

3

The Second Law of Thermodynamics

*All the King's horses and all the King's men
Couldn't put Humpty Dumpty together again*

In addition to the quantity of energy, we must consider its quality, as indicated by its usefulness. As we use energy, its quantity remains constant, but its quality is degraded. Energy degradation is called *entropy increase*. The empirical observation that *there is always net entropy increase in real processes* is the second law of thermodynamics. Entropy, the measure of the quality of the energy of a system, is a state function. This requirement allows us to develop formulas to determine the entropy increase in both the system and its surroundings in any process. These general formulas are applied to a variety of processes involving heating, expansion, phase change, and distortion. The first and second laws of thermodynamics allow us to analyze the limits of performance of heat engines, heat pumps, and refrigerators.

3.1 The Second Law

Although the first law of thermodynamics places useful limits on the processes that can occur in nature, namely those that conserve total energy, it clearly is not

the whole story regarding energy. If the only energy consideration were the first law, there would never be any energy shortages; we could just recycle energy. For example, having used a resistor to convert electrical energy into an equal amount of thermal energy, we could use a different device to convert the thermal energy back into the original amount of electrical energy. Needless to say, such a device has never been invented. As another example, if a brick falls off a table and hits the floor, energy is conserved; the initial potential energy of the brick is converted first into kinetic energy, as the brick accelerates, and then into thermal energy, as it comes to rest on the floor. The brick and floor are slightly warmer at the end of this process. However, no machine has ever been invented that could make use of this thermal energy to raise the brick back up onto the table. Of course, we could just lift up the brick, but then we would be providing the energy to return the brick to its initial state. It is obvious that many processes that occur in nature proceed in one direction, but not in the opposite direction. The generalization of this observation is the second law of thermodynamics, which tells us the direction of real processes.

It should be noted that this property of energy becoming less useful as we use it is purely a characteristic of the macroscopic realm. In the microscopic world, energy is continually transformed between kinetic and potential forms, as in a vibrating molecule, or between molecular energy and radiation, as in a molecule in a laser cavity. How microscopic systems combine to give the very different energy properties of macroscopic systems will be the subject material of [Chapter 5](#).

What is the criterion for the direction of real processes? Because the second law cannot be proved, we must be content to state it as a crystallization of our experience. We will begin by summarizing some examples of real processes. These examples are various types of energy conversion, and we are interested in the *efficiency* of the conversions. Efficiency is defined as the ratio of the amount of the desired product energy produced to the source energy consumed, usually expressed as a percentage.

1. Mechanical potential energy (energy of position) and mechanical kinetic energy (energy of motion) can be efficiently interconverted, as in the example of the falling brick, or more apparent, in the motion of a pendulum clock, in which energy continually shifts between potential and kinetic energy. (The conservation of energy of a pendulum is even more dramatic if it operates in a vacuum, minimizing frictional losses.) Mechanical energy can also be converted into electrical energy with excellent efficiency, as is accomplished by the generators of electrical power plants (which operate with up to 99% efficiency).
2. Electrical energy can be efficiently converted into mechanical energy (with a motor).

3. Both electrical and mechanical energies can be converted with 100% efficiency into thermal energy, the former by collisions of electrons in a resistor and the latter by interactions of moving surfaces. Such *frictional processes* are what cause the disappearance of mechanical or electrical energy in systems.
4. Thermal energy cannot be completely converted into mechanical or electrical energy, as in our example of the slightly warmed brick and floor. As was shown in the discussion of the Carnot cycle engine, the conversion of thermal energy to mechanical or electrical energy is easier when the thermal energy is at high temperature than when it is at low temperature. For example, a candle flame at high temperature can boil a small amount of water, which can move a piston and raise a small weight. On the other hand, it is difficult to see how we could make use of the much larger amount of thermal energy in a lake at ambient temperature to achieve the same result.
5. The thermal energy of a high-temperature object can be transferred to a lower-temperature object by a flow of heat. Heat will not, however, spontaneously flow from a lower to a higher temperature. Of course, because we used the direction of heat flow to define temperature, this is just a reiteration of the zeroth law.
6. Chemical energy, which will be a major interest in this book, can be converted efficiently to heat (by combustion) and often also to electrical energy (as in a battery or fuel cell) or mechanical energy (as in a muscle). Considerations of chemical energy are somewhat complicated and will be deferred until [Chapter 7](#).

The ability to convert one form of energy into other forms indicates the usefulness of the energy. The above considerations of the usefulness of different types of energy show that energy has a *quality*, as well as a *quantity*. There is a *hierarchy* of energy, indicating its quality, which is given in [Fig. 1](#). We have listed electrical energy and mechanical energy as equivalent highest forms of energy, assuming that the slight frictional losses observed in practical interconversion of these forms are not fundamental. Thermal energy is of lower quality, and its quality is lower the lower its temperature. Chemical energy is not considered for the moment. When energy moves up on this scale (i.e., when it is converted to more useful forms), we say the energy has been *upgraded*; when it moves down on the scale, we say that the energy is *degraded*.

Having established the hierarchy of energy, we can now state the second law of thermodynamics (i.e., the principle that tells us the direction of real processes):

In any real process, there is net degradation of energy.

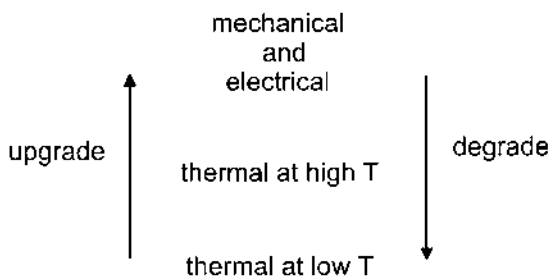


Figure 1 Hierarchy of energy.

The second law explains why we cannot continually reuse energy, as we reuse other resources, such as copper, and why energy recycling is not an effective response to energy shortages. Energy is degraded to less useful forms as we use it!¹ According to the second law, processes that result in net upgrading of energy are not possible. It should be emphasized that we have not proved and cannot prove the second law, just as we did not prove the first law. These laws are a generalization of our experience, and no apparent violation of them has ever survived close scrutiny. Machines that would violate the first law are called *perpetual motion machines of the first type*, whereas those that would violate the second law are called *perpetual motion machines of the second type*. A working model of either of these types of perpetual motion machines has never been delivered to any patent office. You will be wise to keep the laws of thermodynamics in mind when someone approaches you with an opportunity to invest in the development of one of these machines!

There are two innocuous-seeming words in our statement of the second law, *real* and *net*, which are worthy of further discussion. What do we mean by a *real process*? Obviously, any process that is not “real” cannot occur, at least it cannot occur in a finite time. We have already discussed one class of nonreal processes in [Chapter 2](#), the reversible expansions (isothermal and adiabatic) of an ideal gas. These are examples of processes in which there is complete balance between the internal and external forces on a system and, thus, there is no net driving force for the process. We can imagine the process occurring infinitely slowly, but it is not a real process. For example, in the reversible isothermal expansion, the process can be reversed by sliding the grains of sand back onto the piston, with no outside energy cost, assuming that the surfaces are frictionless. A reversible process can only be approached, not attained; it does not degrade energy. We should distinguish between truly reversible processes, which are completely at equilibrium and processes that are slow enough so that we can treat them as reversible with negligible loss of accuracy. The latter type of process is real.

The word *net* is particularly important in discussing the second law, and its neglect is the source of many errors in the application of the law. By net degradation, we mean that we must consider changes of the quality of energy that occur anywhere in the universe, as long as they are associated with the process of interest. If, in a process, a system of interest to us is exchanging energy or matter with its surroundings, there may be energy degradation in the surroundings, and this must be combined with the degradation or upgradation in the system to obtain net degradation. At this point, we will be dealing only with closed and isolated systems, so we will only be interested in energy exchange with the surroundings. In [Chapter 6](#), we will begin considering open systems.

Before continuing, let us decide to define a new thermodynamic function that measures energy degradation. We will call this function the *entropy* and designate it by the symbol S . In terms of entropy our second law becomes

In any real process, there is net entropy increase.

Is entropy a state function? There is no reason that the quality of energy should be less a state function than the quantity of energy. When the system is completely defined, both should be known. Therefore, we assume that entropy is a state function. The state function nature of entropy is critical for the mathematical definition of this thermodynamic quantity. In addition, it allows us to consider processes in which the degradation of energy (entropy increase) is not at all apparent. For example, in a mixing process, such as results when the stopcock connecting containers of two different low-pressure gases is opened, one might think that there is no change in the quality of energy. If the pressure is low enough to neglect intermolecular interactions, the energy of the system is thermal energy (molecular kinetic energy) at the beginning and at the end of the process. Dealing with entropy as a state function, however, will allow us (in [Chapter 4](#)) to calculate the energy degradation (entropy increase) in this spontaneous process by an alternative pathway.

In order to usefully apply the second law, it will be necessary to be able to calculate both ΔS , the entropy change in the system of interest, and ΔS_{sur} , the entropy change of the surroundings. (Thermodynamic functions without the subscript “sur” can be assumed to refer to the system.) The mathematical form of our second law then becomes

$$\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{sur}} \geq 0 \quad (1)$$

Although ΔS_{univ} , the entropy change of the universe, sounds rather formidable, in practice we will only be concerned with a few parts of the universe that interact with our system during the process. In this equation, greater than zero applies to any real process and equal to zero applies to a reversible process. In the latter, change occurs infinitely slowly, eliminating energy degradation due to friction and turbulence.

Of the two terms in Eq. (1), it is easier to calculate ΔS_{sur} , because we, the observers, are in the surroundings and can have more intimate knowledge of the surroundings than of the system. The surroundings are often simple (i.e., masses moving with known velocities or at known heights in gravitational fields or batteries or heat reservoirs) or sometimes they can be idealized as being simple, with little effect on the analysis. The system, on the other hand, is probably complicated at times during the process of interest, with nonuniform temperature, pressure, and concentrations.² Being outside the system, we are not privy to the instantaneous distributions of these variables. Nonetheless, we will be able to establish a method for measuring the entropy change of the system.

In order to calculate the ΔS_{sur} of a process, we note that mechanical and electrical energies are at the top of our hierarchy and we can assume that these types of energy are not degraded at all. Thus, we will not have to consider these forms of energy in calculating entropy changes. In addition, because we are presently not treating open systems, we do not have to consider chemical changes in the surroundings. This leaves only thermal energy changes in the surroundings to be considered.

The addition of thermal energy to a reservoir in the surroundings is $-q$, as our sign convention is that heat is positive when it is removed from reservoirs in the surroundings and added to the system. Thermal energy, however, is less degraded if it is at higher temperature. In order to take this into account, we can multiply the energy added to a heat reservoir by some function that decreases when the reservoir is at higher temperature. Such a function is T^{-m} , where m can have any positive value.³ (We will find that only the value $m = 1$ is compatible with our requirement that entropy is a state function.) This gives for ΔS_{sur} the simple result.

$$\Delta S_{\text{sur}} = -\sum_i \frac{q_i}{T_i^m} \quad (2)$$

We have included the summation because there may be more than one heat reservoir in the surroundings that is involved in the process. For example, in the Carnot cycle engine, we remove heat from a hot reservoir and deposit heat in a cold reservoir.

In order to determine the entropy change of the system, $\Delta S = S_f - S_i$, we conceptualize an *entropy meter*. Although this is not a real device, we can contemplate its construction and mode of operation. Like any other measuring device, an entropy meter is located in the surroundings. It is an instrument containing various masses, batteries, heat reservoirs, and so forth. The distinctive thing about an entropy meter is its instructions, namely the following:

1. In order to measure ΔS of the system in a process, the entropy meter is not employed during the process, but, rather, in a separate measuring

step in which the system goes from the same initial state to the same final state as it does in the process of interest. Because we have agreed that ΔS must be a state function, ΔS must be identical in the actual process and the measuring step.

2. The entropy meter is used reversibly!

3. $\Delta S = -\Delta S_{\text{met}} = \sum_i (q_i/T_i^m)_{\text{rev}}$, as shown in the following analysis:

Requirement 2 guarantees that *in the measuring step*, there is zero net energy degradation (entropy increase) and we can write (with $\Delta S \equiv \Delta S_{\text{system}}$)

$$\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{met}} = 0 \quad (3)$$

or

$$\Delta S = -\Delta S_{\text{met}} = \sum_i \left(\frac{q_i}{T_i^m} \right)_{\text{rev}} \quad (4)$$

We have used Eq. (2) in Eq. (4) because the meter is in the surroundings. The subscript “rev” indicates that in the operation of the entropy meter, the work that it does as well as the heat that it transfers are all done reversibly. As in our previous discussion of the surroundings, it is only the heat reservoirs in the entropy meter that must be considered when calculating ΔS_{sur} .

It turns out that there is only one exponent, m , that will make entropy a state function. This can be seen by considering the simple engine discussed in [Chapter 2](#)—the reversible Carnot cycle engine operating on an ideal gas. Because we require that entropy be a state function, the change of entropy of the engine over one cycle of its operation must be zero. Of the four steps in the Carnot cycle, the reversible adiabatic expansion (step II) and compression (step IV) have $q_{\text{rev}} = 0$ and, thus, zero entropy change. Therefore, the entropy change of the ideal gas over one cycle is just the sum of the changes in steps I and III (or step III') of the cycle:

$$\Delta S_{\text{cycle}} = \Delta S_{\text{I}} + \Delta S_{\text{III}} = \frac{q_{\text{I}}}{T_h^m} + \frac{q_{\text{III}}}{T_c^m} = \frac{RT_h \ln(V_2/V_1)}{T_h^m} - \frac{RT_c \ln(V_2/V_1)}{T_c^m} \quad (5)$$

or

$$\Delta S_{\text{cycle}} = R \ln \left(\frac{V_2}{V_1} \right) (T_h^{1-m} - T_c^{1-m}) \quad (6)$$

which is only zero if $m = 1$.⁴ Because we have developed general procedures for calculating entropy changes of the system and surroundings, these should be

independent of the particular process or system that we have used to determine m , and the general formulas⁵ must be

$$\Delta S_{\text{sur}} = - \sum_i \frac{q_i}{T_i}, \quad dS_{\text{sur}} = - \sum_i \frac{\delta q_i}{T_i} \quad (7)$$

$$\Delta S = \sum_i \frac{q_{i,\text{rev}}}{T_i}, \quad dS = \sum_i \frac{\delta q_{i,\text{rev}}}{T_i} \quad (8)$$

The differential forms of these formulas are useful for processes in which variables, especially temperature, are continuously changing.

The second law of thermodynamics denies the possibility of processes in which the only change is transfer of heat from a higher to a lower temperature. The zeroth law deals with thermal equilibrium and thus, by implication, the direction of heat transfer. However, the zeroth law applies only to heat transfer at a single interface, whereas the second law can deal with processes in which devices accomplish the heat transfer. These devices can have multiple interfaces with the heat reservoirs and can change during the process, as long as their change is cyclic.

The second law of thermodynamics has important philosophical and religious implications. Unlike many other laws of nature, which run equally well with time increasing or decreasing,⁶ the second law states that entropy increases as time increases. Thus, entropy has often been called “time’s arrow.” Since even those who have not studied thermodynamics can usually recognize when a movie is being played backwards,⁷ it appears that humans have an intuitive feeling for entropy. Thus, most moviegoers would know that something was wrong if Humpty Dumpty *spontaneously* came together again.⁸

The second law has not always been used correctly in philosophical discussions. Neglect of the surroundings has been an important error in the arguments of scientific creationists,⁹ who use scientific arguments in support of religious views. The creationists claim that under evolution “theory,” highly structured civilizations have evolved on Earth from the rather amorphous initial state of the planet. Increasing order is equivalent to an entropy decrease of the system, the Earth. Some creationists have argued that this is a clear violation of the second law, which requires entropy to continually increase. Therefore, they claim that the increase in order could not have occurred. The creationists theorize that Earth was created more perfect (with lower entropy) than it is today by a higher force, and its degree of organization has been decreasing with time, as required by the second law. Of course, what is neglected in this argument is that the Earth is not an isolated system. It is a steady-state system that is continually absorbing sunlight and radiating energy to space. Although the magnitudes of these two energy terms are just about equal (the temperature of the Earth has remained roughly constant over time), the qualities of the two types of energy are very different, due to their different temperatures. Over billions of years, the

entropy increase of the surroundings has been more than sufficient to balance any entropy decrease that has occurred on Earth (if this, indeed, has happened) as well as to remove the large amount of entropy produced by dissipative (entropy-producing) processes that have occurred.¹⁰

On a cosmic scale, the second law is in agreement with the currently accepted theory of the expansion of the universe from an initial, highly located “Big Bang.”

3.2 Entropy Changes in Some Simple Processes

Because it takes some practice to be able to use the recipes for calculating entropy changes in the system and surroundings, a few simple examples are presented here.

3.2.1 Reversible Adiabatic Expansion

Here, $q = 0$, giving $\Delta S_{\text{sur}} = 0$, and the process is reversible, so $q = q_{\text{rev}}$ and $q_{\text{rev}} = 0$, giving $\Delta S = 0$. Because entropy is unchanged, reversible adiabatic expansions and contractions are called *isentropic*.

3.2.2 Adiabatic Expansion

Because $q = 0$, $\Delta S_{\text{sur}} = 0$. ΔS depends on the details of the process but must be greater than zero to satisfy the second law.

3.2.3 Reversible Isothermal Expansion of an Ideal Gas

Using Eq. (5) of [Chapter 2](#) and the fact that the energy of an ideal gas depends only on its temperature,

$$\Delta U^{\text{ig}}_{\text{isotherm}} = 0 = q - nRT \ln\left(\frac{V_f}{V_i}\right) \quad (9)$$

Because the process is reversible,

$$q_{\text{rev}} = q = nRT \ln\left(\frac{V_f}{V_i}\right) \quad (10)$$

from which Eq. (8) gives

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) \quad (11)$$

and Eq. (7) gives

$$\Delta S_{\text{sur}} = -nR \ln\left(\frac{V_f}{V_i}\right) \quad (12)$$

so that $\Delta S + \Delta S_{\text{sur}} = 0$, as required for a reversible process.

3.2.4 Isothermal Expansion of an Ideal Gas

Entropy is a state function, so ΔS is the same as for the reversible isothermal expansion, calculated earlier. Because less work is done than in the reversible process and ΔU is the same in both cases, less heat is withdrawn from reservoirs in the surroundings. Therefore, the decrease of entropy of the surroundings is less than in the reversible expansion. In the limit of expansion against a vacuum (Joule process), no work is done and no heat is withdrawn from the surroundings. In this case, $\Delta S_{\text{sur}} = 0$.

3.2.5 Heating at Constant Volume

A differential change in entropy for heating at constant volume is

$$dS_V = \frac{\delta q_{\text{rev},V}}{T} = \frac{C_V dT}{T} = \left(\frac{\partial S}{\partial T}\right)_V dT \quad (13)$$

which tells us that

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad (14)$$

Integrating Eq. (13) from the initial to the final temperature gives

$$\Delta S_V = \int_{T_i}^{T_f} \frac{C_V}{T} dT = C_V \ln\left(\frac{T_f}{T_i}\right) \quad (15)$$

where the last step assumes that the heat capacity can be taken as constant over the temperature range of the integration. This would hold for a monatomic gas or for other substances if the temperature interval were small enough. The entropy change of the surroundings depends on the details of the process. For example, if the heating is accomplished by placing the system in a heat bath at T_2 ,

$$\Delta S_{\text{sur}} = -\frac{q}{T_2} = -\frac{C_V(T_2 - T_1)}{T_2} \quad (16)$$

It can be shown that $\Delta S + \Delta S_{\text{sur}} > 0$.

3.2.6 Heating at Constant Pressure

The results are as given for constant volume heating, with C_V changed to C_P . In particular,

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad (17)$$

Example 1. Calculate the entropy change of 1 mol of Ar, considered an ideal gas, undergoing a change from 0°C and 1.0 atm to 50°C and 3.0 atm.

Solution: Because entropy is a state function, we can calculate ΔS by any path that takes the system from its initial to its final state. For the path, we choose isothermal compression at 0°C from 1.0 atm to 3.0 atm, followed by heating at a constant pressure of 3.0 atm from 0°C to 50°C. The C_P of a monatomic ideal gas is $(5/2)R$, independent of temperature and pressure. Because step 1 is an isothermal compression of an ideal gas, $V_2/V_1 = P_1/P_2$

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 = R \ln\left(\frac{V_2}{V_1}\right) + C_P \ln\left(\frac{T_2}{T_1}\right) = R \ln\left(\frac{1}{3}\right) \\ &+ \frac{5}{2} R \ln\left(\frac{323}{273}\right) = -1.09R + 0.42R = -5.57 \text{ J/K} \end{aligned}$$

Satisfy yourself that the same result is obtained if the gas is first heated at constant pressure to 50°C and then isothermally compressed to 3.0 atm.

3.2.7 Phase Change

During a phase change, such as melting (often called fusion) or boiling, the system temperature remains constant at the phase equilibrium temperature, T_ϕ , while heat is transferred to effect the change. For calculating ΔS , the heat for the phase change must be transferred reversibly (i.e., from a reservoir at the phase equilibrium temperature). (Of course, because there is zero temperature differential driving the flow of heat, the transformation occurs infinitely slowly.) Assuming that the system is exposed to a constant pressure, the required heat is the enthalpy change for the phase transformation ($\Delta_\phi H$):

$$\Delta S = \frac{q_{\text{rev}}}{T_\phi} = \frac{\Delta_\phi H}{T_\phi} \quad (18)$$

The entropy change of the surroundings depends on the actual temperature of the reservoir from which the heat is transferred:

$$\Delta S_{\text{sur}} = -\frac{\Delta_{\phi}H}{T} \quad (19)$$

Because with an endothermic phase change, such as melting or boiling, heat will only flow into the system when $T > T_{\phi}$, $\Delta S + \Delta S_{\text{sur}} > 0$. For an exothermic phase change, such as condensation or freezing, heat will only flow out of the system when $T_{\phi} > T$, so that, once again, $\Delta S + \Delta S_{\text{sur}} > 0$. In Table 1, the phase transition temperatures and the enthalpy and entropy changes on melting and vaporization at 1 atm are given for a number of substances. Entropy changes of vaporization are much larger and show much less variation than those of melting. In fact, the approximation $\Delta_{\text{vap}}S = 85 \text{ J/K mol}$ (Trouton's rule) is reasonably accurate, except for very volatile or polar compounds.

Example 2. An ice tray containing 200 mL of water at 25°C is placed in a freezer at −15°C. What is ΔS and ΔS_{sur} for the resulting process? The heat capacity of ice and water are 2.0 and 4.18 J/K g, respectively. The heat of fusion of water is 6.01 kJ/mol.

Solution: To calculate ΔS for freezing, the freezing must occur at the phase equilibrium temperature (the normal freezing point of water). We break the process down into three parts:

TABLE 1 One atmosphere enthalpies and entropies of melting and vaporization

	T_m K	$\Delta_{\text{fus}}H$ kJ/mol	$\Delta_{\text{fus}}S$ J/K mol	T_b K	$\Delta_{\text{vap}}H$ kJ/mol	$\Delta_{\text{vap}}S$ J/K mol
Ar	83.8	1.12	13.4	87.3	6.43	73.6
N ₂	63.1	0.71	11.2	77.4	5.57	72.0
ethane	90.4	2.86	31.6	185	14.7	79.6
benzene	279	9.95	35.7	353	30.7	87.0
CCl ₄	250	3.28	13.1	350	29.8	85.1
H ₂ O	273	6.01	22.0	373	40.6	109
ethanol	159	5.02	31.6	351	38.6	110
AgCl	728	13.2	18.1	1820	199	109

Source: Handbook of Chem. and Phys., 76 ed., CRC Press (1995)

1. Cooling liquid water from 25°C to 0°C, with

$$\Delta H_a = 200 \text{ g} \times 4.18 \frac{\text{J}}{\text{gK}} \times (-25 \text{ K}) = -20,900 \text{ J}$$

$$\Delta S_a = 200 \text{ g} \times 4.18 \frac{\text{J}}{\text{gK}} \times \ln\left(\frac{273}{298}\right) = -73.2 \frac{\text{J}}{\text{K}}$$

2. Freezing water at 0°C

$$\Delta H_b = 200 \text{ g} \times \frac{\text{mol}}{18 \text{ g}} \times \left(-6010 \frac{\text{J}}{\text{mol}}\right) = -6680 \text{ J}$$

$$\Delta S_b = \frac{-6680 \text{ J}}{273 \text{ K}} = -24.5 \frac{\text{J}}{\text{K}}$$

3. Cooling ice from 0°C to -15°C

$$\Delta H_c = 200 \text{ g} \times 2.0 \frac{\text{J}}{\text{gK}} (-15 \text{ K}) = -6000 \text{ J}$$

$$\Delta S_c = 200 \text{ g} \times 2.0 \frac{\text{J}}{\text{K}} \ln\left(\frac{258}{273}\right) = -22.6 \frac{\text{J}}{\text{K}}$$

For the overall process,

$$\Delta H = \Delta H_a + \Delta H_b + \Delta H_c = -33.6 \text{ kJ}$$

$$\Delta S = \Delta S_a + \Delta S_b + \Delta S_c = -120.3 \frac{\text{J}}{\text{K}}$$

For the surroundings,

$$\Delta H_{\text{sur}} = +33.6 \text{ kJ}$$

$$\Delta S_{\text{sur}} = \frac{33,600 \text{ J}}{258 \text{ K}} = +130.2 \frac{\text{J}}{\text{K}}$$

Note that for this spontaneous process,

$$\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{sur}} = -120.3 + 130.2 = +9.9 \frac{\text{J}}{\text{K}} > 0$$

3.2.8 Isothermal Stretching of an Ideal Rubber

An ideal rubber is defined as one for which

$$\left(\frac{\partial U}{\partial l}\right)_T \stackrel{\text{id. rub}}{=} 0 \quad (20)$$

(a condition similar to that which applies to an ideal gas). This holds at either constant volume or constant pressure, because there is negligible change in

volume as a rubber is stretched. As a result, when an ideal rubber is stretched at constant temperature,

$$\delta q^{\text{id. rub}} - \delta w = -f_{\text{ext}} dl \quad (21)$$

If the stretching is done reversibly (very slowly),

$$\delta q_{\text{rev}} = -f dl \quad (22)$$

and

$$\Delta S = - \int \frac{f}{T} dl = - \frac{1}{T} \int f dl \quad (23)$$

In [Chapter 5](#), we will see that the decrease in entropy of the rubber as it is stretched results from its component macromolecular chains adopting a more elongated configuration. The energy added as work escapes as heat to the surrounding, and in the reversible case,

$$\Delta S_{\text{sur}} = \frac{1}{T} \int f dl, \quad \Delta S + \Delta S_{\text{sur}} = 0 \quad (24)$$

If the rubber is stretched rapidly, more work is done, because $f_{\text{ext}} > f$. As a result, more heat is transferred to the surrounding and the entropy increase of the surroundings is greater than in the reversible case. Because the entropy decrease of the rubber is a state function and the same in both cases, $\Delta S + \Delta S_{\text{sur}} > 0$ when the rubber is stretched rapidly.

3.2.9 Chemical Reactions

When a chemical reaction is proceeding, it is, by definition, not at equilibrium and thus not reversible. Thus, entropy changes in chemical reactions cannot be obtained from heat effects in calorimetric experiments. Entropy changes can be obtained by studying chemical equilibrium ([Chapter 7](#)) or by opposing the tendency of the reaction to proceed with an applied electric potential ([Chapter 10](#)).

3.3 Heat Diagrams

Because $\delta q_{\text{rev}} = T dS$,

$$q_{\text{rev}} = \int_i^f T dS \quad (25)$$

and areas on a graph of T versus S are equal to the heat for the state change carried out reversibly. Noting the similarity to the P versus V diagram, where areas are the work for the state change carried out reversibly, we call the T versus

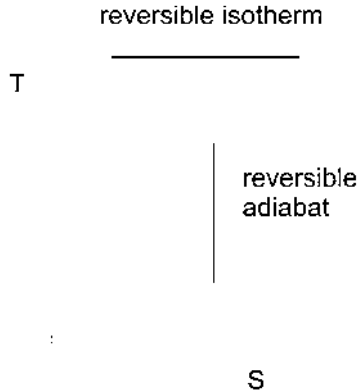


Figure 2 The heat diagram.

S diagram the *heat diagram* for the process. As shown in Fig. 2, on a heat diagram, horizontal lines are reversible isothermal processes, whereas vertical lines are reversible adiabatic (isentropic) processes.

3.4 General Analysis of Thermal Devices

Beginning with the industrial revolution, great improvements in standards of living have been achieved by the use of thermal devices, which interconvert heat and work. Three such devices, which operate with two heat reservoirs, are shown in Fig. 3. For each, the efficiency, ε , is defined as the amount of the type of energy desired divided by the amount of energy that is expended in obtaining it.

In Chapter 2, we have analyzed one particular type of heat engine, the reversible Carnot cycle engine with an ideal gas as the working substance, and found that its efficiency is $\varepsilon = 1 - T_c/T_h$. For both practical and theoretical reasons, we ask if it is possible, with the same two heat reservoirs, to design an engine that achieves a higher efficiency than the reversible Carnot cycle, ideal gas engine. What can thermodynamics tell us about this possibility?

Because we will be looking for the most efficient engine, frictional losses are set equal to zero by running the engine reversibly. The second law then becomes $\Delta S + \Delta S_{\text{sur}} = 0$. In order to keep using the engine, we will require that it operate in a cyclic manner and be unchanged over a cycle of its operation. Because the engine (the system) is unchanged, its entropy, a state function, is also unchanged over the cycle, and $\Delta S = 0$:

$$\Delta S_{\text{sur}} = -\frac{q_h}{T_h} + \frac{q_c}{T_c} = 0 \quad \text{or} \quad \frac{q_h}{q_c} = \frac{T_h}{T_c} \quad (26)$$

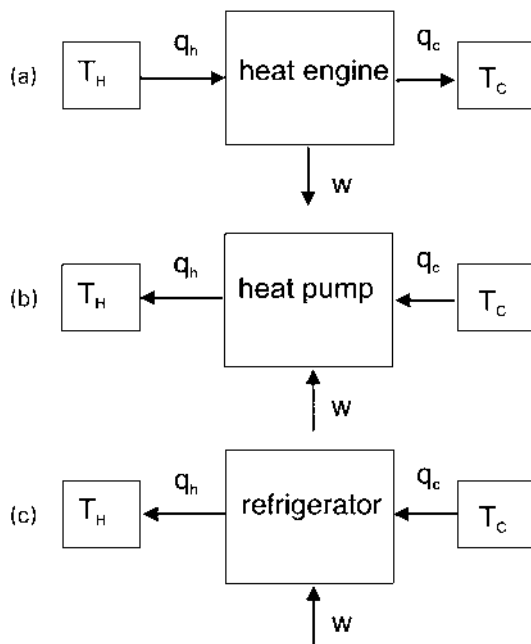


Figure 3 (a) A two-reservoir heat engine, $\varepsilon \equiv w/q_h$; (b) a heat pump, $\varepsilon \equiv q_h/w$; (c) a refrigerator, $\varepsilon \equiv q_c/w$.

Over one cycle, we also have $\Delta U = 0$, and from Fig. 3a, the first law tells us that

$$q_h - q_c - w = 0 \quad (27)$$

The efficiency of a heat engine is defined as what we want from the engine (work) divided by what we pay for (heat from the hot reservoir):

$$\varepsilon \equiv \frac{w}{q_h} = \frac{q_h - q_c}{q_h} = 1 - \frac{T_c}{T_h} \quad (28)$$

(i.e., the same efficiency as the Carnot cycle). Actually, a Carnot cycle engine is the only possible reversible engine that can run with two reservoirs. This follows from the requirement that heat can only be reversibly transferred to or from a single heat reservoir in an isothermal process. The steps in a two-reservoir reversible engine therefore must be either isothermal or adiabatic.

Equation (28) provides us with a means of defining a temperature scale that is as elegant as it is impractical. Our thermometer is a reversible heat engine, the efficiency of which we measure when it is operated between the temperature of interest and a reference temperature, defined as 273.15 K for an ice bath at 1 atm

pressure. For temperatures above that of the ice bath, the ice bath is the cold reservoir; for temperatures colder than the ice bath, the ice bath is the hot reservoir. Such a scale requires only a single calibration point, the defined temperature of the ice bath, and is independent of the working material of the engine. Temperature is determined by Eq. (28) from the measured efficiency of the engine. Temperature measured on this thermodynamic (or Kelvin) scale is identical to that measured on the ideal gas scale discussed in [Chapter 1](#).

As seen in [Fig. 3](#), a heat pump is theoretically just an engine with all its energy flows reversed. Multiplying each term in Eqs. (26) and (27) by -1 does not change these equations. However, ϵ for a heat pump (usually called the coefficient of performance) is defined as q_h/w , because heat pumps are used to heat homes in winter by pumping in heat from the outdoors at lower temperature. This is certainly not the usual direction of heat flow, but it can be achieved by providing work, usually in the form of electrical energy. The coefficient of performance of a heat pump is, using the results of Eqs. (26) and (27),

$$\epsilon \equiv \frac{q_h}{w} = \frac{q_h}{q_h - q_c} = \frac{T_h}{T_h - T_c} \quad (29)$$

Because, under most practical conditions, efficiencies calculated from Eq. (29) are much greater than 1, it predicts that with a heat pump, much more energy can be provided to heat a dwelling than is purchased from the local power company. This, indeed, is found to be the case. One problem that heat pumps do have, however, is providing enough capacity to keep homes warm when the outdoor temperature becomes very low (see Problem 11) and their efficiency is low. Therefore, heat pumps find most use in regions with rather mild winters. Unfortunately, their economic attractiveness in such regions is often diminished by a “capacity fee” that must be paid to the local power company for additional direct heating capacity for days when the heat pump is insufficient to comfortably heat the home. The above-calculated efficiencies assume reversible operation and are called maximum or *theoretical efficiencies*. Actual engines, heat pumps, and refrigerators will have additional losses and operate at some percentage of theoretical efficiency.

The product of the efficiency of a reversible heat engine times the coefficient of performance of a reversible heat pump, both operating between the same two heat reservoirs, is

$$\epsilon_{\text{eng}} \epsilon_{\text{pump}} = \frac{w}{q_h} \frac{q'_h}{w'} = 1$$

If the pump uses all of the work generated by the engine ($w = w'$), it will return to the hot reservoir just the amount of heat withdrawn by the engine. If either of these devices had an efficiency greater than we calculated, it could be used as the pump, taking the work produced by the engine and returning more heat to the hot

reservoir than was used by the engine. This would represent net flow of heat from a cold to a hot reservoir, which is an upgrading of energy and violates the second law of thermodynamics.

Note that in Fig. 3c, what we call a refrigerator is the device that removes heat from the enclosure that stores food and pumps it into the surroundings. The box that stores the food is the cold reservoir. The analysis also applies to an air conditioner. In the analysis of the refrigerator, we get the same result as Eq. (26), but the first law gives

$$q_c - q_h + w = 0 \quad (30)$$

Because the useful quantity for a refrigerator is the amount of heat that it removes from the enclosure, we define its coefficient of performance as

$$\varepsilon \equiv \frac{q_c}{w} = \frac{q_c}{q_h - q_c} = \frac{T_c}{T_h - T_c} \quad (31)$$

a quantity which also is usually considerably greater than 1.

Example 3. What is the maximum rate that a heat pump that uses 1 kW of electrical power can supply heat to a house at 25°C when the outside temperature is 10°C?

Solution: Because we are interested in the maximum heat flow, we assume that the heat pump is reversible. Its coefficient of performance is

$$\varepsilon = \frac{298}{298 - 283} = 19.9 = \frac{q_h}{1.0 \text{ kW}}, \quad q_h = 19.9 \text{ kW} = 19.9 \frac{\text{kJ}}{\text{s}}$$

Questions

1. This chapter is based on the postulate that energy has quality, as well as quantity. List two other properties that have quality as well as quantity. List two properties that have only quantity.
2. For the freezing of water supercooled to -2.0°C , indicate whether each of the following is greater than, equal to, or less than zero: ΔS , ΔS_{sur} , and ΔS_{univ} .
3. Which of the following may be real processes? For those that cannot be real, indicate whether they violate the first or second law of thermodynamics.
 - (a) A “super” heat conductor is discovered that allows heat to flow from a refrigerator to the surrounding room at a higher temperature.
 - (b) A marble in a beaker of water suddenly jumps out of the water, while the water cools.
 - (c) The average temperature of the Earth is increased by a huge volcanic eruption, which deposits a large amount of molten lava on the Earth’s surface.
 - (d) The average temperature of the Earth is increased by a large asteroid that hits the earth.

4. Are any of the following devices perpetual motion machines of the first or second kinds? Which kind are they and why?

- (a) An engine operates by drawing water from a reservoir up a wick by capillary action, followed by the water falling from the top of the wick and turning a water wheel as it returns to the reservoir.
- (b) An engine operates by a rotating magnet being pulled into a magnetic field. When the magnet reaches the field, a mass shifts on the magnet and gravity rotates the magnet out of the field.
- (c) An engine operates by using the relatively warm surface waters of the ocean to evaporate a volatile compound and drive a piston. The resulting gas is passed to the colder lower water of the ocean, where it is compressed and reliquefied.
- (d) A ship is propelled across the ocean in summer using heat from the ocean. (Take the ocean temperature as 18°C and air temperature as 25°C .)
- (e) The same as part (d), but in winter, when the water temperature is 10°C and the air temperature is 2°C .

5. Draw a Carnot cycle on a heat diagram.

6. Sketch a curve representing reversible heating at constant pressure on a heat diagram.

7. Explain why a constant-pressure expansion cannot be included in a reversible engine operating with any finite number of heat reservoirs.

8. Indicate whether each of the following statements is true or false:

- (a) Heat is the increase in the thermal energy of a system.
- (b) $\Delta_{\text{vap}}S$ is always greater than zero.
- (c) q is not a state function, but q_{rev} is a state function.
- (d) In a reversible process, $\Delta S = 0$.
- (e) For one cycle of a refrigerator, $\Delta S = 0$.

9. For each of the following processes, indicate whether ΔS is less than, equal to, or greater than zero, or whether there is insufficient information to decide (note that ΔS refers to the system):

- (a) Melting of ice in a room at 25°C
- (b) Reversible melting of ice at 0°C
- (c) Reversible adiabatic expansion of an ideal gas
- (d) Reversible adiabatic expansion of a van der Waals gas
- (e) Reversible isothermal expansion of an ideal gas
- (f) Joule expansion of an ideal gas
- (g) Joule–Thomson expansion of an ideal gas

10. Rephrase each of the following statements in more exact thermodynamic language:

- (a) The heat of a metallic rod is increased.
- (b) The power company is building a new plant for producing energy.
- (c) The country is suffering from an energy shortage.

11. Which of the following integrals must be zero when integrated over one cycle of a cyclic process (indicated by the symbol \oint):

- (a) $\oint \frac{\delta q}{T}$ (e) $\oint U dT$
 (b) $\oint \frac{\delta q_{\text{rev}}}{T}$ (f) $\oint (P dV + V dP)$
 (c) $\oint P dV$ (g) $\oint U dT$ for an ideal gas
 (d) $\oint dU$

Problems

- Calculate ΔS for vaporization of water at 1.0 atm pressure, given that ΔH for this process is 40.6 kJ/mol.
- Calculate ΔS for increasing the pressure on 1.0 mol of an ideal gas from 2 atm to 7 atm at 300 K. If the process is carried out reversibly, what is ΔS_{sur} ?
- Calculate ΔS for 1 mol of ideal gas expanding isothermally from a pressure of P_1 to a pressure of P_2 against a constant opposing pressure of P_2 . What is ΔS_{sur} ?
- One gram of ice at -10°C is placed in a large amount of liquid water at $+10^\circ\text{C}$. What is the entropy change of the water originally in the ice as it reaches the temperature of the liquid? What is the entropy change of the rest of the water (ΔS_{sur})? What is ΔS_{univ} for this process? Take C_p for ice as 2.1 J/g K and for liquid water as 4.2 J/g K.
- Using data from Table 1 in Chapter 2, find the change of entropy change as ammonia is heated from 25°C to 250°C .
- Using Trouton's rule, estimate $\Delta_{\text{vap}}H$ of naphthalene, which has a normal boiling point of 211°C .
- * Show that for heating at constant volume, with a single heat reservoir at the final temperature, $\Delta S_{\text{univ}} > 0$.
- Did you ever wonder whether the light in your refrigerator stays on when you close the door and whether this is costing you much money? Assume that your refrigerator operates with a box temperature of 5°C in a room at 25°C and that electricity costs \$0.20 per kilowatt-hour. What is the minimum cost per month if the 25-W bulb in the refrigerator stays on continuously? Why is this a "minimum"?
- What is the minimum rate of heat deposition in a river by a 100-MW power plant operating with a boiler at 800°C and using the river water at 30°C to condense steam? Such heat deposition is known as *thermal pollution* and can contribute to making rivers unsuitable for many forms of aquatic life.

10. Considerations of heat losses from homes often show that they are proportional to the temperature difference between the home and its surroundings. Show that as a result of this, the work required by a heat pump will be roughly proportional to the square of the temperature difference between the home and its surroundings.

11.* A reversible heat pump can just keep a house at 25°C when the outside temperature is 10°C . What is the highest temperature that the same pump can maintain in the house when the outside temperature is -10°C ? Assume that the heat loss from the house (which has to be provided by the pump) is proportional to the difference between the inside and outside temperature.

12. The average rate at which solar radiation is absorbed by the earth is 970 W/m^2 of surface. Because the Earth does not change appreciably over a short time (this is called the steady-state approximation), we can assume that the same rate of energy is radiated from Earth to space. The characteristic temperature at which the Earth absorbs radiation is, however, different from the temperature at which it radiates energy. Take an average temperature on the half of the Earth that is receiving solar radiation as 280 K and the temperature of the part of the atmosphere from which the earth radiates as 256 K . Because the steady-state approximation also requires that the entropy of the Earth is constant, what must be the rate of entropy generation of processes on and in the Earth. The radius of the Earth is 6400 km .

13.* A heat engine is proposed that operates with heat reservoirs at temperatures T_1 and T_2 , using a monatomic ideal gas [$C_V = (3/2)R$] as the working fluid. The engine cycle consists of the following three steps:

1. Expansion at constant pressure, P' , from V_1 and T_1 to V_2 and T_2
2. Cooling at constant volume from T_2 to T_1
3. Reversible isothermal compression at T_1 from V_2 to V_1

(a) Draw the cycle on a work (P - V) diagram. Steps 1 and 2, not being reversible, cannot rigorously be drawn on the diagram. Use dashed lines to represent these steps.

(b) Calculate the heat and work for each step in the cycle.

(c) Find ΔS , ΔS_{sur} , and ΔS_{univ} for one cycle of operation of the engine.

(d) Derive an expression for the efficiency of the engine in terms of T_2 and T_1 .

(e) For $T_2 = 600\text{ K}$ and $T_1 = 300\text{ K}$, what is the efficiency of this engine? How does this compare with the efficiency of a Carnot cycle engine operating between reservoirs at the same two temperatures?

14. It has been proposed that temperature gradients in the oceans could be used as a source of power. Assuming that water is at 4°C at lower levels, where it has maximum density, and at upper levels, it has a temperature of 25°C , typical of the tropical ocean, what is the maximum efficiency with which heat could be extracted from the upper ocean to produce work?

15. Derive a formula for the entropy change for stretching an ideal rubber for which $f^* = a\varepsilon - b\varepsilon^2$.

16. What is the temperature of boiling water on a temperature scale defined by the efficiency of a reversible Carnot cycle engine and on which the reference temperature of an ice bath is taken as 100° .
17. A thermometer is based on a reversible heat engine, which operates between a boiling water bath and a heat reservoir at a lower temperature. The boiling water bath is defined to be at 373° . The temperature of the low temperature bath is determined from the efficiency with which the engine converts heat withdrawn from the boiling water bath to mechanical energy. Derive an explicit equation, $T_c = f(\varepsilon)$, from which the temperature of the low-temperature bath can be calculated.
18. Calculate the efficiency of a combined-cycle electricity generating plant. In this plant, the gaseous products of combustion at 1500°C are first directed into a gas turbine, from which the gas exits at 900°C and which operates at 90% of theoretical efficiency. Eighty-five percent of the energy of the effluent from the turbine is used to produce steam at 500°C . This steam is used in a steam electric generating plant which uses a river at 30°C as a cold reservoir and operates at 55% of theoretical efficiency.

Notes

1. Although these less useful forms of energy may still have some use, for example, in *cogeneration*, waste thermal energy from an electric generating plant is used for some other purpose, such as heating residences or greenhouses. In *combined-cycle* energy, generation electricity is produced by two different types of electric generator; for example, hot combustion gases are first directed into a gas turbine and then the effluent from the turbine is used to boil water for a steam electric generating plant.
2. Until [Chapter 10](#), we will require that the system begins and ends the process in equilibrium states.
3. Other monotonically decreasing functions of T can be expanded in terms of the type T^{-m} .
4. $x^\circ = 1$.
5. We have adopted the standard procedure of not explicitly indicating that the temperature is reversible for a reversible process. Because heat is transferred reversibly, the system and surroundings are at thermal equilibrium and the temperature of the system must equal that of the external reservoir.
6. This is because such laws involve forces, which are related to acceleration. The acceleration, being a second derivative, is unchanged when t is replaced by $-t$.
7. Even in the absence of “giveaways,” such as people walking backward and so on.
8. But not necessarily if this change was brought about by all the King’s horses and all the King’s men, whose entropy increase could compensate for Humpty’s decrease in entropy.
9. HM Morris. *Scientific Creationism*. San Diego, CA: Creation Life Publishers, 1974, pp 37–46.
10. Of course, this does not rule out a higher force, a belief in which has been and is presently held by many scientists whose understanding of the second law cannot be questioned.