

# Thermal system

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Part of a book on [Thermodynamics](#)

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**Act One: Entropy meets energy in thermal systems, producing a child—temperature.**

In this most beautiful act of the play of thermodynamics, we watch the union of entropy and energy produce a child—temperature. The child is so prodigious that it is better known than its parents—entropy and energy.

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## Entropy and energy

You have met [entropy](#) and [energy](#). You are ready to critique the paragraph that coined the word “entropy” (Clausius 1865).

“We might call S the transformational content of the body, just as we termed the magnitude U its thermal and ergonal content. But as I hold it to be better to borrow terms for important magnitudes from the ancient languages, so that they may be adopted unchanged in all modern languages, I propose to call the magnitude S the *entropy* of the body, from the Greek word *τροπή*), transformation. I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*; for the two magnitudes to be denoted by these words are so nearly allied in their physical meanings, that a certain similarity in designation appears to be desirable.”

Rudolf Clausius, [The Mechanical Theory of Heat](#), 1867. This book collects papers by Clausius on thermodynamics.

**Exercise.** Are entropy and energy nearly allied in their physical meanings?

## Thermal system is characterized by function $\Omega(U)$

The word *thermal* is an adjective associated with microscopic interaction. By a *thermal system* we mean a part of the world that interacts with the rest of the world in only one mode: transfer energy through microscopic interaction. This mode of interaction is called *thermal contact*.

When the energy of a thermal system is fixed at U, the thermal system becomes an [isolated system](#). The isolated system flips among a set of quantum states. Denote the number of quantum states of this isolated system by  $\Omega(U)$ .

As U changes, the thermal system is a *family of isolated systems*. Each member isolated system has its own value of energy, U, flips among its own set of quantum states, and has its own number of quantum states,  $\Omega(U)$ .

**Hydrogen atom.** A hydrogen atom is a thermal system. The hydrogen atom changes its energy by absorbing photons. When isolated at a particular value of energy, U, the hydrogen atom has a fixed set of quantum states,  $\Omega(U)$ . Each quantum state in the set is characterized by a distinct electron cloud and spin.

The hydrogen atom is a thermal system, characterized by the function

$$\Omega(-13.6\text{eV}) = 2$$

$$\Omega(-3.39\text{eV}) = 8$$

$$\Omega(-1.51\text{eV}) = 18$$

.....

The domain of the function  $\Omega(U)$  is a set of discrete values of energy:  $-13.6\text{eV}$ ,  $-3.39\text{eV}$ ,  $-1.51\text{eV}$ , ... The range of the function  $\Omega(U)$  is a set of integers: 2, 8, 18, .... For the hydrogen atom, the values of energy have large gaps.

**Half bottle of water.** A half bottle of water is a thermal system. In the bottle, some  $\text{H}_2\text{O}$  molecules form liquid, and others form gas. We cap the bottle, so that molecules cannot leak. We make the bottle rigid, so that the bottle cannot change volume. We can change the energy of the molecules in the bottle by placing the bottle over a fire, by shaking the bottle, or by using an electric heater.

For such a system of many particles, the values of energy are so closely spaced that we regard  $\Omega(U)$  as a continuous function.

**Exercise.** Describe a few more thermal systems.

## Entropy and energy meet in thermal system

Recall the definition of [entropy](#):

The entropy of an isolated system is the logarithm of the number of quantum states of the isolated system.

When the energy of a thermal system is fixed at  $U$ , the thermal system becomes an isolated system, and flips among a set of quantum states. We have denoted the number of quantum states of this isolated system by  $\Omega(U)$ . By the definition of entropy, the entropy of this isolated system is

$$S(U) = \log \Omega(U)$$

The two functions,  $S(U)$  and  $\Omega(U)$ , contain the same information. But the function  $S(U)$  has a convenient attribute: both  $S$  and  $U$  are extensive quantities.

In a thermal system, entropy and energy meet through the function  $S(U)$ .

Later we will determine the function  $S(U)$  by experiment—that is, we will [count](#) the number of quantum states experimentally.

## Energy-entropy plane

**Energy and entropy form a two-dimensional vector space.** Energy is an extensive property. The addition of two values of energy gives another value of energy. A value of energy times a real number gives another value of energy. Entropy is also an extensive property. We can add two values of entropy, and multiply a value of entropy by a real number.

A pair of the values of energy and entropy  $(U, S)$  is a *vector*. All pairs of energy and entropy form a *two-dimensional vector space*. We add energy to energy, and add entropy to entropy. But we

never add energy to entropy. We multiply energy and number, and multiply entropy and number. But we do not multiply energy and energy, or entropy and entropy, or energy and entropy.

**Picture a two-dimensional vector space.** In a plane, we draw energy as the horizontal axis, and entropy as the vertical axis. We call this plane the energy-entropy plane. A point in the plane represents a pair of values of energy and entropy. All points in the plane represent the two-dimensional vector space.

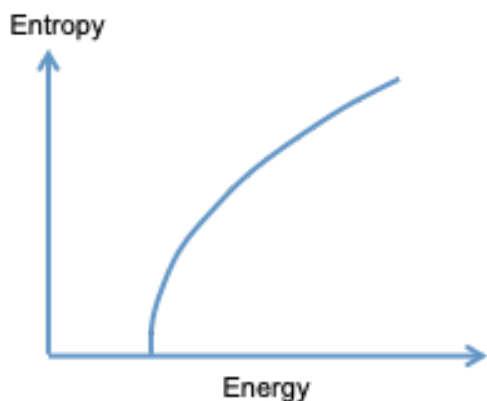
Drawing the two axes perpendicularly in a plane is a convention. What does it even mean that energy is perpendicular to entropy? The statement has no experimental significance. Nature works well if we draw the two axes with an arbitrary angle. But we will follow the convention and draw the two axes perpendicularly in the plane. The perpendicular axes must have pleased us, even if they are unnatural.

In words of linear algebra, energy and entropy form a two-dimensional vector space without inner product.

As we will see, the vector space of energy and entropy is particularly illuminating in the [theory of phase transition](#).

## Common features of function $S(U)$

A thermal system is characterized by entropy as a function of energy,  $S(U)$ . Pictured this function as a *curve* in the energy-entropy plane.



Several features are common to all or many thermal systems. We now list these features in mathematical terms of the curve  $S(U)$ , and will relate these features to experimental observations as we progress. We will also comment if any of these features are absent in a specific thermal system.

1. Because energy is relative, the curve  $S(U)$  can translate horizontally without affecting the behavior of the thermal system.

2. Because [entropy is absolute](#), the curve starts at  $S = 0$ , and cannot be translated up and down.
3. The curve  $S(U)$  is smooth. (There are significant exceptions to this feature, to be discussed in [theory of phase transition](#).)
4. The behavior of a thermal system is often independent of the size of the system. For example, 1 kg of water and 2 kg of water freeze at the same temperature, zero Celsius. Both energy and entropy are extensive properties, linear in the size of the thermal system. As we change the size of the thermal system, the curve  $S(U)$  changes size, but not the shape.
5. The more energy, the more quantum states. Thus,  $\Omega(U)$  is an increasing function. Because logarithm is an increasing function,  $S(U)$  is also an increasing function. That is, the slope of the curve  $S(U)$  is positive,  $dS(U)/dU > 0$ . As we will see, the slope of the curve  $S(U)$  defines [temperature](#)  $T$  by  $1/T = dS(U)/dU$ .
6. As entropy approaches zero, the curve  $S(U)$  approaches the horizontal axis vertically. That is, as  $S \rightarrow 0$ ,  $dS(U)/dU \rightarrow \infty$ .
7. The curve  $S(U)$  is *convex upward*. That is, the slope  $dS(U)/dU$  decreases as  $U$  increases, or equivalently,  $d^2S(U)/dU^2 < 0$ . (There are significant exceptions to this feature. In the [theory of phase transition](#), we will examine thermal systems of which the curve  $S(U)$  is *not* convex upward.) The curvature of the function  $S(U)$  defines [thermal capacity](#)  $C$  by  $1/C = dT(U)/dU$ .

**Exercise.** We have defined temperature  $T$  by  $1/T = dS(U)/dU$ , and defined thermal capacity  $C$  by  $1/C = dT(U)/dU$ . We will soon describe experimental observations that motivate these definitions. But here please derive an identity:

$$1/C = - (d^2S(U)/dU^2) / (dS(U)/dU)^2$$

Thermodynamics is full of such identities. Most of them are useless and ignored. Like nature itself, thermodynamics generates a lot of things useless to people, until people invent uses for them.

## Phrases associated with a family of isolated systems

**One isolated system.** For a single isolated system, as noted before, several phrases are synonymous: a system “isolated for a long time” is a system “flipping to every one of its quantum states with equal probability”, and is a system “in equilibrium”.

Whenever we speak of equilibrium, we identify a system isolated for a long time. Associate the isolated system with a set of quantum states. Out of equilibrium, the isolated system flips to some of its quantum states more often than others. In equilibrium, the isolated system flips to every one of its quantum states with equal probability.

In or out of equilibrium, an isolated system has a fixed sample space, a fixed number of quantum states,  $\Omega$ , and a fixed entropy,  $S = \log \Omega$ .

**A family of isolated systems.** A thermal system is a family of isolated systems. Each member in this family is an isolated system, has its own value of energy and its own set of quantum states.

We describe a family of isolated systems using several additional phrases. These phrases are applicable to any family of isolated systems. Here we make these phrases precise for a family of isolated systems that constitute a thermal system.

**Thermodynamic state.** In a family of isolated systems, a member isolated system, once isolated for a long time, reaches equilibrium. A member isolated system in equilibrium is called a *thermodynamic state*, or a *state* for brevity. The word *state* here means thermodynamic state, not quantum state. A state corresponds to a point on the energy-entropy plane. As energy varies, the thermal system can be in many states.

**Function of state.** We specify a thermodynamic state of the thermal system by a value of energy. Energy is called a *function of state*. A function of state is also called a *thermodynamic property*.

A thermal system is a family of isolated systems of a single variable. Once the energy of the thermal system is fixed, the member isolated system is fixed, and a thermodynamic state is also fixed.

Entropy is also a function of state. We can also specify a thermodynamic state of a thermal system by a value of entropy, a point on the entropy axis.

For a thermal system, we will introduce other thermodynamic properties, including temperature  $T$  and thermal capacity  $C$ .

**Equation of state.** Once the energy  $U$  is fixed, a thermal system becomes an isolated system of a fixed sample space, so that the entropy  $S$  is also fixed. Consequently, given a thermal system, the energy and entropy are related. The relation  $S(U)$  is called an *equation of state*.

In general, an equation of state is an equation that relates the thermodynamic properties of a family of isolated systems. For a thermal system, we will soon introduce several equations of state, in addition to  $S(U)$ .

**Characteristic function.** We will see that, given a thermal system, the function  $S(U)$  can generate all other equations of state. We call  $S(U)$  the *characteristic function* of the thermal system.

# Isolated system conserves energy, but degrades energy

The chapter on [energy](#) describes energy in various forms—thermal, mechanical, chemical, electrical, etc. Energy may not always be differentiated into various forms without ambiguity. We will speak of forms of energy only if they illuminate us.

**Converting chemical energy to thermal energy.** When I shake a half bottle of water, the chemical energy in my muscles transfers to thermal energy in  $\text{H}_2\text{O}$  molecules in the bottle. This transfer of energy goes through several steps. The chemical energy in the muscles moves my hand, the motion of my hand causes the water in the bottle to slosh, and the slosh of water transfers mechanical energy of water to thermal energy in  $\text{H}_2\text{O}$  molecules. The conversion of the chemical energy to thermal energy is *irreversible*: the thermal energy in the  $\text{H}_2\text{O}$  molecules will not become the chemical energy in the muscles.

**Converting electrical energy to thermal energy.** I can also transfer energy to the  $\text{H}_2\text{O}$  molecules in the bottle using an electric current. This transfer of energy goes through several steps. The voltage of the electric outlet moves electrons in the metal wire. The moving electrons impact atoms in the metal wire, and transfer the electrical energy to thermal energy. The metal wire is immersed in the water, and transfers thermal energy in the metal wire to the thermal energy in the  $\text{H}_2\text{O}$  molecules. The conversion of the electrical energy to thermal energy is irreversible: the thermal energy in the  $\text{H}_2\text{O}$  molecules will not become the electrical energy in the outlet.

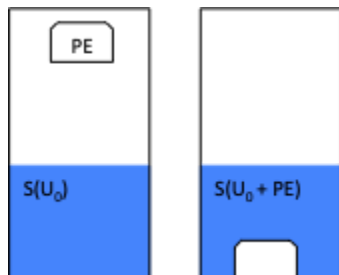
**Converting mechanical energy to thermal energy.** I can also drop a weight from some height into the bottle of water. The weight comes to rest in the water, converting the mechanical energy of the weight to the thermal energy in the  $\text{H}_2\text{O}$  molecules. The conversion is irreversible: the thermal energy in the  $\text{H}_2\text{O}$  molecules will not return to the potential energy of the weight.

**Thermal energy is low-grade energy.** The chemical, electrical, and mechanical energy are said to *degrade*, or *dissipate*, into thermal energy. Thermal energy is called *low-grade energy*.

The dissipation of energy is analogous to the dispersion of ink. In the dispersion of ink, the total number of pigment particles is conserved; the particles disperse, rather than stay localized. In the dissipation of the potential energy of a weight, the total amount of energy is conserved; the potential energy converts into thermal energy, but the thermal energy cannot raise the weight to the initial height.

The irreversibility of the dissipation of energy is understood from the molecular picture. Thermal energy is stored in the motion and interaction at the molecular scale, whereas the jumping up of the weight corresponds to all molecules adding velocity in one direction. The former corresponds to more quantum states than the latter.

To speak of the dissipation of energy, we identify thermal energy and other forms of energy in a single isolated system. The isolated system conserves energy, but increases subset entropy. So long as the system is isolated, the direction of dissipation is irreversible, from other forms of energy to thermal energy.



We next analyze the degradation (dissipation) of energy using the [basic algorithm of thermodynamics](#). We look at one example—the falling weight in water.

**Step 1. Construct an isolated system with an internal variable.** The half bottle of water and the weight together constitute an isolated system. Before the weight drops, the thermal energy of the isolated system is  $U_0$ , and the mechanical energy of the isolated system is the potential energy of the weight  $PE$ . The isolated system conserves energy. After the weight comes to rest in water, the potential energy of the weight vanishes, and the thermal energy of the isolated system is  $U_0 + PE$ . The thermal energy,  $U$ , is an internal variable of the isolated system, increasing from the initial value  $U_0$  to the final value  $U_0 + PE$ .

**Step 2. Find the subset entropy of the isolated system as a function of the internal variable.** The subset entropy of the isolated system is a function of the thermal energy,  $S(U)$ , which is an increasing function. As the weight drops, the entropy of weight does not change.

**Step 3. Maximize the subset entropy to reach equilibrium.** Before the weight drops, the subset entropy is  $S(U_0)$ . After the weight comes to rest in the water, the subset entropy is  $S(U_0 + PE)$ . Because  $S(U)$  is an increasing function, the isolated system maximizes the subset entropy when the mechanical energy fully changes to the thermal energy, the weight comes to rest, and the isolated system reaches equilibrium.

**Step 4. Increase the subset entropy for any irreversible process.** The reverse change would violate the law of the generation of entropy. The weight, after resting in water, will not draw thermal energy and jump up. Dissipation is irreversible. What makes thermal energy low-grade energy is its high entropy.

Thus, the dissipation of energy—the conversion of potential energy to thermal energy—results from two facts:

- A thermal system has an increasing function  $S(U)$ .



- As a weight lowers its height, the potential energy of the weight reduces, but entropy of the weight does not change.

**The Kelvin-Planck statement of the second law of thermodynamics.** This analysis confirms an empirical fact. It is impossible to produce no effect other than the raising of a weight by drawing thermal energy from a single thermal system. This fact is called the *Kelvin-Planck statement of the second law of thermodynamics*.

**Exercise.** Use the basic algorithm of thermodynamics to analyze adding energy to a pot of water by an electric current in a resistor.

**Exercise.** In [\*Heat considered as a Mode of Motion\*](#), published in 1863, John Tyndall described numerous experiments that tested the hypothesis of thermal energy. Wiki [Julius Robert von Mayer](#). Wiki [James Prescott Joule](#). The following passage is taken from the book by Tyndall.

“A bullet, in passing through the air, is warmed by the friction, and the most probable theory of shooting stars is that they are small planetary bodies, revolving round the sun, which are caused to swerve from their orbits by the attraction of the earth, and are raised to incandescence by friction against our atmosphere.”

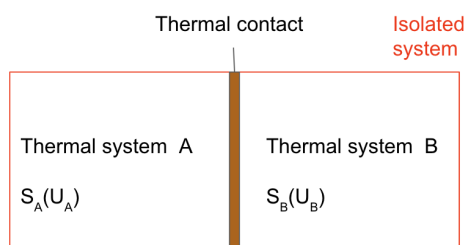
**Assignment.** Use the basic algorithm to analyze heating by friction. Identify an isolated system with an internal variable  $x$ . Identify the function  $S(x)$ . Interpret equilibrium. Interpret irreversibility.

## Thermal contact

We have just analyzed the dissipation of energy from a high grade to a low grade—that is, conversion from mechanical energy to thermal energy. We now look at the transfer of energy from one thermal system to another thermal system.

Two thermal systems are said to be in *thermal contact* if the following conditions hold.

1. The two thermal systems interact in one mode only: transfer energy by microscopic interaction.
2. The two thermal systems together form an isolated system.



In thermal contact, the two thermal systems transfer energy through molecular vibration, for example. The principle of the conservation of energy requires that an isolated system should

have a fixed amount of energy. It allows arbitrary partition of energy between the two thermal systems, so long as the sum of the energies of the two thermal systems remains constant. Our everyday experience indicates two facts:

1. When two thermal systems are in thermal contact, energy transfers from one thermal system to the other thermal system, one-way and *irreversible*.
2. After some time, the energy transfer stops, and the two thermal systems equilibrate. Two thermal systems are said to reach *thermal equilibrium*.

We now trace these empirical facts to the fundamental postulate. That is, we run the [basic algorithm of thermodynamics](#) on two thermal systems in thermal contact.

**Step 1. Construct an isolated system with an internal variable.** The two thermal systems, A and B, together constitute an isolated system. Let  $U_A$  be the energy of thermal system A, and  $U_B$  be the energy of thermal system B. The energy of the isolated system is a sum:

$$U_{\text{iso}} = U_A + U_B$$

The principle of the conservation of energy requires that the isolated system to have a fixed amount of energy:

$$U_{\text{iso}} = \text{constant}$$

When system A gains an amount of energy, system B loses the same amount of energy. For energy, thermal contact is a zero-sum game. Consequently, the isolated system has a single independent internal variable, say, the energy of one of the thermal systems,  $U_A$ .

**Step 2. Find the subset entropy of the isolated system as a function of the internal variable.** The two thermal systems are characterized by two functions,  $S_A(U_A)$  and  $S_B(U_B)$ . Once the internal variable  $U_A$  is fixed, the isolated system flips among a subset of its quantum states. The subset entropy of the isolated system is a sum:

$$S_{\text{iso}} = S_A(U_A) + S_B(U_B)$$

Because  $U_A + U_B = \text{constant}$ , the subset entropy of the isolated system is a function of a single independent internal variable,  $S_{\text{iso}}(U_A)$ .

**Step 3. Maximize the subset entropy of the isolated system to reach equilibrium.** According to calculus,

$$dS_{\text{iso}}(U_A) = (dS_A(U_A)/dU_A)dU_A + (dS_B(U_B)/dU_B)dU_B$$

According to the principle of the conservation of energy, when system A gains an amount of energy  $dU_A$ , system B loses energy by the same amount:

$$dU_B = -dU_A$$

Write

$$dS_{\text{iso}}(U_A) = (dS_A(U_A)/dU_A - dS_B(U_B)/dU_B)dU_A$$

After being isolated for a long time, the isolated system equilibrates, and the subset entropy of the isolated system maximizes, so that

$$dS_{\text{composite}}(U_A) = 0$$

Thus,

$$dS_A(U_A)/dU_A = dS_B(U_B)/dU_B$$

This equation is the condition of *thermal equilibrium*. This condition, along with the conservation of energy,  $U_A + U_B = \text{constant}$ , partitions energy between the two thermal systems A and B in equilibrium.

For entropy, thermal contact is not a zero-sum game. Thermal contact increases the subset entropy of the isolated system.

**Step 4. Increase the subset entropy of the isolated system for an irreversible process.**

Prior to reaching equilibrium, the subset entropy of the isolated system increases in time:

$$dS_{\text{composite}}(U_A) > 0$$

The increase of the subset entropy requires that

$$(dS_A(U_A)/dU_A - dS_B(U_B)/dU_B)dU_A > 0$$

Distinguish two possibilities:

- If  $dS_A(U_A)/dU_A > dS_B(U_B)/dU_B$ , the increase of the subset entropy requires that  $dU_A > 0$ , so that system A gains energy from system B.
- If  $dS_A(U_A)/dU_A < dS_B(U_B)/dU_B$ , the increase of the subset entropy requires that  $dU_A < 0$ , so that system A loses energy to system B.

**The algorithm confirms two empirical facts of thermal contact:**

1. In thermal contact, the direction of energy transfer is one-way, from a thermal system of a low slope to a thermal system of high slope. For example, when  $dS_A(U_A)/dU_A > dS_B(U_B)/dU_B$ , the energy transfers from system B to system A.

2. We further assume that  $S_A(U_A)$  and  $S_B(U_B)$  are *convex functions*. Consequently, as system A gains energy, the slope  $dS_A(U_A)/dU_A$  decreases. As system B loses energy, the slope  $dS_B(U_B)/dU_B$  increases. Our analysis shows that the transfer of energy continues until the two slopes are equal,  $dS_A(U_A)/dU_A = dS_B(U_B)/dU_B$ , i.e., when the two thermal systems reach thermal equilibrium.

**Caution.** The word “heat” serves no purpose in analyzing thermal contact. In running the basic algorithm of thermodynamics, we only invoke the principle of the conservation of energy, and the principle of the increase of subset entropy. The word “heat” does not appear in the analysis. Of course, the energy transfer from one thermal system to the other thermal system is called heat by definition. But so long as we keep track of the energy of one thermal system,  $U_A$ , the word “heat” is superfluous, and serves no purpose.

## Definition of temperature

A thermal system is characterized by a function  $S(U)$ . The basic algorithm of thermodynamics identifies the significance of the slope of the function,  $dS(U)/dU$ .

Define temperature  $T$  by

$$1/T = dS(U)/dU$$

This equation defines temperature as a *derivative* of entropy and energy. A child is born.

**Temperature is absolute.** Entropy is an absolute property, but energy is a relative property. Because the definition of temperature only uses the difference in energy, temperature is an absolute property.

**Temperature is intensive.** Both entropy and energy are extensive thermodynamic properties, but temperature is an intensive thermodynamic property. Two thermal systems in equilibrium have the same temperature.

**Flexibility in defining temperature.** But wait a minute! Any decreasing function of  $dS(U)/dU$  also serves as a definition of temperature. What is so special about the choice made above? Nothing. It is just a choice. Indeed, all that matters is the slope  $dS(U)/dU$ . Nature is indifferent to what humans call this slope.

**The roles of temperature.** We can use the word *temperature* to paraphrase the above analysis of thermal contact.

1. When two thermal systems are brought into thermal contact, energy transfers from the thermal system of higher temperature to the thermal system of lower temperature. This fact is called the *Clausius statement of the second law of thermodynamics*.

2. After some time in thermal contact, energy transfer stops, and the two thermal systems have the same temperature. The two thermal systems reach *thermal equilibrium*.

**Range of temperature.** For a thermal system, the function  $S(U)$  is a monotonically increasing function. The more energy, the more quantum states, and the more entropy. Thus, the definition  $1/T = dS(U)/dU$  makes temperature positive. Usually we only measure temperature within some interval. Extremely low temperatures are studied in the science of cryogenics. Extremely high temperatures are realized in stars, and other special conditions.

**What can you do for temperature?** An essential step to grasp thermodynamics is to get to know this prodigious child of entropy and energy—temperature. We define temperature by running the basic algorithm of thermodynamics on an everyday experience—thermal contact. How does temperature rise up as an abstraction from everyday experience? How does temperature come down from the union of energy and entropy?

Let me paraphrase a better-known Bostonian. And so, my fellow thermodynamicist: ask not what temperature can do for you—ask what you can do for temperature.

## Circular statements

What is temperature? Temperature is a property shared by two bodies in thermal contact when they stop exchanging energy by heat.

What is heat? Heat is the transfer of energy caused by difference in temperature.

The circular statements define neither heat nor temperature. They are correct and useful statements: they link heat and temperature.

By heat we mean energy transfer by microscopic interaction. By temperature we mean  $T$  defined by  $1/T = dS(U)/dU$ .

Heat and temperature are distinct quantities, and can be determined by separate experiments. The art of measuring heat is called [calorimetry](#), and the art of measuring temperature is called [thermometry](#).

## Fake unit of entropy

Because entropy is a dimensionless number,  $S = \log \Omega$ , temperature has the same unit as energy, Joule.

However, we often report temperature in the unit of Kelvin. By definition, the two units of temperature—Kelvin and Joule—are related as

$$1 \text{ Kelvin} = 1.380649 \times 10^{-23} \text{ Joules}$$

The factor of conversion between the two units is called the [Boltzmann constant](#)  $k_B$ .

To maintain the equation  $1/T = dS(U)/dU$ , the entropy need be in the fake unit of the Boltzmann constant:

$$S = k_B \log \Omega$$

Twitter [What does the Boltzmann constant mean?](#)

## Temperature finds parents: entropy and energy

The relation between entropy, energy, and temperature was invented by Clausius (1854). At the time of invention, both temperature and energy had been accepted, but entropy was imagined by Clausius. He used energy and temperature to define entropy:

$$dS = T^{-1}dU$$

His logic gives the wrong impression that entropy is derived from energy and temperature. This confusion has been propagated through textbooks to this day.

Energy is one of several supporting actors of equal importance, along with space, matter, and change. Singling energy out to define entropy confuses the structure of the play of thermodynamics.

Clausius's definition of entropy leaves the question unanswered: what is temperature?

By contrast, the [new synthesis of thermodynamics](#) does not follow Clausius's logic. The new synthesis first formulates [energy](#) and [entropy](#), and then uses them to define temperature:

$$1/T = dS(U)/dU$$

The origin of temperature is obscure until it is related to its parents, entropy and energy. Do not let temperature be an orphan again.

## The zeroth law of thermodynamics

If two thermal systems A and B are separately in thermal equilibrium with a third thermal system C, the two thermal systems A and B are in thermal equilibrium with each other. This empirical fact is called the *zeroth law of thermodynamics*. This law dates back at least to Maxwell (1871), who called it the *law of equal temperatures*.

The zeroth law is fundamental to thermometry—the art of measuring temperature.

It is commonly claimed that the zeroth law establishes temperature as a thermodynamic property. This claim is false.

Consider many thermal systems. We bring two of them into thermal contact, and check if they are in thermal equilibrium. If they are in thermal equilibrium, we say that they are at the same temperature. If they are not in thermal equilibrium, we say that they are at different temperatures.

Assume that we can “check” thermal equilibrium without disturbing each thermal system appreciably. All these thermal systems constitute a library of temperatures. For instance, we can use many different pure substances, such as gold, silver, iron, lead... Their melting points constitute a library of temperatures. We can name each temperature by the name of the substance.

For a new thermal system X, we check if it is in thermal equilibrium with any one thermal system in the library. If X is in thermal equilibrium with one of the thermal systems in the library, we have just measured the temperature of system X. If X is not in thermal equilibrium with any system in the library, we have just discovered a new temperature, and add X to the library. Thus, the growing library of temperatures functions as a thermometer.

The zeroth law, however, does *not* order the library of temperatures in a one-dimensional array. To do so we need to invoke another empirical fact. When thermal systems A and B are in thermal contact, if energy goes from B to A, energy will not go in the opposite direction. This fact is a version of the second law.

In any event, the zeroth law leaves the nature of temperature opaque, reminiscent of blind men feeling an elephant.

**Exercise.** Write an essay with the title, *What is the temperature?* How does temperature result from everyday experience of thermal contact? How is temperature born from the union of energy and entropy?

**Exercise.** Hotness and happiness are two common feelings. We measure hotness by an experimental quantity, temperature. Can we do so for happiness? Why?

**Exercise.** Replace the word “happiness” in the above exercise with any attribute that people wish to measure, such as intelligence, beauty, and love.

**Nobel lecture.** Onnes, [Investigations into the Properties of Substances at Low Temperatures, which Have Led, amongst Other Things, to the Preparation of Liquid Helium](#), 1913.

# Grade thermal systems by temperature

Thermal energy is low-grade energy: all other forms of energy can convert into thermal energy. Now we can grade all thermal systems. When two thermal systems are in thermal contact, the thermal system of a high grade transfers energy to the thermal system of a low grade. We grade each thermal energy by its temperature.

**Degrade energy by transferring energy from a high-temperature thermal system to a low-temperature thermal system.** Consider two thermal systems characterized by functions  $S_A(U_A)$  and  $S_B(U_B)$ . In thermal contact, one thermal system transfers energy to the other, but the two thermal systems together constitute an isolated system. The sum of the energies of the two thermal systems is conserved:

$$U_A + U_B = \text{constant}$$

When the energy can transfer between the two thermal systems, the composite—the isolated system—has a sample space of quantum states. When the energies of the two subsystems are fixed at  $U_A$  and  $U_B$ , the isolated system flips among a subset of quantum states, and the subset entropy is

$$S_A(U_A) + S_B(U_B)$$

To increase the subset entropy, the energy transfers from a thermal system with a lower slope  $dS/dU$  to a thermal system with a higher slope  $dS/dU$ . That is, energy degrades by transferring from a high-temperature thermal system to a low-temperature thermal system.

## Features of the function $T(U)$ common to all thermal systems

Recall the definition of temperature,  $1/T = dS(U)/dU$ . We plot the function  $T(U)$  on the energy-temperature plane. We use energy as the horizontal axis, and temperature as the vertical axis. Each point on the curve represents a thermal system isolated at a particular value of energy. That is, each point on the curve represents a thermodynamic state of the thermal system. Note several general features of the curve  $T(U)$ .

1. Energy is defined up to an additive constant, so that the curve  $T(U)$  can be translated along the axis of energy by an arbitrary amount.
2. Temperature  $T$  starts at absolute zero, is positive, and has no upper bound.
3. For the time being, we assume that  $T(U)$  is an increasing function.

These features of  $T(U)$  should be compared with those of  $S(U)$ .



**Exercise.** A thermal system can also be characterized by function  $S(T)$ . Discuss the general features of the curve  $S(T)$  on the entropy-temperature plane.

## Thermal capacity

When the energy of a thermal system changes by  $dU$ , the temperature changes by  $dT$ . Define the *thermal capacity* by

$$1/C = dT(U)/dU$$

Because energy is an extensive quantity and temperature is an intensive quantity, thermal capacity is an extensive quantity. Thermal capacity is a function of state. When we report temperature in the unit of energy, thermal capacity is dimensionless. When we report temperature in the unit Kelvin, the thermal capacity has the fake unit of entropy,  $\text{JK}^{-1}$ .

The thermal capacity is a function of energy,  $C(U)$ . We assume that the thermal capacity is positive. This assumption is equivalent to that the function  $T(U)$  has positive slope, and that the function  $S(U)$  is convex. Recall the definition of temperature,  $1/T = dS(U)/dU$ .

**Caution.** Thermal capacity is commonly called heat capacity. Thermal capacity is a function of state, and is independent of the method of energy transfer. For example, we can add energy to a half bottle of water by work, such as shaking the bottle, or electric heating. Once we commit to the modern usage of the word heat as a method of energy transfer, it is inappropriate to name a function of state using the word heat.

**Specific thermal capacity.** The energy needed to raise the temperature of a unit mass of a substance by a degree is called the *specific thermal capacity* of the substance. Liquid water has approximately a constant specific thermal capacity of  $4.18 \text{ kJ/kg-K}$ . Ice has approximately a constant specific thermal capacity of  $2.06 \text{ kJ/kg-K}$ .

**Exercise.** (a) We immerse a  $100 \text{ W}$  light bulb in  $1 \text{ kg}$  of water for  $10$  minutes. Assume that all electric energy applied to the bulb converts to the thermal energy of water. How much does the temperature of the water increase? (b) How much does the temperature of the water increase when an apple falls from a height of  $1 \text{ m}$  into the water and converts all its potential energy to the thermal energy of the water? Similar experiments were conducted in the 1840s to establish that heat is a form of energy.

**Exercise.** What are the changes in energy and entropy of  $1 \text{ kg}$  of water when raised from the freezing to the boiling temperature?

**Exercise.** When  $1 \text{ kg}$  of water at the freezing point is mixed with  $2 \text{ kg}$  of water at the boiling point, what is the temperature in equilibrium? What is the change of entropy associated with this mixing?

**Exercise.** For a solid or a liquid, the change of volume is small when temperature increases. We model the solid or liquid as a thermal system, and measure the temperature-energy curve experimentally. For a small range of temperature, the thermal energy is approximately linear in temperature,  $U(T) = CT$ , where the thermal capacity  $C$  is taken to be a constant. Derive the characteristic function  $S(U)$ .

## Temperature as an independent variable

For the time being, we assume that the function  $T(U)$  is an increasing function. That is, on receiving energy, a thermal system increases temperature. Any monotonic function is invertible. Write the inverse function as  $U(T)$ . The two functions,  $U(T)$  and  $T(U)$ , correspond to the same curve on the energy-temperature plane, and contain the same information.

Recall the definition of temperature:

$$1/T = dS(U)/dU$$

Also recall the definition of thermal capacitor:

$$1/C = dT(U)/dU$$

Regard temperature as the independent variable. Write.

$$C(T) = dU(T)/dT$$
$$dS(T)/dT = C(T)/T$$

## Thermostat

A thermostat is a device that uses a feedback mechanism to fix temperature. A thermostat measures the temperature of a thermal system and switches heating or cooling equipment on. A thermostat is used widely to set the temperature of a refrigerator or a room.

## Sous-vide

Sous-vide (su:'vi:d) is a method of cooking, also called low-temperature, long-time cooking. Food (e.g., a piece of meat) is sealed in an airtight plastic bag, and placed in water for a longer time and at a lower temperature than those used for normal cooking. The temperature of water is fixed by a thermostat. Because of the long time and low temperature, sous-vide cooking keeps the temperature evenly in the entire volume of the food. The inside is properly cooked without overcooking the outside. A sous-vide recipe is specified by temperature as a function of time. The airtight bag retains moisture in the food.

At home, energy is supplied to the water by an electric current, and is dissipated to the room. The temperature is fixed by regulating the electric current. Sous-vide is also commonly done at a hot spring, where the temperature of a pool is fixed by regulating the rate of flow of the hot spring.

YouTube [Dave Arnold on low-temperature cooking of eggs](#)

## Thermal reservoir

Recall the definition of temperature:

$$1/T = dS(U)/dU$$

A *thermal reservoir* is a thermal system of a constant temperature  $T_R$  when energy changes. Thus, a thermal reservoir is characterized by a linear function  $S(U)$ , with a constant slope of  $1/T_R$ .

Integrating the equation  $1/T = dS(U)/dU$  from energy  $U$  to energy  $U + Q$ , we find that

$$S(U + Q) - S(U) = Q/T_R$$

This result should be committed to memory. Upon gaining energy  $Q$ , a thermal reservoir of temperature  $T_R$  increases entropy by  $Q/T_R$ .

A thermal reservoir is analogous to a water reservoir. The level of a water reservoir remains nearly unchanged when a small cup of water is taken out from the water reservoir. The amount of water in a water reservoir is analogous to the amount of energy in a thermal reservoir. The level of a water reservoir is analogous to the temperature of a thermal reservoir.

A thermal reservoir is approximately realized by using a large tank of liquid. When the liquid loses or gains a small amount of energy, the temperature of the liquid is nearly unchanged.

A mixture of ice and water is also approximately a thermal reservoir. At the atmospheric pressure, the temperature of the ice-water mixture is fixed at the melting point, zero Celsius. Upon gaining or losing energy, the mixture changes the ratio of ice and water, but keeps the temperature fixed.

## Debye model

To illustrate the determination of the characteristic function  $S(U)$ , consider the Debye model (1912). Near absolute zero, the thermal energy of a solid takes the form

$$U = aT^4$$

where  $a$  is a constant. Debye obtained this expression from a microscopic model.

Invert the above equation, and we have  $T = (U/a)^{1/4}$ . Integrating  $dS = T^{-1}dU$ , we obtain that

$$S(U) = (4/3)a^{1/4}U^{3/4}$$

We have used the condition  $S = 0$  at  $T = 0$ .

**Exercise.** Calculate the function  $C(T)$  for the Debye model.

**Nobel lecture.** Debye, [Methods to Determine the Electrical and Geometrical Structure of Molecules](#), 1936.

## Calorimetry

The art of measuring thermal energy is called *calorimetry*. A device that measures thermal energy is called a *calorimeter*.

Calorimetry has become an art of high sophistication. It is too much of a tangent to talk about current practice of calorimetry in a beginning course in thermodynamics. All we need to know is that energy transfer by thermal contact is measured routinely.

This said, it is good to have a specific method of calorimetry in mind. Just think of an electric current in a resistor. As the electric current flows, electrons bump the atoms of the resistor, and the vibration of the atoms of the resistor transfers energy to the molecules in the thermal system. The electric outlet supplies energy (current)(voltage)(time). This energy is assumed to be fully transferred into the thermal system.

Wikipedia [Calorimetry](#).

## Thermometry

Temperature is defined by  $1/T = dS(U)/dU$ . The art of measuring temperature is called *thermometry*. A device that measures temperature is called a *thermometer*.

Temperature affects all properties of all materials. In principle, any property of any material can serve as a thermometer. The choice is a matter of convenience, accuracy, and cost. For example, our fingers are thermometers. So are many parts of our bodies. But these thermometers are unreliable and work in a narrow range of temperature. We next describe two commonly used thermometers.

**Exercise.** A block of steel and a block of wood have the same temperature, which is higher than our body temperature. On touching them with a finger, you feel the steel is hotter than the wood. Why?

**Liquid-in-glass thermometer.** A liquid-in-glass thermometer relies on a property of liquid: the volume expands as temperature increases. Thus, a volume indicates a temperature.

**Gas thermometer.** An ideal gas obeys the equation of state:

$$PV = Nk_B T$$

This equation defines temperature  $T$  in terms of  $P$ ,  $V$ , and  $N$ . We will show later that the temperature defined by the ideal gas law coincides with the temperature defined by the equation

$$1/T = dS(U)/dU$$

The quantities  $P$ ,  $V$ , and  $N$  can be measured, so that an ideal gas serves as a thermometer, called the *gas thermometer*.

**Exercise.** Watch a video of a [gas thermometer at constant volume](#). Explain how this thermometer works.

**A division of labor.** How does a doctor determine the temperature of a patient? Certainly she does not count the number of quantum states of her patient. Instead, she brings a thermometer into thermal contact with the patient. Say that she uses a liquid-in-glass thermometer. Upon reaching thermal equilibrium with the patient, the liquid expands a certain amount, giving a reading of the temperature of the patient.

The manufacturer of the thermometer must assign a volume of the liquid to a temperature. This he can do by bringing the thermometer into thermal contact with a flask of an ideal gas. He determines the temperature of the gas by measuring its volume, pressure, and number of molecules. He varies the temperature of the gas and gives the liquid-in-glass thermometer a series of markings.

Thermometry follows these basic steps:

1. For an idealized system, formulate a theory that relates temperature to measurable quantities.
2. Use the idealized system to calibrate a thermometer by thermal contact.
3. Use the thermometer to measure temperatures of any other system by thermal contact.

Steps 2 and 3 are sufficient to set up an arbitrary scale of temperature. It is Step 1 that maps the arbitrary scale of temperature to the definition  $1/T = dS(U)/dU$ .

Our understanding of temperature now divides the labor of measuring temperature among a doctor (Step 3), a manufacturer (Step 2), and a theorist (Step 1). Only the theorist needs to count the number of quantum states, and only for very few idealized systems. The definition of temperature helps us understand thermometry and design thermometers.

Twitter [Thermometry](#)

**Exercise.** YouTube [temperature sensor](#). Explain how the thermocouple works.

## Count the number of quantum states of an isolated system experimentally

This heading captures a magic between nature and humans. We can count experimentally the number of quantum states of an isolated system of any complexity, knowing nothing about the quantum states themselves. We illustrate the method of counting using a thermal system—a family of isolated systems characterized by a function  $S(U)$ .

**Division of labor.** Recall the definition of entropy:

$$S = \log \Omega$$

Counting the number of quantum states of an isolated system is equivalent to determining its entropy.

Some things are easy to calculate theoretically, others are easy to measure experimentally. A division of labor improves the economics of getting things done. Much of thermodynamics is only sensible in terms of the division of labor between theory and experiment, and between people and machines. For most isolated systems, counting quantum states experimentally is far more economic than computing them theoretically

Here is a statement of the task. Given a thermal system, such as a bottle of water, measure its characteristic function  $S(U)$ . Recall the definition of temperature:

$$1/T = dS(U)/dU$$

Counting the number of quantum states requires a combination of thermometry to measure  $T$  and calorimetry to measure  $U$ .

**Experimental measurement of the function  $T(U)$ .** We add energy to the thermal system by, say, passing an electric current through a resistor. The change in energy  $U$  is determined by  $(\text{time})(\text{resistance})(\text{current})^2$ . At each increment of energy, we isolate the system, wait until the system reaches equilibrium, and measure temperature  $T$ . These incremental measurements determine the function  $T(U)$ .

**Determination of entropy.** Once  $T(U)$  is measured, integrating the equation  $1/T = dS(U)/dU$ , we obtain the function  $S(U)$ . In this integration, set  $S = 0$  as  $T \rightarrow 0$ . That is, at the ground state, the number of quantum states is low, and is set to be one. This statement is called *the third law of thermodynamics*. On the energy-entropy plane, the curve  $S(U)$  approaches the horizontal axis vertically.

Recall  $S(U) = \log \Omega(U)$ . Thus, this method counts the number of quantum states of the system isolated at each value of  $U$ .

**Temperature as an independent variable.** In practice, temperature is often regarded as an independent variable. Assuming  $T(U)$  is an increasing function, the measurement also gives the function  $U(T)$ .

Recall that

$$C = dU(T)/dT$$

As we measure the increment energy and increment temperature, their ratio determines the thermal capacity as a function temperature,  $C(T)$ .

Recall that

$$dS(T)/dT = C(T)/T$$

Integrating, we obtain that

$$S(T) = \int_0^T \frac{C(T)}{T} dT$$

Often, the measurement only extends to some temperature above absolute zero. Say  $C(T)$  is determined in a range of temperature from  $T_0$  and  $T$ . Write

$$S(T) - S(T_0) = \int_{T_0}^T \frac{C(T)}{T} dT$$

Such an experiment leaves the absolute entropy undetermined. The [Debye model](#) has been used to extrapolate experimental measurement of entropy to temperature zero. For the extrapolation to be reliable, one has to cool the thermal system to temperature close to the absolute zero. We will learn about refrigeration later.

The function  $U(T)$  and  $S(T)$  together give the function  $S(U)$ .