

## **C. Energy and Entropy**

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*PT-C-110*

# Chapter 7. Energy

## Chapter Introduction

### A. Why?

Although physics was constructed on the basis of Newton's understanding of force and momentum, later discoveries have shown that *energy* (such as energy of motion) is at least as important. Unfortunately, arguments based on force and momentum are often confused with energy considerations, one of the most common sources of error in physics textbooks.

### B. What to Look For

In contrast to force and momentum, energy has no directional characteristic. Furthermore, it may change its form — energy of motion may disappear, reappearing as energy of position or as thermal energy or other “hidden” forms such as electronic or chemical or nuclear energy.

### C. Pre-Test for Prior Comprehension

- a. What is meant by *kinetic energy*?
- b. What is meant by *potential energy*?
- c. What is meant by *thermal energy*?
- d. According to the principle of “equipartition of energy”, what is equal to what?
- e. What is the meaning of the familiar equation  $E = mc^2$ ?

### D. Inquiry Questions

A. If energy is conserved, does that require that it will be preserved? If energy is preserved, does that require that it will be conserved? How can these two questions be better phrased?

B. We stipulate that potential energy must be readily convertible to kinetic energy (or simply other forms of mechanical energy). Often one sees the expression that force is (minus) the derivative of potential energy with position.

- i. Are these two restrictions compatible with each other?
- ii. Does either of these restrictions follow from the other, or is it possible to have one restriction without the other?

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**N**ewton laid a solid base for classical physics with the concepts of force, mass, acceleration, and momentum. At the same time, Leibniz was attempting to develop his alternative structure for physics giving primary emphasis to  $m\mathbf{v}^2$ . He had selected a path that was initially far more difficult, but proved over the following two centuries to be extremely powerful.

In one sense, momentum is a more difficult concept because direction is important. Momentum is a vector quantity, with components that are fully independent of each other. Each component is conserved, so the total  $p_x$  for the universe (or for system and surroundings) is constant for every kind of process;  $p_y$  is constant; and  $p_z$  is constant, regardless of the type of

### Short Answers to Pre-Test Questions.

a. Kinetic energy is energy of motion, typically (but *not* necessarily) describing motion in a straight line or an approximation to a straight line. For low speeds, it is  $\frac{1}{2} m v^2$ . To avoid confusion, some forms of energy of motion (such as rotational energy) are usually excluded from kinetic energy.

b. Potential energy is energy that depends on position, but may be readily converted to kinetic energy.

c. Thermal energy is the energy contained within a body or substance that changes with temperature, or with change of phase, as in melting or boiling.

d. The principle of equipartition of energy, applicable in its simple form at customary temperatures, is a statement that thermal energy is equally distributed among the various modes of (thermal) energy storage, with the amount in each mode proportional to temperature.

e. Mass is a measure of the total energy of any body or substance. Hence mass *cannot* be converted to anything else, nor can energy be converted to (or from) mass or anything else.

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interaction.

On the other hand, momentum is far simpler because it is *always* a product of a mass and a velocity,  $\mathbf{p} = m\mathbf{v}$ . Equally important, it is *always* transferred from one body, or system, to another by a force acting for a time interval,

$$\Delta\mathbf{p} = \int \mathbf{f} \cdot dt$$

where  $\mathbf{f}$  may vary with time,  $\mathbf{f} = \mathbf{f}(t)$ .

By contrast, to understand energy, we must recognize that energy may exist in different “modes”. It may be kinetic energy, it may be rotational energy, it may be vibrational energy, or it may be any of the various “hidden” forms of energy such as gravitational, or electrical, or magnetic, or internal energy modes including thermal or chemical or nuclear. It may involve obvious motion, or it may depend on relative positions. Until you have learned to recognize the various modes of energy storage, energy will appear very mysterious. Many people have difficulty identifying where energy is stored and how it is transferred.

In contrast to momentum, energy may be transferred between objects, or systems, in a variety of ways. Sometimes (but not always) a force acts through a distance. Sometimes energy is transferred primarily, or entirely, because of a temperature difference. It is often a temptation to generalize, but this is quite likely to lead us astray.

“Energy”, as *vis viva*, or roughly “live power” or “live force”, was first introduced by Leibnitz (in contrast to the “dead force”, *vis mortua*, attributed by Leibnitz to Newton). Leibnitz introduced  $mv^2$ , and argued vehemently that Newton was misleading people with his  $mv$ . (The importance of a factor of one half was not recognized until it was introduced by Coriolis in 1835.)

In 1699, Huygens recognized the seemingly improbable result that in collisions of “elastic” bodies, not only was momentum conserved but also  $mv^2$  was preserved — constant for the impacting bodies.<sup>1</sup> Thomas Young, early in the 19<sup>th</sup> century, proposed the name *energy* with a broader definition. Energy of motion became known as “actual” or “dynamic” energy, a term replaced in 1856 by Kelvin with *kinetic energy*.

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<sup>1</sup> An “elastic” body is defined by this property that kinetic energy is preserved.

Although energy was exploited heavily in solving many problems, including orbit problems in astronomy, it was not until 1850 that energy was shown to be one of the unifying concepts for all of physics, and more than another half century before the underlying importance of energy to Newton's concepts of force, mass, and acceleration was revealed. Even today, there is substantial disagreement and misunderstanding of this very important concept that underlies much of modern science.

We will follow a semi-historical development of energy primarily because such an approach begins with simple, relatively concrete ideas and gradually adds sophistication, leading from Newtonian physics to the physics developed during the twentieth century.

When discussing position, acceleration, momentum, and angular momentum it is generally clear that we ascribe these properties to a specific object. It will often be convenient to refer to the object as the *system*. As we enter the discussion of energy, which can often be hidden from view, we will want to consider the movement of energy from one system to another, or from the system to its *surroundings*. For the present, however, it will be sufficient to ascribe energy, whether it is kinetic energy, rotational energy, or other forms, solely to the system, *except* in discussions of potential energy.

## 7.1 Kinetic Energy

Energy of motion, or *kinetic energy*, is usually defined as the difference between the total energy of an object and the energy of that object with center of mass at rest (with respect to the observer), in the same location.<sup>2</sup>

$$K.E. = E - E_0$$

For speeds that are not too large (much less than the speed of light in vacuum), the kinetic energy has a very simple form,

$$K.E. = \frac{1}{2} m v^2 = p^2/2m$$

Energy of motion, or kinetic energy, always depends on the square of a speed or speed-like coordinate. (The speed is measured relative to the observer.) The SI unit of energy is  $1 \text{ kg}\cdot\text{m}^2/\text{s}^2$ , which is called a *joule* (rhymes with pool), with symbol J.

Like momentum, energy of motion must be measured relative to some arbitrary reference frame, with the value dependent on the choice of frame. For example, a car parked at the curb has no kinetic energy (or momentum) in the reference frame of the curb, but it does have kinetic energy (and momentum) in the reference frame of a passing bus. The total energy of the car depends also on other properties, such as location and temperature. In Newtonian mechanics, we cannot measure energy on an absolute scale. We can only measure energy differences.

Thus, although we typically represent energy by  $E$ , or equivalent form, the meaning (in Newtonian physics) is always  $\Delta E$ . There is an implicit understanding that we are measuring an energy difference above some implicit reference level in an implicit frame. For example, if we are

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<sup>2</sup> Strictly interpreted, this common definition eliminates rotational energy from kinetic energy, which is a common, but certainly not universal, choice. We will encounter ambiguous examples, such as a rolling body, where it appears preferable to relax the definitions.

discussing kinetic energy,  $E$  will represent energy of motion of an object relative to the object at rest in the observer's frame. The reference level and the reference frame will usually be apparent, but that does not make the choice of reference frame unimportant.

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Examples 7.1. A. A satellite with  $M = 1000$  kg has a speed of 8000 m/s. What is the kinetic energy of the satellite?

B. The satellite launches a probe of mass  $m = 1$  kg in the forward direction with a (relative) speed of 1000 m/s. What energy must the satellite give the probe?

C. An observer on the ground notes the probe moving at a speed of 9000 m/s. What energy does he calculate for the probe?

D. Where did the probe get, or lose, the extra energy?

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Energies measured within any single reference frame are additive. The total energy of any system is the sum of all the different forms of energy. When energies are measured in different frames, extra care is required because of the  $v^2$  dependence of energy on reference frame.

7.1.1. *Particles.* Newton's laws, and the implications he drew from them, are applicable to any body. Clearly the first law and third law say nothing about the size or shape of the body in uniform motion or interacting with some other body. But the second law, also, describes the motion of the center of mass of an object, acted on by a force, independent of the size or shape of the body. Even the point of application of the force, or forces, is irrelevant. Newton's mechanics dealt with the motions of the centers of mass of bodies, as if they are equivalent to spherical bodies interacting with each other.

Other investigators later added more details, including torques and their consequences, and developed equations that are applicable *only* for certain bodies that are often called *particles*. Usually we interpret "particle" to mean a small body. In mathematics a *point particle* has zero size, but point particles are of limited value in physics because point particles necessarily have zero (or infinitesimal) chance of collision. In nuclear physics a particle usually refers to one of the family of particles that come from nuclei and atoms: electrons, protons, neutrons, neutrinos, and the particles with very short lives, for example. Other times, a particle may be a bit of sand or a blood cell or some other bit of matter of what we might consider intermediate size.

In physics, particularly with respect to kinetic energy, it is convenient to introduce a distinctive definition of a particle, which we therefore call a "physical particle":

*A physical particle is an object of any size or shape that may have kinetic energy, but cannot (or does not in the processes we consider) change its energy in any way except a change of kinetic energy.*

More explicit attention is given to physical particles in section 8.13. Failure to distinguish between general equations of physics and equations that are applicable only to particles has caused many errors.

## 7.2 Potential Energy

Understanding energy is made more difficult by the lack of a sufficiently sensitive general-purpose energy meter. Energy is often “hidden” from us, only becoming apparent when it is changed into one of the more recognizable forms. The existence of this “latent *vis viva*” was first recognized in 1803 by Lazare Carnot (father of Sadi Carnot; section 9.5). Such hidden energy forms tend to cause confusion as to where (and how much) energy is stored. In 1853 the non-moving energy source was called *potential energy* by W.J.M. Rankine. We now include such potential energy as a form of real energy, but retain the archaic name, potential energy.

Because potential energy was initially defined somewhat indirectly, it was not given a clear operational definition. Following customary current practice, we include within potential energy

- a) only those forms of energy that depend on (relative) position, and
- b) only those forms that are directly convertible to kinetic energy.

For example, a force applied to a spring produces a distortion and storage of energy, as potential energy, that is given back when the spring is released slowly. But if we (permanently) bend a piece of metal, the energy is increased a measurable amount because of strain energy. That energy is convertible to kinetic energy only through a multi-step process, so it is not generally included in potential energy. (It will show up, for example, if the strained metal is substituted for unstrained metal in an electrochemical cell.) Although an applied force causes the strain, relief of the strain does not yield a force, as it would from the potential energy in a spring. Energy may be stored also in other forms, such as chemical energy, not convertible to kinetic energy in a single step.

*7.2.1. The Field Model.* Newtonian physics is based on a very simple concept. When any object is pushed or pulled (*i.e.*, acted on by a net force), the motion of the object will be changed. That push or pull must come from some other object, which implies a subtle problem. Two objects, whether large or small, seldom if ever actually come into contact.<sup>3</sup> But if the two interacting objects are not “in contact”, then we must consider the two as “acting at a distance”. How can a far-away object exert a force?

The first satisfactory answer to this problem was to define certain “fields”. A field is a description of a region of space where forces are exerted on an object not in physical contact with whatever object is exerting the force. For example, we say that the Earth is surrounded by a “gravitational field” that exerts a force on objects near the surface or far away. (Similarly, a charged rod is surrounded by an “electrostatic field” and a magnet is surrounded by a “magnetic field”.) Then it is the field, produced by one object (*e.g.*, the Earth), that interacts with the system we are considering. (Mathematically, the two objects enter the equations symmetrically, so we could say it is the ball that is attracting the Earth, as implied by Newton’s third law. We could go a step farther and describe interactions as occurring between two fields, but it is seldom, if ever, advantageous to do so.)

The field model has two advantages. First, it is all inclusive, because even touching objects

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<sup>3</sup> Typically when we think two bodies are in contact, closer examination reveals a separation. One nuclear particle invading another might be very close to contact, but even there true contact is unlikely.

Answers 7.1. A.  $K.E. = \frac{1}{2} m v^2 = \frac{1}{2} \times 1000 \times (8000)^2 = 3.2 \times 10^{10} \text{ J} (= 3.2 \times 10^7 \text{ J/kg})$

B.  $\Delta(K.E.) = \frac{1}{2} \times 1 \times (1000)^2 = 5 \times 10^5 \text{ J}.$

C.  $\frac{1}{2} \times 1 \times (9000)^2 = 4.05 \times 10^7 \text{ J}.$

D. Apparently the probe had an energy of  $3.2 \times 10^7 \text{ J}$  and was given a  $\Delta(K.E.)$  of  $5 \times 10^5 \text{ J}$ , for a total kinetic energy of  $3.25 \times 10^7 \text{ J}$ , except that these values are measured in different reference frames so the energies are not simply additive.

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have some very small separation in practice, especially between the bulk of the two objects, so we can say that *all* interactions occur by means of these invisible fields. You may believe you are in contact with the Earth, but in fact you are, effectively, about  $6.4 \times 10^6 \text{ m}$  (4000 mi) from the center of the Earth, which may be considered the center of the attractive force. Even the repulsive force between atoms and molecules of your feet and the surface on which you stand is an interaction through the electrostatic fields of the electrons and with the electrostatic fields of the nuclei in which the electrons move. Second, by defining a field, we can introduce mechanisms that introduce a time for interaction over a distance, so that we don't violate logic by having a very distant object instantaneously affect local objects. The fastest that any signal can move is the speed of light in vacuum, so when the Sun moves, it must take at least 8 minutes or so for the Earth to be affected by that motion. Fields allow us to provide such delays.<sup>4</sup>

A *disadvantage* of the field model is a matter of notation. We nearly always define each symbol, unless specifically marked otherwise, as describing a property belonging to the object, or system. When we introduce a field we ascribe certain properties to the field, rather than the system. In particular, we typically define  $E$  and  $V$  as energy, or potential energy, assigned to the field that is interacting with our system. There is some ambiguity in the assignment, which we will return to later, but special care is required to keep the energy attribution consistent.

Force and energy are often directly related. The rate of change of height with distance as you go up a hill is called the *gradient* of the hill, and is measured along the steepest path. Similarly, when we can associate a potential energy with a body in a field, the force acting on that body depends on the rate of change (in space) of that energy. For example, a body of mass  $m$  at a height  $h$  in a uniform gravitational field of strength  $g$  has an associated potential energy

$$E = V = mgh$$

The *rate of change of V*, with respect to height, tells us the force acting on that body.

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<sup>4</sup> An alternative method, which is powerful but more difficult to visualize, is to assume "third party" bodies that carry the interaction. The electromagnetic force is carried by photons. The gravitational force has been assigned to particles called *gravitons*. Other interactions, between nuclear and sub-nuclear particles, have been assigned to other particles, some of which have only recently been confirmed experimentally or are still being sought. It is not hard to imagine particles carrying energy between bodies. It is not difficult to imagine particles exerting repulsive forces. (Think of throwing a medicine ball back and forth.) It is more difficult to visualize particles exerting attractive forces on separated bodies. We will usually not be concerned with the model that describes particles as carrying interactive forces.

We may write this

$$f = -\frac{\Delta V}{\Delta h} \quad \left( \text{with other variables held constant} \right)$$

or, more compactly, as

$$f = -\frac{\partial E}{\partial h} = -\frac{\partial V}{\partial h} = m g$$

For example, if you lift a box in a gravitational field, energy is stored (in the field)<sup>5</sup> and that stored energy may be recovered, as kinetic energy, if the box is dropped.

Quite generally, if potential energy is defined in the problem under consideration, the force is the (negative) *gradient* of the potential energy,  $V$ , which is measured along the direction of greatest rate of change. By contrast, there is no potential energy associated with a frictional force, and chemical energy does not fit this expression for potential energy.

Potential energy may also be defined for a single object. When we compress a spring, energy is stored in the spring. That energy may be recovered, as kinetic energy, if we anchor one end of the spring and allow the loose end of the spring to push against a cart when the spring is released. The energy stored in a spring, when it is stretched or compressed by an amount  $\Delta x$ , is

$$\Delta V = \frac{1}{2} k \Delta x^2$$

The force exerted by the spring (on whatever had compressed or stretched the spring, or whatever retards its return to normal) is

$$f = -\frac{\partial V}{\partial(\Delta x)} = -\frac{\partial}{\partial(\Delta x)} \left( \frac{1}{2} k \Delta x^2 \right) = -k \Delta x$$

The constant  $k$  is called the *spring constant*, or the *Hooke's law constant*. The minus sign indicates that the force exerted by the spring is opposite in direction to  $\Delta x$ . The force exerted by the spring tends to restore  $\Delta x$  to zero. Hence the force is zero only when  $\Delta x = 0$ .

### 7.3 Rotational Energy

As we saw in Chapter 6, a special form of motion is a mass moving, under the constraint of a radial force, in a circular path. In the simplest form, we let  $v = \omega r$ , with  $r$  constant. Then the

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<sup>5</sup> Mathematical notation is generally a means to an end — an attempt to represent a physical situation in a convenient and compact form. The partial derivative notation is an example, with some good features and some weak features. Here we represent a derivative with respect to a vector quantity, which tells us to be aware of directional properties but does not specifically tell us whether the force and height should be a scalar product (intended here) or a vector product (as in some later examples). The field exerts a force on the body so, as previously mentioned, we describe such stored energy as stored in the gravitational field. It will be necessary to refine this definition later (secs. 13.3-13.4 and 14.3-14.4).

energy of motion is the kinetic energy of the mass, which may be written as

$$\frac{1}{2} m v^2 = \frac{1}{2} m (\omega r)^2 = \frac{1}{2} (m r^2) \omega^2$$

The product  $m r^2$  that appears in most problems involving rotation, which is the *second moment* (i.e., involving  $r^2$ ) of the mass,  $m$ , about the origin, is called the “moment of inertia”. It is generally represented as  $I$ . The simplest type of rotational motion therefore has an energy that may be written as

$$E = \frac{1}{2} I \omega^2$$

If the rotating object is more complex, with different values of the moment of inertia in different directions, or if the rotation is about a point other than the center of mass, the equations for energy of rotation become more involved. In particular,  $I$  may no longer be a simple number. We will consider some of these complexities later. For now, the simple formula is adequate.

Although rotational energy is a form of energy of motion, and therefore can be called kinetic energy, it is usually important to distinguish between the energy of motion *of* the center of mass and the energy of motion *about* the center of mass, so we call the former *kinetic energy* and the latter *rotational energy*.

A rolling body has both kinetic energy,  $\frac{1}{2} m v^2$ , and rotational energy,  $\frac{1}{2} I \omega^2$ . We will find it is possible to combine the two parts of the equation to define a new moment of inertia for rolling:

$$E = \frac{1}{2} m v^2 + \frac{1}{2} I \omega^2 = \frac{1}{2} I' \omega^2$$

and will find similar alternative values for  $I$  when rotations are about other axes in section 10.1.

## 7.4 Oscillatory Motion

If a mass is attached to the end of a spring, which is anchored at the other end, the mass may acquire kinetic energy,  $\frac{1}{2} m v^2$ , and the spring may acquire potential energy,  $\frac{1}{2} k(L - L_0)^2$ . Consider a system that includes both the spring and the mass. The total energy, of mass and spring, at any moment is then

$$E = \frac{1}{2} m v^2 + \frac{1}{2} k(L - L_0)^2$$

That energy is called *vibrational energy*.

As the mass moves toward the equilibrium position of the spring ( $L = L_0$ ), the spring gives up (potential) energy to the mass, increasing the (kinetic) energy of the mass. As the mass moves away from the equilibrium position of the spring, it gives up its (kinetic) energy to the spring, increasing the (potential) energy of the spring. The vibrational energy of this system is preserved, to a good approximation, as energy is transferred back and forth within the system.

Similar oscillatory behavior is shown by a pendulum in a uniform gravitational field. A simple pendulum consists of a mass, called a *bob*, at the end of a rod or a cord. It is assumed that the rod or cord has negligible mass and that the mass of the bob is concentrated at a point. Position of the bob is described by the length,  $\ell$ , and the angle from the vertical,  $\theta$ . The displacement is  $\ell\theta$  so the speed of the bob at any point is  $v = d\ell/dt$ . The kinetic energy of the pendulum bob is the energy of swinging of the bob (rotational energy with respect to the point

of suspension),<sup>6</sup> at the radius  $r = \ell$ .

$$\frac{1}{2} m v^2 = \frac{1}{2} m (\dot{\vartheta} \ell)^2 = \frac{1}{2} (m \ell^2) \dot{\vartheta}^2 = \frac{1}{2} I \dot{\vartheta}^2$$

The potential energy of the bob plus the gravitational field, when the bob has risen through the angle  $\theta$ , is

$$V = f \cdot h = mgh = mg\ell \sin \theta$$

For small values of  $\theta$ , this is adequately approximated by

$$V = m g \ell \theta$$

Again, energy is passed back and forth between the kinetic energy of the bob and the potential energy of the bob *and field*, with total energy constant.

Kinetic energy, rotational energy, vibrational energy, and potential energy are conveniently lumped as *mechanical energy*. Mechanical energy may be exchanged without loss between different forms, for idealized systems. Thus mechanical energy is often, but not always, very nearly a *constant of the motion* for a system that includes both the donor and the recipient of the energy. That is, mechanical energy is often *preserved*. Only *total* energy is conserved.

## 7.5 Internal Energy and Temperature

Brevity and accuracy often conflict. We define kinetic energy as  $K.E. = E - E_0$ , where  $E_0$  is the energy of the system at rest (with respect to the observer). We define internal energy as energy of the system at rest (with respect to the observer). Potential energy is energy of position (easily convertible to kinetic energy), usually attributable to a field. Potential and vibrational energy of the system are forms of energy of motion not usually included in kinetic energy nor in internal energy. We must be aware of the difficulties of labeling, which vary with our purposes.

All ordinary matter is constructed from atoms and molecules, which in turn are constructed from electrons and other small particles. Changes of energy associated with changes of position or changes of motion of the particles within a system are generally described as internal energy.

There are important limitations, or quantum effects, that restrict the exchange of energy between the small parts of the system. Even so, much of the energy may be exchanged freely between different modes of energy storage. Kinetic energy associated with a velocity component  $v_x$  may be converted to energy associated with  $v_y$  or  $v_z$ , or passed in whole or in part to another particle. Kinetic energy may be converted from translational energy to rotational energy or vibrational energy. Because the particles themselves are so small, the amounts of energy so

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<sup>6</sup> There is an unfortunate conflict of symbols here. For circular motion,  $d\theta/dt$  is equal to the angular speed,  $\omega = \omega_s$ . For the pendulum bob,  $\theta$  measures the angle and  $\omega = \omega_\theta = 2\pi\nu$  is the angular frequency. These two  $\omega$ 's are different;  $\omega_\theta = \text{angular frequency}$  is constant for the pendulum motion but  $\omega_s = d\theta/dt = \text{angular speed}$  changes constantly during the motion. See secs. [12.1, 12.3]. Therefore, in this section, we choose  $\dot{\vartheta}$  for angular speed and  $2\pi\nu$  for angular frequency.

transferred are extremely small (typically on the order of  $10^{-21}$  J). We may think of the energy as moving from one substance to another in very small lumps (or *quanta*) of energy, like grains of sand or molecules of a liquid. Hence the energy flow, although inherently discontinuous, may be compared to the flow of a “continuous” fluid. The way in which this supply of energy is distributed within any system at equilibrium turns out to be important, in theory and in practice.

Imagine a very large number of mountain lakes. Some of these lakes are isolated from their neighbors. The levels of the isolated lakes will be individually determined. But many other of the lakes are connected by pipes or by small, horizontal streams. They have not only the same width, but also the same bottom, or zero level. Furthermore, all lakes that are connected maintain the same upper level of water in each. Over a substantial range of water depth, the water is equally divided, or *equally partitioned*, between the connected lakes. The same amount of water is required to raise each lake to the same height.

The distribution of energy among different energy states, or storage modes, in matter is quite similar to the mountain lakes. There are isolated lakes (such as those corresponding to nuclear and electronic energy states). Energy is not easily passed back and forth between these isolated states. But there are also many interconnected lakes, corresponding to (internal) translational kinetic energy, rotational energy, and vibrational energy (at least for low-frequency vibrations). A thermometer in contact with the substance reports a value that corresponds to the upper surface of the energy reservoirs — *i.e.*, the energy level of each of the interconnected energy reservoirs. A thermometer gives the same reading whether it samples translational energy, or rotational energy, or any other form of energy shared between the many molecules. This principle is known as the *equipartition of energy*.

Thus, for example (*considering for convenience at the moment **only** average values*), a molecule of water at 25°C has a velocity component along the  $x$  axis such that the energy is

$$\frac{1}{2} m v_x^2 = \frac{1}{2} kT = \frac{1}{2} \times k \times 298 \text{ K}$$

and has rotational energy, about *each* of three axes, of<sup>7</sup>

$$\frac{1}{2} I_i \omega_i^2 = \frac{1}{2} kT = \frac{1}{2} \times 298 \text{ K}$$

whereas the same molecule, at 125°C, has energies

$$\frac{1}{2} m v_x^2 = \frac{1}{2} kT = \frac{1}{2} \times k \times 398 \text{ K}$$

and

$$\frac{1}{2} I_i \omega_i^2 = \frac{1}{2} kT = \frac{1}{2} \times 398 \text{ K}$$

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<sup>7</sup> Rotational energy may be written in terms of angular momentum components.

$$\frac{1}{2} I_i \omega_i^2 = L_i^2 / 2I_i$$

It is worth noting that conservation laws apply to the angular momentum values, but this has no effect in determining the values of  $L_a$  vs.  $L_b$  vs.  $L_c$ .

This is despite the facts that

a) the translational motion was restricted by quantum effects to a lattice motion at lower temperature (in ice) and lattice motions only approximate unrestricted translational energies at higher temperatures;

b) the conversion of ice to liquid, partially freeing up the translational freedom, requires 330 J/mol (at 0°C);

c) the conversion of liquid water to water vapor (at 100°C) requires 2.25 kJ/mol;

d) the rotations are largely “frozen” at low temperatures (in ice) and only partially “unfrozen” in liquid water; and

e) the moments of inertia ( $I_a$ ,  $I_b$ ,  $I_c$ ) are quite different, and therefore — at any given temperature — the angular speeds are quite different.

The equipartition principle is easily summarized:

The average amount of energy in each of the reservoirs is

$$E_i = \frac{1}{2} kT$$

where  $k$  is the constant  $1.38066 \times 10^{-23}$  J/K, known as the Boltzmann constant, and  $T$  is the temperature, in kelvin. Thus, for example, the kinetic energy of a single molecule is the sum of the energies in the  $v_x$ ,  $v_y$ , and  $v_z$  reservoirs of that molecule, or the average value<sup>8</sup> is

$$\langle K.E. \rangle = \frac{3}{2} kT$$

which, for room temperature (298 K) is  $6.2 \times 10^{-21}$  J. The total molecular translational kinetic energy per mole at ordinary temperatures is

$$\langle K.E. \rangle = \frac{3}{2} RT$$

where  $R$  is the gas constant, or Avogadro’s number times  $k$ ,

$$R = N_A k$$

for a total translational kinetic energy of 3.72 kJ/mol.

There are two significant points. First, although the expressions for the different forms of energy (translational kinetic energy along each axis, rotational energy about different axes, and potential and kinetic energies of various low-frequency vibrational modes) involve quite different

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<sup>8</sup> Usually kinetic energy follows quite closely the classical expression,  $\frac{1}{2} m \vec{v}^2$ , not only in gases but also in liquids and even in solids. There is a more general form of the equipartition principle applicable to energy states that do not fit the quadratic dependence. The average value of a coordinate,  $q_i$ , times the rate of change of energy with respect to that coordinate is equal to  $kT$ :  $\left\langle q_i \frac{\partial E_i}{\partial q_i} \right\rangle = kT$ . But even this more general result breaks down at quite low temperatures where quantum effects become important.

constants, the *average energy* in each of these modes is the same. Second, it is this average energy that is measured by a thermometer within the range of ordinary temperatures.

*Temperature is a measure of average energy  
in each of the internal degrees of freedom in equilibrium.*

All of the energy of an object, at rest in the observer's reference frame, may be called *internal energy*. (For convenience, we may arbitrarily include here rotation and/or vibration of the system about its center of mass as internal energy.) Most of the internal energy is in isolated reservoirs (primarily nuclear, chemical, and electronic). We will usually be primarily concerned with the relatively small portion of the internal energy that changes when the temperature of the system changes. This portion, which is in equilibrium between modes, is called the *thermal energy*. It is *only* the thermal energy that is described by the law of equipartition of energy.

## 7.6 Conservation of Energy

The best known of all the conservation laws is the law of conservation of energy. Unfortunately, it is often misunderstood and misquoted. To begin with (as for other conservation laws), the law of conservation of energy *does not* usually tell us anything about whether energy is constant for the system. Conservation of energy applies only for the system *and* its surroundings.

Also, there are no conservation laws that apply to portions of the energy. There is no law of conservation of mechanical energy. Sometimes mechanical energy is preserved (*i.e.*, is constant for the system); sometimes it is not; but in neither case is it helpful to claim that mechanical energy is conserved.

Conservation laws are often expressed as a condition that the quantity (*e.g.*, energy) is a constant for an *isolated system*. But an "isolated system" is not defined. It is not possible to hold the volume, energy, and momentum of a system constant without exerting forces, or pressures, on the system by the surroundings. Furthermore, we could not carry out an experiment on an isolated system. Isolated systems are a convenient fiction, but for very limited purposes, only. The meaning of "isolated system" must be defined each time it appears.

As for other conservation laws, the simplest statement is:

*E is constant (for system plus surroundings).*

Conservation of energy is an experimental law. It cannot be derived from theory.<sup>9</sup> Because it tells us nothing directly about whether the energy of a system is constant, it has very limited applicability. Yet it is one of the most important principles in physics. It tells us some very important things about how any system interacts with its surroundings.

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<sup>9</sup> Although it cannot be derived from theory, it is fundamental to construction of theories in physics. It can be tied to symmetry of space and time, as was shown by Emmy Noether (1882-1935) in 1915-18; that is, energy is *not* a function of time. Kinetic energy is tied to momentum through Newton's laws *for a physical particle*, but this is a limited link that did not prevent serious questioning of conservation of energy by some prominent physicists in the 20<sup>th</sup> century. Conservation of energy is now widely accepted as universally valid.

## 7.7 Other Properties of Energy

Well before Galileo there was a general acceptance that heat and light were associated. The discovery of the Bologna rock, a naturally occurring piece of barium sulfide, BaS, that phosphoresced, without heat, was an early step toward separating the concepts. Whereas Galileo attempted to explain thermal energy as “atoms” of heat, Newton proposed that internal vibrations were responsible, which was backed by the discoveries of Count Rumford a century later.

Joseph Black (1728-1799) studied medicine at Glasgow, which included newly instituted lectures in chemistry by William Cullen. When Cullen moved to Edinburgh, Black took over his positions in chemistry and medicine and undertook a series of experiments on heat and temperature (stimulated by meeting James Watt). It was Black who is given credit for the “Zeroth law of thermodynamics” which he called the “equilibrium of heat”, the observation that objects in equilibrium with each other come to the same temperature.<sup>10</sup> He also recognized that different materials have different heat capacities (per gram, per mole, or per unit volume) and gave the first account of the heat of fusion and heat of vaporization, which acquired the label of “latent heat” because the “heat” involved in the phase transition had no apparent effect (on temperature). He was the first to attempt the distinction between “heat” (meaning thermal energy,  $E$ , and thermal energy transfer,  $Q$ ) and temperature. He also studied reactions involving gases and showed that weight was preserved in such chemical reactions.

Antoine Lavoisier (1743-1794) developed the first cohesive theory of chemistry. He refuted the phlogiston model of combustion — *i.e.*, the idea that combustion was the escape of a mysterious substance, “phlogiston”, from the burning material. He advocated a model of “heat” as a fluid, which he called *caloric*<sup>11</sup>. A few years later, Rumford showed, by his cannon-boring experiments, that the supply of caloric must be unlimited and, in fact, more was released from the metal when the metal was *not* cut (because of a dull cutter) than when it was cut.<sup>12</sup>

Half a century later, the relationship of thermal energy to mechanical energy was first generally recognized. The theory was developed by Julius Robert von Mayer, a physician, James Prescott Joule (1818-1889), inheritor of a family brewery, William Thomson (1824-1907), later Lord Kelvin, and Hermann von Helmholtz (1821-1894), a physician recognized for work on physiological optics, nerve impulses, electricity and magnetism, and many other fields. The quantitative conversion of mechanical energy to thermal energy was recognized and this was

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<sup>10</sup> The equilibrium of heat may be considered a precursor of the law of equipartition of energy, which extends the equilibrium from bulk matter to each of the modes of thermal energy storage. We now recognize that the “Zeroth law” is one of the consequences of the Second law of thermodynamics.

<sup>11</sup> Caloric, or calorique, is the French word equivalent to “heat” in English. Lavoisier’s model appears, lightly disguised in Black’s terminology, in many current science books.

<sup>12</sup> Rumford supported the earlier arguments of Newton, but his interpretation was largely rejected because Lavoisier’s theory was “more modern”. Lavoisier lost his head during the Revolution. His conclusion was that “the Revolution has no need of chemists.” Rumford subsequently married Lavoisier’s widow. (Some said Lavoisier got the better end of the deal.)

correlated with the conversion of thermal energy to mechanical energy by steam engines. By about 1850 the basic understanding required for a statement of conservation of energy had been gained.

7.7.1. *Quantization of Light.* The equipartition principle soon followed, but then was brought into question by measurements of radiation as a function of temperature. It could be shown, by what seemed to be fundamental physics, that the energy radiated should be proportional to the square of the frequency of the radiation (the Rayleigh-Jeans law). But this predicted that infinite energy would be radiated in the limit of high frequencies, a conclusion backed neither by experiment nor logic. It was called “the ultraviolet catastrophe” for its wild prediction and, especially, for its apparently devastating effect on the underlying physics. Max Planck attempted to find a way around this problem by means of a model in which energy would be transferred from a solid to the radiation field in chunks, with the intent that the size of the chunks would then be permitted to shrink and become infinitely small. He found, however, in 1900 that the model worked too well — it appeared to fit new experimental data precisely, but *only* if he kept the size of the chunks, or *quanta*, finite. Specifically, the energy had to be transferred in units of

$$\Delta E = h \nu$$

with  $h = 6.6 \times 10^{-34}$  J·s. Planck was uncomfortable with the result, stressing that it did *not* mean that the radiation itself was in any sense lumpy.

About the same time, the photoelectric effect was under investigation. When ultraviolet light is shone on an active metal surface, such as zinc, electrons are given off. Einstein rejected the theory proposed to explain this effect, turning instead to Planck’s result and re-interpreting it to say that the radiation itself consisted of quanta of size

$$E = h \nu$$

With this new model, in 1905 Einstein made predictions of the energies of electrons emitted, as a function of the incident frequency, and the lack of a time delay in first emission when the light source was very weak. Experimental results continued to support the earlier theory for several years,<sup>13</sup> but Einstein’s model was subsequently confirmed by experiments. This “particle” model of electromagnetic radiation proved to be extremely important in the development of physics. It was the photoelectric effect, rather than some seemingly more important contributions, for which Einstein received the Nobel prize.

7.7.2. *Mass as a Measure of Energy.* Einstein also provided a new understanding of the principle of relativity. It was necessary that the speed of light in vacuum should be constant for all observers and all sources. The Galilean formula for addition of velocities had to be replaced by a new formula when the speeds were not small compared to the speed of light. This, in turn,

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<sup>13</sup> The subject can easily be followed through *Science Abstracts* (later *Physics Abstracts*) which gives a brief summary of each step in the investigations.

predicted the apparent contraction of lengths and the expansion, or dilation, of time intervals, when the measurements are made by an observer moving with respect to the rulers and clocks. Mass lost its independence.

Newton's second law tells us that an object at rest or in uniform motion will not change its state of motion without the application of a non-zero net, or total, force, which can only be an externally applied force. It follows that an object cannot change the position of its center of mass at all (beyond any uniform motion described by the first law — *i.e.*, as measured in its local unaccelerated frame) unless an external force is applied.

Einstein proposed a *gedanken* (thought) experiment. Consider a railroad car with a cannon inside pointed toward the opposite end of the car. If the cannon is fired, a shell, carrying mass and momentum, passes from one end of the car to the other. To satisfy conservation of momentum, the car must move in the direction opposite to the shell motion, but will be brought to rest when the shell hits the opposite wall. (We assume it does not pass through!) The center of mass of the car, including cannon and shell, cannot move during this process, according to Newton's laws. If the shell is fired toward the east, the car must move toward the west. The center of mass remains unmoved, which means the center of mass must now be closer to the eastern end of the car.

Consider then, Einstein suggested, a similar experiment in which a photon, or a pulse of light, replaces the shell. When the photon moves from one end of the car to the other, it carries with it a predictable quantity of momentum,  $E/c$ , according to electromagnetic theory. The car must move, while the photon is traveling, but come to rest when the photon is absorbed. At the end, the center of mass of the car (plus photon, although the photon no longer exists; only its energy remains) must be in the same location as at the beginning, despite the car motion. Thus we must conclude that the photon has carried with it a predictable amount of mass. That mass, which may be calculated from this *gedanken* experiment or from other paths, is

$$m = \frac{h\nu}{c^2} = \frac{E}{c^2}$$

Expressed another way, Einstein recognized that one cannot have momentum without mass.<sup>14</sup> From other arguments, Einstein had already predicted this general relationship between mass and energy.

The interpretation has proven difficult for many people. Basically, it tells us that the quantity we know as the mass of an object is a measure of the (total) energy of that object. Thus every kilogram of matter, at rest with respect to the observer, represents an energy of  $8.99 \times 10^{16}$  J. This is the internal energy and is subject to change if the object loses energy or is given additional energy. A nucleus may give off energy, falling to a lower energy state, reducing its proper mass. (Both the energy and the mass then appear in the surroundings.) Also, if the object is given a high speed, the mass, as well as the energy, may increase dramatically. This effect is well known for small particles, such as electrons, which increase in mass by a large factor when they move in

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<sup>14</sup> A photon does not exist, as such, at rest, so it is meaningless to speak of a mass of a photon at rest. Moving at the speed  $c$ , in vacuum, the photon has energy  $h\nu$  and the mass  $h\nu/c^2$ .

large accelerators.

It is often necessary, therefore, to distinguish between the internal energy or rest energy, also called the *proper energy*, which we label  $m_0$ , and the total energy. The total, or actual, energy will be greater than  $m_0$  if the body is moving with respect to us. The general equation<sup>15</sup> is

$$E = mc^2$$

with the special case, for the observer and mass in the same reference frame (*i.e.*, at rest with respect to each other),

$$E_0 = m_0c^2$$

The general expression, therefore, for the kinetic energy of an object, at any speed  $v$ , is

$$K.E. = mc^2 - m_0c^2$$

if we include the energy of (overall) vibration and rotation as part of  $m_0$ . For speeds that are small compared to  $c$ , this expression for the kinetic energy reduces to

$$K.E. = \frac{1}{2} m v^2$$

7.73. *Special equations for physical particles.* Most systems, or most objects, are not physical particles; that is, they can change energy in ways other than a change of kinetic energy. In special relativity, however, emphasis is often placed on physical particles because they are simpler to deal with and yet allow illustration of many of the important points.

The change in energy of a physical particle may be written

$$dE = f dx = \frac{dp}{dt} dx = v dp$$

which has been confirmed, experimentally, as valid in special relativity. We add the definition of momentum,

$$p = mv \quad \text{or} \quad m = \frac{p}{v}$$

and therefore

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<sup>15</sup> Recall that we have no fundamental definition of mass except the operational definition based on Newton's second law (and/or on Newton's gravitational equation). The definition requires that we supply an artifact as a standard mass. This is accomplished with a platinum-iridium block and its replicates stored in various countries around the world. Any measurement of mass is then a comparison with the standard kilogram. What is measured, or compared, is always the total mass,  $m = E/c^2$ . Although the differences are beyond present measurement sensitivities, this means that if we were to warm the standard mass, we would increase its energy, and therefore its mass. It is necessary (in principle, and achieved in practice) to have the standard and the comparison mass at the same temperature, at the same gravitational height, and at the same speed, relative to the observer. Keep in mind that  $m$  and  $m_0$  are fully equivalent descriptions, except that one is limited to objects at rest with respect to the observer.

$$E = mc^2 = \frac{pc^2}{v}$$

The product of equations gives

$$E dE = \frac{pc^2}{v} v dp = c^2 p dp$$

which integrates (between  $E = E_0$  and  $E = E$ , and  $p = 0$  and  $p = p$ ) to give, for the physical particle,

$$E^2 = E_0^2 + (pc)^2$$

Provided  $m_0 > 0$  (*not*, for example, a photon, which doesn't exist at rest and thus doesn't have a defined  $m_0$ ), we may substitute  $E = mc^2$ ,  $E_0 = m_0c^2$ , and  $p = mv$  to obtain

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} = \gamma m_0$$

Here the restriction to physical particles is particularly apparent. For example, if we consider the energy transformations within a hydrogen molecule, we know that the vibration (at  $1.3 \times 10^{14}$  Hz) gives the hydrogen atoms a variable speed, yet there is no change in energy or mass of the molecule with time.

It has recently become popular to represent  $m_0$  by  $m$  and represent  $m$  by  $\gamma m$ . Then the previous equation may be simplified.

$$K.E. = mc^2 - m_0c^2 = (\gamma - 1)mc^2 \quad (\text{Letting } m \equiv m_0)$$

This has the advantage of eliminating a subscript, but the disadvantage of accurately representing *only* physical particles. We therefore avoid this shortcut.

**7.7.4. Conservation of Mass.** We have already seen that energy is a conserved quantity. Although the energy of a system may change, the change is equal and opposite to the change in energy of the surroundings, so the energy of system plus surroundings remains constant.

Now we see that mass is a measure of energy. Einstein immediately recognized that this implies that mass is also conserved. There is no experiment yet recognized in which the total mass of system plus surroundings changes, just as there is no experiment in which the total energy of system plus surroundings changes. Although conservation of mass had been assumed previously, the measurements were insufficiently sensitive before the 20<sup>th</sup> century (and measurements of radioactive processes) to detect changes of mass associated with changes of energy. Einstein's results show that mass is indeed conserved, but it is not an independent result.

Rather, it follows from conservation of energy.<sup>16</sup>

7.7.5. *Geodesics*. The theory of relativity as initially proposed by Einstein, usually called the *special theory of relativity*, is quite satisfactory in the types of problems we have considered. There are difficulties, however, when the theory is pushed a little farther.

For example, we know there is a change of energy of a body in a gravitational field, but a change in energy implies a change in mass and it is the mass, interacting with the field, that determines the energy. Thus the argument becomes circular.

Newtonian mechanics, and thus the special theory, requires reference of all motions to an unaccelerated reference frame, or an “inertial” frame. Furthermore, there is a gap in the theory because there is no explanation within Newtonian mechanics, or the special theory, for the *equivalence principle*, which is the statement that a gravitational field is indistinguishable, by local measurements, from an accelerated reference frame. Because this principle is not otherwise explained, Einstein concluded that it must, itself, be a fundamental principle.

Looking for a foothold to construct a more comprehensive theory, Einstein recognized that every experiment requires that the measuring apparatus and the object of the measurement must be in the same place at the same time. Under these conditions, the question of whether the observer and apparatus is in an inertial frame or an accelerated frame becomes irrelevant. Physics becomes (comparatively) simple when it is analyzed locally, considering only one time and place at a time.

When we introduce fields and potential energy, we can express a force (for idealized cases, at least) as a *gradient*, or rate of change of energy with position. Einstein showed that some problems in physics cannot be adequately solved with classical interactions through fields.

If we plot the motion of an object as position vs. time, as shown in Figure 7.1, and we see a change in slope, we can easily recognize that the velocity has changed, so the object has been accelerated. From this we conclude a force must have acted on the object. But if we look at Figure 7.2, we see the same motion is represented by a straight-line trajectory, which is the shortest distance between two points (called a *geodesic*). In this representation, it is the

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<sup>16</sup> This brings us back to the frequent confusion between conservation laws and preservation statements. It has often been noted that, in a nuclear reaction, for example, mass is not preserved. The mass of the nucleus changes when energy is emitted. But in every such case, mass is conserved, because the loss of mass by the nucleus is equal to the gain in mass by the surroundings, just as the loss of energy by the nucleus is equal to the gain in energy by the surroundings. The same argument, with smaller numbers, applies to chemical reactions and other processes. Einstein’s wording (“Does the Inertia of a Body Depend Upon Its Energy Content”, *Annalen der Physik*, **17**, 1905; Dover, *The Principle of Relativity*) was, “The mass of a body is a measure of its energy-content; if the energy changes by  $E$ , the mass changes in the same sense by  $E/c^2$ .” Note especially that the relationship is *not* an “either-or”, Jekyll and Hyde connection in which one form is converted to the other, an unfortunate misunderstanding as if  $\Delta E = - \Delta mc^2$ .

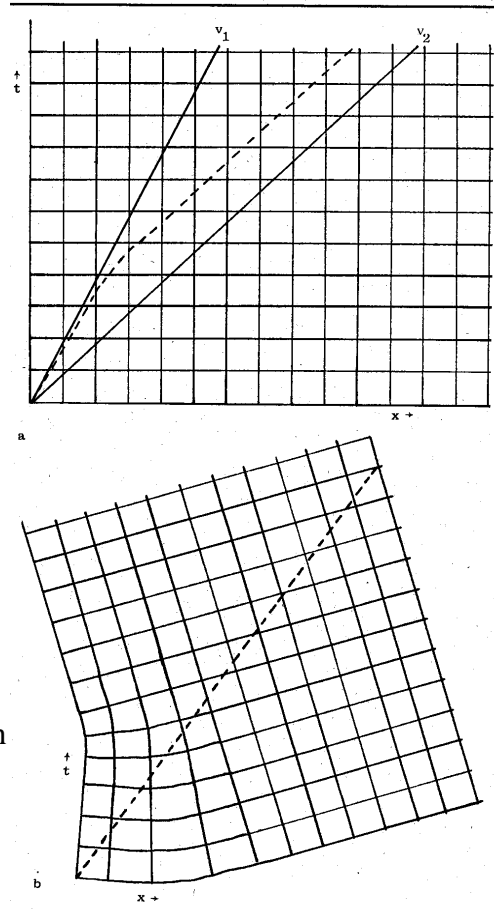
Figure 7.1 The straight lines,  $v_1$  and  $v_2$ , represent bodies moving at constant speed. The curved (dashed) line shows a change of slope, hence an acceleration, caused by a force acting.

Figure 7.2 The dotted line is now straight, in the curved space-time coordinate frame. The freely-falling body follows a geodesic (shortest distance path) in curved space-time.

coordinate system representing space-time that is curved. Whatever would exert a force, in Newton's description, must be responsible for distorting space-time, in Einstein's description. We already know a typical cause of a force on a body is a large mass. A massive body, such as the Earth or the Sun, exerts a force on an object nearby and thus accelerates the body. Alternatively, we may say that the large mass distorts space-time, so the object follows a straight line in curved space-time, but its path is no longer a straight line in uncurved space-time (Figure 7.1).

Recognizing that any experiment requires the object under study and the detectors for measuring the state of the object to be in the same place, at the same time,<sup>17</sup> he removed the concept of force from the center of attention. Newton's laws are no less important for applications of physics, but they should now be considered as a consequence of more general principles, rather than as fundamental postulates. The more general principles show how concepts such as force, mass, and momentum are obtained from energy and space-time.

But then, we can recognize that the large mass,  $M$ , is equal to a large energy,  $E = Mc^2$ . So rather than describing space-time as curved by a large mass, we may equally well say that space-time is curved by the presence of a large energy. In this sense, then, it is energy that gives rise to forces. The presence of energy = mass causes space-time to curve. Space-time, in turn, tells matter how to move. Furthermore, because space-time is connected from one region to another, a curvature of space-time in one region necessarily causes a curvature in space-time in other regions. Thus matter "here" affects the motion of matter "there", a result we had previously achieved by introducing a *force field*. Forces are replaced by geometrical properties of space-time.



<sup>17</sup> It might seem that we can measure objects at a distance by means of light beams — we can see the Sun without touching it. But the light that travels from an object to our detector is part of the measuring apparatus. Thus, for example, we lose all information about what is happening at the Sun while we are waiting (8 minutes) for the emitted light to arrive.

It is important, however, to distinguish between curved space-time, as shown here, and curved space. At present there is no evidence to indicate that space, itself, is curved.

One of the goals of the new formulation was to provide an understanding of the equivalence principle. Nothing in Newtonian mechanics explains why a gravitational field should have an effect indistinguishable, by local measurements, from an acceleration. Because acceleration, curvature of space-time, and forces are unified into a single model in the new theory, the equivalence principle is automatically satisfied.

This new approach to describing physics is far more powerful than Newton's description. Commonly known as *general relativity*, it was introduced in 1915. Techniques for solving many problems with this mechanism have been developed in the succeeding years. The theory has been extensively tested and found necessary for very large distances and for very large masses. Unfortunately it leads to more difficult mathematics than Newtonian physics, so we will not pursue this alternative except in a very cursory fashion.

Newtonian mechanics predicts the behavior of matter for objects that are not too small, not too large, and not moving too fast. Modified as necessary, for high speeds and very small particles or very large energies and distances, Newtonian mechanics works very well for *almost* every problem we will need to consider, so we will follow the easier mathematical path, dealing with forces and, when necessary or helpful, with fields that link remote objects.

#### Chapter Summary

Kinetic energy is energy of motion, which for moderate speeds is  $\frac{1}{2} m v^2$ . We define a *physical particle* as an object (of any size) that changes *only* its kinetic energy. Potential energy is energy of position that is directly convertible to kinetic energy. Potential energy is usually associated with a field that transmits forces between non-touching objects. The rate of change of potential energy with position is (minus) the force exerted by the field. Rotational energy of a body with moment of inertia  $I = mr^2$  is  $E = \frac{1}{2} I \omega^2$ . Vibrational energy is of the form  $E = \frac{1}{2} m v^2 + \frac{1}{2} k (\Delta x)^2$ , where  $v$  is the relative speed ( $v = d/dt(\Delta x)$ ). For a pendulum,  $mgh = mg\ell \sin \theta$  or, approximately,  $mgh = mg\ell \theta$  for small angles. For normal temperatures, most forms of thermal energy have an average energy of  $\frac{1}{2} kT$ , so temperature is a measure of the average energy, for each such contributing mode of thermal energy. This is known as the equipartition of energy. Energy is constant for system plus surroundings for every process; *i.e.*, energy is conserved. Energy of a beam of light may be considered as a sum of energies of particles, or photons, each with energy  $E = hv$ . Mass is a measure of total energy;  $E = mc^2$ . Mass is therefore also conserved. Physics may be extended to large distances, large masses, and accelerated systems with Einstein's general relativity, or geodesics.

## Chapter 8. Transfer of Energy

### Chapter Introduction

#### A. Why?

Energy is important because of the ways in which it is transferred. In particular, the transfer of thermal energy (as “heat”) causes the sensation of warmth and coldness, and the transfer of energy as work is associated with changes of motion and/or of potential energy.

#### B. What to Look For

In practice, most energy transfers are neither classifiable as heat nor work, but are only approximations to these idealized processes, or are transfers associated with the transfer of matter (as in delivery of fuel or addition of material to a system). Distinguishing real processes from idealizations often requires thoughtful analysis but is omitted from most discussions.

#### C. Pre-Test for Prior Comprehension

- What are the several distinct meanings of “heat” within the context of physics?
- How is “work” defined?
- What is the “imposter” equation that is often confused with “work”?
- What is the “first-law equation” and how is it related to the first law of thermodynamics?

#### D. Inquiry Question

Nomenclature has been a difficulty in describing energy and its transfers from the very beginning. Select a standard physics textbook and decide, each place in which the term “heat” appears, whether the author is intending to describe

- thermal energy
- transfer of thermal energy
- temperature
- warming of an object
- other, or indeterminate

For the same textbook, each place that the term “work” appears, decide whether the author is describing

- a transfer of energy between a system and its surroundings, by means of a force acting through a distance, or
- a dissipation of energy, within a system or with transfer of energy to surroundings
- other, or indeterminate

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**I**n the opening chapters we have looked at changes of position, including time-rate-distance equations, and how an applied force changes the motion, introducing acceleration. We considered momentum as a description of motion, and introduced angular speed and torque to describe

## Short Answers to Pre-Test Questions

a. “Heat” may mean

- i. thermal energy
- ii. the transfer of thermal energy between system and surroundings, represented by  $Q$
- iii. temperature (typically discouraged, but ancient and still common)
- iv. the verb meaning to add thermal energy and/or to raise the temperature of the system

b. The only important, consistent definition of work within the context of physics is as an example of transfer of energy to or from a system, involving a (macroscopic) motion. A subsidiary (provisional) definition is that work is equal to the (scalar) product of an applied force and the distance through which the applied force acts, summed over all the applied forces acting on the system.

c. Work is *defined* as the amount of energy transferred to the system as a consequence of a force acting through a distance. The “simplified” equation,  $W = \text{force} \times \text{distance}$  is sometimes valid but often not valid, unless the system acted on is simple enough (*a physical particle*) so that *only* the kinetic energy of the system can change, or when a single (uniform) force acts on all parts of a system equally (*e.g.*, a gravitational field). In these special cases,  $W = \Delta(K.E.)$ . The “imposter” equation is the second-law integral (*SLI*),

$$SLI = \int \left( \sum_i f_i \right) dx_{cm} \equiv \int f_{net} dx_{cm}$$

which typically is *not* equal to work.

d. The “first-law equation” is  $\Delta E = Q + W$ , so named because it often arises in connection with the first law of thermodynamics. It is *not* a fully general equation and, itself, does not express a conservation law.

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motions relative to a point, including circular motions. Then, in Chapter 7, we added energy, with its many disguises and names — kinetic, potential, rotational, *etc.* — and its important but obscure ties to temperature, mass, and force.

Now we consider ways in which energy can be transferred between objects or, as we generally prefer to describe it, between a system and its surroundings. Keeping track of energy as it is moved back and forth may be considered as a type of bookkeeping, known as *thermodynamics* because many of the transfers of interest occur because of temperature differences (thermo) or because of forces (dynamics). It is here that conservation of energy becomes important because it assures us that

$$\Delta E_{system} = - \Delta E_{surroundings}$$

The law of conservation of energy is called the first law of thermodynamics.

It will be very important that we choose, and carefully specify, what we want to include in our system. Then everything else becomes part of the surroundings. However, to avoid problems of cosmology, we define the surroundings as everything in the universe, except the system, that may be affected by the process under consideration.

We will look first at energy transfer processes classified as work, then take a look at

“imposter” expressions that are easily confused with work or are at risk of being substituted as approximations to work. Next we consider “heat” before concluding with other modes of energy transfer that are neither work nor heat, or close approximations to either. In the following chapter we will look at why things happen, and why all important processes must be explained in terms of probabilities.

## 8.1 Work

Work is one method (of several) for transfer of energy between two systems, or between a system and its surroundings. Thus

$$W = (\Delta E)_w$$

where the right-hand symbol represents the portion of the total energy transfer,  $\Delta E$ , occurring by the mechanism called work, involving forces and motions.

We have already seen, when the system exists in an external force field for which potential energy,  $V$ , is defined, that the force (due to the field) acting on the system is

$$f = - \frac{\partial V}{\partial x} \quad (\text{if } V \text{ is defined})$$

Careful attention to signs is typically required. For example, if a mass  $m$  is in a uniform gravitational field of strength  $g$ , the potential energy of the gravitational field is  $mgh$  or  $-m \mathbf{g} \cdot \mathbf{h}$ , with  $\mathbf{g}$  downward and  $\mathbf{h}$  upward. Thus the force acting on the mass (the system) is

$$f = - \frac{\partial V}{\partial h} = +mg$$

(downward) and therefore the change in potential energy of the field (surroundings) is

$$\Delta V_{\text{field}} = - \int f \cdot dh$$

The potential energy (of the field) increases as the mass moves upward ( $f \cdot h < 0$ ). This tells us that the integral of the force, exerted by the field *on the system*, integrated over the displacement of *the system*, is equal to the *decrease* in energy of the field, and therefore, invoking conservation of energy, equal to the *increase* in energy of the system. Typically, during the same process, energy is being supplied to the mass by some *other* external lifting force, so the energy of the mass remains constant while the energy of the field increases. Alternatively, the mass may be thrown upward, losing kinetic energy as the field gains potential energy, or the mass may drop, gaining kinetic energy as the field loses potential energy.

Such a process of energy transfer associated with a displacement is called *work*. Note the assumptions that are part of the definition:

- a. We know the force acting on *each* mass particle (easily satisfied for a uniform gravitational field because the force/mass ratio is the same for all parts of the body), and
- b. We know the distance through which *each* force acts (easily satisfied for the uniform

gravitational field because each mass element moves through the same distance under the action of the gravitational force).

However, most energy transfers do not meet the stringent conditions we assumed here, so we

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Examples 8.1. A. The product  $f dx$  appears quite simple and straightforward. Can you think of a process in which this simplified statement of work done on the system would be inappropriate?

B. How do we know that work done on the system is the negative of work done on the surroundings? (Or is it always true?)

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must be more careful in finding the work done in more general processes.

8.1.1. *Definition of Work.* It is easy to find examples for which the equation obtained above does not give a reasonable answer if we assume that  $dx$  describes the displacement of the system. For example, if you spin a bicycle wheel in place, you impart energy to the wheel but the center of mass of the wheel does not move. If you jump off the floor, your center of mass moves but the floor, which is exerting the upward force on you, does not provide you with any energy. If you apply equal and opposite forces to an enclosed gas, you can increase the energy of the gas by compressing it, even though there is no *net* force acting on the gas and the center of mass of the gas does not move. Later we will find that frictional forces are incompatible with the evaluation of work.

In other words, we cannot simply accept the overly broad generalization that force times distance is equal to work done. We require, first of all, from the fundamental definition, that

a) the work done is equal to the amount of energy transferred from the surroundings to the system,<sup>18</sup> because of the action of the force, and then we add the provisional<sup>19</sup> stipulation that

b) work is equal to the integral of the scalar product of the individual force and the displacement of the point of application of that force. Individual work contributions may be added together, but in general the forces may not be added before the individual integrations. Work done *on the system* is represented by  $W$ , so

$$W = \int \mathbf{f}_i \cdot d\mathbf{x}_i$$

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<sup>18</sup> This is now the most common sign convention. Early investigations emphasized steam engines and the work they did, and therefore chose the opposite sign for  $W$ . American authors retained this alternative sign convention long after European authors converted to a more consistent choice emphasizing properties of the system.

<sup>19</sup> Interestingly, there is apparently no published proof that this general definition of work done on a system is universally valid, but no exceptions seem to be known so we will consider the definition adequate. Recent attempts to introduce alternative expressions for “work” or for “work-like” terms lead to serious conflicts because they abandon the fundamental definition of work as  $W = (\Delta E)_w$ , and therefore they are not recommended.

where  $f_i$  and  $x_i$  indicate a single force and its point of application.

If more than one force is acting on the system, the work done on the system is a sum of such integrals,<sup>20</sup>

$$W = \sum_i \left( \int f_i \cdot dx_i \right)$$

If energy is transferred, because of forces, *within* a system, we are free to redefine the system(s) so these transfers, which are between different parts of the original system, become transfers between the new systems, or subsystems, and may be analyzed as work terms. Without such a redefinition of the system, we cannot legitimately describe internal transfers as work without violating the definition of work. “*Internal work*” is a contradiction of terms.

We are often interested in the integrand,  $f_i \cdot dx_i$ , the quantity appearing inside the integral, which is the infinitesimal amount of work that will be summed to find the total amount done on the system. Because

$$W = \Delta E$$

it is not appropriate to write an infinitesimal amount as  $dW$ , as if it were a differential (*i.e.*, an infinitesimal *change* in the quantity  $W$ ). This would lead to the equation

$$dW = d(\Delta E)$$

which is not at all what we want. We therefore introduce the symbol  $w$  for an infinitesimal *amount* of work. Then, quite appropriately,

$$w = dE$$

in the absence of other forms of energy transfer.

Work is a scalar quantity, which may be positive or negative. Positive work (in the usual convention) means that energy is transferred from the surroundings to the system. Negative work means the energy is transferred from the system to the surroundings.

*Because the system and surroundings labels are arbitrary, we may interchange system and surroundings without any change in  $W$  except its sign*

provided we can identify, at each stage of the transfer, the forces acting and the displacements of the points of applications of those individual forces.

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<sup>20</sup> Note especially that generally we would get a different, and incorrect, answer if we took the sum of the applied forces first, or if we substituted the displacement of the center of mass of the system. We return to this comparison in section 8.13.

Answers 8.1. A. Three common examples we discuss more carefully above are

- a. spinning a wheel: typically the work is done on the rim of the wheel, which moves in the direction of the force, but the displacement is not the displacement of the center of mass of the wheel, which remains stationary;
- b. when you jump from the floor, you move, but the force is acting on your feet only while your feet are in contact with the floor, so the force does not move and thus no work is done — no energy is transferred from the floor to you; and
- c. frictional force is at the molecular level and differs from one point along the surface to another and varies with time at each point. It is neither possible to calculate nor to measure energy transferred as work in any frictional process.

B. So long as “work” is well defined (forces and displacements of the points of application of those forces known) we may argue by the third law that the forces are equal and opposite and/or by conservation of energy that the energy transfers are equal and opposite, we know that work done on the system is the negative of work done on the surroundings.

We will usually assume the “reversible work” model is adequate. Then, for example, we can quite freely exchange labels on “system” and “surroundings” and apply our definition of work to the “new” system (formerly the surroundings).

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Examples 8.2. A. The simplest type of system on which we may do work is a physical particle. Applying Newton’s second law, find the effect of applying a constant force,  $f$ , to a physical particle of mass  $m$ , over a distance  $d$  for which the speed increases from  $v = 0$  to  $v = v$ .

B. Find the effect on a mass,  $m$ , in a uniform gravitational field,  $g$ , of applying a constant upward force,  $f$ , over a distance  $d$ .

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8.1.2. *Effects of Work Done on the System.* Although “work” stipulates how energy is transferred, it does not give us any clue as to the form the energy takes after the transfer. If the work is positive ( $W > 0$ ),

- a) the kinetic energy of the system may increase;
- b) the potential energy *of the system* may increase (*e.g.*, when a spring is stretched or compressed);
- c) the vibrational energy of the system may increase;
- d) the rotational energy of the system may increase; and/or
- e) the internal energy of the system (apart from *b*, *c*, and *d*, large-scale potential energy, vibrational energy, or rotational energy) may increase.

For example, if a net force acts on a piston that compresses a fluid, the energy of the fluid increases. To find the work done on the fluid, we apply the fundamental equation for work. The force acting *on the system* (the fluid) is the product of the pressure *of the fluid* times the area. The area times the displacement,  $dx$ , is the change in volume of the system. We add a minus sign because the pressure (of the system) acts in the direction *opposite* to the applied force,  $f$ . Thus, if

$P$  is well defined (fluid in equilibrium),

$$W = \int f dx = - \int P A dx = - \int P dV$$

The work done in compressing a fluid is equal to (minus) the pressure of the fluid times the change in volume of the fluid.<sup>21</sup> In a compression,  $\Delta V$  is negative, so the work done is positive.

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Examples 8.3. A. Liquids are typically “incompressible”, meaning that even a large pressure increase causes a change in volume small enough to be generally considered negligible.

a. Art says increasing the pressure must increase the energy of the liquid, even if the volume change is negligible.

b. Betty says that  $W = - \int P dV$  but  $\int V dP$  does not give any change in energy.

c. Charlie says  $\int V dP$  changes the product  $PV$ , so that must change the energy even though  $W = 0$ .

Which of these arguments (if any) would you concur with?

B. An old textbook problem asked for the work done *by* a gas as it expanded into a vacuum, from an initial pressure of 1 atm to a final pressure of 1/4 atm.

a. Ann found an equation that said  $W = - \int P_{ext} dV$  and reasoned that external pressure was  $P_{ext} = 0$ , so  $W' = W_{by\ system} = 0$ .

b. Bruce argues that  $P_{ext} = 0$  only initially. It then increased to a final value  $P_{ext} = 1/4$  atm. He said  $W' > 0$  but  $W' < 1/4 \text{ atm} \times \Delta V$ . He suggested  $W' \approx 1/8 \text{ atm} \times \Delta V$ .

c. Carol objected to substituting an external pressure for the pressure of the gas. She suggested inserting a piston (perhaps an ideal massless piston) to simplify the problem.

Which of these arguments (if any) would you support?

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Work done on a system by a gravitational field is a common problem. The force acting on the object acts equally on all parts of the object, and all parts of the object undergo the same displacement, so the work done on a falling body ( $\mathbf{g}$  parallel to  $d\mathbf{x}$ , opposite to  $d\mathbf{h}$ , which decreases) is

$$W = \int \mathbf{f} \cdot d\mathbf{x} = \int m\mathbf{g} \cdot d\mathbf{x} = -mg\Delta h > 0$$

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<sup>21</sup> Sometimes, because of friction or acceleration of the piston, the pressure exerted on the piston is quite different from the pressure exerted on (and by) the fluid. We have no particular interest here in what is happening to the surroundings. We must deal with the pressure and the volume of the system to find the work done on the system.

Answers 8.2. A.  $\int f dx = \int ma dx = \int m(dv/dt) dx = \int m(dx/dt) dv = \int m v dv = \frac{1}{2} mv^2$ . The work done on the physical particle starting at rest is equal to the final kinetic energy of the particle.

B.  $\int \mathbf{f} \cdot d\mathbf{x} = - \int m\mathbf{g} \cdot d\mathbf{x} = - mg \cdot \mathbf{h} > 0$ . The work done on the mass is positive, equal to the energy required to lift the mass through a height  $h$ , which is also equal and opposite to the work done by the gravitational field on the mass. Thus there is no net change in energy of the mass, but energy is transferred to the gravitational field (which may be recovered from the field if the mass is released and allowed to fall).

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Answers 8.3. A. Even though the product  $PV$  has the same dimensions and units as energy, it is not a measure of energy. Consider, for example, attempting to find the best “energy” value for  $PV$ . For an ideal gas,  $PV = nRT$ , but  $PV \neq nRT$  for a liquid. Also, even though the increase in pressure may be slow so that every part of the change is reversible, if  $\Delta V \approx 0$ , you will not be able to recover any energy put into the fluid by a large  $\Delta P$  when the pressure is again reduced. Thus answer  $b$  is the best of the three.

B. Without a piston, the gas exerts a force only on the walls of the (evacuated) container, which do not move, so  $a$  is correct for the wrong reason. If a piston is added to the problem, it cannot be massless (otherwise the acceleration should be infinite), the pressure exerted on the piston is indeterminate, and the work done by the gas goes to accelerate the piston. The students were misled by an incorrect starting equation.

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Because the object gains energy ( $W > 0$ ), it gains speed and kinetic energy.

Work done on a spring is

$$W = \int \mathbf{f} \cdot d\mathbf{x} = \int kx dx = \frac{1}{2} k(x_2^2 - x_1^2)$$

where  $x_2 \equiv x_f - x_0$  is the final extension and  $x_1 \equiv x_i - x_0$  is the initial extension, showing that the energy of the spring is increased, by work ( $W > 0$ ) done on it, if the final displacement,  $|x_2|$ , is larger than the initial displacement,  $|x_1|$ , whether these displacements are positive or negative with respect to the equilibrium position.

The last result confirms the answer obtained earlier, where we began with an expression for the energy of the spring and from that obtained the force acting on the spring. Here we start with the force and determine the energy change.

*8.1.3 Approximate Calculations of Work and an Imposter Equation.* The basic equation for work is (apparently) adequate for any type of process, provided we know the individual forces acting and the displacements of the points of application of those forces. Not all processes fit these criteria.

A common difficulty is a calculation of work done against friction, where the equation for work is surreptitiously replaced by an imposter equation. See if you can spot the sleight of hand.

If a block slides down a plane at constant speed, we might calculate work done on the block (for  $\Delta h$  negative, opposite in sign to  $\mathbf{g}$ ) as  $-mg\Delta h > 0$  for the work done by gravity and  $W = \int f_{friction} ds < 0$  for the (negative) work done by the plane on the sliding block. (The sliding block gives up energy to the plane.) The forces are equal and opposite if there is no acceleration of the block, and the distances are the same. Because these integrals are equal and opposite, the net work would appear to be zero which is consistent with the assumption that the block sliding at constant speed would not change energy.

However, we know that the block will be warmer at the bottom of the slope than at the top. On closer examination, we may recognize that the force of friction is a collection of small forces, acting on molecules of the block and molecules of the plane, and the displacements are displacements of the molecules before they break away and snap back to their initial equilibrium positions. Thus we do not know either the actual forces acting or the actual displacements of the points of application of those forces. We know only the sum of the forces, which is the quantity we call the force of friction. The equation for work, the sum of each force times the displacement of its point of application, has been replaced by a *net* force and a displacement of the *center of mass*.

Putting invalid quantities into the equations, we obtained an invalid answer. Certainly the surface does (positive or negative) work on the block, but we can only guess at the amount. We know quite a bit about the block sliding down the plane, but not the amount of work done on the block.

Similarly, if we allow a gas to expand against a light piston with only a small external pressure acting on the piston, the equation for work requires a value for the pressure of the gas to obtain the force acting on the piston. But in a rapidly expanding gas, there is no uniform pressure. (The problem is only made more severe by the typical trick of imagining the piston to have zero mass, because it must then have infinite acceleration.) We can only estimate the actual pressure on the piston, which is less than the equilibrium pressure (because the gas molecules do not fully catch up with the retreating piston) and therefore gives us an estimate of the work done by the gas, which is less than if the gas expanded under equilibrium conditions.

The initial consideration above of work done on an object in a field led us to an expression that appeared to be the net force exerted on the object times the displacement of the center of mass of the object. That result was correct, but it was for a special case and therefore misleading. Because the field acts equally on all parts of the object, the forces are all the same and the displacements are all the same, so we get the same answer if we substitute net force and displacement of center of mass for the individual forces and their displacements.

Consider the application of Newton's second law to a body being acted on by a net force. Newton's second law tells us how the *center of mass* of any object, or system, will change its motion when acted on by a (net) force. We may call this the "second-law integral" (*SLI*).

$$SLI = \int \mathbf{f}_{net} \cdot d\mathbf{x}_{cm} = \int m \mathbf{a}_{cm} \cdot d\mathbf{x}_{cm} = \int m \frac{d\mathbf{v}_{cm}}{dt} \cdot d\mathbf{x}_{cm}$$

Here we can treat the derivative as a ratio of differentials. Assuming the displacement and velocity are in the same direction (usually satisfied for such problems), we can write a general condition for change in kinetic energy,

$$\int \mathbf{f}_{\text{net}} \cdot d\mathbf{x}_{\text{cm}} = \int m \frac{dx_{\text{cm}}}{dt} d\mathbf{v}_{\text{cm}} = \int m \mathbf{v}_{\text{cm}} d\mathbf{v}_{\text{cm}} = \Delta \left( \frac{1}{2} m \mathbf{v}^2 \right)$$

This equation looks very much like the equation for work, but it is an imposter.<sup>22</sup>

To make the situation more confusing, as we saw for the field equation, sometimes the imposter equation gives the same values as the expression for work. Other times, it gives an absurd answer if interpreted as work. Consider again the person jumping off the floor. The point of application of the force (acting on the person) is the surface of the floor. The motion of the center of mass is the motion of the center of mass of the jumper. The integral gives the change in kinetic energy of the jumper. But the floor cannot supply any energy to the jumper. The floor does no work, although the floor (and Earth) does supply the momentum to lift the jumper. (Work done because of deflection of the floor is negligibly small and of opposite sign).

Be on the lookout for this imposter. It has made its way without warning into many textbooks. It links a legitimate calculation of a transfer of momentum to the system (and an equal but opposite transfer of momentum to the surroundings) to an apparent, but fallacious, calculation of transfer of energy (as work) from the surroundings to the system.

8.14 *Work, Energy, and Physical Particles.* Physical particles are an idealization, with special properties, subject to special equations. Some of these (including equations from sec. 7.73) are listed in Table I.

Table 8.1. Equations for Physical Particles<sup>a</sup>

$$W = \Delta(K.E.)$$

$$E^2 = E_0^2 + (pc)^2$$

$$m = \gamma m_0 = \frac{m_0}{\sqrt{1 - \frac{\mathbf{v}^2}{c^2}}}$$

<sup>a</sup>Generally not valid *except* for physical particles.

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<sup>22</sup> The expression has even been called “pseudo-work” (which means “not work”), but that has the unfortunate consequence of verbally linking this imposter equation with work. An alternative, less than fully satisfactory, name for the equation from Newton’s second law is the *momentum-kinetic energy equation*, emphasizing the dependence on Newtonian variables.

a. There can be no friction between a physical particle and any surface or medium, because friction involves conversion of kinetic energy to thermal energy (distributed between the objects or surfaces in contact) and change of thermal energy is forbidden for a physical particle.

b. Any work done on a physical particle changes the kinetic energy of the physical particle.

$$W = \Delta(K.E.)$$

This special condition has been labeled *the work-energy theorem* (or the *work-kinetic energy theorem*) and widely applied to other systems, for which it is *not* valid.

c. By integration of  $dE = v dp$  we obtain

$$E^2 = E_o^2 + (pc)^2$$

showing that, for physical particles ( $E_o$  not a function of  $p$ ) the rest energy and kinetic energy terms are orthogonal.

d. Because the energy of a physical particle is a function of speed, *only*,

$$m = \gamma m_o = \frac{m_o}{\sqrt{1 - \frac{v^2}{c^2}}}$$

Because these equations are typically derived in a context in which physical particles are tacitly assumed, the equations often enter the mainstream of physics expressions and appear under circumstances for which they are not valid.

## 8.2 Heat

Our understanding of heat progressed over several centuries, from the “atoms” of heat advocated by Galileo, to “caloric” fluid that moved unchanged from one body to another, to the modern interpretation in terms of certain forms of internal energy. Along the way, terminology was added and modified, with little attention to removing the litter from earlier, faulty models. We will find that “heat” is not a satisfactory technical term (even though it is frequently regarded as such). Not only does it not have an operational definition, it actually lacks a clear definition that can be agreed upon by a majority of physicists.

8.2.1. *Definition of Heat.* Today, “heat” has three quite distinct meanings, as a noun, in physics.

a) Heat means temperature. When we speak of a heat wave, or say “It’s not the heat, it’s the humidity”, we are speaking of high temperatures. Similarly, temperatures of metals are often characterized as “red heat” or “white heat”, because the apparent color of radiation from a body depends on the temperature of the body. Physicists usually reject this usage, but it is embedded in everyday language, and will not go away. (It’s part of the language most physicists use at home.) When there is no rise in temperature when a rise was expected, the heat is said to be “latent”.

b) In technical writing, heat most often means a portion of the internal energy. Specifically, it means that part of the internal energy that changes when the temperature changes, or when a substance changes phase, as for melting ice or boiling water. This portion of the internal energy is

best called *thermal energy*.

c) Nearly every careful writer on the subject introduces the subject with a definition of “heat” as equal to a quantity designated with the symbol  $Q$ , which is the amount of thermal energy transferred to a system from the surroundings. However, having given this definition, the writers uniformly revert to the terminology of heat equal to thermal energy.<sup>23</sup>

The consequence of this confusion of terminology is that often it is not possible, without great effort, to determine what meaning is assigned to the term “heat” by a writer or speaker. (The writer or speaker may not have consciously made that decision.) To avoid such confusion here, we choose the following definitions:

a) Temperature is called *temperature* (never heat).

b) The portion of internal energy that varies with temperature is called *thermal energy*.

c) The amount of thermal energy transferred to the system from the surroundings in contact with the system, solely as a consequence of the difference in temperature of the system and that portion of the surroundings, is designated by the symbol  $Q$  and, for lack of a better label, is called the *thermal energy transfer*.

$$Q = (\Delta E)_Q$$

Consistent with the notation for infinitesimal amounts of work, we will designate by the symbol  $q$  an infinitesimal amount of thermal energy transferred, so

$$q = dE$$

in the absence of other forms of energy transfer. If energy is transferred as *both* work and thermal energy transfer, we would obtain for an infinitesimal change

$$dE = q + w$$

or for finite changes,

$$\Delta E = Q + W \equiv (\Delta E)_Q + (\Delta E)_W$$

Unless otherwise restricted,  $\Delta E$  is the change in total energy, including kinetic and potential energies. This equation is known as the *first law equation*. It frequently occurs in problems where we are considering energy transfer between the system and surroundings, which is, like every other process, subject to the law of conservation of energy.

8.2.2 *Effects of Thermal Energy Transfer*. As might be expected from the definition of thermal energy, the addition of thermal energy to a system generally raises its temperature, with  $\Delta T$  proportional to the amount of thermal energy added.

$$Q = C \Delta T$$

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<sup>23</sup> Confusion of  $Q$  and thermal energy is closely analogous to an accountant confusing net income and net worth (or perhaps, closer to home, confusing net deposits for the month with your bank balance at the end of the month). It would be disastrous in business or for your finances and is (subtly) equally disastrous in thermodynamics.

where  $C$  is a constant that depends on the nature of the substance, the amount of substance, and, to a smaller extent, on the temperature and the nature of the process (e.g.,  $C$  is different if volume of the system is held constant, or if pressure on the system is constant). The constant,  $C$ , is called the *heat capacity*. It is often expressed as a value per unit of mass and called *specific heat*.<sup>24</sup>

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Examples 8.4. A. The heat capacity of liquid water at room temperature is 4.2 kJ/kg·K. How much thermal energy was added to 150 cm<sup>3</sup> of water (i.e., what was  $Q$ ) if the water is warmed by 35°C?

B. What  $Q$  is required to melt 250 g of ice, at 0°C? The *heat of fusion* of ice is 333.5 kJ/kg.

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However, when thermal energy is added to a mixture of ice and water, the temperature does not change. Similar effects are observed for water conversion to steam (at constant pressure) and other phase changes. The absence of a temperature increase was labeled “latent heat”, an anachronism that still appears today.

8.2.3 *Heat and Warm as Verbs*. As much as we might wish to speak and write clearly about the quantities of thermal physics, you will probably find it impossible to avoid vernacular terminology. We started with the idea that “heat” represented (primarily) either a portion of the internal energy or a transfer of thermal energy. Even those definitions are inadequate.

The overlap and confusion of “heat” and “temperature” is especially obvious, and inevitable, when we compare the verbs *to heat* or *to warm* with the adjectives *hot* and *warm*. For example, to heat a pan of water, you put the water over a flame or a “heater”. Usually this means that thermal energy is added (to the water),  $Q > 0$ , and (the water) gets warmer. But if the pan contains water and ice, or if the water was originally at its boiling point, heating the water may melt ice or boil water with no change of temperature. The “heat” was said to be “latent”, or “hidden”.

Also, it is possible to heat a system without adding thermal energy to it. The ancient practice of rubbing two sticks together produces enough rise in temperature to start a fire (under favorable conditions). Stirring some chemicals, or adding a spark of negligible energy, may cause them to react, releasing thermal energy, thus “heating them up”, releasing thermal energy that increases the temperature even though  $Q = 0$  (and often  $\Delta E = 0$ ). Or a gas may be heated by compressing it. Work is done on the gas, which raises the temperature of the gas.

One alternative might be to choose a single meaning of “heat” and attempt to exclude all other meanings, but we know that will not work. A better solution appears to be to accept “heat”

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<sup>24</sup> “Specific” quantities generally indicate the dimensionless ratio of a property for one substance to the same property for another. *Specific gravity* is the ratio of the density of a solid or liquid to the density of water, or the ratio of the density of a gas to the density of air. *Specific heat* was defined as the ratio of the heat capacity of a substance to the heat capacity of water, but with a change in units (from calories or BTU to SI) the definition has changed to “absolute”, rather than “relative” values, requiring units.

Answers 8.4. A.  $Q = 35 \text{ K} \times 0.150 \text{ kg} \times 4.2 \text{ kJ/kg}\cdot\text{K} = 22 \text{ kJ}$ .

B.  $Q = 0.250 \text{ kg} \times 333.5 \text{ kJ/kg} = 83.375 \text{ kJ}$ .

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in any of its traditional meanings, but substitute for it a “proper”, well-defined term when we wish to be clear.

8.2.4 *Uncertainties and Approximations in Measuring  $Q$* . It may seem that  $Q$  could always be measured. In practice, various difficulties arise. In principle, one can always find  $\Delta E$ , the gain in energy of the system, because  $E$  is a property of the system, or a “state function”, not dependent on the details of how the system reached the final state. But how that energy was transferred may well remain indeterminate. We saw, for a block sliding down a plane, that thermal changes are mixed with the transfer of energy as work. Similarly, if a gas is compressed or, especially, is expanded rapidly, turbulence can mix thermal changes with work. In general, we will find that anything that makes the system deviate from equilibrium conditions during a process will lead to mixed modes of energy transfer. We can then only estimate, or approximate, the value of  $Q$ .

A similar uncertainty arises when energy is transferred by radiation between objects at different temperatures. The radiation is, at least in principle, capable of producing a photoelectric effect, which can generate electrons at a voltage capable of doing work elsewhere.<sup>25</sup>

### 8.3 Other Modes of Energy Transfer

In an attempt to simplify thermodynamics, the “first-law equation,” written

$$\Delta E = Q + W$$

is often called the first law of thermodynamics. That is unfortunate. Not only does the equation fail to express the law of conservation of energy. It also is incomplete in describing energy transfers to and from a system. We need not go into all the methods of energy transfer, which may include electric, magnetic, and gravitational fields as well as surface tension and linear tension. Simply remember that there are terms missing from the abbreviated equation, which may be important.

One missing term that does require special consideration is the addition of material to a system. There can be several effects. First, there may be a reaction between the added substance and the material of the system. You may recall, for example, that concentrated sulfuric acid added to water causes strong heating of the solution. Adding “hypo” (sodium hyposulfite = sodium thiosulfate, long employed as a photographic “fixer”) to water causes the solution to cool. And, more generally, simply adding any substance adds mass and therefore

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<sup>25</sup> The reader may wonder why the definitions of  $Q$  and  $W$  are considered so important. To preserve the equations of thermodynamics it is necessary that  $Q$  and  $W$  represent transfers of energy between system and surroundings. The first-law equation suggests that it is only the sum of  $Q$  and  $W$  that must be known. However, we will find a cross link between  $Q$  and the property called *entropy* that requires an understanding of what is, or is not, included in  $Q$ .

energy to the system.<sup>26</sup>

A more subtle example, where  $Q$  and  $W$  are mixed along with material transfer, is a phase change such as boiling water. Although the process appears simple, there is a natural selection process occurring, in which the most energetic molecules selectively leave the liquid phase. This part of the energy transfer does not easily fit our idealized division into  $Q$  and  $W$ .

These variations from the ideal classification of energy transfers do not, in any sense, make thermodynamics wrong. They simply emphasize that the idealizations to which we become accustomed — reversible processes for which  $Q$  and  $W$  are sharply defined, like ideal gases, frictionless surfaces, and fluids without viscosity, represent simplified models that are a good starting point, but may require adjustment or refinement to fit realistic experiments.

### Chapter Summary

Energy may be transferred between a system and its surroundings as work, as “heat”, or in other ways. Work,  $W$ , is  $\Sigma(\int \mathbf{f}_i \cdot d\mathbf{x}_i)$  where  $\mathbf{x}_i$  is the displacement of the point of application of the force,  $\mathbf{f}_i$ . An imposter expression,  $\int \Sigma(\mathbf{f}_i) \cdot d\mathbf{x}_{cm}$ , often appears, which is sometimes equal to  $W$  but generally has no connection to  $W$ . “Heat”, or  $Q$ , is the transfer of thermal energy from a warmer body to a cooler body as a consequence of a temperature difference. Under non-equilibrium conditions, only approximate values of  $Q$  and  $W$  may be measured or calculated. Thermal energy transfer,  $Q$ , is typically measured by a change in temperature,  $Q = C \Delta T$ . Energy may also be transferred to a system by adding material, or by non-equilibrium processes that resemble  $Q$  and/or  $W$ .

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<sup>26</sup> The energy added is  $c^2$  times the mass added, but for most purposes we would look at a small part of this increase, above the rest energies of selected reference states.

7/27/07

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# Chapter 9. Probability and Heat Engines

## Chapter Introduction

### A. Why?

We have looked at how to describe what happens (kinematics) and at how things happen (dynamics and energy balance). Now we look at whether a process will occur — that is, at why things happen.

### B. What to Look For

In one sense, we can never say something will or will not happen. We can only say that some processes are more probable than others. But we will find that some processes are so probable, or so improbable, that they may safely be regarded as certain outcomes.

### C. Pre-Test for Prior Comprehension

- a. If there are 10 equally probable states available, what is the probability a system will be in any one specific state?
- b. How many ways can  $n$  objects be arranged (*e.g.*, in a straight line)?
- c. How many ways can  $m$  objects be put into  $n$  boxes?

### D. Inquiry Question

Describe a universe in which there existed a class of object for which there were no atoms and molecules, and thus no internal structure and, in particular, no internal degrees of freedom. For example, what probability would you predict for a ball (of such substance) rolling uphill rather than downhill? Could the conservation laws be satisfied? Would the physics be self consistent? Would it be necessary to postulate other changes in physical laws?

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**W**hy does a ball roll downhill? The obvious answer is that it moves to a lower-energy state, but that is clearly not correct, or at least not adequate. Overall, there is no change in energy in the process. Energy has no interest in “beauty pageants”; energy does not have a preference for one form over another. When the ball rolls downhill, potential energy (of the gravitational field) is converted to kinetic (translational and rotational) energy of the ball, but the total amount of energy remains unchanged. We might even expect the ball to keep rolling until it reaches the top of the next hill, at (almost) the same height where it began. Energy is important — nothing happens that does not satisfy the law of conservation of energy — but energy is not a sufficient explanation of why the ball rolls downhill, from rest, but will not roll uphill, from rest. For that we must look at probabilities.

## 9.1 Probability and Number of States

Dice have six faces, with numbers from one to six, so two dice can give values from 2 ( $1 + 1$ ) to 12 ( $6 + 6$ ). A value of five may be achieved in four ways ( $1 + 4$ ;  $2 + 3$ ;  $3 + 2$ ;  $4 + 1$ ) and

Short Answers to Pre-Test Questions

- a. With 10 possibilities, the probability of any one occurring is 1/10.
- b. There are  $n$  choices for the first position and one less for each subsequent position, or a total of  $n$  factorial =  $n! = n(n - 1)(n - 2) \dots(2)(1)$ .
- c. Assuming the objects are, at least in principle, distinguishable, there are  $n!/[(m!(n - m)!]$ . (Arrange the  $n$  objects, then divide by the arrangements of  $m$  boxes and arrangements of  $n - m$  “leftovers”.)

The point here is simply that if  $n$  is a large number (e.g., comparable to  $10^{23}$ ), the numbers of arrangements (permutations and combinations) is extremely large.

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seven in six ways (1 + 6, 2 + 5; 3 + 4; 4 + 3; 5 + 2; 6 + 1) as shown in Tables 1 and 2. So the probabilities of 7 to 5 and 7 to 2 or 12 are 6/4 and 6/1. Thrown properly, each (detailed) possible outcome is equally likely, but some (overall) outcomes are more likely than others. Such a

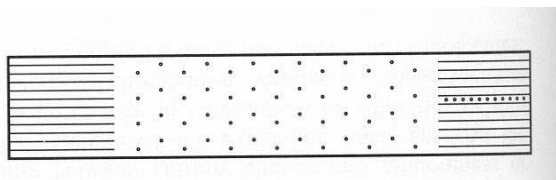
Die A	Die B	Sum	Die A	Die B	Sum	Die A	Die B	Sum
1	1	2	3	1	4	5	1	6
1	2	3	3	2	5	5	2	7
1	3	4	3	3	6	5	3	8
1	4	5	3	4	7	5	4	9
1	5	6	3	5	8	5	5	10
1	6	7	3	6	9	5	6	11
2	1	3	4	1	5	6	1	7
2	2	4	4	2	6	6	2	8
2	3	5	4	3	7	6	3	9
2	4	6	4	4	8	6	4	10
2	5	7	4	5	9	6	5	11
2	6	8	4	6	10	6	6	12

Sum	“Internal States”	No. Int. States
2	1+1	1
3	1+2, 2+1	2
4	1+3, 2+2, 3+1	3
5	1+4, 2+3, 3+2, 4+1	4
6	1+5, 2+4, 3+3, 4+2, 5+1	5
7	1+6, 2+5, 3+4, 4+3, 5+2, 6+1	6
8	2+6, 3+5, 4+4, 5+3, 6+2	5
9	3+6, 4+5, 5+4, 6+3	4
10	4+6, 5+5, 6+4	3
11	5+6, 6+5	2
12	6+6	1

The two faces of a pair of dice give the sum of the values shown in the third column of Table 1 (and subsequently across the table). These values are rearranged in Table 2 to show the number of ways in which each of the possible sums is achieved. Because emphasis is on the sum, the individual value pairs may be called “internal states”. Seven may be achieved in more ways (6) than five (4 ways) or 2 or 12 (1 way each).

process, in which the outcome is determined by chance depending on the relative number of possibilities, is called a *random* process.

Now consider a very large number of coins distributed randomly among a very large number of cups, so that each cup is likely to have a large number of coins but the actual number of coins in any one cup is totally unpredictable. Then we should expect that the most likely outcome would be a nearly equal distribution of coins among the cups. Furthermore, there will be a very large number of distributions that are essentially indistinguishable from an equal distribution. When we collect together all these essentially equivalent distributions, the relative probability becomes very much greater than other states in which the coins are distributed quite unequally. Careful mathematical analysis confirms these relative probabilities.



*Figure 9.1 Simple Pinball Machine*

Similar considerations apply, in a somewhat different way, to a very simple pinball machine consisting of a set of nails in a flat board, with channels at each end. If all the balls are initially in the center channel on the right, when the board is tipped the distribution will be symmetrical with a maximum in the center on the left. However, tipping the board back the other way does *not* return the balls to the center channel on the right, even though the individual collisions with pins are essentially reversible. Instead, balls from each channel on the left contribute to a symmetric distribution *about that channel* on the right, so the total distribution tends toward a uniform spread. Given an opportunity, the balls move toward a greater spread in states. The final state depends on the initial state, as well as the tendency toward a spreading of states.

What happens if an elastic ball is dropped onto a hard surface and bounces repeatedly? With each bounce, some of the kinetic energy of the ball is transformed into molecular kinetic energy, or thermal energy, within the ball. There are so many molecules in the ball (typically more than  $10^{20}$ ), and therefore so many “degrees of freedom”, or places for the energy to go (several modes per molecule), that the energy will be widely spread among the molecules. One place for any small quantity of energy to go is back into motion of the ball, but with so many other equally attractive destinations, each small quantity of energy has typically less than one chance in  $10^{21}$  of remaining in the single degree of freedom associated with kinetic energy of the ball as a whole.

If the energy is spread among the particles, as thermal energy, can it be gathered together again? Yes, but only because of spreading of a different kind. For example, a drop of water spilled onto the sidewalk soon disappears, even though energy must be supplied from the surroundings to evaporate the water. The “driving force” is that there are so many more possible locations for water molecules after they have escaped into the surrounding air than there were in the water droplet, that a molecule that has escaped is very unlikely to return to the water droplet. Thus in addition to spreading in energy space (or momentum space), we get spreading in ordinary space (coordinate space). One type of spreading may overcome another type, if the numbers work out.

We will define (below) a “spread” function,  $S$ , that will serve as a measure of probability. The technical name for the quantity  $S$  is *entropy*.<sup>1</sup> A positive change in entropy corresponds to an increase in probability; a decrease in entropy corresponds to a decrease in probability.

## 9.2. Reversibility and Equilibrium

We introduce idealizations into the equations of physics from time to time. For example, it is often convenient to imagine an object on a surface with no *friction* between them. For liquids or gases, this takes the form of assuming no *viscosity*, or friction within the liquid or with the walls. We may assume some objects or substances are *incompressible*, so there is no change in volume no matter how much we increase the pressure applied to them. We treat ideal gases, which follow the equation  $PV = nRT$  and for which energy is independent of volume.

We know there are no frictionless surfaces and no fluids without viscosity (at ordinary temperatures). There are no incompressible substances, nor ideal gases. Nevertheless, such idealizations are often quite adequate approximations to real systems. Even when the differences are significant, it is often helpful to undertake analyses and make calculations first with the idealizations, then find correction terms to achieve better agreement between calculations and experiments.

Similarly, real processes are seldom, if ever, truly reversible. Yet thermodynamics is built upon consideration of reversible processes.<sup>2</sup>

When can a process be reversed (in either direction), with no significant outside help? The previous section offers a guide. If the final state has approximately the same amount of spreading, in momentum and coordinate space, as the initial state, then there is no reason the system cannot return to the initial state. The process is then said to be *reversible*, or the states are said to be in *equilibrium*. From a macroscopic, or non-molecular, point of view, many reversible processes are described simply as “nothing happening”. For example, in a gas, molecular states are in constant flux, yet the temperature, pressure, volume, and other properties remain constant. More generally, we may describe a reversible process, such as a very slow expansion or compression, as one that can be reversed by an infinitesimal decrease in the driving force, or an infinitesimal increase in the opposing force, where for this purpose we interpret “force” as a cause that may be a real force, or a temperature difference, or a concentration difference, or anything else that will tend to cause the system to change from one state to another.

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<sup>1</sup> The name was chosen by Clausius from the Greek verb *entrepo* (*εντρεπω*), meaning “to turn,” implying “change”, and because it somewhat resembles the word *energy*, one of the important quantities involved in finding the number of states. Entropy,  $S$ , is proportional to (or for suitable units, equal to) the *logarithm* of the relative probability, *i.e.*, to the logarithm of the number of accessible states.

<sup>2</sup> There are some processes, such as scrambling an egg, that cannot be reversed even with external intervention. For economy of terminology, we almost always distinguish only between processes that can be reversed with external intervention, called *irreversible*, and processes that do not require significant external intervention to be reversed, called *thermodynamically reversible*, or simply *reversible*.

Time does not enter into thermodynamic equations. Nevertheless, because the net driving force is vanishingly small in a reversible process, it can be shown that a reversible process must be extremely slow, requiring an infinite amount of time.<sup>3</sup> Thus real processes are seldom, if ever, truly reversible. The thermodynamic equations therefore give us limiting values, for ideal processes or reversible processes.

Some variables, such as temperature, pressure, volume, and energy, are *properties* of the system that depend only on the state of the system, not on its history. Such quantities are therefore called *state functions*. Because the value of a state function does not depend on how the system arrived at the final state, values of changes of state functions do not depend on whether processes are reversible or irreversible. That is, values of  $\Delta T$ ,  $\Delta P$ ,  $\Delta V$ ,  $\Delta E$ , and  $\Delta S$  depend on the initial state and the final state but do not depend on the “path” the system follows in getting from the initial state to the final state.<sup>4</sup> When reversible and irreversible processes would naturally lead to different final states, we must add an extra step to bring the system to the same chosen final state for each case.

Reversibility and equilibrium are two descriptions of essentially the same thing. They are among the most important idealizations, or approximations, for describing change. Any study of *why* things happen leads directly to an exploration of relative probabilities and whether a change is between overall states of similar probabilities, and is therefore a reversible change, and hence a change between equilibrium states.

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<sup>3</sup> Assume the value of the entropy of the system with time may be described by some parameter,  $\lambda$ ;  $S = S(\lambda)$ . Then the change in entropy with time,  $(dS/dt)$ , may be written as a function of, or equation involving,  $(d\lambda/dt)$ . In general, such an equation may always be written in terms of powers of the variable,  $(d\lambda/dt)$ . Thus

$$\frac{dS}{dt} = a_0 + a_1 \left( \frac{d\lambda}{dt} \right) + a_2 \left( \frac{d\lambda}{dt} \right)^2 + a_3 \left( \frac{d\lambda}{dt} \right)^3 + \dots$$

If  $\lambda$  doesn't change,  $S$  cannot change, so  $a_0 = 0$ . If  $\lambda$  changes sign, then  $dS/dt = a_1(d\lambda/dt)$  would change sign, but we know  $dS/dt \geq 0$ . Therefore  $a_1 = 0$ , also. Thus we find

$$\frac{dS}{dt} = a_2 \left( \frac{d\lambda}{dt} \right)^2$$

plus higher-order terms and so  $dS/dt$  is zero, or very nearly zero (reversible process), if and only if  $d\lambda/dt \approx 0$ . A reversible process must be very slow.

<sup>4</sup> We are describing here only possible differences in the state of the *system*. If the system goes from state A to state B by an irreversible process, the changes in the *surroundings* may be quite different than if the change had been by a reversible path for the system.

### 9.3. Probability and Thermal Energy Transfer

Information about the relative probabilities of thermodynamic states (*i.e.*, states described by specific values of state functions, such as  $P$ ,  $V$ ,  $T$ , and  $E$ ) would not be of much help if it were necessary to find all the billions of internal states contributing to each state under consideration. Fortunately, there is a simple laboratory measurement that gives us direct information about relative probabilities. We look first at the procedure, then look at why we should expect the connection with probabilities.

9.3.1  $Q_{rev}/T$  as a Measure of Increase of Spreading. First we decide which of two states of the system we wish to compare. Call them, arbitrarily, states A and B. Then we find a suitable path that will take us from state A to state B. “Suitable” in this instance means we find a path that is sufficiently close to reversible, all the way, but within our available time frame. Then we measure the amount of thermal energy that is transferred from the surroundings to the system when the system changes along the reversible path. Call this amount  $Q_{rev}$

The amount of thermal energy absorbed by the system, in a reversible process, gives us information about the additional number of “packets” of energy spread around in the system. Now we want to know whether that number is very important or negligible. If there are already lots of such “packets” of energy available, a few more may be of minor importance. If there are not very many available in the system, even a few added may make a substantial difference. We know that temperature is a measure of average thermal energy (per degree of freedom), so we divide  $Q_{rev}$  by  $T$  to find  $\Delta S$ , the measure of the increase in the spread function.

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Examples 9.1. A. The “spreading function”,  $S$ , is a measure of spreading of energy or spreading in space (or both). What can you predict, from this, about the sign of  $Q_{rev}$  for a chemical reaction of dissociation, such as  $N_2O_4 \rightarrow 2 NO_2$  ?

B. Would you expect higher entropy or lower entropy for soft iron when it is magnetized compared to demagnetized iron?

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If  $Q_{rev}$  is divided by the temperature (on an absolute scale) at each step, the answer tells us whether state B is, by itself, more or less probable than state A. But it *does not* tell us whether the system will change from state A to state B, or from state B to state A. Consider lowering a mass of 1 kg by a distance of 1 m. That would seem pretty trivial, and likely to happen *spontaneously* (meaning not necessarily fast, but “on its own”, without interference). But suppose that mass is on an equal-arm teeter totter, with 10 kg (part of the surroundings) at the far end. Then lowering the 1 kg mass would not be expected to happen spontaneously. What happens to the surroundings can be important in determining what will happen to the system.

We must therefore also make the *same* type of calculation for the surroundings. That is, as the *system* changes, along a reversible path, from state A to state B, the surroundings change from what we may call state C to state D. We find the amount of thermal energy transferred to the surroundings (positive or negative) when the surroundings change from state C to state D along a reversible path. Call this amount  $(Q_{rev})_{surr}$ . This amount, divided by the temperature of the surroundings at each step, tells us whether the state of the *surroundings* is more or less probable when the system is in state A or state B.

Now we compare the two results. If the sum of the probability change for the system and the probability change for the surroundings is positive, the change is probable. That is, if

$$\frac{Q_{rev}}{T} + \left( \frac{Q_{rev}}{T} \right)_{surr} > 0$$

or more generally, if

$$\int \frac{q_{rev}}{T} + \left( \int \frac{q_{rev}}{T} \right)_{surr} > 0$$

(where  $q_{rev}$  is the infinitesimal amount of thermal energy transferred along the reversible path), then the change of the system from state A to state B is probable and may occur. We are taking the amount of thermal energy absorbed, divided by the temperature, along a reversible path, as our measure of probability increase.

The work done *on* the system is a minimum for a reversible process,

$$w_{rev} = w_{min}$$

but the change in energy is independent of path, because  $E$  is a state function. Therefore, assuming all energy transfer to be as  $Q$  or  $W$ ,

$$dE = dE_{rev} = q_{rev} + w_{rev} = q_{rev} + w_{min} = q_{max} + w_{min}$$

from which we see that  $q_{rev}$  must be a maximum. The maximum increase in the spread function,  $S$ , occurs for a reversible path. Therefore  $Q_{rev}/T$  gives the maximum percentage increase in spread of energy, and the best measure of the increase in probability of the final state in comparison to the initial state.

Because the number of molecules is enormous, the ratios of probabilities for states of different  $S$  are also enormous. Thus we may conclude (or demonstrate with more detailed calculations) that an increase in entropy for the system plus the surroundings is probable,<sup>5</sup> but any significant decrease in entropy, for system plus surroundings, is so highly improbable that it will not happen in the lifetime of the universe.

The probability principle can now be expressed, without any concern for molecules and internal states.

The change in entropy of the system ( $\Delta S_{system}$ ) plus the change in entropy of the surroundings ( $\Delta S_{surroundings}$ ) is greater than zero for any process that can actually occur, or is zero for a process at equilibrium which can go in either direction but would require a very, very long time (forever) to occur.

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<sup>5</sup> Processes are often more complex than they appear. Even if a process is “probable”, as judged by initial and final states, it may not occur because of intervening states. An iron ball dropped to the floor will not likely roll down to the lowest point of the ocean floor. Diamond is unstable relative to graphite, but does not convert at room temperature.

Answers 9.1. A. More particles corresponds to more degrees of freedom and therefore higher entropy. For the reaction as shown,  $\Delta S = + 175.8 \text{ J/mol}\cdot\text{K}$ .

B. Magnetized iron is more ordered and therefore has lower entropy.

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Often we can more easily predict the direction of a process than estimate the magnitude of the entropy change involved. Consider a drinking glass dropped onto a hard floor, or the reverse process in which the broken glass reassembles. We know the first process will go smashingly well; the second process does not happen. In principle we could experimentally determine the entropy change of the breaking of glass by devising a series of reversible steps, some of which would have to be carried out in reverse. For example, in this instance, we could warm the glass fragments and melt them. Then we could carry out the same process starting with an equivalent unbroken glass, ending again with molten glass. With careful measurements of  $Q_{rev}/T$ , we could find the entropy difference for the two processes. The difference then gives us  $\Delta S$  for breaking of the glass. (The uncertainty in the measurements, especially when we attempt to include the momentum in the initial state that caused the fracturing, would very likely be too large to make this measurement practical, but we feel very comfortable predicting the sign of  $\Delta S$ .)

*9.3.2 Another Example of Entropy Change.* Another familiar example of increase in entropy is a change of phase. Melting of ice, for example, involves breaking apart many moderately loose bonds between adjacent water molecules, replacing these with much weaker bonds in a more random structure in the liquid. Melting a gram of ice, at  $0^\circ\text{C}$  ( $= 273.15 \text{ K}$ ) requires a transfer of  $333.5 \text{ joule}$ . Dividing  $333.5 \text{ J}$  by the temperature of  $273.15$  gives a value of  $1.221 \text{ joule per kelvin}$ . If we make the calculation for the surroundings, which give up the  $333.5 \text{ J}$ , or absorb  $-333.5 \text{ J}$ , at the same temperature, the answer is  $-1.221 \text{ joule per kelvin}$ . Adding these together gives  $+1.221 + (-1.221) = 0$ , which shows, first, that the ice (starting point) and liquid water (end point), at  $0^\circ\text{C}$ , are in equilibrium. The process can go in either direction, ice to water or water to ice. It also reminds us that it will take a very, very long time to melt ice, or to freeze liquid water, if the surroundings are also at  $0^\circ\text{C}$ .

If, on the other hand, the surroundings of the ice are at a higher temperature than  $273.15 \text{ K}$ , the denominator is larger and the calculation for the surroundings gives a smaller (less negative) value. Then the sum, for system plus surroundings, is positive for melting ice (it will happen), but negative for the process of freezing liquid water (it won't happen, with the surroundings warmer). Similarly, if the surroundings are at a lower temperature, the calculation shows that the liquid water will freeze to ice, but the ice will not melt. The calculation gives results that we all knew beforehand.

In summary,

$$\Delta S_{\text{total}} = \left(\frac{Q_{rev}}{T}\right)_{\text{system}} + \left(\frac{Q_{rev}}{T}\right)_{\text{surroundings}}$$

and  $\Delta S_{\text{total}} \geq 0$  for any process that can occur. The probability principle, expressed in this form,

is known as *the second law of thermodynamics*.<sup>6</sup>

9.3.3 *Evaluation of Entropies*. The two important ideas underlying these calculations are, first, that molecules have no preference whatever for one internal, or microscopic, state over another, so they occupy such states randomly. Second, although we may easily imagine dice or a pinball machine in which the number of accessible internal states changes by a factor of 5 or 10 or 100, the number of molecules in any normal sample of matter is billions of billions of times greater. For even one gram of the simplest substance the number of possible states is likely to exceed, by far, a number with 23 digits before the decimal point. Consequently, what we calculate as a probability can be regarded, for most purposes, as a certainty.

Furthermore, the number of states increases markedly with temperature, volume, and mixing of substances. A change of temperature gives an increase in entropy on the order of

$$\Delta S = nC \ln T_2 / T_1$$

with the heat capacity,  $C$ , depending on the experimental conditions (but typically on the order of  $R = 8 \text{ J/mol}\cdot\text{K}$ ).<sup>7</sup> A change in volume is subject to a similar relationship,

$$\Delta S = nR \ln V_2 / V_1$$

which gives even larger factors because accessible volumes may change by much larger factors than accessible temperatures.

A third consideration is the spreading associated with mixing. If two distinct materials, such as oxygen and nitrogen gases, are put into the same container, they mix thoroughly, greatly increasing the number of possible microscopic states, which, of course, increases the entropy. The entropy of mixing, for ideal solutions, is

$$\Delta S = -nR \sum_i X_i \ln X_i > 0$$

where  $X_i$ , the *mole fraction*, is the number of moles of substance  $i$  divided by the total number of moles of all substances.

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Examples 9.2. A. What is the increase per mole if  $C = R$  and  $T$  increases from  $0^\circ\text{C}$  to  $100^\circ\text{C}$ ?

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<sup>6</sup> From this inequality, one may draw conclusions about steam engines and other processes, or the arguments may be reversed. Thus the second law of thermodynamics may be expressed in a variety of ways, all of which lead to the same final results.

<sup>7</sup> Because  $T$  and  $V$  are not dimensionless,  $\ln T$  and  $\ln V$  are not defined. As implied by the  $\Delta S$ , we are actually looking for differences, hence for  $\ln T - \ln T_0$  and  $\ln V - \ln V_0$ , or  $\ln(T/T_0)$  and  $\ln(V/V_0)$ . Our final equations always contain such reference levels.

B. What is the increase in entropy per mole for a gas that expands by a factor of 1000?

C. What is the increase in entropy for a substance going into solution at a mole fraction of 1/100?

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9.3.4 “*Absolute*” Entropies. A conceptually and theoretically important problem is the entropy of a crystalline solid. Imagine that we can build up a crystal by placing, by hand, individual atoms or molecules. We place one atom or molecule at a selected point. Then place a second atom or molecule (of the same kind) in any direction at a distance determined naturally by the character of the particles. Then a third particle must go at a fixed position with respect to the first two but it can be placed at an arbitrary angle of rotation about the line of the first two. The positions of the fourth, fifth, and any subsequent atoms or molecules are then fully determined. The crystal structure has no more variability. That is what we mean by saying the crystal has a uniform, prescribed structure. (Different materials have different crystal structures, but for our selected substance, at a particular temperature and pressure, in general only one crystal structure is stable.)

This perfect crystal structure has the smallest possible number of choices of position, and therefore the lowest possible entropy, or randomness, or probability. In fact, if we can minimize motions of the particles about their equilibrium positions — for example, by cooling the crystal to zero temperature on the absolute temperature scale (0 K) — then we may assign a value of zero entropy to this, and to every other, perfect crystal at the same temperature.

We cannot directly check this value for two reasons. First, there is no way to reach exactly 0 K. That is an important statement, which has been called the *third law of thermodynamics*. Second, and more important, we have no way to measure absolute entropy, so we cannot confirm whether the entropy is or is not zero at 0 K. On the other hand, through slightly indirect methods, we can show that all perfect crystals (that can be interconverted) have the *same* entropy at 0 K. Then, because we cannot measure the actual value of entropy, we are free to *assign* a value of zero entropy to this common value, even though we know that there are some internal degrees of freedom that we ignore in this evaluation.

There is a very good experimental check on this treatment of entropy at 0 K. Certain molecules are *almost* symmetric, end to end. For example, carbon monoxide, CO, can fit *almost* as well into its own crystal if one molecule, or more, is put in backward, so the sequence along one direction might be

CO CO CO OC CO CO CO CO

*Figure 9.2 Possible sequential arrangement of CO molecules in a crystal.*

and so forth. As the gas is cooled, to form the crystal, there is nothing to prevent some molecules from inserting themselves backward, like the “stray” OC in the example shown. When a molecule once gets into the crystal at low temperature, there is not enough energy available to allow it to flip over. The *energy* difference to the crystal of this misalignment is extremely small, but the effect of this disorder on *entropy* is large enough to be easily measured.

Experiments show that crystals such as carbon monoxide have exactly as much “excess

entropy” (5.76 J/mol·K) as predicted.<sup>8</sup> There is no other apparent source of this excess entropy than random orientation of molecules within the crystal, so the quantitative agreement with the prediction is an excellent test of the theory.

**9.3.5 Achieving Low Entropy.** We have seen that *every* process has the effect of increasing entropy, of system plus surroundings, or else the process cannot happen in a finite time. We also have seen that crystals, for example, are low entropy states. That may raise the question: If entropy always increases, how can we produce crystals and other low-probability (low-entropy) states?

The answer simply requires that we distinguish between the system and the surroundings. We can always lower the entropy of a system at the cost of increasing the entropy of the surroundings.

High probability, or high entropy, corresponds to a randomized distribution of the molecules over a large number of (internal) states. Spreading things around, in an unordered fashion, can be called “chaos”. Thus we are led to some observations about how the universe works.

The second law of thermodynamics does not prohibit increasing the ordering of anything we choose. We regularly form new crystals, build elaborate buildings and machines, and grow plants and animals. But a decrease in entropy of the system can only happen when there is an increase in entropy, at least as large, in the surroundings. Highly ordered, or structured, forms, such as crystals or living beings, require a trade-off in the form of large “expenditures” (increases) of disorder or probability or randomness or chaos or entropy — call it what you will — in the universe. The universe undergoes change in the direction that increases the total chaos (system + surroundings).

That is, we can increase the order, or *decrease* the chaos, in any system we choose. The cost of this is that we *increase* the chaos, even more, elsewhere in the universe (that is, in the surroundings). You might say that we spread chaos wherever we live.

## 9.4 Simplifications to Calculations

The method of calculation described would be sufficient for deciding which processes occur and which will not occur. However, usually we are only interested in knowing how the system will change. Making calculations for the surroundings can be a nuisance and, in a sense, irrelevant. An effective method has been devised for eliminating the need for a second calculation for the surroundings. We introduce a brief diversion, not because introductory physics requires an understanding of the techniques of calculating and applying these short cuts but simply to inform readers that a short cut exists, so that in principle one need not always worry about what is happening in the surroundings to make predictions for what will happen in a system.

Consider first the relatively simple problem of measuring the amount of thermal energy required to melt a gram of ice. Assuming the first-law equation in the form

$$\Delta E = Q + W$$

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<sup>8</sup> Because each molecule has two possible orientations,  $\Delta S = R \ln 2 = 5.76 \text{ J/mol}\cdot\text{K}$ .

- Answers 9.2. A.  $8.314 \times \ln(373/273) = 2.59 \text{ J/mol}\cdot\text{K}$   
 B.  $8.314 \times \ln(1000) = 54.4 \text{ J/mol}\cdot\text{K}$   
 C.  $-8.314 [0.01 \ln 0.01 + 0.99 \ln 0.99] = 0.466$ , where we have included the effect of the mixing on the solute with mole fraction  $1 - 0.01$ .

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the quantity we typically measure is  $Q$ . To find  $\Delta E$  from this, we must correct for the small  $W$ , the work done on the ice as it changes volume during the melting process. Although the value of  $W$  is sufficiently small to often be neglected, its determination requires knowing accurately the volume of ice and of water, at  $0^\circ\text{C}$  and, assuming the pressure is constant, finding  $-P \Delta V$ .

It is much more convenient to define a new quantity,

$$H = E + PV$$

which has been named *enthalpy* (similar to energy and entropy, but distinct from each). Then, in any process at constant pressure, such as melting ice,

$$(P) \quad \Delta H = \Delta E + P \Delta V = Q + W + P \Delta V = Q - P \Delta V + P \Delta V = Q$$

Thus we see that the change in enthalpy is equal to the amount of thermal energy transfer (provided pressure is constant and there is no work done other than  $-P \Delta V$  work). In practice, therefore, it is  $\Delta H$  that is listed in handbooks, rather than  $\Delta E$ , for most processes involving measurements of  $Q$ .

Similarly, we define other functions, such as two quantities known as “free energy” — the Helmholtz free energy,

$$F = E - TS$$

and the Gibbs free energy<sup>9</sup>

$$G = H - TS$$

Changes in these functions effectively take the place of entropy,  $S$ , for most processes because they include *both* the change in entropy of the system *and* the changes associated with changes of entropy of the surroundings, under conditions of constant temperature and volume (for  $F$ ) or constant temperature and pressure (for  $G$ ). They differ from entropy in that *a*) we calculate  $\Delta F$  or  $\Delta G$  for the system, only, and *b*) a process will proceed (*i.e.*, is spontaneous) if the free energy ( $F$  or  $G$ ) *decreases*.

## 9.5. Engines and Heat Pumps

One interpretation of thermodynamics is that the first law, conservation of energy, tells us we can't get something for nothing. The best we can do is break even. The second law, the

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<sup>9</sup> Notation has changed in recent decades. Especially in America, Gibbs free energy was previously represented by  $F$  and Helmholtz free energy by  $A$ . The several new functions introduced here ( $H$ ,  $G$ ,  $F$ ) are less strange, or more predictable, than they may appear at first. See problem 9.xx at the end of the chapter.

probability principle, tells us we can never break even. We always lose. That is, the first law tells us when energy is changed in form, or transferred between objects, the amount of energy never changes. The second law tells us every time something happens, energy gets spread around, or dissipated, or “spilled”. Disorder, or entropy, increases. So even though we have the same amount of energy, some of it is in a less useful form.

Even so, we can get what we need, including converting thermal energy to mechanical energy. We look here at some of these results, and their limitations.

**9.5.1 Gaining Mechanical Energy: Heat Engines.** Mechanical energy is a name applied to kinetic energy and to the forms of energy most readily convertible into kinetic energy. In particular, it includes translational kinetic energy, rotational energy, potential energy, and vibrational energy. (It may also be interpreted to include electrical energy.) Many things we wish to do require mechanical energy — running machinery and lifting and transporting ourselves or our goods, are examples.

Thermal energy is relatively easy to obtain. We burn wood, or coal, or gasoline, for example. But to operate machinery, we must have mechanical energy. There are many ways of converting thermal energy to mechanical energy (so-called<sup>10</sup> “heat to work”).

Hero of Alexandria, in 130 B.C., constructed a primitive reaction steam turbine but there was no significant advance in gaining motive power, other than direct power from windmills, water wheels, and animals, until the end of the 17<sup>th</sup> century. By that time, the British Isles were running low on wood for heating and were turning to coal. After a short time, however, surface mines were depleted and deep mines quickly filled with water. Thomas Savery developed a steam-driven water pump in 1698. It was not very efficient, but that was of minor concern because it operated at the mine head where coal was plentiful.<sup>11</sup> A few years later, Thomas Newcomen produced the first engine with a steam-driven piston. It served for several decades until substantial improvements in design by James Watt, between 1763 and 1782, gave us the basic design still incorporated in steam engines today. Watt’s steam engines drove the British Empire to world dominance throughout most of the 19<sup>th</sup> century. In France, a recently retired officer, Sadi Carnot,<sup>12</sup> recognized that steam engines “seem destined to produce a great

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<sup>10</sup> In such a phrase, the implication is quite clearly  $Q$  and  $W$ . But  $Q$  and  $W$  are mutually exclusive ways of transferring energy between systems, or system and surroundings, so technically it is meaningless to speak of “converting heat to work” or *vice versa*.

<sup>11</sup> There is validity to the generalization that necessity is the mother of invention. There was no incentive to produce a working steam engine at the time of Hero because needs for motive force were adequately met by slave labor. The industrial revolution caused, and was caused by, the creation of more powerful engines for manufacture and transportation in 18<sup>th</sup> century England.

<sup>12</sup> Lazare Carnot was a mathematician, engineer, administrator, and general who served under Napoleon. He introduced the concept of potential energy (as “latent *vis viva*”) and recognized that jerks, or sudden accelerations, decreased efficiency in engines. His son, Sadi (named after a medieval Persian poet), born in 1796, followed Lazare’s army career, but when

revolution in the civilized world” and undertook a study of the underlying principles.

Ideally, we prefer to operate through a cycle, so the system returns to its initial state and we can run through the cycle again and again. Unfortunately, none of the methods of conversion is very efficient. We cannot get mechanical energy without putting in a lot of “high grade” (that is, high temperature) thermal energy, most of which comes back to us as “low grade” (low temperature) thermal energy. The limitations are clearly related to the second law, so there is no way to avoid the difficulty except, as we will see later, by avoiding a path through thermal energy.

Carnot studied a cycle in which an ideal gas is heated at constant temperature, expanded without heat exchange, doing work on the surroundings, then cooled at constant temperature and compressed, without heat exchange, while work is done on the engine.

It is easy to follow the ideal gas around a cycle, but it is easier, and more general, to treat the cycle without regard to the substance. The steps of Carnot’s cycle are then described as:

1. an isothermal process, taking in thermal energy, at the higher temperature,  $T_H$ ; for example, the gas expanding against a piston as it is heated by a boiler.
2. an adiabatic<sup>13</sup> process ( $Q = 0$ ) with the system changing from  $T_H$  to the cooler temperature,  $T_C$ ; for example, the gas further expanding against a piston without heating.
3. an isothermal process, where the system gives off thermal energy, at  $T_C$ ; for example, the gas being compressed by a piston, giving off thermal energy to cooling water.
4. an adiabatic process ( $Q = 0$ ) with the system changing from  $T_C$  to  $T_H$ ; for example, the gas being further compressed, without transfer of thermal energy.

The entropy changes around the cycle (with all steps reversible) are

1.  $\Delta S_H = Q_H/T_H$  [high temperature]
2.  $\Delta S_a = 0$  [adiabatic cooling]
3.  $\Delta S_C = Q_C/T_C$  [cool temperature]
4.  $\Delta S_a = 0$  [adiabatic warming]

and, because  $S$  is a state function,  $\Delta S = 0$  for the total cycle, so  $\Delta S_H + \Delta S_C = 0$ .

$$\frac{Q_H}{T_H} = -\frac{Q_C}{T_C}$$

Also, for energy balance, the total (*i.e.*, net) thermal energy transfer into the engine must be balanced by the total (*i.e.*, net) energy transfer, as work, out of the engine to make  $\Delta E = 0$  for a complete cycle. Therefore

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Napoleon lost power, Sadi retired (in 1820, at age 24) and devoted much of his remaining life to the study of steam engines. He died at age 36, probably of cholera, while recovering from scarlet fever.

<sup>13</sup> *Diabatic* (like diabetic) indicates “passing through”. Adiabatic means no flow, specifically no “heat” flow, or passage of thermal energy across a boundary between system and surroundings.

$$Q_H + Q_C + W = 0$$

Therefore

$$-W = Q_H + Q_C = Q_H \left( 1 - \frac{T_C}{T_H} \right) = \frac{Q_H}{T_H} (T_H - T_C)$$

or

$$\frac{-W}{\Delta T} = \frac{Q_H}{T_H} = -\frac{Q_C}{T_C}$$

Because  $W$  and  $Q_C$  are negative, each of these three terms is positive.

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Examples 9.3. A. What is the predicted Carnot efficiency of a heat engine operating between 25°C (298 K) and the boiling point of water (100°C = 373 K)?

B. What is the predicted efficiency if the upper temperature is increased to 600°C?

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The Carnot equations may be summarized in the form (with  $\kappa = \Delta S_H = -\Delta S_C$ )

$$\begin{aligned} Q_H &= \kappa T_H \\ -Q_C &= \kappa T_C \\ -W &= \kappa \Delta T \end{aligned}$$

so

$$efficiency = \frac{-W}{Q_H} = \frac{T_H - T_C}{T_H} = \frac{\Delta T}{T_H} = 1 - \frac{T_C}{T_H}$$

We must put in a large amount of thermal energy to get out a small amount of mechanical energy. The results also show why “low level” thermal energy is not very valuable.

It is not possible to create an engine that takes in thermal energy and puts out mechanical energy with an efficiency greater than that given by Carnot’s equation. This is a direct consequence of, and considered as an alternative statement of, the second law.

9.5.2 *Heat Pumps*. Because our heat engine is made to operate reversibly, it should be possible to run the engine backward. The “efficiency” then becomes the (thermal energy) output divided by the (mechanical energy) input. This “efficiency” for an engine that puts out thermal energy at the higher temperature is

$$"efficiency" = \frac{\text{output}}{\text{input}} = \frac{-Q_H}{W} = \frac{T_H}{\Delta T} = \frac{T_H}{T_H - T_C}$$

Answers 9.3. A.  $Efficiency = output/input = \Delta T/T_H = 75/373 = 20\%$ .

B.  $Efficiency = 575/873 = 66\%$ .

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which is greater than one. (It is often called a *coefficient of performance* to avoid labeling a quantity greater than one as an efficiency.)

Consider a heat engine operating in reverse between room temperature of 25°C and 0°C. The efficiency, or coefficient of performance, is  $298/25 = 11.9$ . That is, we can put nearly 12 times as much thermal energy into the room by pumping energy, from outside at freezing temperature, than by an electric heater inside the room. Actual coefficients of performance are, however, much lower (typically 3 to 5).

9.5.3 *Practical Engines*. The theory of heat engines describes any devices that convert thermal energy to mechanical energy or, running in reverse, pump thermal energy from one temperature level to another. The idealized cycle depicted by Carnot represents the best that we could possibly achieve. However, there is a serious limitation that prevents us from doing even that well. The theory describes the operation of a reversible engine, meaning one that is in equilibrium at all times, and which therefore must operate *extremely* slowly. We get maximum *efficiency* (output divided by input) but no *power* (energy transfer divided by time).

The rate at which thermal energy is conducted from one point to another (heat transfer rate) depends on the temperature difference between the points. If the working substance (usually a gas) in the heat engine is to be at the same temperature as the source of the thermal energy, or at the same temperature as the cooling water, it will take forever to conduct thermal energy from one place to another. To maximize the rate of transfer, the temperature differences should be as great as possible. But if the temperature differences are too great, the engine will operate at zero efficiency.

It was shown in 1975, by Frank L. Curzon and Boye K. Ahlborn, that a happy medium gives the maximum possible power output of a heat engine. The maximum power is independent of the heat transfer properties of the engine materials. In particular, the optimum performance of a heat engine gives an efficiency of

$$efficiency = \frac{\sqrt{T_H} - \sqrt{T_C}}{\sqrt{T_H}} = 1 - \sqrt{\frac{T_C}{T_H}}$$

This Curzon-Ahlborn efficiency is lower than the Carnot value, but with higher power than for reversible engines (which would have zero power output).

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Examples 9.4. A. Find the anticipated efficiency for a heat engine operating between 25°C and 100°C according to the Curzon-Ahlborn description.

B. Find the anticipated efficiency for a heat engine operating between 25°C and 600°C according to the Curzon-Ahlborn description.

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Actual steam engines operate very close to this revised theoretical limitation. Consequently, actual efficiencies are significantly lower than Carnot efficiencies.

There is no similar calculation for the optimum efficiency, or coefficient of performance, of heat pumps, where the performance depends strongly on heat transfer properties but is not otherwise limited. The temperature difference between engine and surroundings can be made as large as desired, but with consequent degradation of efficiency. There are other practical limits, as well, such as a tendency for the cooler surroundings to freeze, which greatly decreases the rate of transfer of thermal energy.

### Chapter Summary

Because energy is often visible (as motion or position), there is a widespread conception that processes go in the direction that will lower energy. Understanding the direction of change requires some knowledge of the atomic and molecular structure of matter, and how that influences probabilities. When many states are accessible to a system, the system components tend to spread among all the accessible states (both momentum and spatial). By predicting the relative numbers of such states, we can predict the relative probabilities of “look alike” sets of states, which have nearly the same values for properties such as energy, temperature, and pressure. Fortunately, we can avoid most numerical comparisons by measuring thermal energy transfer and temperature to measure the change in the ‘spread function,’  $S$ , which is given the name *entropy*. An early, and important, application is to conversions between thermal energy and mechanical energy, including steam engines and refrigerators.

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[Advanced] Problem 9.xx. We introduced new functions — enthalpy,  $H$ , and free energy,  $F$  and  $G$ , to meet specific needs, but seemingly “out of the blue”. Looking back, we can see that there is a logical structure that leads to the new functions when we look for them.

Let  $f$  represent a function of  $x$  and  $y$ , such that  $df = u dx + z dy$ . (That is,

$$\left(\frac{\partial f}{\partial x}\right)_y = u \quad \text{and} \quad \left(\frac{\partial f}{\partial y}\right)_x = z$$

Basic properties of differentials tell us that  $d(ux) = u dx + x du$ , and similarly  $d(zy) = z dy + y dz$  (where  $u$ ,  $x$ ,  $y$ , and  $z$  may be functions). Therefore

$$d(f - ux) = df - d(ux) = u dx + z dy - u dx - x du = z dy - x du$$

and

$$d(f - zy) = df - d(zy) = u dx + z dy - z dy - y dz = u dx - y dz$$

From these purely mathematical relationships,

a. show that from

$$dE = T dS - P dV$$

we can obtain

$$d(E + PV) = T dS - P dV + P dV + V dP = T dS + V dP$$

b. show that, from the definitions  $F = E - TS$  and  $G = H - TS$ , we may obtain

$$dF = d(E - TS) = T dS - P dV - T dS - S dT = -S dT - P dV$$

and

Answers 9.4. *Efficiency* =  $1 - \sqrt{(298/373)} = 11\%$ .

B. *Efficiency* =  $1 - \sqrt{(298/873)} = 42\%$ . The assumption of 25oC cooling water is too optimistic for most installations.

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$$dG = d(H - TS) = T dS + V dP - T dS - S dT = V dP - S dT$$

Thus the “magic function”,  $H$ ,  $F$ , and  $G$ , and their equations are obtained by simple mathematical processes. (These are called Legendre transforms, fr the French mathematician Adrien-Marie Legendre (1752-1833),)

### Addendum: Energy Transfer and Work

Energy is an extensive property. Therefore any transfer of energy,  $\Delta E$ , must be a product of an extensive property and (perhaps) one or more intensive property. For example, transfer of thermal energy is typically  $C \Delta T$ , where  $C$  (the choice depending on experimental conditions) is an extensive property and temperature is an intensive property. Transfer of material depends on the amount of material, an extensive measure.

Elementary discussions often “define” work as force times distance. The more fundamental conditions to be satisfied is that work is a transfer of energy,  $W = (\Delta E)_w$ . That is, work is the portion of the *energy transfer* that satisfied the requirement of involving some type of generalized force and some type of generalized displacement. This often involves subtle distinctions. An example of selection of work terms is given in Table 9.1 below.

Table 9.1. Examples of work terms.<sup>14</sup>

Extensive	Intensive	$w$
$s$ , displacement	$\mathbf{f}$ , force	$\mathbf{f} \cdot d\mathbf{s}$
$x_i$ , “generalized displacement”	$F_i$ , “generalized force”	$F_i dx_i$
$L$ , length	$\mathcal{T}$ , tension	$\mathcal{T} dL$
$A$ , area	$\gamma$ , surface tension	$\gamma dA$
$V$ , volume	$-P$ , pressure	$-P dV$
$m$ , mass	$\Phi$ , gravitational potential	$-m d\Phi$
$q$ , charge	$V_E$ , electric potential	$q dV_E$
$V\mathbf{P}$ , polarization	$\mathbf{E}$ , electric field	$\frac{1}{2}V(\mathbf{P} \cdot d\mathbf{E} + \mathbf{E} \cdot d\mathbf{P})$
$V\mathbf{M}$ , magnetization	$\mathbf{H}$ , magnetic field	$\frac{1}{2}\mu_0 V(\mathbf{H} \cdot d\mathbf{M} + \mathbf{M} \cdot d\mathbf{H})$

<sup>14</sup> Robert P. Bauman, *Modern Thermodynamics with Statistical Mechanics*, Macmillan, 1992.

As previously discussed, the traditional “force times distance” is often misleading because there is a tendency to multiply a sum of forces that move through different distances, or a force (such as a frictional force) times a distance that has nothing to do with that force (*e.g.*, the distance the center of mass of the body moves), or a contact force and motion of a body away from that contact surface. But other difficulties are also widely recognized (*e.g.*,  $\int V dP$ , which appears hidden in derivations of Bernoulli’s equation, or lie hidden beneath the surface waiting the unwary). For example, gravitational potential energy is  $E = m\phi$ , and therefore we could write  $dE = m d\phi + \phi dm$ , but the second term is not work, and similar distinctions appear for other entries in the table.

The “first-law equation”, in complete form, must include all energy transfer terms, including the more obscure forms of work. Particular care is required in examining terms such as  $A d\gamma$  or  $L dT$  (corresponding to changes in surface tension or tension), where the energy of the system may or may not change. (There may be an internal conversion of energy.) In practice, we typically write the “easy”  $\Delta E = Q + W$ , but must keep in mind that this short-hand version is only an approximation.

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