

### Energy and Fundamental Postulate

We have described two great principles of our world: the fundamental postulate (<http://imechanica.org/node/290>) and the conservation of energy (<http://imechanica.org/node/11297>). The former is the foundation of thermodynamics, as we have learned in a previous lecture. The latter is not specific to thermodynamics: we borrow the concept of energy—along with the principle of the conservation of energy—from other branches of science, such as mechanics and electrodynamics. Both principles are abstracted from many empirical observations.

The two great principles are combined here to study an everyday experience: thermal contact. Of thermal contact we have recounted a large number of empirical observations (<http://imechanica.org/node/11298>). These observations have enabled us to formulate a property—a function of state—temperature. In our past studies, we took these empirical observations as given, and did not probe their origins.

We now wish to show that all the empirical observations of thermal contact are consequences of the two great principles. The fundamental postulate gives us one property—entropy  $S$ , the principle of the conservation of energy gives us another property—internal energy  $U$ . The combination of the two great principles gives us a third property—temperature  $T$ . The three properties are connected through a beautiful relation:  $dS = dU/T$ . Consequently, the entropy of a system can be determined by independently measuring temperature (thermometry) and measuring energy (calorimetry).

An essential step to understand how thermodynamics works is to get to know temperature. How does temperature come down as an abstraction from everyday experience? How does temperature rise up as a consequence of the fundamental postulate and the principle of the conservation of energy?

And so, my fellow enthusiasts of thermodynamics: ask not what temperature can do for you—ask what you can do for temperature.

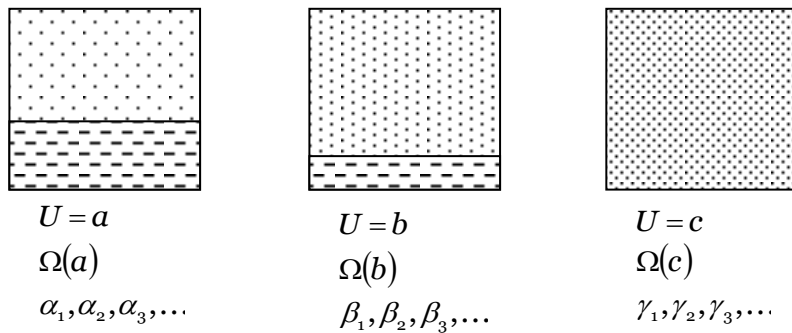
**A thermodynamic system of one independent variation.** We now allow a system to interact with the rest of the world in only one way: the system can gain or lose energy by thermal contact. Such a system is not an isolated system. However, when the energy of the system is fixed at any particular value  $U$ , the system is isolated, and has a specific number of quantum states,  $\Omega$ . Consequently, we can regard the system of variable energy as a family of isolated systems, characterized by the function  $\Omega(U)$ . Each member in the family is a distinct isolated system, with its own amount of energy, and flipping among its own set of quantum states. The family of isolated systems has a single

independent thermodynamic variable, the energy. We choose to focus exclusively on thermal contact, and block all other modes of interaction between the system and the rest of the world.

**Hydrogen atom.** For example, a hydrogen atom is a system that can change its energy by absorbing photons. Thus, the hydrogen atom may be viewed as a family of isolated systems. According to quantum mechanics, this family of isolated systems is characterized by the function  $\Omega(U)$ :

$$\Omega(-13.6\text{eV})=2, \quad \Omega(-3.39\text{eV})=8, \quad \Omega(-1.51\text{eV})=18, \dots$$

The domain of the function  $\Omega(U)$  is a set of discrete values of energy:  $-13.6\text{eV}, -3.39\text{eV}, -1.51\text{eV}, \dots$ . The range of the function is a set of integers: 2, 8, 18, .... Each quantum state is characterized by a distinct wave function and spin. For the hydrogen atom, the gaps between the values of energy happen to be large.



**A tank of water molecules.** For a complex system like a tank of water molecules, the gaps between energy levels are so small that we regard the energy of the tank of water as a continuous real variable. The number of water molecules in the tank is fixed. To make the tank of water molecules an isolated system, we make the tank with a rigid material, so that pressure in the tank does no work to the rest of the world. We also insulate the tank, so that no transfer of energy by heat. We can make the tank of water molecules into a family of isolated systems of different values of energy. The figure illustrates the tank of water molecules in three thermodynamic states, each being an isolated system of a particular value of energy. When isolated at energy  $U = a$ , the tank contains a mixture of liquid and vapor, and the system flips amount a total number of  $\Omega(a)$  quantum states, labeled as  $\alpha_1, \alpha_2, \alpha_3, \dots$ . When isolated at a higher energy,  $U = b$ , the more liquid transforms into the vapor, and the system flips amount a total number of  $\Omega(b)$  quantum states, labeled as  $\beta_1, \beta_2, \beta_3, \dots$ . When isolated with at an

even higher energy,  $U = c$ , the tank contains vapor only, and the system flips amount a total number of  $\Omega(c)$  quantum states, labeled as  $\gamma_1, \gamma_2, \gamma_3, \dots$

The tank of water molecules is modeled as a system of a single independent property, energy. The system has a set of quantum states. A value of energy specifies a thermodynamic state of the system. Each thermodynamic state corresponds to a subset of quantum states that have the same value of energy. In past studies we have viewed a property of a system as a function whose domain is the thermodynamic states of the system. We can also regard the property as a random variable—a function whose domain is the quantum states of the system.

**Entropy of the family of isolated systems.** Once again, when the energy of the system is fixed at any particular value  $U$ , the system is an isolated system, and has a specific number of quantum states,  $\Omega(U)$ . Recall the definition of entropy, the entropy of the isolated system of energy  $U$  is

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

The function  $S(U)$  describes the entropy of the family of isolated systems.

The two functions,  $\Omega(U)$  and  $S(U)$ , contain the same information. For me, speaking of  $\Omega(U)$  gives me a movie of jiggling molecules, and speaking of  $S(U)$  allows me to simplify mathematics from multiplication to addition.

**Thermal contact analyzed by the conservation of energy.** When a glass of wine and a piece of cheese are in thermal contact, energy may go from the wine to the cheese, or the other way around. We make the composite of the wine and cheese an isolated system. According to the principle of the conservation of energy, the composite has a fixed amount of total energy, which is designated as  $U_{\text{total}}$ . Consider a specific partition of energy: the wine has energy  $U'$ , and the cheese has energy  $U''$ . According to the principle of the conservation of energy, we write

$$U' + U'' = U_{\text{total}}.$$

The central mystery is this. The principle of the conservation of energy allows arbitrary partition of energy between the wine and the cheese, so long as the total energy in the wine and cheese remains constant. Our everyday experience indicates, however, when the wine and the cheese are brought into thermal contact, energy flows only in one direction. Furthermore, after some time, the flow of energy stops, and the wine and the cheese reaches thermal

equilibrium. In the state of equilibrium, the wine and the cheese divide the total energy into two definite amounts.

To sum up, according to the principle of the conservation of energy, the energy of the isolated system—the composite of the wine and the cheese—is a constant. The gain of energy in the wine equals the loss of energy in the cheese. Consequently, the partition of energy between the wine and the cheese is an internal variable of the isolated system. How the energy is partitioned is determined by the fundamental postulate.

### **Thermal constant analyzed by the fundamental postulate.**

Isolated at energy  $U'$ , the wine has a total of  $\Omega'(U')$  number of quantum states, labeled as  $\{\alpha'_1, \alpha'_2, \dots\}$ . Isolated at energy  $U''$ , the cheese has a total of  $\Omega''(U'')$  number of quantum states, labeled as  $\{\alpha''_1, \alpha''_2, \dots\}$ . A quantum state of the composite can be any combination of a quantum state chosen from the set  $\{\alpha'_1, \alpha'_2, \dots\}$  and a quantum state chosen from the  $\{\alpha''_1, \alpha''_2, \dots\}$ . For example, one quantum state of the composite is when the wine is in quantum state  $\alpha'_2$  and the cheese is in quantum state  $\alpha''_3$ . The total number of all such combinations is

$$\Omega'(U')\Omega''(U'').$$

This is the number of quantum states of the composite in the subset that energy is partitioned as  $U'$  and  $U''$  between the wine and the cheese. Thus, when energy is partitioned as  $U'$  and  $U''$  between the wine and the cheese, the entropy of wine  $S' = \log\Omega'(U')$ , the entropy of the cheese is  $S'' = \log\Omega''(U'')$ . We call this composite of partition A. The entropy of the composite of partition A is

$$S'(U') + S''(U'').$$

Consider another partition of energy: the wine has energy  $U' + dU$ , and the cheese has energy  $U'' - dU$ . That is, the wine gains energy  $dU$  and the cheese loses energy by the same amount, as required by the principle of the conservation of energy. Isolated at energy  $U' + dU$ , the wine has a total of  $\Omega'(U' + dU)$  number of quantum states, labeled as  $\{\beta'_1, \beta'_2, \dots\}$ . Isolated at energy  $U'' - dU$ , the cheese has a total of  $\Omega''(U'' - dU)$  number of quantum states, labeled as  $\{\beta''_1, \beta''_2, \dots\}$ . A quantum state of the composite can be any combination of a quantum state chosen from the set  $\{\beta'_1, \beta'_2, \dots\}$  and a quantum state chosen from the  $\{\beta''_1, \beta''_2, \dots\}$ . The total number of all such combinations is

$$\Omega'(U' + dU)\Omega''(U'' - dU).$$

Thus, when energy is partitioned as  $U' + dU$  and  $U'' - dU$  between the wine and the cheese, the entropy of the composite is

$$S'(U' + dU) + S''(U'' - dU).$$

Both systems—the wine and the cheese—are so large that the partition of energy may be regarded as a continuous variable, and that the functions  $S'(U')$  and  $S''(U'')$  are differentiable. Consequently, the entropy of the composite of partition B is

$$S'(U' + dU) + S''(U'' - dU) = S'(U') + S''(U'') + \left( \frac{dS'(U')}{dU'} - \frac{dS''(U'')}{dU''} \right) dU.$$

$U'$	$U''$	$U' + dU$	$U'' - dU$
$\Omega'(U')$	$\Omega''(U'')$	$\Omega'(U' + dU)$	$\Omega''(U'' - dU)$
$\alpha'_1, \alpha'_2, \dots$	$\alpha''_1, \alpha''_2, \dots$	$\beta'_1, \beta'_2, \dots$	$\beta''_1, \beta''_2, \dots$

partition A

partition B

The partition of energy is an internal variable of the isolated system, the composite. For a specific partition of energy, the composite flips among a specific subset of the quantum states. According to the fundamental postulate, all the quantum states of the composite are equally probable, so that a subset of more quantum states is more probable. The two partitions of energy—A and B—corresponds to two subsets of quantum states of the composite. According to the fundamental postulate, partition A is less probable than partition B if the former corresponds to fewer quantum states than the latter, namely,

$$\left( \frac{dS'(U')}{dU'} - \frac{dS''(U'')}{dU''} \right) dU > 0.$$

Consequently, it is more probable for energy to go from the cheese to the wine if

$$\frac{dS'(U')}{dU'} > \frac{dS''(U'')}{dU''}.$$

It is more probable for energy to go from the wine to the cheese if

$$\frac{dS'(U')}{dU'} < \frac{dS''(U'')}{dU''}.$$

Furthermore, when the two quantities are equal,

$$\frac{dS'(U')}{dU'} = \frac{dS''(U'')}{dU''},$$

energy is equally probable to go in either direction—that is, the wine and the cheese are in thermal equilibrium.

**Thermodynamic temperature scale.** The function  $S(U)$  is specific to a system of variable energy, so is the quantity  $dS(U)/dU$ . The previous paragraph, however, shows that the value  $dS(U)/dU$  is the same for all systems in thermal equilibrium. Consequently, the values of  $dS(U)/dU$  can be used to define a scale of temperature. We will use a particular scale of temperature,  $T$ , set up by

$$\frac{1}{T} = \frac{dS(U)}{dU}.$$

This scale of temperature is called the thermodynamic temperature scale.

The combination of the two great principles—the fundamental postulate and the conservation of energy—relates temperature to two other quantities: the number of quantum states and energy. You can revisit all the empirical observations of thermal contact described before, and convince yourself they are logical consequences of the fundamental postulate, applied in conjunction with the conservation of energy.

The function  $S(U)$  is expected to be a monotonically increasing function: the more energy, the more quantum states. The above definition makes all levels of temperature positive.

This scale of temperature also accounts for another empirical observation. As indicated by the above inequality, when two systems are brought into thermal contact, energy flows from the system with a higher temperature to the system with a lower temperature.

**Ideal gas.** We can calculate the absolute temperature of a system by counting the number of states of the system as a function of energy,  $\Omega(U)$ . Such counting can be carried out for simple systems, but is prohibitively expensive for most systems. As an example, consider an ideal gas, in which the molecules are so far apart that their interaction is negligible. For the ideal gas, a counting of the number of states recovers the law of ideal gases:

$$T = pV/N,$$

where  $p$  is the pressure,  $V$  the volume, and  $N$  the number of molecules. This equation relates the absolute temperature  $T$  to measurable quantities  $p$ ,  $V$  and  $N$ .

Historically the law of ideal gases was discovered empirically. However, this empirical discovery does not make it clear that the temperature scale set up by the law of ideal gases is the same as that set by  $T^{-1} = dS(U)/dU$ . In a later lecture, we will derive the law of ideal gases by counting the number of quantum states.

### **Experimental determination of temperature (thermometry).**

How does a doctor determine the temperature of a patient? Certainly she has no patience to count the number of quantum states of her patient. She uses a thermometer. Let us say that she brought a mercury thermometer into thermal contact with the patient. Upon reaching thermal equilibrium with the patient, the mercury expands a certain amount, giving a reading of the temperature of the mercury, which is also the temperature of the patient.

The manufacturer of the thermometer must assign an amount of expansion of the mercury to a value of temperature. This he does 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. Also, by heating or cooling the gas, he varies the temperature and gives the thermometer a series of markings.

Any experimental determination of the absolute temperature follows these basic steps:

- (1) Calculate the temperature of a simple system by counting the number of states. The result expresses the absolute temperature in terms of measurable quantities.
- (2) Use the simple 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 absolute scale.

**Division of labor.** Our understanding of temperature now divides the labor of measuring absolute temperature among a doctor (Step 3), a manufacturer (Step 2), and a theorist (Step 1). Only the theorist needs to count the number of state, and only for a very few idealized systems, such as an ideal gas. The art of measuring temperature is called *thermometry*.

As with all divisions of labor, the goal is to improve the economics of doing things. One way to view any area of knowledge is to see how labor is divided and why. One way to make a contribution to an area of knowledge is to

perceive a new economic change (e.g., computation is getting cheaper, or a new instrument is just invented) and devise a new division of labor.

### Experimental determination of the number of quantum states.

Given a system, its number of quantum states,  $\Omega$ , can be determined by separately measuring temperature  $T$  and energy  $U$ . We open the system in a single way by adding energy to the system, while blocking all other modes of interaction. That is, the system interacts with the rest of the world by pure thermal contact. At each increment of energy, we wait until the system regains equilibrium, and then measure the temperature of the system.

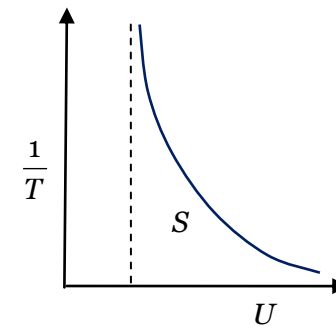
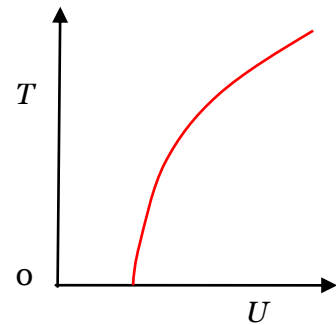
The experimental data are plotted as the  $U$ - $T$  curve. The temperature starts at the absolute zero. The energy is defined up to an additive constant, so that the curve can be translated horizontally by an arbitrarily amount. Each point on the curve represents the system isolated at a particular value of energy. The whole curve represents the system as a family of isolated systems.

For a small amount of energy  $dU$  added to the system, from the definition of temperature, we have

$$dS = \frac{dU}{T}.$$

The temperature is that of the system after regaining equilibrium. This method allows us to determine the function  $\Omega(U)$  of a system up to a multiplicative factor. To fix the multiplication factor, we set  $\Omega=1$  as  $T \rightarrow 0$ . That is, at the ground state, the number of quantum states is low, and may be set to be one. This is a version of the *third law of thermodynamics*.

The above equation suggests a graphic representation. For a given system, we plot the experimentally determined  $U$ - $T$  curve into a  $U$ - $T^{-1}$  curve. The area under this curve is  $\log \Omega$ .



**A commonly used irrational unit of entropy.** The entropy  $S$  of an isolated system is defined by

$$S = \log \Omega.$$

Entropy so defined is a pure number, and has no unit.

When temperature is given in the unit of Kelvin, to preserve the relation  $dS = T^{-1}dU$ , one includes the conversion factor  $k$  in the definition and write

$$S = k \log \Omega.$$

This practice will give the entropy a unit J/K. Of course, this unit is as silly as a unit like inch/meter, or a unit like joule/calorie. Worse, this unit gives an impression that the concept of entropy is logically dependent on the concepts of energy and temperature. This impression is wrong. Entropy is simply the shorthand for “the logarithm of the number of quantum states”. The concept of entropy is more primitive than either energy or temperature. We happen to be interested in thermal contact, where energy and temperature are involved.

At a more elementary level, entropy is a pure number associated with any probability distribution, not just the probability distribution of quantum states of an isolated system. For example, we can talk about the entropy of rolling a fair die ( $S = \log 6$ ), or the entropy of tossing a fair coin ( $S = \log 2$ ).

**Heat capacity.** A system is in thermal contact with the rest of world, while all other modes of interaction are blocked. Associated with a small change in the energy of a system,  $dU$ , the temperature of the system changes by  $dT$ . Define the *heat capacity* of the system  $C$  by the relation

$$\frac{1}{C} = \frac{dT(U)}{dU}.$$

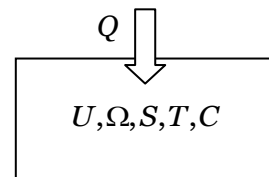
Because the temperature has the unit of energy, heat capacity is dimensionless. If you'd like to use a different unit for temperature,  $kT$  has the unit of energy, and the heat capacity is given in units of  $k$ . The heat capacity is also a function of energy,  $C(U)$ .

**Energy as the independent variable.** We have already introduced quite a few functions of state, or properties:

$$\Omega, S, U, T, C.$$

Because the system is capable of a single independent variation, we may choose one of the five properties as the independent variable, and plot any one of the other properties as a function of the independent variable.

Consider a plane with two coordinates  $S$  and  $U$ . On this plane, a system with variable energy is represented by a curve  $S(U)$ . A point on the curve represents the system isolated at energy  $U$ , flipping



among  $\exp(S)$  number of quantum states. The slope of the curve  $S(U)$  gives the inverse of  $T$ . We can also plot the function  $T(U)$  on the plane with coordinates  $U$  and  $T$ . The slope of the curve  $T(U)$  gives the inverse of  $C$ .

The horizontal positions of both curves have no empirical significance, because energy is meaningful up to an additive constant. By contrast, the vertical positions of the curves do have empirical significance. We know  $\Omega \approx 1$  or  $S \approx 0$  at the ground state of the system  $T \rightarrow 0$ .

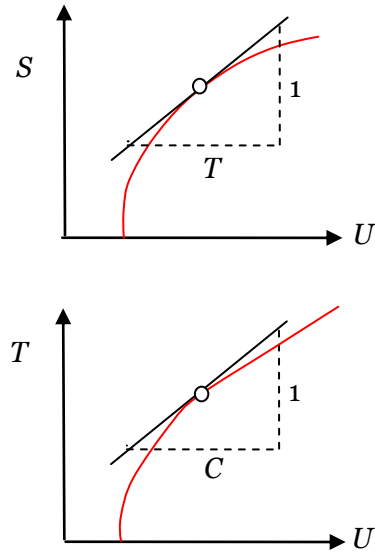
The more energy the system has, the more quantum states the system has. That is, the function  $S(U)$  is a monotonically increasing function. The temperature is positive.

If the function  $S(U)$  is convex, the function  $T(U)$  is a monotonically increasing function, and  $C > 0$ . That is, the system must receive energy to increase its temperature.

**Entropy as the independent variable.** One difficulty in learning thermodynamics is to learn alternative choices of the independent variable. So far we have been dealing systems with a single independent variable. The number of choices will proliferate when we look at systems with more independent variables. At this stage, it is helpful to look at several choices of independent variable for a system of a single independent variable.

For a given system, such as the bottle of wine in thermal contact with the rest of the world, the function  $S(U)$  is a monotonically increasing function. The more energy the system has, the larger the number of quantum states among which the system flips. Any monotonic function can be inverted. Consequently, the function  $S(U)$  can be inverted to obtain the function  $U(S)$ . The two functions,  $S(U)$  and  $U(S)$ , are alternative and equivalent ways to describe the same system in thermal contact with the rest of the world. The two functions correspond to the same curve on the  $(S, U)$  plane. We can always choose to plot the independent variable as the horizontal axis.

In terms of the function  $U(S)$ , the temperature is



$$T = \frac{dU(S)}{dS}.$$

This equation expresses the temperature as a function of the entropy,  $T(S)$ . The temperature is the slope of the  $U(S)$  curve, while the energy is the area under the  $T(S)$  curve. Another way to write the above equation is

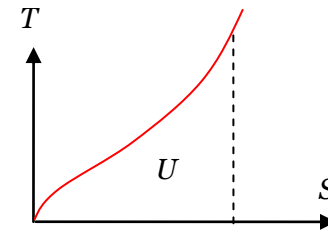
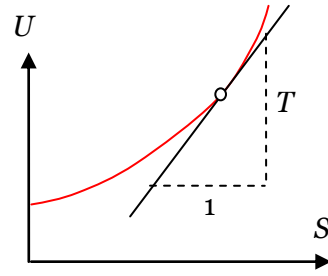
$$dU = TdS.$$

The heat capacity is defined as

$$\frac{1}{C} = \frac{dT(U)}{dU}.$$

In terms of the function  $U(S)$ , the heat capacity is

$$C = \frac{dU(S)/dS}{dT(S)/dS} = \frac{dU(S)/dS}{d^2U(S)/dS^2}$$



**Temperature as the independent variable.** We often use  $T$  as the independent variable. This choice can be tricky because temperature and the members of the family of the isolated systems may have a one-to-many mapping. For example, when ice is melting into water, energy is absorbed, but temperature does not change, so that associated with the melting temperature are many members in the family of the isolated systems.

If we stay away from such a phase transition, the function  $S(U)$  is convex. Recall the definition of temperature,

$$\frac{1}{T} = \frac{dS(U)}{dU}.$$

This equation defines the temperature as a function of the energy,  $T(U)$ . When the function  $S(U)$  is convex, the function  $T(U)$  increases monotonically. Consequently, the function  $T(U)$  can be inverted to obtain  $U(T)$ .

In terms of the function  $U(T)$ , the heat capacity is

$$C = \frac{dU(T)}{dT}.$$

This expression defines the function  $C(T)$ . A combination of the above two equations gives that

$$dS = \frac{C(T)}{T} dT.$$

The function  $U(T)$  is typically determined by a combination of thermometry and calorimetry. Once  $U(T)$  is known, the pair of equations above can be used to obtain  $C(T)$  and  $S(T)$ .

**Summary.** Consider a system that interacts with the rest of the world in only one way: thermal contact. We block all other modes of interactions. That is, the system is a closed system, which does not exchange matter with the rest of the world. The system exchanges energy with the rest of the world by heat, but not by work. When a quantity of heat  $Q$  is transferred from the rest of the world to the system, according to the principle of the conservation of energy, the energy of the system increases by

$$\Delta U = Q.$$

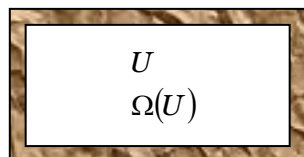
Thus, the energy of the system  $U$  can be measured incrementally by the quantity of heat transferred to the system. This is the art of calorimetry.

The system can be in many thermodynamic states. Each thermodynamic state of the system is specified by a value of a single variable, the energy  $U$ . The energy of the system is a function of state, or a property, of the system. When the value of the energy is fixed, the system becomes an isolated system. According to the fundamental postulate, after being isolated for a long time, the system flips to every one of a set of quantum states with equal probability. The number of the set of quantum state is designated by  $\Omega$ , which is a function of the energy,  $\Omega(U)$ . The entropy is designated by

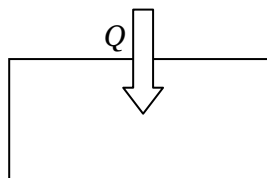
$$S = \log \Omega.$$

When a quantity of heat  $\delta Q$  is transferred from the rest of the world to the system, the energy of the system increases by  $dU = \delta Q$ , and the entropy of the system increases by

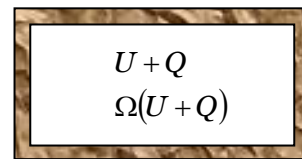
$$dS = \frac{dU}{T}.$$



Isolate the system at energy  $U$



Transfer energy to the system by a quantity of heat  $Q$



Isolate the system at energy  $U + Q$

This equation defines the thermodynamic temperature scale  $T$ . The art of measuring temperature is called thermometry. The entropy of the system can be determined incrementally by separately measuring the energy and the temperature.

The heat capacity  $C$  is defined by

$$dU = CdT .$$

The heat capacity can be determined by separately measuring the energy and the temperature.