. The powers in the scaling laws are multiples of approximately $1/4$: heart rates in mammals $\propto M^{-1/4}$, growth rates $\propto M^{-1/4}$, DNA nucleotide substitution rates $\propto M^{-1/4}$, densities of mitochondria, chloroplasts, and ribosomes $\propto M^{-1/4}$, and lifespans $\propto M^{1/4}$. Are all these processes related to each other? Such $1/4$-power scaling laws have been explained by the rates at which supply networks (such as networks of blood vessels) transport energy to cells. For optimal efficiency, blood vessels, like the streets and highways that supply cities, should have a hierarchy of sizes; large roads are needed for rapid global transport and small roads are needed for local transport.

EXAMPLE 3.5 Elephants metabolize more efficiently than mice. Dividing the BMR (energy per unit time used by the whole organism), which scales as $M^{3/4}$, by the body mass $M$ shows that the energy used by an organism per unit mass is

$$\frac{\text{BMR}}{M} \propto M^{-1/4},$$

so larger animals expend less energy per unit mass than smaller animals do.

The question of whether metabolic scaling exponents are $2/3$ or $3/4$ or some other value remains a matter of active research [3].

In short, the world’s commerce, climate and environment, and living systems are dependent on the thermophysical principles of energy balance. Below, we develop the quantitative basis for these principles. We start with a little historical background.
Before 1800, a major mystery of physical science was why heat flows from hot objects to cold objects. Is heat like a fluid that equalizes its levels in two connected containers? This was the view until thermodynamics emerged. Heat was mistakenly thought to be conserved, like the volume of a flowing fluid. The correction to this misunderstanding was captured in the First Law of Thermodynamics.

Some Physical Quantities Obey Conservation Laws

The origin of ideas about molecules and their energies is deeply rooted in laws of conservation, which are central to physical science. The law of conservation of momentum was discovered in 1668 by J Wallis. Wallis observed that when objects collide, their velocities, positions, and accelerations can change, but the sum of the mass × velocity of all the objects does not. The quantity mass × velocity, called the momentum, is special because it is conserved.

Other functions of the position, time, velocity, and acceleration depend on the details of the collision process. For example, the quantity velocity or the quantity mass × acceleration squared will generally change when one particle collides with another. Such quantities are different for every situation and depend on the angles of the collisions and the shapes of the objects. However, conservation laws describe properties that are exceptionally simple because they are not dependent on particular details. The total momentum (mass × velocity) is the same before and after a collision, no matter how the collision occurs. Similar laws describe the conservation of mass, of angular momentum, and of energy. A property that is conserved is neither created nor destroyed as collisions take place. Because they are conserved, mass, momentum, and energy can only ‘flow’ from one place to another.

Conservation laws help to predict the behaviors of physical and chemical systems. For example, because the total momentum does not change in a collision, you can predict the final velocities of colliding objects on the basis of their masses and initial velocities. Another conserved quantity is the energy. Like momentum, the total energy cannot be created or destroyed. Properties that are conserved, such as matter, momentum, and energy, can flow from one place to another, since they cannot be destroyed. The importance of energy derives from two properties. Energy describes a capacity to perform work. And, because it is conserved, that capacity to perform work can move from one place to another.

**Total Energy.** The total energy \( E \) of a mechanical system is defined by the law of conservation of energy:

\[
K + V = E = \text{constant.} \tag{3.4}
\]

where the kinetic energy \( K \) is the work that an object can perform by virtue of its motion and \( V \) is the work that an object can perform by virtue of its spatial position.

**Kinetic Energy.** The kinetic energy \( K \) of an object of mass \( m \) moving at velocity \( v \) is defined as

\[
K = \frac{1}{2} mv^2. \tag{3.5}
\]

A moving object slows down as it does work, losing kinetic energy.
**Potential Energy.** In contrast, the potential energy $V$ is the work that an object can perform by virtue of its position, or the positions of its subcomponents. If an object is raised above the Earth, it gains the gravitational potential to do work when it comes back down. The potential to do work can be stored in a stretched or compressed spring, or in a battery through the separation of electrical charges. Like the kinetic energy, the potential energy of a system can change. The potential energy of a ball changes as it rolls downhill, as in Example 2.1. The potential energy of a mass attached to a spring changes as the mass bounces.

The conservation of energy is a fundamental observation about nature. Although the kinetic and potential energies each change throughout a process, their sum, the total energy $E$, is constant. The total energy is an invariant of the motion. That is, the sum of all the kinetic energies plus all the potential energies of a system is the same at any stage before, after, and during a process. Any change in the kinetic energy of an object as it does work, or as work is done upon it, is balanced by an equal and opposite change in the potential energy of the system. A system performs work by virtue of its ability to exert a force.

**Forces and Work**

**Force.** Newton’s second law defines the force in terms of the acceleration of an object:

$$f = ma = \frac{d^2x}{dt^2}, \quad (3.6)$$

where the mass $m$ of an object represents its resistance to acceleration, $x$ is its position, the acceleration $a = \frac{d^2x}{dt^2}$, and the velocity $v = \frac{dx}{dt}$.

**Work.** Consider a ball located at $x = 0$ that can move along the $x$ axis (see Figure 3.6). One force acting on the ball is from a spring attached to a wall pulling the ball to the left. Call this the intrinsic force $f$. For a spring, you have

$$f = -k_s x, \quad (3.7)$$

called Hooke’s law, named after 17th century British physicist R Hooke, where $k_s$ is the spring constant. The minus sign shows that the spring acts in the $-x$ direction. Suppose you apply an approximately equal opposing force to stretch the spring $f_{ap} = -f$. (It must be slightly greater, and not exactly equal, to stretch the spring. However, the near equality ensures that there is approximately no net force or acceleration.) The work $\delta w$ you perform on the system by moving the ball a distance $dx$ to the right is

$$\delta w = f_{ap} dx = -f dx. \quad (3.8)$$

The total work $w$ performed on the system in stretching the spring from $x_1$ to $x_2$ is the integral

$$w = \int_{x_1}^{x_2} f_{ap} dx = -\int_{x_1}^{x_2} f dx. \quad (3.9)$$
Examples 3.6 and 3.7 calculate the work of stretching a spring and the work of lifting a weight.

**EXAMPLE 3.6 The work of stretching a spring.** The work $w$ to stretch a spring from 0 to $x_0$ is

$$w = \int_0^{x_0} k_s x \, dx = \frac{1}{2} k_s x_0^2.$$

**EXAMPLE 3.7 The work of lifting a weight.** Gravity acts downward with a force $f = mg$, where $m$ is the mass of the weight and $g$ is the gravitational acceleration constant (see Appendix H). Suppose that you lift a weight from the floor, $z = 0$, to a height $z = h$ (see Figure 3.7). The downward force defines the direction $x > 0$, but positive $z$ is in the upward direction, so $dz = -dx$. Substituting $f = mg$ and $dx = -dz$ into Equation (3.9) gives the work of lifting the weight

$$w = -\int_0^h (mg)(-dz) = mgh.$$

**Conservative Forces.** The forces operating on the ball on the hill in Example 2.1 are conservative forces, because there is no frictional loss, no turbulence, and no other dissipation of energy. For a conservative force $f$, no net work is performed in moving an object through any cycle that returns it to its starting point. For a force acting in the $x$ direction, the work performed in the cycle from $A$ to $B$ to $A$ is zero,

$$w(A,B) + w(B,A) = -\int_A^B f \, dx - \int_B^A f \, dx$$

$$= -\int_A^B f \, dx + \int_A^B f \, dx = 0. \quad (3.10)$$

In contrast, for nonconservative forces, the work around a cycle does not sum to zero, for example when the friction is different in one direction than the other. So far, we have described how work arises from the actions of forces. Work can be done by different types of forces: stretching springs, lifting weights, or moving electrical charges or magnets, for example. What is the role of heat? Let’s look at the history of the thought that led to the First Law of Thermodynamics.

**Heat Was Thought to Be a Fluid**

The ability to flow is an aspect of conserved properties: mass, momentum, and energy can all flow. What about heat? When a hot object contacts a cold one, heat flows. Does it follow that heat is a conserved quantity? It does not. Heat is not a conserved quantity. All conserved properties can flow, but not all properties that flow are conserved.
Until the mid-1800s, heat was (incorrectly) thought to be a conserved form of matter, a fluid called calorique. The calorique model explained that materials expand upon heating because the added heat (calorique fluid) occupied space. The flow of heat from hot to cold objects was attributed to repulsions between the more crowded calorique particles in the hot material. Calorique particles escaped to cold materials, where they were less crowded. Because all known materials could absorb heat, it was thought that calorique particles were attracted to all materials, filling them in proportion to the volume of the material. The temperature of a substance was known to increase on heating, so it was thought that temperature directly measured the amount of calorique in a material.

The misconception that calorique obeyed a law of conservation had important implications for industry and commerce. The industrial revolution began with J. Watt’s steam engine around 1780. During the late 1700s and early 1800s, power generated from steam gained major economic importance. The industrial quest for efficient steam engines drove the development of thermodynamics. How is heat converted to work in steam engines? It was thought that the heat flow in a steam engine was like the water flow in a water wheel. In a water wheel, water goes in at the top, falls down to turn the wheel, and comes out the bottom (see Figure 3.8). The water is conserved: the flow of water from the bottom equals the water flow into the top. The amount of heat flowing out of the exhaust of a steam piston was believed to equal the amount of heat in the steam that enters the piston chamber.

The view of heat as a fluid began to change in the mid-1700s. The first step was the concept of heat capacity, developed by J. Black around 1760: he heated mercury and water over the same flame and discovered that the temperature of the mercury was higher than the temperature of the water. He concluded that heat could not be a simple fluid, because the amount taken up depended on the material that contained it. Different materials have different capacities to take up heat. The heat capacity of a material was defined as the amount of heat required to raise its temperature by 1°C.

The next step was Black’s discovery of latent heat, which showed that temperature and heat are different properties. Liquid water slightly below 100°C can absorb heat and boil to become steam slightly above 100°C. In this case, the uptake of heat causes a change of phase, not a change of temperature. This heat is latent because it is ‘stored’ in the vapor and can be recovered in a condenser that converts the steam back to liquid water. The melting of ice also involves a latent heat. Although the discovery of latent heat showed that heat and temperature are different properties, heat was still regarded as a conserved fluid until the 1800s. And the question remained: What is temperature? We develop a conceptual model of temperature in Chapter 12, after laying the groundwork in thermodynamics and statistical mechanics.

The development of quantitative thermodynamics ultimately caused the downfall of the calorique theory of heat. The early 1800s were years of intensive development of engines driven by steam (see Figure 3.9), by hot air, and later by internal combustion. In 1853, J. Ericsson launched a magnificent engine, designed using the calorique theory, with pistons 14 feet in diameter driven by hot air. Ericsson hoped the calorique engine would achieve 600 horsepower and compete with the steam engine. A set of ‘regenerator’ coils were supposed to
collect exhaust heat and re-use it, on the basis of the assumption that heat was a conserved and recyclable fluid. But the calorique engine and the calorique theory ultimately failed because heat is not a conserved fluid. One of the main uses of the Second Law of Thermodynamics in its early days was to debunk such ‘perpetual motion’ machines. The Second Law, now the centerpiece of statistical thermodynamics, is little needed for that purpose any longer.

Other problems with the theory of calorique emerged at that time. First, it was shown that radiant heat could be transmitted through a vacuum by electromagnetic radiation. If heat is a form of matter, how could it pass through a vacuum that is devoid of matter?

Second, careful measurements showed that work could be converted to heat quantitatively. In 1798, Count Rumford showed that the mechanical work involved in boring cannons was converted to heat. In 1799, H Davy showed that the mechanical work involved in rubbing ice cubes together was sufficient to melt them. In the 1850s, J P Joule produced heat from work in many ways: a falling weight rotating a paddle wheel and imparting heat to a liquid, electrical work heating a resistor, and others. These experiments were difficult to reconcile with the view that heat is a conserved fluid. How could heat be created by work?


These experiments led to two paradigm-changing conclusions: (1) heat is not conserved, and (2) heat and work can be interconverted. This new understanding, first formulated by J R von Mayer in 1842, came to be known as the First Law of Thermodynamics. It is not the heat $q$ that is conserved ($q_{\text{in}} = q_{\text{out}}$). Rather, it is the sum $q + w$ of the heat $q$ plus the work $w$ that has special properties. This sum is called the internal energy change $\Delta U = q + w$. $\Delta U$ of a system will rise or fall as a system does work or takes in or gives off heat, but any gain in $\Delta U$ of the system must balance a loss in energy somewhere else; $\Delta U$ is conserved between the system and its surroundings. Various forms of work were known before the 1800s, including mechanical, electrical, and magnetic. The advance embodied in the First Law was the recognition that heat can be added to this list, and that heat is a form of energy transfer, not a form of matter.

**The First Law of Thermodynamics** The internal energy $\Delta U$ changes when a system takes up or gives off heat $q$ or work $w$:

$$\Delta U = q + w$$

This is a statement of the equivalence of heat and work. The internal energy is conserved; if $\Delta U$ increases in the system, the energy decreases in the surroundings.
Energy is a property of a system, while heat and work are properties of a process of energy transfer across a boundary. As a metaphor, the level of water in a lake is like the amount of internal energy in a system, and the different modes of water exchange between the lake and its surroundings are like heat and work [4]. Say that rainfall corresponds to the process of heat going into the system \( q > 0 \), evaporation corresponds to the process of heat going out of the system \( q < 0 \), streams flowing into the lake correspond to work done on the system \( w > 0 \), and streams flowing out of the lake correspond to work done by the system \( w < 0 \). The change in internal energy \( \Delta U = q_{\text{in}} - q_{\text{out}} + w_{\text{in}} - w_{\text{out}} \) is the sum of the heat and work into the system minus the heat and work out of the system, just as the change in the water level of the lake is the sum of rainfall plus river flows in minus evaporation and river flows out. Once the water is in the lake, you cannot tell whether it came from rainfall or from streams. Similarly, you cannot tell whether the amount of internal energy in a system was acquired as heat or work. In this analogy, the internal energy corresponds to a property of the lake, while heat and work correspond to processes of the transfer across the boundaries of the lake.

**Atoms and Molecules have Energies**

**The Kinetic Theory of Gases**

The modern conception of particulate atoms and molecules developed in parallel with the modern view of heat. What is the microscopic nature of heat? This question was addressed in the kinetic theory of gases, a radically different view of heat that superseded the model of calorique, owing to the efforts of Clausius, Maxwell, Boltzmann, and others during the late 1800s. The concept of calorique had been intimately tied to the concept of the ether, a hypothetical pervasive medium that could transmit vibrations. Atoms were thought to be at fixed positions in the ether. The kinetic theory introduced three novel concepts:

1. Matter is composed of molecules that are not located at fixed positions in space, but are free to move through a space that is otherwise empty.
2. Heat is the exchange of energy that takes place owing to the motions and collisions of molecules. In the kinetic theory, molecules collide and exchange energy like Newtonian billiard balls.
3. Electromagnetic radiation can influence the motions of molecules. This is the basis for radiant heat.

How does the kinetic theory of gases explain the conversion of heat to work? How does a gas lose heat and push the piston in a steam engine? The kinetic theory of gases is a mechanical model on a microscopic scale (see Figure 3.10). According to the kinetic theory, when molecules collide, they exchange energy and momentum. At high temperature, gas particles move with high velocities. When a molecule collides with a piston, it imparts momentum, loses kinetic energy, moves the piston, and produces work. Alternatively, a high-energy particle colliding with its container can impart energy to the container wall, and the container wall can impart this kinetic energy to the surroundings as heat.
Because the collisions between the gas and the piston are random, some collisions will perform work, owing to motion in the direction of the piston’s trajectory. Other collisions will produce only heat, molecular motions in all other directions that result in a flow of energy out of the container.

The kinetic theory is remarkably successful. It predicts the ideal gas law and other properties of gases, including diffusion rates, viscosities, thermal conductivities, and the velocities of sound in gases. It provides a model in which every molecule has its own energy, different molecules have different energies, and molecules can exchange their energies. The kinetic theory predicts that the temperature $T$ of a gas is proportional to the average kinetic energy of the gas particles:

$$\frac{3}{2} kT = \frac{m \langle v^2 \rangle}{2},$$

(3.11)

where $m$ is the mass of one particle, $\langle v^2 \rangle$ is the square of the particle velocity averaged over all the particles, $m \langle v^2 \rangle / 2$ is the average kinetic energy of the gas molecules, and $k$ is Boltzmann’s constant (see Appendix H).

**A Better Model: Energy Is Quantized**

Despite the tremendous advances that resulted from the kinetic theory of gases, it wasn’t perfect either. The kinetic theory described gas particles as mechanical objects like billiard balls, with a continuum of possible energies. But 20th century quantum theory, describing the motions of particles at the atomic level, showed that the energies of atoms and molecules are quantized. Each particle has discrete amounts of energy associated with each of its allowed degrees of freedom, some of which are translations, rotations, vibrations, and electronic excitations. For example, quantum mechanics might dictate that the molecules in a given system have energies of 1, 5, 16, 21, and 26 units, and no other energies are allowed. The allowed energies for a given system are indicated in *energy-level diagrams*, as shown in Figure 3.11. Although these diagrams seem to contain very little information, this information is sufficient to predict the thermodynamic properties.

For simple systems of independent particles such as ideal gases, we can express the total internal energy of a thermodynamic system as the sum of the particle energies:

$$U = \sum_i N_i \varepsilon_i,$$

(3.12)

where $\varepsilon_i$ is the energy of any particle at level $i$ and $N_i$ is the number of particles at energy level $i$. When the total internal energy of a system is increased by heating it, the energy levels do not change: the populations $N_i$ change. Then more particles occupy higher energy levels.

What drives molecules or materials to exchange energy with each other? Why does heat flow? The answer is not found in an equalization principle or a conservation law like the First Law. Heat flow is a consequence of the tendency toward maximum multiplicity, which is the *Second Law of Thermodynamics*.

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*Figure 3.11* The quantum mechanical view: the quantized energies of particles are given by energy-level diagrams.
Why Does Heat Flow?

In Example 2.2, we found that gases expand because the multiplicity $W(V)$ increases with volume $V$. The dependence of $W$ on $V$ defines the force called pressure. In Example 2.3, we found that particles mix because the multiplicity $W(N)$ increases as the particle segregation decreases. This tendency defines the chemical potential. These are manifestations of the principle that systems tend toward their states of maximum multiplicity, also known as the Second Law of Thermodynamics.

The following examples illustrate in two steps that the flow of heat from hot to cold objects is also driven by a tendency to maximize multiplicity. First, Example 3.8 shows a model for how the multiplicity $W(U)$ of an object depends on its energy. Then Example 3.9 uses that result to show that heat flow maximizes multiplicity.

**EXAMPLE 3.8 Why do materials absorb heat?** Here is a miniaturized model of a material. The material has three distinguishable particles. Each particle can have energy $\varepsilon = 0, 1, 2, 3$ units. (For now, it doesn’t matter that our energy rule is simple. In Chapter 11, we’ll get energies from quantum mechanics.) There are different ways of getting different total energies $U$. What is the total number $W(U)$ of ways the system can partition its energy $U$ among its component particles? Figure 3.12 shows four different states, $U = 0, 1, 2, 3$, and their different multiplicities.

![Figure 3.12](image)

Each case represents a system with a different given energy $U$. Each card represents a different distribution of the three particles over the four energy levels. The numbers shown at the top of each card are the individual energies of the particles. $W$ is the number of configurations (cards).
Case D shows that there is only one way to achieve a total energy of \( U = 0 \): each particle must have zero energy. Case C shows the three ways of achieving \( U = 1 \): two particles must have zero energy and one particle must have \( \varepsilon = 1 \). Case B shows the six different ways to get \( U = 2 \). And case A shows the 10 different ways of achieving a total energy \( U = \sum_{i=0}^{t} N_i \varepsilon_i = 3 \). Collecting these results together, Figure 3.13 shows that the number of configurations \( W \) is an increasing function of the total energy \( U \), for the system shown in Figure 3.12. The higher the energy \( U \) the material has, the higher is its multiplicity of states.

So, because systems tend towards states having high multiplicities, materials tend to take up heat from their surroundings. Now why does heat flow from hot objects to cold ones? Example 3.9 addresses this question.

**EXAMPLE 3.9 Why does energy exchange?** Consider the two systems, A and B, shown in Figure 3.14. Each system has 10 particles. Each particle has two possible energies, \( \varepsilon = 0 \) or \( \varepsilon = 1 \). Suppose that system A starts with energy \( U_A = 2 \) and system B starts with energy \( U_B = 4 \). We show here that if the two systems were in thermal contact and could instead share their energies equally, \( U_A = U_B = 3 \), it would increase the multiplicity of the combined system, so heat will flow from B to A to reach this state. Because each system A and B has only two energy levels, the multiplicities \( W(U) \) are given by binomial statistics. Count the number of ways that A can have two particles in its ‘excited state’ (\( \varepsilon = 1 \)), and eight in its ‘ground state’ (\( \varepsilon = 0 \)), for a total energy of \( U_A = 2 \). Then make the corresponding count for B.

![Figure 3.14](image-url) Energy-level diagrams for the two different systems in Example 3.9 with 10 particles each. System A has total energy \( U_A = 2 \), and B has \( U_B = 4 \). System B has the greater multiplicity of states.
The multiplicities of isolated systems $A$ and $B$ are

$$W_A = \frac{10!}{2!8!} = 45, \quad \text{and} \quad W_B = \frac{10!}{4!6!} = 210.$$ 

If $A$ and $B$ do not exchange energies, the total multiplicity is $W_{\text{total}} = W_A W_B = 9450$. Now suppose that you bring $A$ and $B$ into ‘thermal contact’ so that they can exchange energy. Now the system can change values of $U_A$ and $U_B$ subject to conservation of energy ($U_A + U_B$ will be unchanged). One possibility is $U_A = 3$ and $U_B = 3$. Then the total multiplicity $W_{\text{total}}$ will be

$$W_{\text{total}} = \frac{10!}{3!7!} \frac{10!}{3!7!} = 14,400.$$ 

This shows that a principle of maximum multiplicity predicts that heat will flow from $B$ to $A$ to equalize energies in this case. Consider the alternative. Suppose $A$ were to lower its energy to $U_A = 1$ while $B$ wound up with $U_B = 5$. Then the multiplicity of states would be

$$W_{\text{total}} = \frac{10!}{1!9!} \frac{10!}{5!5!} = 2520.$$ 

A principle of maximal multiplicity predicts that this inequitable distribution is unlikely. That is, heat will not flow from the cold to the hot object.

**EXAMPLE 3.10** However, energy doesn’t always flow downhill. Example 3.9 predicts that energies tend to equalize. But here’s a more interesting case, which shows that the tendency to maximize multiplicity does not always result in a draining of energy from higher to lower. Consider two systems having the same energies, but different particle numbers. Suppose system $A$ has 10 particles and an energy $U_A = 2$ and system $B$ is smaller, with only four particles, but also has energy $U_B = 2$. The multiplicity is

$$W = W_A W_B = \frac{10!}{2!8!} \frac{4!}{2!2!} = 45 \times 6 = 270.$$ 

Now suppose that $A$ and $B$ come into thermal contact and the larger system absorbs energy from the smaller one, so $U_A = 3$ and $U_B = 1$. This causes the multiplicity to increase:

$$W = W_A W_B = \frac{10!}{3!7!} \frac{4!}{1!3!} = 120 \times 4 = 480.$$ 

The tendency for heat to flow is not always a tendency to equalize energies. It is a tendency to maximize multiplicity. We will see later that the concept of temperature describes the driving force for energy exchange. The tendency toward maximum multiplicity is a tendency toward equal temperatures, not equal energies. Temperature is the quantity that describes the tendency toward maximum multiplicity when energies can exchange. This is the topic of Chapter 12.
The Second Law of Thermodynamics Is an Extremum Principle

In this and the preceding chapter we have used simple models to predict that gases expand to fill the volume available to them, molecules mix and diffuse to uniform concentrations, rubber retracts when pulled, and heat flows from hot bodies to colder ones. All these tendencies are predicted by a principle of maximum multiplicity: a system will change its degrees of freedom to reach the microscopic arrangement with the maximum possible multiplicity. This principle is the Second Law of Thermodynamics, and is much broader than the simple models that we have used to illustrate it.

Why do systems tend toward their states of maximum multiplicity? It is because every microstate is just as likely as every other. So, in the same way that a series of coin flips is most likely to lead to half heads and half tails, the probability of observing any particular macrostate in a physical system depends on how many microstates it has. In the following chapters, we explore the Second Law in more detail.

Summary

We have described the concept of energy and traced a little of the history of thermodynamics. The First Law of Thermodynamics says that heat is a form of energy exchange, and that the sum of heat plus work is a quantity $\Delta U$ that is conserved between a system and its surroundings. The First Law is a bookkeeping tool. It catalogs the balance of heat and work. It doesn’t tell us why heat flows. The Second Law of Thermodynamics says that systems tend toward their states of maximum multiplicity. Heat flows to maximize multiplicity. A simple example shows that transferring internal energy from one system to another can change the multiplicity.

To make these principles more useful, we need some mathematical tools and then, beginning in Chapter 6, the definitions of thermodynamics.
Problems

1. The time dependence of a mass on a spring
(a) For the harmonic motion of a mass on a spring, the kinetic energy is \( K = (1/2)mv^2 \), and the potential energy is \( V = (1/2)kx^2 \), where \( k \) is the spring constant. Using the conservation of energy, find the time-dependent spring displacement \( x(t) \).
(b) Compute the force \( f(t) \) on the mass.

2. Equalizing energies. For the two 10-particle two-state systems of Example 3.9, suppose the total energy to be shared between the two objects is \( U = U_A + U_B = 4 \). What is the distribution of energies that gives the highest multiplicity?

3. Energy conversion. When you drink a cup of juice, you get about 100 Cal (1 food Cal = 1 kcal). You can work this off on an exercise bicycle in about 10 minutes. If you hook your exercise bicycle to a generator, what wattage of light bulb could you light up, assuming 100% efficiency? (1 watt = 1 J s\(^{-1}\) = power, i.e., energy per unit time.)

4. Kinetic energy of a car. How much kinetic energy does a 1700 kg car have, if it travels at 100 km h\(^{-1}\)?

5. Root-mean-square (rms) velocity of a gas. Using \( (1/2)kT = (1/2)m\langle v_x^2 \rangle \), for \( T = 300 \) K, compute the rms velocity, \( \langle v_x^2 \rangle^{1/2} \), of O\(_2\) gas.

6. Earth's energy balance. Figure 3.3 in the text shows energy inputs and outputs to the Earth, in W m\(^{-2}\), which is a measure of energy per unit area per unit time (1 W = 1 J V\(^{-1}\) A\(^{-1}\)).
(a) Suppose your backyard has an area of 1000 m\(^2\). Your yard only receives sunlight about one-third of each day, and, because of overcast skies, let's say the total flux is reduced by another factor of one-half. What average energy flux, in W m\(^{-2}\), does your yard receive?
(b) Your cell phone uses about 2 W. Assuming 20% efficiency, how big a solar cell would you need to power it?
(c) If we had no natural greenhouse gases (CO\(_2\) and water vapor), how would that shift the Earth's energy balance?
(d) How much energy, in W h, is in a gallon of gasoline? Assume that 100% of the gasoline is octane (C\(_8\)H\(_{18}\)). The density of gasoline is about 1 g cm\(^{-3}\), and each carbon–carbon covalent bond is worth about 60 kcal mol\(^{-1}\). Assume 50% efficiency in burning.

7. Taking the Earth's temperature. A physical law, called the Stefan–Boltzmann (SB) law, relates the transfer rate of electromagnetic radiation of a body (called black-body radiation) to its temperature. The SB law is a relative of the Wein law, the principle that explains why an object that is hot enough will emit visible light, as when a burning ember in a fire glows red, or glows blue if is even hotter.

An object having a nonzero temperature will emit electromagnetic radiation. Conversely, an object that absorbs energy via radiation increases its temperature. The SB law says that the electromagnetic power \( P \) is related to the temperature \( T \) by
\[
P = \left(5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}\right) T^4
\]  \hspace{1cm} (3.13)
(a) If the incoming solar power hitting the Earth is \( P = 342 \text{ W m}^{-2} \), what would you predict should be the Earth’s temperature?
(b) Now, turn around this argument around. The Earth’s actual average temperature is \( T = 288 \text{ K or} +15^\circ\text{C} \). Use the SB law to compute the power of radiated heat from the Earth’s core.

8. Why do elephants live longer than mice? Let \( L \) represent the lifespan of an organism. It is known that all mammalian species live, on average, to have about 1.5 \times 10^9 heartbeats (HB), independent of their size. Assume that an organism will have a total of \( HB = L \times HR \) = constant heartbeats during its lifetime, where \( HR \) is its heart rate. What assumptions would you need to make to explain the observation that the lifespans of organisms grow with body mass \( M \) as \( L \propto (HB/HR) \propto M^{1/4} \)?

References


Suggested Reading

