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Thermodynamics: The Zeroth and First Laws

A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates and the more extended its area of applicability.

Albert Einstein on thermodynamics

Facility with thermodynamics requires understanding the precise definition of many concepts, including different types of systems, properties, processes, and equilibria. We begin by considering systems isolated from their surroundings and systems into which energy, but not matter, can flow from the surroundings (closed systems). Measurements, including those of heat and work, are made on systems by observers in the surroundings. Thermodynamically, temperature is defined as the property that determines the propensity of a system to transfer heat, and the zeroth law asserts that this property is unique. In the reversible limit of real processes, a system is in equilibrium with its surroundings and processes can be represented on P versus V work diagrams. The first law states that the energy of the universe is constant in any process. The internal energy of a system, U , is a state function, and the change of U in a constant-volume process is the heat added

to the system. Likewise, the change of enthalpy, H , is the heat added in a constant-pressure process. Heat capacities at constant volume and pressure are related to the rate of change of U and H , respectively, with temperature in such processes. The Joule and Joule–Thomson processes provide information on the variation of U and H with volume and pressure, respectively. The efficiency of a Carnot cycle engine (a reversible engine that transforms heat to work on a continuous basis) is analyzed using the first law of thermodynamics.

2.1 The Nature of Thermodynamics

Few endeavors reward precise thinking and penalize sloppy thinking as much as the study of thermodynamics. In this subject, we take familiar concepts, such as heat and energy, rigorously define them, and derive a multitude of relationships that are useful in many branches of science. By the above criteria of Einstein, thermodynamics is impressive indeed!

Thermodynamics is applicable to the types of substances and occurrences that we are familiar with in our daily lives or can easily create in the laboratory. As a result, it is easy to compare the predictions of thermodynamics with “real-world” behavior. Needless to say, there are impressive amounts of data that verify the conclusions of this subject. Relatively few examples of the agreement of experiment with thermodynamic theory are given in this volume. The reader is referred elsewhere for additional examples of the conformity of thermodynamic theory and experiment.¹

Thermodynamics is not unique in dealing with energy. Energy considerations are also of paramount importance in fields such as mechanics, electricity and magnetism, and atomic and molecular structures. In these other fields, the energy of individual particles are discussed. The types of energy that they recognize are kinetic energy (the energy of motion), potential energy (the energy of position), and the energy of electric and magnetic fields. Thermodynamics is different from these other fields in that it considers the energy of entire systems, consisting of huge numbers of particles (and perhaps radiation fields). The approach of thermodynamics is totally macroscopic and its conclusions are not based on any particular model for the behavior and nature of the microscopic particles.

2.2 Systems

We live in a very complicated universe. Clearly, not even with the most powerful computers would we be able to study the details of all parts of the universe. If we are to make any progress in thinking about energy, we must focus our attention on

only part of the universe. This part we call the *system*. The remainder of the universe is termed the *surroundings*.

In some cases, it will be possible to consider the system as *isolated* (i.e., not interacting with the surroundings). In order to be isolated, the boundaries of a system must be impermeable to mass and energy. Such boundaries cannot allow any interaction with external mechanical or electrical forces. For example, if there is an external pressure, the walls of the system must be rigid so that they cannot be moved by the pressure. In addition, the system must also be *adiabatic* (i.e., not allowing any energy to flow through the walls in the absence of such forces).

In most cases, we will be forced to define our system in such a way that it exchanges mass or energy with the surroundings. Systems that can exchange energy, but not mass, with the surroundings are called *closed* systems; those that can exchange both energy and mass are called *open* systems. It is not necessary to consider systems that exchange mass, but not energy, with the surroundings, because the transferring mass will bring its internal energy with it into the system. We will start by dealing exclusively with isolated and closed systems and then extend our considerations to open systems, beginning with [Chapter 6](#).

2.3 Equilibrium

Equilibrium is a very important concept in discussions of thermodynamics. An isolated system is at equilibrium when it has no tendency to change—a condition that is called *internal equilibrium*. This implies that the system is at *mechanical equilibrium* (i.e., it has no tendency for bulk movement of material), *thermal equilibrium* [i.e., it has no tendency for transport of energy (without bulk movement of material)], and *material equilibrium* [i.e., it has no tendency for material to change form (such as by a phase transformation or a chemical reaction)].

It is somewhat more difficult to decide whether a system with no tendency to change is at equilibrium if it is not isolated (i.e., when it is closed or open). In such cases, we apply the mental test of removing the interaction between the system and its surroundings. If the system still has no tendency to change, then we say that (1) the original system was at internal equilibrium and (2) the original system was at *equilibrium with its surroundings*.

A system that relies on its surrounding to remain unchanged, such as a living organism, is at *steady state*. In the first 11 chapters of this volume, we will discuss properties of systems at equilibrium and processes in which systems change from one equilibrium state to another (each defined by appropriate constraints). In [Chapter 12](#), we will briefly touch on systems at steady state.

We are rarely interested in systems at complete equilibrium, where all conceivable chemical (and nuclear) reactions have no tendency to occur. Usually,

there are real or imagined *constraints* in our system, related to the *rates* of certain processes. For example, at most temperatures, we can completely ignore nuclear reactions. Also, in a mixture of H_2 and O_2 at low temperature, without catalysts, we may choose to ignore the formation of water, because it is very slow in reality. An imagined constraint is often convenient to use in treating chemical reactions, where the actual reaction step is separated from an additional step, in which the energy liberated in the reaction is used to heat the reaction products.

2.4 Properties

A complete description of a system, of sufficient detail to describe its macroscopic behavior, is called the *state* of the system. A system has a particular state independent of the way in which it has arrived at that state. A system is characterized by measuring its *properties*. For systems at equilibrium, specification of a few properties will suffice to determine all other properties of the system and, thus, its state. Quantities that are determined by defining the equilibrium state are called *state functions*. After a short period of adjusting to their constraints, gases and liquids can usually be assumed to be at equilibrium for all physical changes² (but not necessarily for chemical reactions). For solids with strong bonds, such as high-melting-point metals, properties may depend on the previous history of a particular sample (e.g., heat treatment) and differ from the equilibrium properties for a very long time.

In thermodynamics, the observer is outside the system and properties are measured in the surroundings. For example, pressure is measured by an external observer reading a pressure gauge on the system. Volume can be determined by measuring the dimensions of the system and calculating the volume or, in the case of complex shapes, by using the system to displace a liquid from a filled container. Important thermodynamic properties have low information content (i.e., they can be expressed by relatively few numbers). The details of the shape of a system are usually not important in thermodynamics, except, sometimes, a characteristic of the shape, such as the surface-to-volume ratio, or radii of particles, may also be considered. Information only accessible to an observer within the system, such as the positions and velocities of the molecules, is not considered in thermodynamics. However, in [Chapter 5](#) on statistical mechanics, we will learn how suitable averages of such microscopic properties determine the variables we study in thermodynamics.

As discussed in [Chapter 1](#), properties are either *extensive* or *intensive*, depending on whether they are proportional to the size of the system or not. Thus, mass and volume are extensive properties; temperature and pressure are intensive properties. An extensive property multiplied by an intensive property remains extensive. Because the ratio of two extensive properties is intensive, dividing an

extensive property by the number of moles, the mass, or the volume of a system gives an intensive property. An example of an intensive property is the density $\rho \equiv m/V$. An intensive property has a value in each region of a system. A *uniform* intensive property is constant throughout the system; if a system has all of its intensive properties uniform, it is *homogeneous*, compared to a *heterogeneous* system, in which some properties vary in the system. In heterogeneous systems, properties may vary continuously or discontinuously in space.

2.5 Processes

In thermodynamics, we are interested in *processes*, during which the state of a system changes. A process is defined by the external constraints that exist during the changes. The *path* of a process is the continuous sequence of states in which the system exists during the process. Often, a system will begin a process in some initial state in which it is in equilibrium and end the process in a final state in which it is also in equilibrium. The intermediate states of the process in general will have tendency for change and will, thus, be nonequilibrium states. Nonequilibrium states are very complicated; their properties are usually not uniform and very difficult to specify. However, the properties of the initial and final states, being state functions, are independent of the process by which the system changes between these two states. Therefore, the change of all state properties during the process are also independent of the path of the process. Sometimes, we will want to consider systems, such as engines, which undergo a *cyclic* process. In these cases, if we chose the initial and final states to be at the same place in the cycle, they are identical states with identical properties and the change in any state function for such a process is zero.

2.6 Heat and the Zeroth Law of Thermodynamics

When a system originally at equilibrium is brought into contact with its surroundings, through boundaries that do not permit any mechanical, electrical, or magnetic forces to affect the system or any transfer of matter between the system and its surroundings, two things can happen: the system can change—in this case, we say that thermal energy has transferred between the system and the surroundings. Alternatively, the system may remain unchanged, indicating that no thermal energy has been transferred. Thermal energy is the energy of random motion of particles and its transfer between the surroundings and the system is called *heat*, given the symbol q . In keeping with measuring thermodynamic quantities from outside the system, we define heat as follows: *Heat is the decrease in the thermal energy of the surroundings*. By this definition, our

sign convention is that positive heat corresponds to thermal energy entering the system. Strictly speaking, it is redundant to talk of “heat transfer” or “heat flow,” as heat already is a transfer of thermal energy. However, these phrases are so commonly used that a statement such as “there is heat between A and B” sounds awkward and “thermal energy is transferred between A and B” is ponderous. Therefore, we will not hesitate to use the terms “heat transfer” and “heat flow.”

The absence of heat flow may be a result of the walls not permitting the transfer of thermal energy. Boundaries of this kind are called *adiabatic*. (Adiabatic walls are infinitely good thermal insulators.) If the walls are *non-adiabatic* (sometimes called diabatic or diathermal) and do permit heat transfer, but it does not occur, we say that the system is at *thermal equilibrium* with its surroundings.

The laws of thermodynamics are generalizations of experience. They are accepted as fundamental postulates because exceptions to them have never been observed. There are four laws of thermodynamics, labeled the zeroth, first, second, and third laws. The numbering results from the fact that the zeroth law was so intuitive that it was not realized that it was a basic postulate, which, for logical consistency, was necessary for the derivation of the other laws until after the numbering of those laws had become generally accepted. It is the zeroth law that enables us to define temperature scales. The zeroth law is a generalization of what happens when we bring two systems, each in internal thermal equilibrium, in contact through nonadiabatic walls. We will state the zeroth law as follows:

There is a single property of systems at thermal equilibrium that determines their propensity to transfer thermal energy.

We call this property the *temperature*, and when two systems at the same temperature are brought into thermal contact through nonadiabatic walls, there is no heat transferred between them and they remain at thermal equilibrium. If they are not at the same temperature, heat is transferred spontaneously from the system at higher temperature to the system at lower temperature. All systems that are at thermal equilibrium with one another are at the same temperature.

Heat transfer between two systems is a process that occurs at the surface of each system, and it is the propensity for this surface heat transfer that is dealt with in the zeroth law. Strictly speaking, the zeroth law only deals with the direction of heat transfer and the absence of heat transfer when the systems have finally reached thermal equilibrium with each other. During the process of heat transfer, the two systems are not at thermal equilibrium and they do not each have a unique temperature. The rate of heat transfer during the process also depends on properties of the systems, such as their thermal conductivity.

When dealing with heat transferred between a system and its surroundings, we often idealize the surroundings by considering it as a *heat reservoir*. A heat reservoir is a store of thermal energy in the surroundings at a single temperature

and sufficient thermal capacity so that arbitrary amounts of thermal energy can be withdrawn or added to it without noticeably changing its temperature.

Although we will not deal with the rate of heat transfer in this book, thermodynamics does require that it rise monotonically as the temperature difference between the system and its surroundings increases. In addition to considering thermal equilibrium as the condition of zero heat transfer between a system and its surroundings, it is sometimes useful to consider it as the limit of the nonequilibrium situation—as the temperature difference between the system and the surroundings approaches zero. In the limit, the rate of heat transfer approaches zero, a uniform temperature is maintained in the system, and it takes an infinite amount of time for any finite amount of heat to be transferred. Because the direction of heat transfer in this case can be reversed with the slightest change of temperature of the system or surroundings, we say that this heat transfer is *reversible*. Because in the real world we are not able to wait an infinite amount of time to observe changes in systems, we say that reversible processes are not real. However, the reversible limit of processes is of great importance in thermodynamics. It is an easily considered idealized situation against which real processes can be compared.

Of course, it is one thing to say that there is a unique property that determines the propensity to transfer heat and another thing to actually measure that property—the temperature. Usually, it is rather inconvenient to measure temperature by determining a system's tendency to transfer heat to other systems,³ and we determine it by measuring some property that varies monotonically with temperature. The volume of a given mass of reference material (with pressure held approximately constant or kept very low), such as that of the mercury in the common household thermometer, is usually chosen for this purpose. A measurement of the length of the mercury column is equivalent to a volume measurement, because, to a very good approximation, the dimensions of the glass tube are independent of temperature. We allow the system to reach thermal equilibrium with our *thermometer*, at which point the system and thermometer have the same temperature, and then measure the volume of the reference material. It is assumed that the mass of the thermometer is so much less than that of the system that the system temperature will not be changed in the process of reaching thermal equilibrium. Two systems that give the same reading when they reach thermal equilibrium with a thermometer have the same temperature, and the zeroth law assures us that there will be no heat transferred if these two systems are brought in contact.

Temperature scales such as the centigrade scale discussed in [Chapter 1](#) are quite arbitrary, requiring a choice of two calibration points and the material and property used to interpolate between them. We saw that we could alternatively use a single-calibration-point scale based on a broad class of materials—the ideal

gases. A conceptually much simpler temperature scale, based on the second law of thermodynamics, will be discussed in [Chapter 3](#).

2.7 Work

Heat is one way of transferring energy to or from a system; work, the transfer of energy due to a force, is another way. Work is the product of a force and the distance that the point of application of the force moves. For example, a body of mass M in the Earth's gravitational field experiences a gravitation force of magnitude Mg directed downward (g is the acceleration of gravity). If the body moves downward by a distance h , the gravitational field has done work equal to Mgh on the body. An alternative way of describing this process is to say that the body's potential energy in the gravitational field has been reduced by Mgh . These are alternative ways of describing the same process. It is important to not include both the work and the decrease of potential energy in analyzing systems.

As an example more important to thermodynamics, we consider a gas at equilibrium, confined in a cylinder topped by a movable, leak-free, and massless piston, as illustrated in Fig. 1. A mass, M , on the piston exerts a force of Mg on the piston. If the system is at *mechanical equilibrium* with its surroundings, the external and internal forces at the piston boundary are in balance. The pressure in the gas must therefore be $P = Mg/A$, where A is the area of the piston. No work is done at mechanical equilibrium, because there is no motion of the boundary, and work is the product of a force and the distance its point of application moves. If the piston does move, the work is positive if the motion is in the direction of the force. In Fig. 1, if the gas is compressed, the piston moves in the direction of the force and the force does positive work on the system.

Let us say that the mass on the piston is increased to M' . The system is no longer in mechanical equilibrium and the piston will move down, compressing

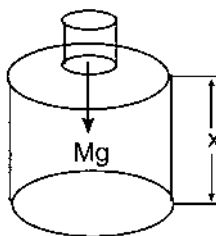


Figure 1 Gas in a cylinder.

the gas, and increasing its pressure until mechanical equilibrium is restored. With the force in the negative x direction, the work done on the gas is

$$w = F\Delta x = (-M'g)\Delta x = -\left(\frac{M'g}{A}\right)(A\Delta x) = -P_{\text{ext}}\Delta V \quad (1)$$

The symbol Δ is used generally to express the change of a state function during a process. It is equal to the value of the state function at the end of the process less its value at the beginning of the process. The work is positive, because ΔV is negative (the force and displacement are in the same direction). P_{ext} is the external pressure on the system. We can also discuss work in terms of potential energy. The potential energy of a mass in the Earth's gravitational field is Mgh , where h is measured from some arbitrary reference elevation. From this perspective, the change of mechanical potential energy in the surroundings is $M'g[(h_0 + \Delta x) - h_0] = M'g\Delta x$. We will find it most convenient to define work in the following manner:

Work is the decrease in mechanical or electrical energy of the surroundings.

This gives $-M'g\Delta x$ for the work—the same result that was calculated in Eq. (1).

From the vantage point of the system, the above process is really very complicated. When the mass on the piston is increased, the downward force on the piston is greater than the upward force, and the piston accelerates downward. During this motion, the gas in the cylinder is unevenly compressed, turbulence is generated, and the gas pressure and temperature rise. Because of its momentum, the piston passes the point of equilibrium and compresses the gas to where its pressure is greater than the pressure caused by the external mass. There is some oscillation of the piston, causing further heating of the gas. After a while, the piston comes to rest and nonuniformity in the temperature and pressure of the gas disappear. However, from the point of view of the surroundings, the process is much simpler; we have a force moving a distance Δx or an external pressure changing the volume of a system by ΔV . If the system is not perfectly insulated, then there may also be heat transferred between the system and the surroundings. This does not affect our calculation of the work. This is the usual agenda of thermodynamics. Measurements are made in the surroundings.

Example 1. A gas is confined in the bore of a cannon of length L by a shell of mass M and cross-sectional area A . Initially, the shell is at a distance L_i from the end of the cannon. Assuming 1 atm pressure, find an expression for the ejection velocity of the shell in terms of the work done by the expanding gas.

Solution: We will define the system as the confined gas. Mechanical energy is increasing in the surroundings, due to compression of the

atmosphere and acceleration of the shell. The sum of these is $-w$, the work done by the gas on the surroundings:

$$-w = P_{\text{ext}}\Delta V + \frac{1}{2}Mv^2 = (1 \text{ atm})(L - L_i)A + \frac{1}{2}Mv^2$$

$$v = \left(\frac{2}{M}(-w - (1 \text{ atm})(L - L_i)A) \right)^{1/2}$$

Thus, not all the work done by the expanding gas goes to accelerate the shell; some goes to compress the atmosphere.

Electrical energy is considered to allow us to discuss batteries and electrochemical cells, as well as motors and resistance heating. If a charge Q is transferred to a system at an electrostatic potential (voltage) ϕ with respect to the surroundings, the work done is $Q\phi$:

$$w_{\text{elec}} = \phi Q = \phi I \Delta t \quad (2)$$

where I is the electric current which flows for time Δt . The SI unit for Q is the Coulomb and ϕ has the derived unit of the electrical potential through which unit charge must be moved to do 1.0 J of work. This unit is called a volt.

In the limit of an infinitesimal amount of motion, an infinitesimal amount of work is done. We write this as

$$\delta w = -P_{\text{ext}} dV \quad (3)$$

or

$$\delta w_{\text{elec}} = \phi dQ \quad (4)$$

The differential symbol, d , means an infinitesimal change in, and we use the symbol δ to mean an infinitesimal amount of. We make this distinction to emphasize that w is a transfer of energy through the boundaries of a system; it is not a property of the system, like V , that can change. (Note that $\int_i^f dX = X_f - X_i \equiv \Delta X$, whereas $\int \delta x = x$.) The total work done in a process is just the sum of the little bits of work done in each stage of the process. In the limit of a true infinitesimal, we must integrate Eq. (3) to get

$$w = \int \delta w = - \int P_{\text{ext}} dV \quad (5)$$

which gives Eq. (1), when P_{ext} is constant.

It is very important to remember that because work is measured in the surroundings, it is the external pressure that determines the work. There are, however, a number of circumstances in which P_{ext} equals P , the system pressure, and this substitution can be made in Eq. (5). These cases are both important practical processes and useful standards against which to compare such processes, and their careful discussion is necessary. One of these situations is

where the system is in complete equilibrium, including mechanical equilibrium with the surroundings. In this case, because there is no unbalanced force at the boundary of the system, there is no movement and no work.

To be exact, we should say that in mechanical equilibrium, there is no movement in a finite time. We could imagine, in Fig. 1, doing work by horizontally sliding an infinite number of individual grains of sand from an infinite number of appropriately located platforms onto the piston. In the limit of infinitely small particles of sand, P_{ext} would be equal to P and we would maintain mechanical equilibrium. Do not worry if you cannot imagine just how this could be done. This is an example of a process that is impossible in practice, but does not violate any of the laws of physics. It is called by the German name, a *gedanken* (thought) process. Such a *gedanken* process is called reversible. Because the compression is infinitely slow, any process going on in the system (such as a pressure-dependent chemical reaction) will remain at equilibrium.

Assuming no friction, the above process can be reversed without the addition of energy by sliding the grains back onto the platforms. Consideration of reversible processes will be very important in our theoretical development of thermodynamics. Although reversible processes are not real, there are some real processes which occur so slowly that the system may be considered to be at equilibrium. Geological processes are usually of this type.

Replacement of P_{ext} by P , however, does not require complete equilibrium; mechanical equilibrium with the surroundings is sufficient. In many slow processes, the system pressure closely tracks the external pressure and can be substituted for it in Eq. (5). The most commonly encountered of these is the *constant-pressure process*. Because we define our constraints in the surroundings, a constant-pressure process has constant P_{ext} . If the system has a moveable boundary and *the system is initially in mechanical equilibrium with the surroundings* ($P_i = P_{\text{ext},i}$), then P will remain equal to P_{ext} for the following two processes:

1. The process has no tendency to change the pressure of the system. For example, it may be a chemical reaction that is both thermoneutral and for which the number of moles of gaseous reactants and products are equal.
2. The process does tend to change the pressure of the system, but it occurs slowly enough so that the system boundary can move to maintain $P = P_{\text{ext}}$. Reactions occurring in the liquid or solid phase exposed to atmospheric pressure are of this sort. The boundary in this case is just the upper surface of the liquid or solid, which, having negligible momentum, responds almost instantaneously to pressure changes in the system. Similarly, gaseous reactants confined by a weightless, or very light, piston will also allow the system pressure to

remain at the constant P_{ext} , unless the reaction occurs very rapidly (such as an explosion). Because we will not usually be considering explosions, we will generally assume that in constant-pressure processes, $P = P_{\text{ext}}$. In an explosion, such a substitution would actually be meaningless, as the pressure in the system is not uniform.

In the case of a reversible process, $P_{\text{ext}} = P$ and the work is given by

$$\delta w_{\text{rev}} = -PdV, \quad w_{\text{rev}} = - \int_i^f P dV \quad (6)$$

where we have explicitly shown that this integral is from some *initial* to some *final* state. By the definition of an integral, work done by the system under reversible conditions is given by the area on a P versus V diagram under the curve $P(V)$. P versus V diagrams, such as shown in Fig. 2, are known as a *work diagrams*. Only reversible processes can be shown on work diagrams.

In thermodynamic systems, pressure is usually a function of at least two other variables (e.g., $P = RT/V_m$ for an ideal gas), so the integral in Eq. (6) is not defined until more information concerning the process is given. For example, in the work diagram of Fig. 2, three different reversible *paths* going from an initial state i to a final state f are shown. This diagram emphasizes that the work done in going between two states is not specified by defining these states and, thus, work is not a state function. In the upper path, the expansion is carried out at constant pressure to state 2, followed by a reduction of pressure (by lowering the temperature) to get to the final state. The area and, thus, the reversible work done by the system is $P_i \Delta V$ ($w = -P_i \Delta V$) and is greatest in this case. The lowest

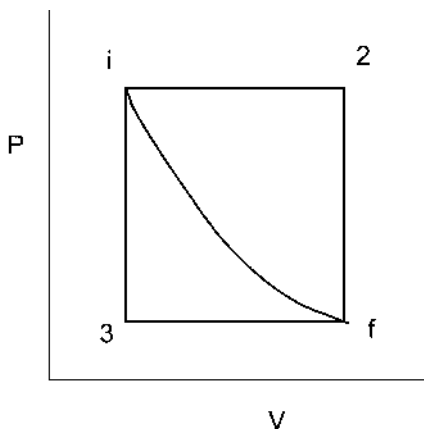


Figure 2 Work diagram for an expansion.

amount of reversible work done by the system $P_f \Delta V$ ($w = -P_f \Delta V$), is by the path through state 3, where pressure reduction precedes expansion. By taking the curved path between the initial and final state, an intermediate amount of reversible work is done.

One specific reversible expansion of an ideal gas that will be of particular interest to us is the one in which the system remains at constant temperature (by being immersed in a thermostat). Such a process is called *isothermal*. For this case, we can use Eq. (6), with $P = nRT/V$:

$$w_{\text{rev}} = - \int_i^f P dV \stackrel{\text{ig}}{=} - \int_i^f \frac{nRT}{V} dV \stackrel{\text{isotherm}}{=} - nRT \int_i^f \frac{dV}{V} = -nRT \ln\left(\frac{V_f}{V_i}\right) \quad (7)$$

The work is negative because the system is expanding.

In this book, when equalities are restricted to certain conditions or certain substances, we will often indicate these restrictions by notations above the equals sign. The designations “ig” (ideal gas) and “isotherm” (isothermal) have been used in Eq. (7).

The type of work that we will deal with most often in this book is work of expansion and contraction, which we will call PV work. Usually, the expansion or contraction is against the pressure of the atmosphere. In cases in which other types of work are involved, such as the work required to stretch an object or increase its surface area or the work of electrochemical cells or driving chemical reactions, we will usually designate these as w_{oth} or δw_{oth} . We then have

$$\delta w = -P_{\text{ext}} dV + \delta w_{\text{oth}} \quad (8)$$

or, in the reversible case,

$$\delta w_{\text{rev}} = -P dV + \delta w_{\text{oth,rev}} \quad (9)$$

The term $\delta w_{\text{oth,rev}}$ can be written in a form analogous to $-P dV$ (i.e., as the sum of products of changes in generalized displacement coordinates, dl_i , times the intensive forces conjugate to these displacement coordinates, L_i).

$$\delta w_{\text{rev}} = -P dV + \sum_i L_i dl_i \quad (10)$$

where the sum is over all forms of “other” work). One example of other work is electrical, where $L_{\text{elec}} = \phi$ (the electrical potential) and $dl_{\text{elec}} = dQ$ (the charge transferred). Another example is stretching a surface, where $L_{\text{surf}} = \gamma$ [the surface tension (discussed in [Chapter 11](#))] and $dl_{\text{surf}} = d\sigma$ (the increase in surface area).

2.8 Internal Energy

In elementary physics, we are taught to recognize the different types of energy of simple bodies. These may include the translational and rotational kinetic energies of motion of the body as a whole, which we call K , and the potential energy due to the position of the body in a gravitational or electrical external field, V . From Newton's laws, it can be shown that energy is conserved in motion. A falling body converts its potential energy in a gravitational field into kinetic energy of motion; conversely, an upward-moving body will be brought to rest for an instant,⁴ its initial kinetic energy being converted into potential energy in the gravitational field. In the presence of air, these conversions are not perfect; some energy is consumed by friction and causes a slight heating of the air and the body. We account for heating of the air by including its thermal energy in our considerations. In order to account for the energy absorbed by the body, we invoke its *internal energy*, U . U is the energy of motion or of position of one part of a body relative to other parts. Most importantly, it includes the energy of the random motions of the atoms and molecules of which the body is composed. For example, for a monatomic ideal gas, U is just the total kinetic energy of the atom discussed in [Chapter 1](#). U is a state function; it depends only on the properties of the body, primarily its temperature. We are usually only interested in changes in the internal energy of systems and are thus free to arbitrarily fix a "minimum set" of internal energies at a particular temperature. We will see in [Chapter 7](#) that a convenient minimum set is the internal energy of each chemical element in the state that it is found under ambient conditions. We can set these values equal to zero.

Internal energy is an extensive property of a system. If we double the size of a system, keeping intensive variables such as temperature and pressure constant, we double the system's internal energy. If we divide the internal energy of a system by the number of moles in the system, we obtain the *molar internal energy*, $U_m = U/n$, which is an intensive quantity. Other molar properties, such as the molar volume, are also indicated by the subscript m .

2.9 The First Law

The first law of thermodynamics is the recognition that

In any process, the energy of the universe is conserved.

Discussing the universe might seem grandiose, but it is just a way of reminding ourselves that we must consider both the system and the surroundings. Energy can flow between the system and surroundings and it is only the sum of these energies that is constant. The law is trivially applied to isolated systems, because,

by definition, such systems cannot exchange mass or energy with the surroundings. Thus, a corollary of the first law is as follows:

The energy of an isolated system is constant in any process.

We will be more interested in closed systems, which can exchange energy with their surroundings by either heat transfer or work at the system boundary. A sign convention will be used where both heat and work are positive if they represent transfer of energy from the surroundings to the system. Because heat and work are decreases in the thermal and mechanical energy of the surroundings, they must show up as increases in the energy of the system. The mathematical form of the first law for closed systems is therefore

$$\Delta E = q + w \quad (11)$$

If there is more than one heat or work term, q and w are the net heat and work. E is the total energy of the system—the sum of its overall kinetic and potential energy plus its internal energy. Therefore, we can write

$$\Delta E = \Delta K + \Delta V + \Delta U = q + w \quad (12)$$

where ΔK is the change of the kinetic energy of motion of the system as a whole, ΔV is its change of potential energy due to its position in an external field, and ΔU is its change of internal energy. The change of the kinetic energy of the motion of the system as a whole and the change of its potential energy are usually the concern of mechanics rather than thermodynamics and we will deal only with processes in which ΔK and ΔV are both equal to zero. Our mathematical statement of the first law then becomes

$$\Delta U = q + w \quad (13)$$

This equation also applies to isolated systems, where $\Delta U = 0$ because q and w are zero.

In applying Eq. (13), the variables that determine q and w will often be continuously changing. Such change can be handled by adding up very small changes of U or, more exactly, by integrating over infinitesimal changes in U . The differential form of Eq. (13) is

$$dU = \delta q + \delta w \quad (14)$$

Although the first law might seem logically obvious to us today, it was only around 1800 that Rumford showed that a body could be heated by doing work on it, as well as by transferring heat to it. Prior to this, the *caloric* theory of heat was in vogue. Caloric was supposedly a fluid contained in bodies and transferred from hot bodies to cold bodies in the process of heating. It was not recognized that caloric was a form of energy. The amount of this fluid required to heat 1 g of water 1°C was defined as the *calorie*.⁵ By the mid-19th century, Joule had

measured the heat equivalent of a number of different types of mechanical energy, showing that $1 \text{ cal} = 4.184 \text{ J}$. Because many energy terms in chemistry are still given in calories, it will be worthwhile to memorize this conversion.

Example 2. What is the heat flow for an ideal gas undergoing an expansion by each of the three reversible paths shown in Fig. 2? States i and f are at the same temperature and the curved path is the isotherm between these states.

Solution: Because the initial and final states are at the same temperature, there is no change in the internal energy of the ideal gas in the overall process. Therefore, $q = -w$.

$$\begin{array}{ll}\text{Path i-2-f:} & q = P_i \Delta V \\ \text{Path i-3-f:} & q = P_f \Delta V \\ \text{Isothermal path} & q = nRT \ln(V_f/V_i)\end{array}$$

Example 3. The ideal gas discussed in Example 2 could also undergo a single-stage expansion to the final state f, by suddenly reducing the pressure on the confining piston to P_f . How does this process differ from the reversible path i-3-f discussed in Example 2?

Solution: The final state in all four processes is the same. The work done is $P_f \Delta V$ ($w = -P_f \Delta V$). Therefore, $q = P_f \Delta V$, just as in path 1-3-f. There are some subtle differences, however. The single-stage expansion is not reversible and cannot be represented on a work diagram. Temperature and pressure are not uniform during the process. The system is held in a heat reservoir at a single temperature, and all the heat transferred is withdrawn from that single heat reservoir.

In the reversible process through path 1-3-f, heat transfer must be reversible. The system temperature is reduced in order to lower the pressure at constant volume. Therefore, heat must be transferred from an infinite number of heat reservoirs in the surroundings, all at a lower temperature than the final temperature of the system. We will see when we discuss entropy, in Chapter 3, that this is a very significant difference.

2.10 Heat Capacities

The heat required to heat a substance depends on just how that heating is conducted. The most common ways of heating are at constant volume or at constant pressure. In applying the first law to the process of heating a system at

constant volume, no expansion work is done as $dV = 0$. Assuming that there is no other work ($\delta w_{\text{oth}} = 0$), the first law gives

$$\delta q_V = dU_V \quad (15)$$

where the subscript V indicates that the process occurs at constant volume. All of the added heat goes into the internal energy of the system. Dividing this equation by dT_V results in

$$\frac{\delta q_V}{dT_V} \equiv C_V = \frac{dU_V}{dT_V} \equiv \left(\frac{\partial U}{\partial T} \right)_V \quad (16)$$

C_V is the *heat capacity* at constant volume. We have used the partial derivative notation (see [Appendix A](#)) for dU_V/dT_V , the rate of change of internal energy with temperature when volume is held constant. We cannot use a partial derivative for $\delta q_V/dT_V$ because, as we discussed, δq_V is the *amount* of heat transferred and not the change in something, which is required for a derivative. The added heat for a finite temperature range may be found by integrating Eq. (16) in the form $\delta q_V = C_V dT_V$:

$$q_V = \int_{T_1}^{T_2} C_V dT = \int_{T_1}^{T_2} dU_V = U_2 - U_1 \equiv \Delta U \quad (17)$$

The heat capacity per unit mass, c_V , is called the *specific heat* at constant volume. The heat capacity per mole is called the *molar heat capacity* at constant volume, $C_{V,m}$. For homogeneous systems, the system heat capacity can be calculated as

$$C_V = mc_V = nC_{V,m} \quad (18)$$

For solids and liquids, heating is almost always at constant pressure. Heating such substances in constant-volume containers would build up very high stresses in the walls of the container to counter the tendency of the substances to expand as they are heated. If volume is not held constant, some expansion will occur and work can be done. Assuming $\delta w_{\text{oth}} = 0$,

$$\delta q = dU - \delta w = dU + P_{\text{ext}} dV = dU + P dV \quad (19)$$

Constant pressure means constant P_{ext} , because we define our constraints with respect to the surroundings, where we control the process. In the last step, we assume mechanical equilibrium between the system and the surroundings. This is an excellent assumption for slow processes with systems with movable boundaries, for which we will generally take $P_{\text{ext}} = P$. It is not a good assumption for processes in which there is a sudden change of constraints, such as an explosion or the removal of a “stop” which secures a piston. In such cases, the system may not even have a uniform pressure.

For a constant-pressure process, we can write Eq. (19) as

$$\delta q_P = dU + P dV + V dP \quad (20)$$

where the last term may be added, because it is zero in this case. Using the formula for the differential of a product, $d(xy) = x dy + y dx$, gives

$$\delta q_P = d(U + PV) \quad (21)$$

Defining a function, H (the *enthalpy*) by

$$H \equiv U + PV \quad (22)$$

$$\delta q_P = dH_P \quad (23)$$

If there are other work terms, the reversible forms of which are $\delta w_{\text{oth}} = L dl$, where l is a displacement coordinate and L is the force conjugate to the displacement coordinate, we will include additional terms of the form $-Ll$ in the definition of the enthalpy. Although not all authors adopt this extended definition, it is necessary, as shown below, to maintain the form of Eq. (23).

$$H \equiv U + PV - \sum_i L_i l_i \quad (24)$$

With δw_{oth} , the first law becomes

$$dU = \delta q - P dV + \sum_i L_i dl_i \quad (25)$$

This gives

$$\begin{aligned} \delta q &= dH - P dV - V dP + \sum_i L_i dl_i + \sum_i l_i dL_i + P dV - \sum_i L_i dl_i \\ &= dH - V dP + \sum_i l_i dL_i \end{aligned} \quad (26)$$

so that at constant pressure and forces (the usual situation), the heat absorbed remains the enthalpy change.

Enthalpy plays a role in constant-pressure processes similar to that of internal energy in constant-volume processes. The heat added to a system in a constant-pressure process is the enthalpy increase of the system. Because U , P , and V (and l_i and L_i) are all state functions, H is also a state function. It is extensive. The molar enthalpy, $H_m \equiv H/n$, is intensive. Dividing Eq. (23) by dT_P gives

$$\frac{\delta q_P}{dT_P} \equiv C_P = \frac{dH_P}{dT_P} = \left(\frac{\partial H}{\partial T} \right)_P \quad (27)$$

The specific heat at constant pressure, c_p , and the molar heat capacity at constant pressure, $C_{P,m}$, are defined by

$$C_P = mc_P = nC_{P,m} \quad (28)$$

Figure 3 is a graph of molar heat capacities for a number of gaseous substances as a function of temperature. Although for most substances, heat capacities rise as temperature increases, for the noble gases, heat capacities are remarkably independent of temperature. Equation (17) of [Chapter 1](#) gives $\frac{3}{2}kT$ for the average translational kinetic energy of ideal gas molecules. To a very good approximation, this is the only type of energy that can change in noble gas molecules at low and moderate temperatures and pressures. Multiplying by Avogadro's number, the energy per mole is $\frac{3}{2}RT$ and $C_{V,m}$ from Eq. (16), is $\frac{3}{2}R$, in agreement with Fig. 3. Molecules containing two or more atoms can also store energy as vibrational energy and rotational energy, which increases their

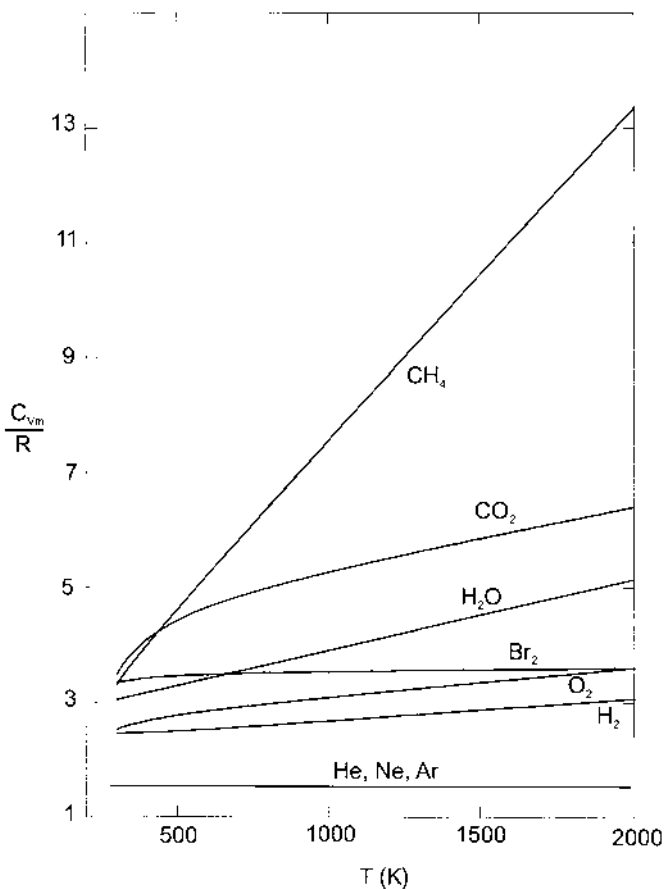


Figure 3 Heat capacities of gases.

heat capacities over that of the noble gases. Although the detailed shapes of all the curves in Fig. 3 can be calculated, such calculations involve statistical mechanics and quantum mechanics. Statistical mechanics will be treated in Chapter 5, but quantum mechanics will not be discussed in this book.

For substances with temperature-independent heat capacity, C_V can be removed from the integral in Eq. (17):

$$\Delta U = q_V = C_V(T_2 - T_1) = C_V\Delta T \quad (29)$$

Equation (29) may be an adequate approximation for substances with temperature-dependent heat capacities if the temperature range is small enough. In addition, the substance must remain in a single phase (e.g., solid, liquid or gas) over the temperature range considered. The temperature variation of heat capacities is often represented by a multiterm empirical equation. Data for a number of gases in one often-employed representation are given in Table 1. Note that if $10^3b = 3.26 \text{ J/K}^2 \text{ mol}$; $b = 3.26 \times 10^{-3} \text{ J/K}^2 \text{ mol}$.

Example 4. One reason that temperature drops as we go to high elevations is that rising air expands as it moves to regions of lower pressure. Assuming that a parcel of air behaves adiabatically and reversibly as it rises, calculate its *lapse rate*, the temperature decrease

TABLE 1 Molar Heat Capacities of Gases

Gas	$C_{P,m} = a + bT + c/T^2$		
	$a \text{ (J/K mol)}$	$10^3b \text{ (J/K}^2 \text{ mol)}$	$10^{-5}c \text{ (J K/mol)}$
He, Ne, Ar, Kr, Xe	20.786	0	0
H ₂	27.28	3.26	0.50
O ₂	29.96	4.18	−1.67
N ₂	28.58	3.77	−0.50
F ₂	34.56	2.51	−3.51
Cl ₂	37.03	0.67	−2.85
Br ₂	37.32	0.50	−1.26
CO ₂	44.22	8.79	−8.62
H ₂ O	30.54	10.29	0
NH ₃	29.75	25.10	−1.55
CH ₄	23.64	47.86	−1.92
SO ₂	49.77	4.56	−11.05
H ₂ S	32.68	12.38	−1.92

Note: Valid for 298–2000 K.

Source: Data from A James, M Lord. Index of Chemical and Physical Data. New York: Van Nostrand Reinhold, 1992.

for each kilometer that the air rises. Assume dry air, so that no moisture condenses out. Consider the air to be ideal with a heat capacity $C_{P,m} = (7/2)R$.

Solution: Because we found the pressure variation in the atmosphere in [Chapter 1](#), it is convenient to use pressure as the independent variable. Enthalpy is used when dealing with pressure. The rise of the parcel is slow enough so that it can be considered reversible:

$$dU \stackrel{\text{ad}}{=} -P_{\text{ext}} dV \stackrel{\text{rev}}{=} -P dV$$

$$dH = d(U + PV) = dU + P dV + V dP = V dP$$

Arbitrarily treating 1 mol of gas,

$$dH = C_{P,m} dT = RT \frac{dP}{P}$$

Using Eq. (59) of Chapter 1 for the pressure variation,

$$C_{P,m} dT = -Mg dz$$

or

$$\frac{dT}{dz} = -\frac{Mg}{C_{P,m}} = -\frac{0.029 \text{ kg/mol} (9.8 \text{ m/s}^2) 1000 \text{ m/km}}{29 \text{ J/mol K}} = -9.8 \text{ K/km}$$

which is the dry, adiabatic lapse rate.

We will now derive a general relationship between C_P and C_V :

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial(U + PV)}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \quad (30)$$

because $(\partial P / \partial T)_P = 0$. Comparison with Eq. (16) shows that $(\partial U / \partial T)_P$ is not C_V , because P , rather than V , is held constant in the derivative. To relate $(\partial U / \partial T)_P$ to C_V , we apply Eq. (10), of [Appendix A](#), with $F = U$, $x = T$, $y = P$, and $z = V$, to get

$$\left(\frac{\partial U}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V + \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P = C_V + \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \quad (31)$$

giving as our final result

$$C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P \quad (32)$$

Equation (32) shows that there are two additional energies that must be supplied when heating at constant pressure compared with constant volume. The term $P(\partial V / \partial T)_P$ is the work done in expanding against the external pressure P .

Because the term $(\partial U/\partial V)_T(\partial V/\partial T)_P$ is of similar form, the quantity $(\partial U/\partial V)_T$ is called the *internal pressure*. This term represents additional energy stored *within the system*, due to the change in the average separation of the molecules when heating is performed at constant pressure. It is nonzero when forces exist between molecules.

In the Bernoulli model of the ideal gas, discussed in [Chapter 1](#), there are no interactions between molecules. The internal energy, U , therefore does not depend on how far apart the molecules are, and $(\partial U/\partial V)_T = 0$. For an ideal gas $(\partial V/\partial T)_P = nR/P$, and

$$C_P^{\text{ig}} = C_V + nR \quad \text{or} \quad C_{P,m}^{\text{ig}} = C_{V,m} + R \quad (33)$$

In [Chapter 3](#), we will see how the difference in C_P and C_V can generally be obtained from the equation of state. For condensed phases, $(\partial V/\partial T)_P$ is very small, but $(\partial U/\partial V)_T$ is very large, and substantial differences between C_P and C_V can result.

Heat capacities can be measured by supplying energy to a system and observing its rise in temperature under adiabatic conditions. The energy is most easily supplied as an electrical current I passing through a known resistance for a given time:

$$w_{\text{elec}} = \phi Q = (IR)(I\Delta t) = I^2 R \Delta t \quad (34)$$

At constant volume,

$$\Delta U \stackrel{\text{ad}}{\underset{\text{const}}{=}}_V w_{\text{elec}} \quad (35)$$

At constant pressure,

$$\Delta H = \Delta U + \Delta(PV) - \Delta(\phi Q) \stackrel{\text{ad}}{\underset{\text{const}}{=}}_P w_{\text{elec}} - P\Delta V + P\Delta V = w_{\text{elec}} \quad (36)$$

For the last equality, we have assumed that the process begins before the current is turned on and ends after it is turned off. There is, then, no change of ϕ or Q of the system. The current is on while ϕ is not a uniform property of the system.

Example 5. When a voltage of 0.4 V is impressed on a well-insulated piece of iron of mass 44 g, exposed to the atmosphere, a current of 43 A results. After 10 s, the current is terminated and the sample is allowed to reach a uniform temperature. Its temperature is found to have risen 8.7°C. What is the heat capacity of iron? Is this value a better approximation to $C_{V,m}$ or $C_{P,m}$?

Solution: Because this system is well insulated, we will assume adiabaticity, $\delta q = 0$. In addition, we will assume that heat capacities

are constant over the small temperature range of the measurements.

$$\Delta U \stackrel{\text{ad}}{=} w_{\text{elec}} - P_{\text{ext}}\Delta V = C_V\Delta T + \int_i^f \left(\frac{\partial U}{\partial V}\right)_T dV$$

Although $P_{\text{ext}}\Delta V$ is negligible, $(\partial U/\partial V)_T$ is very large for a solid and is not easily evaluated. Thus, the described measurement is not a good way to measure C_V :

$$\Delta H \stackrel{\text{ad}}{\underset{\text{const } P}{=}} w_{\text{elec}} = C_P\Delta T$$

$$C_{P,m} = \frac{(0.4 \text{ V})(43 \text{ A})(10 \text{ s})}{(8.7 \text{ K})(44 \text{ g})} \left(\frac{55.8 \text{ g}}{\text{mol}}\right) = 25.1 \frac{\text{J}}{\text{K mol}}$$

Heat capacities can be defined for processes that occur under conditions other than constant volume or constant temperature. For example, we could define a heat capacity at constant length of a sample. However, regardless of the nature of the process, the heat capacity will always be positive. This is ensured by the zeroth law of thermodynamics, which requires that as positive heat is transferred from a heat reservoir to a colder body, the temperature of the body will rise toward that of the reservoir in approaching the state of thermal equilibrium, regardless of the constraints of the heat-transfer process.

2.11 The Joule Process

The internal pressure, $(\partial U/\partial V)_T$, is so important that we should consider how it might be measured for real gases. In 1843, Joule showed that $(\partial U/\partial V)_T$ could be obtained from the simple process diagrammed in [Fig. 4](#).

In the Joule process, a gas expands into a vacuum in a well-insulated container and the change in temperature with the change in volume of the gas is measured. The system is all of the gas, which we imagine surrounded by a flexible boundary. (The boundary expands with the gas; no gas passes through the boundary.) Because there is no opposing force as the boundary expands into vacuum, the work done is equal to zero. Assuming perfect insulation, the heat transferred to the system is also zero and $\Delta U = q + w = 0$. Thus, the Joule expansion is a constant-energy process and we measure $\Delta T_U/\Delta V_U$. If a series of measurements at different ΔV 's are made, they can be extrapolated to zero ΔV_U to give $(\partial T/\partial V)_U$, which is known as the *Joule coefficient*, μ_J . From Eq. (7) of [Appendix A](#), we can write μ_J as

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T \quad (37)$$

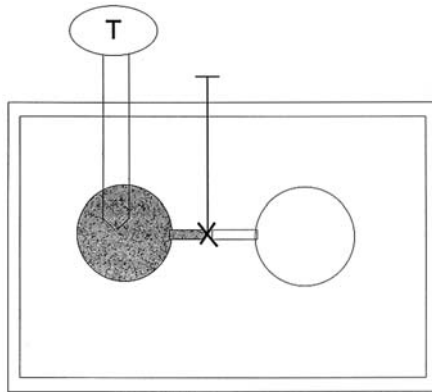


Figure 4 The Joule process.

Using Eq. (16),

$$\left(\frac{\partial U}{\partial V}\right)_T = -C_V \mu_J \quad (38)$$

The problem with the Joule experiment in practice is that although it is possible to insulate the vessel containing the gas, the vessel itself and the temperature-measuring device will be heated with the gas, greatly reducing the observed temperature change. Because the Joule coefficient is zero for ideal gases, we expect it to be small for real gases. Joule observed no temperature change when he did the experiment in the 1840s. Later, more careful measurements gave observable results, but with little precision.

2.12 The Joule–Thomson Process

An alternative, and much more accurate, method for obtaining information on the interactions between molecules is the Joule–Thomson expansion, shown in [Fig. 5](#). This process also forms the experimental basis for much of the science of cryogenics (the study of phenomena at low temperatures), which we will discuss in [Chapter 4](#). Industrially, cryogenic liquids, such as liquid N_2 , O_2 , H_2 , and He , are produced by the Linde process, which uses Joule–Thomson expansions. N_2 and O_2 (and noble gases) are obtained in this process by producing and then

initial state: P_1, V_1, T_1



final state: P_2, V_2, T_2

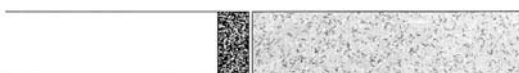


Figure 5 The Joule–Thomson process.

fractionally distilling liquid air. O_2 and N_2 are among the top five chemicals in terms of the amount produced in the United States.

In the Joule–Thomson process, a compressed gas is allowed to rapidly expand through a porous plug. Because the apparatus is insulated and the gas expands very rapidly, no appreciable heat transfer occurs and the process is adiabatic. We will analyze the system as a quantity of gas moves through the plug. The gas is our system and it is shown in its initial and final states in Fig. 4. The process is certainly not reversible. However, the initial and final states are at internal equilibrium, with uniform temperature and pressure. The boundary of the system moves with the gas through the plug. Because of flow resistance, there is a considerable pressure drop as the gas passes through the tortuous channels of the plug. The much smaller pressure drops in the tubes upstream and downstream of the plug are neglected. Work equal to $P_1 V_1$ is done on the system by the upstream pressure, which pushes the gas through the plug. Work equal to $P_2 V_2$ is done by the system in pushing the downstream gas out of the way as it comes out of the plug. Applying the first law to this process,

$$\Delta U = U_2 - U_1 \stackrel{\text{ad}}{=} w = P_1 V_1 - P_2 V_2 \quad (39)$$

Rewriting, we obtain

$$U_2 + P_2 V_2 = H_2 = U_1 + P_1 V_1 = H_1 \quad (40)$$

Thus, the initial and final states of a Joule–Thomson expansion lie on a curve of constant enthalpy (*isoenthalp*) and the Joule–Thomson process occurs at constant enthalpy. The Joule–Thomson coefficient, μ_{JT} , is defined as

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P} \right)_H \quad (41)$$

and can be determined from the limit of measurements of $\Delta T/\Delta P$ made as shown in Fig. 5. Alternatively, a single isoenthalp can be determined by expanding from an initial T_1 and the highest P_1 available to a succession of lower P_2 's, measuring the resulting temperature each time. Some isoenthalps of N_2 are shown in Fig. 6. The dashed curve indicates the Joule–Thomson inversion temperature, T_i , below which $\mu_{JT} > 0$.

The Joule–Thomson coefficient is the slope of the isoenthalp and is a function of both temperature and pressure. From Eq. (23) and Eq. (7) of Appendix A, we can write

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P} \right)_H = - \left(\frac{\partial T}{\partial H} \right)_P \left(\frac{\partial H}{\partial P} \right)_T = - \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T \quad (42)$$

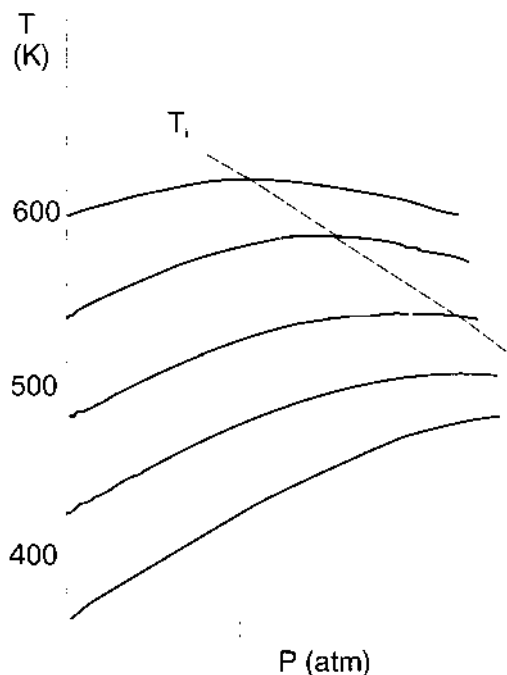


Figure 6 Isoenthalps of N_2 . (Data from JR Roebuck, H Osterberg. Phys Rev 48:450, 1948.)

showing that measurements of the Joule–Thomson coefficient provide the variation of enthalpy with pressure at constant temperature. The reader should note the parallel between the Joule process for a change of volume and the Joule–Thomson process for a change in pressure.

The Joule–Thomson coefficient can be shown to be zero for ideal gases. For real gases, its magnitude is usually less than a few degrees Kelvin per atmosphere. Its sign can be either positive or negative, corresponding to the slope of the isoenthalp, as shown in Fig. 5. For gases (fluids, if we are above the critical temperature) at high temperatures, $\mu_{JT} \equiv (\partial T / \partial P)_H$ is generally negative, corresponding to heating the gas upon expansion. However, at lower temperatures and pressures, μ_{JT} is positive, corresponding to a cooling of the gas upon expansion. The temperature above which $\mu_{JT} < 0$ and below which $\mu_{JT} > 0$ is known as the *Joule–Thomson inversion temperature* at the given pressure. At this temperature, $\mu_{JT} = 0$. Most gases have $\mu_{JT} > 0$ at room temperature and moderate pressures and they cool upon expansion. Nitrogen and oxygen, for example, can be liquefied by a Joule–Thomson expansion from room temperature. For hydrogen and helium, however, the Joule–Thomson inversion temperature is lower than room temperature and these gases must be cooled (e.g., by liquid nitrogen) before they can be liquefied by further expansion. The Joule–Thomson expansion is adiabatic, but clearly nonreversible. Because it occurs in a finite time (actually quite quickly), it can be used for practical processes. A different, distinctly nonpractical, type of adiabatic process will be considered in the next section.

2.13 Reversible Adiabatic Expansion of an Ideal Gas

A reversible adiabatic expansion of an ideal gas is infinitely slow, so the system maintains internal equilibrium (mechanical, thermal, and material) and equilibrium with its surroundings. Mechanical equilibrium with the surroundings requires that the external pressure be only infinitesimally less than the internal pressure. We can therefore set $P = P_{\text{ext}}$. Thermal and material equilibria with the surroundings are not at issue, because the system is closed with adiabatic walls. A reversible adiabatic expansion is a highly idealized process! Nevertheless, it will serve as a cornerstone in our discussions of thermodynamics. Applying the first law to such a process,

$$dU = \delta q + \delta w^{\text{ad}} = -P_{\text{ext}} dV^{\text{rev}} = -P dV \quad (43)$$

For an ideal gas, U is only a function of temperature, so that we can also write

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \stackrel{\text{ig}}{=} \left(\frac{\partial U}{\partial T} \right)_V dT = C_V dT \quad (44)$$

Equating these two expressions and setting $P = nRT/V$ gives

$$C_{V,m} dT = -RT \frac{dV}{V} \quad (45)$$

Separating variables,

$$C_{V,m} \frac{dT}{T} = -R \frac{dV}{V} \quad (46)$$

which can be integrated from initial conditions T_1 and V_1 to final conditions T_2 and V_2 . If the ideal gas is monatomic or if the temperature range is small, $C_{V,m}$ may be taken as a constant and integration gives directly:

$$\ln\left(\frac{T_2}{T_1}\right) = -\frac{R}{C_{V,m}} \ln\left(\frac{V_2}{V_1}\right) \quad (47)$$

In the more general case, an average $C_{V,m}$, $\overline{C_{V,m}}$, must be used. [Actually, because $dT/T = d(\ln T)$, this should be an average over the logarithm of temperature.] If the final temperature is not known, $\overline{C_{V,m}}$ can be estimated by successive approximations, as in Example 6.

Example 6. Methane gas, originally at 800°C, undergoes a reversible adiabatic expansion that doubles its volume. Estimate the final temperature, considering the gas to be ideal.

Solution: For the first estimate, we will use $C_{V,m}$ at 800°C. Using data from Table 1, $C_{P,m}$ at 800°C for methane is $23.67 + 0.04786(1073) - (1.92 \times 10^5)/(1073)^2 = 74.85 \text{ J/mol K}$ and $C_{V,m} = C_{P,m} - R = 66.53 \text{ J/mol K}$. Then,

$$\ln\left(\frac{T_2}{T_1}\right) = -\frac{8.314}{66.53} \ln 2 = -0.0866$$

$$\begin{aligned} T_2 &= T_1 \exp(-0.0866) \\ &= (1073 \text{ K})(0.917) = 984 \text{ K} = 711^\circ\text{C} \end{aligned}$$

For a better estimate, we use $C_{V,m}$ at $\ln T$, the average of $\ln(1073)$ and $\ln(984)$. $\ln T = 6.935$ K, $T = 1028$ K, $C_{P,m} = 72.69 \text{ J/mol K}$ and $C_{V,m} = 64.37 \text{ J/mol K}$. Then,

$$\ln\left(\frac{T_2}{T_1}\right) = -\frac{8.314}{64.37} \ln 2 = -0.0895$$

$$\begin{aligned} T_2 &= T_1 \exp(-0.0895) \\ &= (1073 \text{ K})(0.914) = 981 \text{ K} = 708^\circ\text{C} \end{aligned}$$

(This example is done more exactly in Problem 7.)

Assuming constant $C_{V,m}$ and setting $R = C_{P,m} - C_{V,m}$ for an ideal gas, we get

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_1}{V_2}\right)^{(C_{P,m}-C_{V,m})/C_{V,m}} = \ln\left(\frac{V_1}{V_2}\right)^{\gamma-1} \quad (48)$$

where $\gamma \equiv C_{P,m}/C_{V,m}$ is called the *heat capacity ratio*. For gases, the heat capacity ratio is always greater than unity. If the logarithms of two functions are equal, the functions must be equal:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \frac{P_2 V_2}{P_1 V_1} \quad (49)$$

or

$$P_1 V_1^\gamma = P_2 V_2^\gamma = \text{const.} \quad (50)$$

Thus, a reversible adiabatic expansion of an ideal gas occurs with constant PV^γ . Figure 6 shows two reversible processes of an ideal gas—a reversible isothermal process and a reversible adiabatic process—plotted on a work diagram. The pressure for the adiabatic expansion falls faster than that for the isothermal expansion (because $\gamma > 1$). The area under each curve is the amount of work that the expanding gas does on the surroundings in the process. More work is done in the isothermal process, because heat is added to the system to keep its temperature constant. Because the energy of the system remains constant with constant temperature, the added heat must end up as work done on the surroundings. In the adiabatic process, the work done on the surroundings comes exclusively from the internal energy of the system. Therefore, there is a reduction of temperature and less work is done on the surroundings in the reversible adiabatic process.

2.14 A Simple Heat Engine

A heat engine is a device that converts heat into work, the starting process for much of what is done in a modern industrial society. We have seen that this conversion can be accomplished by an isothermal expansion of a gas. If the gas is ideal, all the work done on the surroundings in such an expansion is provided by heat withdrawn from the surroundings (say, from a hot reservoir at temperature T_h). In order to continue obtaining work from a system undergoing isothermal expansion, it would have to continue expanding, and soon it would become inconveniently large. We will thus additionally require that a heat engine return to its initial state (i.e., that it undergoes a *cyclic process*). Because the system comes back to its initial state after one cycle in a cyclic process, all of the resulting change for the cycle is in the surroundings. How can we return a system (an

engine) to its initial state after an isothermal expansion? One way to do this would be to perform an isothermal compression at the same temperature, T_h . In this case, however, we would just be traversing the same isotherm in the opposite direction and have to supply to the engine exactly the amount of work that we (in the surroundings) received from it in the original expansion. This would not be much of an engine at all; over one cycle, we would achieve exactly zero.⁶

One way to obtain net work over one cycle of our engine is to return it to its initial state by an isothermal expansion at a lower temperature, T_c , the temperature of a cold reservoir. The area under the lower-temperature compression on the work diagram would be lower than that under the expansion, and we would have net work. The only problem in doing this is that isotherms at different temperatures do not intersect on a work diagram. We need some way to get from the higher temperature of the expansion to the lower temperature of the compression and then back to the initial high-temperature state of the engine. This suggests that we need two additional steps to complete our cycle, as shown in Fig. 7. If these steps are adiabatic (and reversible so that they can be shown on the work diagram), we have the *Carnot cycle*, which has played a key theoretical role in the development of thermodynamics.

In Fig. 8, step I is an isothermal expansion, step II is an adiabatic expansion, step III is an isothermal compression, and step IV is an adiabatic compression. Note that zero heat is transferred in the adiabatic expansion and compression (steps II and IV) that we have added to complete the cycle, and that the work terms in these two steps exactly cancel, being equal to $\int_{T_h}^{T_c} C_V dT$ in the expansion and $\int_{T_c}^{T_h} C_V dT$ in the compression. (The work in an adiabatic

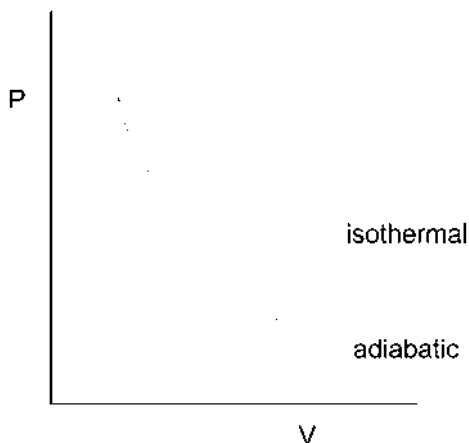


Figure 7 Reversal isothermal and reversible adiabatic expansions.

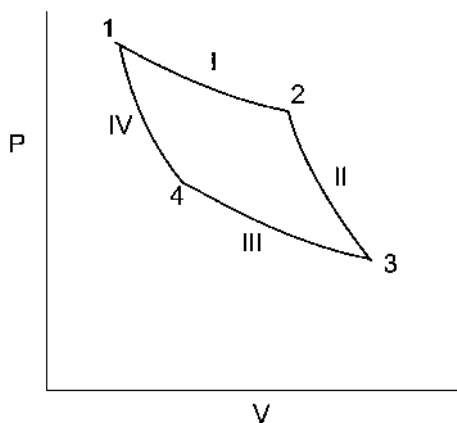


Figure 8 The Carnot cycle.

expansion comes at the expense of the internal energy of the gas.) Thus, to consider the effect on the surroundings of one cycle of the engine, we must consider only steps I and III of the Carnot cycle [i.e., the isothermal expansion (at T_h) and compression (at T_c)]. The heat and work terms in steps I and III are given in Table 2. In step III', we have made use of the fact that because V_4/V_1 and V_3/V_2 are volume ratios for adiabatic expansion and contraction between the same two temperatures, from Eq. (49) we have

$$\left(\frac{T_h}{T_c}\right) = \left(\frac{V_4}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \quad \text{or} \quad \left(\frac{V_4}{V_1}\right) = \left(\frac{V_3}{V_2}\right) \quad (51)$$

The Carnot cycle engine achieves what we are looking for, a conversion of heat into work, with return of the engine to its initial state. We note, however, that in order to complete the cycle, we have paid a price. In the isothermal compression at T_c , some of the work produced in the expansion has to be used up to compress the system, finding its way into heat at the cold reservoir temperature.

TABLE 2 Heat and Work in a Carnot Cycle

Step	Heat	Work
I	$nRT_h \ln\left(\frac{V_2}{V_1}\right)$	$-nRT_h \ln\left(\frac{V_2}{V_1}\right)$
III	$-nRT_c \ln\left(\frac{V_3}{V_4}\right)$	$nRT_c \ln\left(\frac{V_3}{V_4}\right)$
III'	$-nRT_c \ln\left(\frac{V_2}{V_1}\right)$	$nRT_c \ln\left(\frac{V_2}{V_1}\right)$

An important measure of the quality of an engine is its *efficiency*, ε [the fraction of the energy that it removes from a high temperature reservoir (the heat term in step I) that it converts into work].⁷ For the Carnot cycle engine to work as efficiently as possible, the heat transfers should be reversible. Thus, the heat transferred to the system in step I should be from a heat reservoir at temperature T_h , and the heat transferred from the system in step III should be to a reservoir at T_c . From Table 2, we see that the efficiency of a Carnot cycle engine is

$$\varepsilon = \frac{(-w_I) + (-w_{III})}{q_I} = \frac{[nR \ln(V_2/V_1)](T_h - T_c)}{nRT_h \ln(V_2/V_1)} = \frac{T_h - T_c}{T_h} \quad (52)$$

The Carnot cycle engine is actually the only reversible engine that we can design with two heat reservoirs. We see that because of the need to reject heat when returning the engine to its initial state, the engine cannot operate with unit efficiency. In Chapter 3, we will elevate this observation to one of the basic tenets of thermodynamics—the second law.

Questions

1. Indicate whether each of the following systems would be best described as an isolated, closed, or open system:

- (a) An empty microwave oven during a 3-min cycle.
- (b) Food is placed in the above microwave oven during the same cycle and then the cooked food is removed from the oven.
- (c) A bomb explodes in a cargo container in an airplane. (The system is the container and contents, and the analysis concludes before the walls of the system distort or rupture.)

2. Are the following isolated systems at internal equilibrium? If not, which types of internal equilibrium (thermal, mechanical, or material) do not hold?

- (a) A glass of water that has been untouched for a considerable time
- (b) A glass of room-temperature water into which some ice cubes have recently been placed
- (c) A diamond ring at ambient conditions

3. Would each of the following unchanging systems be better described as at equilibrium or at steady state?

- (a) A rock sitting at the bottom of a lake
- (b) A fish swimming in the lake
- (c) A Styrofoam cooler filled with a large amount of partially melted ice (take only the cooler, not its contents as the system)

4. Is each of the following systems homogeneous or heterogeneous?
 - (a) Some crystalline sugar
 - (b) An aqueous salt solution
 - (c) The same solution as in part (b), after more salt is added than will dissolve
 - (d) A molten solution of iron and carbon
 - (e) The solution in part (d) after it has solidified into steel
5. An explosion is usually considered to be adiabatic, indicating negligible heat transfer, even though its rapidly expanding gaseous products are not at the same temperature as the surroundings, and the boundary does permit heat transfer. Can you explain this?
6. Does a real expansion produce more or less work than a reversible expansion? Does a real compression require more or less work than a reversible compression?
7. Express the definition of each of the following in mathematical form:
 - (a) An adiabatic process
 - (b) An isothermal process
 - (c) A process in an isolated system
 - (d) The Joule–Thomson expansion
8. The caloric theory of heat pictured heat as a fluid which permeates all materials. What experimental evidence clearly made this theory untenable, regardless of the properties assigned to the caloric fluid? Why?
9. Write expressions for H and dH in terms of U and dU for processes that include the following:
 - (a) Electrical work
 - (b) Stretching of an elastomer
10. One of the most common types of error made by students of thermodynamics is using formulas for conditions under which they do not apply. Indicate the physical conditions under which each of the following formulas holds:
 - (a) $dU = \delta q - P dV$
 - (b) $PV^\gamma = \text{const.}$
 - (c) $dU = 0$ (when $dV \neq 0$)
 - (d) $dH = C_p dT$
11. A gas expands from V_1 to V_2 . For which of the following processes will the final temperature be the highest and for which will the final temperature be the lowest:
 - (a) The process is reversible and adiabatic.
 - (b) The process is a Joule expansion.
 - (c) The process is an adiabatic irreversible expansion against the final pressure.
12. Which of the following pairs is larger:
 - (a) ΔU or ΔH for an expansion against the atmosphere
 - (b) $C_{p,m}$ of N_2 at 1000°C or at 25°C
 - (c) $C_{p,m}$ of H_2 at 500°C or $C_{p,m}$ of Ar at 500°C

13. Draw a work diagram for a reversible heat engine that operates with two isothermal steps and two constant-pressure steps. How many heat reservoirs are needed to operate this engine?
14. An ideal rubber is defined as one for which $\left(\frac{\partial U}{\partial l}\right)_{T,V} = 0$. What does this definition imply for the direction of heat flow as an ideal rubber is extended? Verify your conclusion by holding a rubber band against your lips while rapidly extending it.
15. Rationalize the statement “The Carnot cycle engine is the only reversible engine that operates with just two heat reservoirs.”

Problems

1. Consider the doubling of volume of 1 mol of an ideal gas at 298 K from 22.4 L (1.0 atm) to 44.8 L (0.5 atm). [Figure 2](#) shows three paths by which this expansion can be performed. Calculate the work done on the surroundings by each path.
2. A waterfall is 200 ft high. If the water at the top has a temperature of 21.50°C, what is its temperature at the bottom?
3. A 1.0-kg iron mass falls from a height of 5.0 m into a well-insulated vessel containing 1.0 L of water. Neglecting splashing, if the original temperature of both the mass and the water was 25.00°C, what is their temperature when the final system has reached thermal equilibrium?
4. What is the temperature rise of 2.0 L of water if 2.0 A of electrical current is passed through a 200-Ω resistor in the water for 2 min? Assume the process is adiabatic and neglect the heat capacity of the resistor. The heat capacity of water is 75 J/K mol. (Note: 1.0 ΩA = 1.0 V.)
5. Find the work required to produce a strain ϵ in a metal following Hook’s law and in a rubber following Eq. (54) of [Chapter 1](#).
- 6*. (a) Derive the relation

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T \left[\left(\frac{\partial U}{\partial V}\right)_T + P \right] + V$$

- (b) Show that for an ideal gas

$$\left(\frac{\partial H}{\partial P}\right)_T = 0$$

7. Find a formula relating $(\partial H/\partial T)_V$ to $C_P = (\partial H/\partial T)_P$.
8. Calculate q , w , ΔU , and ΔH when 1 mol of NH_3 is heated from 300 K to 500 K at constant 1.0 atm pressure.

9. Calculate q , w , ΔU , and ΔH when 1 mol of an ideal gas expands isothermally from a pressure P_1 to a pressure P_2 against a constant opposing pressure of P_2 . Put your results in terms of P_1 , P_2 and T . Note that in this process, P_{ext} is constant, but P is not constant.
10. The pressure on Ar gas, originally at 25°C , is increased reversibly and adiabatically from 1.0 to 10.0 atm. What is the final temperature of the gas?
- 11*. (a) Using the form of $C_{p,m}$ from Table 1, integrate Eq. (46).
 - (b) Using the result in part (a), find the final temperature when N_2 at 25°C expands reversibly and adiabatically from a pressure of 1.0 atm to a pressure of 0.1 atm.
 - (c) Find a solution for Example 6, using the result in part (a). A program such as MathCad is useful for finding the root of the resulting equation.
12. ΔH_{vap} of water is 6.01 kJ/mol. Find ΔU_{vap} of water.
13. After finishing the measurement described in Example 5, the same iron resistor is placed in an insulated container with 75 g of an unknown substance. A current of 37 A through the resistor for 15 s raises the temperature of the system by 7.6°C . What is the specific heat of the unknown substance?
14. Give a formula for the work done in each of the following processes (use only the variables given in the problem):
 - (a) A gas is heated from T_1 to T_2 at constant volume.
 - (b) A battery produces a current I at a voltage ϕ for a time t .
 - (c) A gas passes through a porous plug in a Joule–Thompson expansion.
 - (d) An adiabatic expansion of an ideal gas in which its temperature falls from T_1 to T_2 .

Notes

1. An excellent source is *Thermodynamics* by Kenneth S. Pitzer (McGraw-Hill, 1995), an update of an early classic in the field.
2. This period is much longer for liquids than for gases, and care must be taken to adequately mix liquids (and high-pressure gases) in the laboratory.
3. Although we may do something like this when we measure someone's body temperature by placing our hand on her forehead.
4. This assumes that the initial velocity is below that needed to escape from the influence of the Earth's gravitational field, the so-called escape velocity.
5. More precisely, from 14.5°C to 15.5°C at 1 atm pressure.
6. This assumes that the engine is reversible. If it were a real engine and operated at a finite speed, due to friction, we would have actually achieved a conversion of work into heat.
7. This is because we usually pay for the fuel to maintain the hot reservoir at T_h . We consider the cold reservoir as "free" (e.g., it might be a river to which we add our waste heat). Recently, it has been recognized that there are costs involved in rejecting waste heat, in the form of thermal pollution. These are not considered in the definition of thermodynamic efficiency.