Temperature

Thermal contact. Consider a glass of wine and a piece of cheese. They have been kept as two separate isolated systems long enough so that each by itself is in equilibrium. However, the two systems are not in equilibrium with each other. When we allow the two systems to interact in a particular way, with one system gaining energy at the expense of the other, we observe that energy does go from one system to the other. To focus on this particular mode of interaction, we block all other modes of interaction: the two systems do not exchange volume, molecules, etc. Will energy go from the wine to the cheese, or the other way around?

This mode of interaction between two systems, allowing only exchange in energy, is called *thermal contact*. The amount of energy that goes from one system to the other is called *heat*. Energy can "go" from one place to another in several familiar ways:

- *Conduction*. Energy can go through a material, which itself remains stationary at a macroscopic scale. At a microscopic scale, energy is carried by flow of electrons and vibration of atoms.

- *Convection*. Energy can be carried by the motion of a fluid. This way of energy transfer is not analyzed now because it involves mass transfer between systems.

- *Radiation*. Energy can be carried by electromagnetic waves. Because electromagnetic waves can propagate in vacuum, two systems in thermal contact need not be in proximity with each other.

Weakly interacting systems. In reality, the contact of two systems inevitably does more than just re-allocating energy from one system to the other. For example, when two bodies touch each other, they may form atomic bonds. As another example, the presence of two bodies in space modifies the electromagnetic field. For the time being, we assume that such effects are

negligible. The two systems are said to *interact weakly* if all they do is that one system gains

energy at the expense of the other.

Hotness and temperature are synonymous. To distill everyday experience of hotness,

we note the following observations:

(1) When two systems are brought into thermal contact, energy goes from the hotter system

to the less hot system.

(2) After the two systems are in thermal contact for a long time, they cease to exchange

energy. We say that they are in thermal equilibrium. Two systems in thermal equilibrium

are equally hot.

(3) When two systems are separately in thermal equilibrium with a third system, the two

systems are in thermal equilibrium with each other.

These observations allow us to assign a scale of hotness. For example, we could set up a

scale of hotness by the melting points of several substances: nitrogen, water, lead, aluminum,

and gold. We could name a level of hotness by the substance that melts at this hotness. We

would know that the hotness "nitrogen" is lower than the hotness "water" because of the

following empirical observation.   We would first make system A in thermal equilibrium with

the melting nitrogen, and system B in thermal equilibrium with the melting water. Afterwards,

upon bringing system A into thermal contact with system B, we observe that energy goes from

system B to system A. Similar experiments would show us that the hotness "water" is lower

than the hotness "lead", "lead" is lower than "aluminum", and "aluminum" is lower than "gold".

We may even assign a continuous variable to various levels of hotness. For example,

around 1720, Fahrenheit suggested that the freezing point of water be given the number 32, and

the boiling point of water (under the normal pressure) be given the number 212. What could we

do for other levels of hotness? Mercury is a liquid for this hotness range and beyond, sufficient

for most purposes for everyday life. Mercury expands as it becomes hotter. We could define the change in the hotness to be proportional to the change in the volume of mercury.

What would we do for a high level of hotness when mercury is a vapor, or a low level of hotness when mercury is a solid? We could switch to materials other than mercury, or phenomena other than thermal expansion.

Relative scales of temperature. A scale of hotness set up by thermal contact is a relative one. While the rank order of hotness is independent of the phenomenon used to set up the scale, the numerical values of hotness do depend on the phenomenon. Once a scale of hotness is set up experimentally, any monotonically increasing function of the scale gives another scale of hotness. For example, in the Celsius scale, the freezing point of water is set to be 0C, and the boiling point of water 100C. We further require that the Celsius (C) be linear in the Fahrenheit (F) scale. These prescriptions give the transformation between C and F:

$$C = \frac{5}{9}(F - 32) \ .$$

In general, however, the transformation between two scales of hotness need not be linear. So long as the transformation is a monotonically increasing function, the transformation will preserve the rank order of hotness. We have yet attached any fundamental significance to the numerical values of hotness.

Classify the configurations of a composite by the partition of energy. To set up an absolute scale of hotness will require us to go deeper than our everyday experience. This we will do now. The exercise will also relate the everyday experience about hotness to the fundamental postulate.

When the two systems are in thermal contact, energy may go from one system to the other, but the composite of the two systems is an isolated system. Consequently, we may use the

partition of energy between the two systems to dissect the set of all states of the composite into a family of configurations. Of all possible ways to partition energy between the two systems, which one is most probable?

We call two systems A' and A''. When the two systems are separately isolated, A' has energy U' and the numbers of state $\Omega'(U')$, while A'' has energy U'' and the number of states $\Omega''(U'')$. The composite of the two systems has the number of states

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

To progress further, we assume that both systems are large so that energy transfer may be regarded as a continuous variable, and the functions $\Omega'(U')$ and $\Omega''(U'')$ are differentiable. Let a small amount of energy dU go from system A'' to A'. For system A', the energy changes to $U' + dU$, and the number of states changes to

$$\Omega'(U' + dU) = \Omega'(U') + \frac{\partial \Omega'}{\partial U'}dU.$$

We have retained the Taylor expansion up to the first power in dU. Similarly for system A'', the energy changes to $U'' - dU$, and the number of states changes to

$$\Omega''(U'' - dU) = \Omega''(U'') - \frac{\partial \Omega''}{\partial U''}dU.$$

Consequently, when a small amount of energy dU goes from system A'' to A', the number of states of the composite changes by

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

According to the fundamental postulate, a partition of energy is more probable if the partition consists of more states of the composite, so that the more probable direction of energy transfer will be such that

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

For energy to go from A'' to A', $dU > 0$. Consequently, it is more probable for energy to go from system A'' to A' than the other way around if

$$\Omega''\frac{\partial\Omega'}{\partial U'} > \Omega'\frac{\partial\Omega''}{\partial U''}\,.$$

When the two quantities are equal, energy is equally probable to go in either direction, and the two systems are said to be in *thermal equilibrium*.

Once we know the two functions for the systems, $\Omega'(U')$ and $\Omega''(U'')$, the above analysis determines the probable direction of energy flow when the two systems are brought into thermal contact, and the most probable partition of energy after the two systems are in thermal contact for a long time.

The absolute temperature. In the above inequality, either side involves quantities of both systems. We can modify the inequality into a form that either side only involves quantities of one system. Divide both sides of the inequality by $\Omega''\Omega'$, and recall a formula in calculus, $\partial\log x/\partial x = 1/x$. We find that it is more probable for energy to flow from system A'' to A' if

$$\frac{\partial\log\Omega'}{\partial U'} > \frac{\partial\log\Omega''}{\partial U''}\,.$$

For a system characterized by a function $\Omega(U)$, we define the temperature T of the system by

$$\frac{1}{T} = \frac{\partial\log\Omega}{\partial U}\,.$$

The temperature so defined is called the absolute temperature in that both the rank order and the numerical value are independent of any substances used in thermal contact. While the definition

of the absolute temperature relies on deeper insight into the fundamental nature of our world, the behavior of the absolute temperature does conform to everyday experience of hotness.

Experimental determination of the absolute temperature. We can calculate the absolute temperature of a system by counting the number of states of the system. For example, for an ideal gas, such a calculation gives

$$T = pV/N ,$$

where p is the pressure, V the pressure, and N the number of molecules. Such calculations can be carried out for a few systems, but is prohibitively expensive for most systems.

How does a doctor determine the temperature of her patient? Certainly not by counting the number of states of the 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.

(2) Use the simple system to calibrate a thermometer by thermal contact.

(3) Use the thermometer to measure temperatures of any other systems by thermal contact.

Steps (2) and (3) are sufficient to measure the relative temperature. It is Step (1) that links the experiments to the absolute temperature.

The units of temperature. The absolute temperature has the same dimension as energy. We will use the same unit for energy and temperature. An international convention, however, specifies the unit of energy by Joule (J), and the unit of temperature by Kelvin (K). The latter is so defined that the triple point of pure water is 273.16K exactly. The conversion factor between the two units is known as Boltzmann's constant, with experimental value $k \approx 1.38 \times 10^{-23} \, \text{J/K}$. Another useful unit for energy is $1 \, \text{eV} = 1.60 \times 10^{-19} \, \text{J}$, giving a conversion factor $1 \text{K} = 0.863 \times 10^{-4} \, \text{eV}$.

Any temperature scale is an increasing function of the absolute temperature *T*. The Celsius temperature scale, *C*, relates to *T* by $C = T - 273.15 \text{K}$ (in the Kelvin unit). The merit of use Celsius in everyday life is evident. It feels more pleasant to hear that today's temperature is 20C than 0.0253eV or 293K. Our melting-point hotness scale can be mapped to the Kelvin scale or the energy scale as follows:

Melting-point scale	Kelvin scale	Energy scale
Nitrogen	63.14 K	0.0054 eV
Water	273.15 K	0.0236 eV
Lead	600.65 K	0.0518 eV
Aluminum	933.60 K	0.0806 eV
Gold	1337.78 K	0.1155 eV

Experimental determination of heat. Although energy and temperature have the same dimension, their experimental measurements can be independent of each other. For example, we can pass an electric current through a metal wire immersed in a pot of water. The Joule heating of the metal wire adds energy to the water, and a measurement of the electrical power, *IV*, over some time tells us the amount energy added to the water. As another example, the energy absorbed by a mixture of ice and water is proportional to the volume of the ice melted. Consequently, once this proportionality constant is measured, e.g., by using the method of Joule

heating, we can subsequently measure energy gained or lost by a system by placing it in thermal contact with a mixture of ice and water. The volume of the ice remaining in the mixture can be used to determine the energy transferred to the system.

Heat capacitance and latent heat. Once again, we add energy to a system by thermal contact alone. Associated with a small change in the energy of the system, dU, the temperature of the system changes by dT. Define the heat capacitance of the system by

$$dU = CdT .$$

Because the temperature has the unit of energy, heat capacitance is dimensionless. If you'd like to use a different unit for temperature, so that kT has the unit of energy, to preserve the relation $dU = CdT$, heat capacitance is given in units of k.

When ice melts into water, energy is absorbed, but temperature does not change. The amount energy needed to complete such a transition is known as the latent heat of the transition. Thus, the experimental record of the function $U(T)$ may look like this:
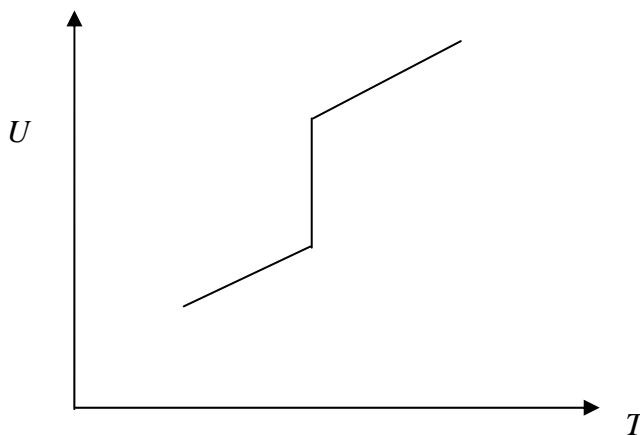
The slope defines the heat capacitance, and the jump defines the latent heat.

Experimental determination of the number of states. Once we know how to measure temperature and energy, we can determine the number of states Ω. We open the system in a single way by adding energy to the system, while blocking all other modes of

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

$$d \log \Omega = \frac{dU}{T}.$$

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 $T \to 0$.

Entropy of an isolated system. If you are tired of the phase "the logarithm of the number of states of an isolated system", you may as well join the crowd and replace the phrase by a cryptic word: entropy. You define the entropy S of an isolated system by

$$S = \log \Omega.$$

The entropy is dimensionless. When the Kelvin scale is adopted as a unit for temperature, to preserve the relation

$$dS = dU / T,$$

you can include the conversion factor k in the definition and write $S = k \log \Omega$. This practice will give the entropy an apparent unit J/K. Of course, this unit is as silly as a unit like inch/meter.

By change a phrase you should not trick yourself into believing that you have learned anything new. You simply paraphrase what you already know about "the logarithm of the number of states of an isolated system", $\log \Omega$. The following statements are banal, but may sound profound if you forget what entropy is.

- Entropy is well defined for an isolated system even when the system is not in equilibrium. Thus, entropy is a property of an isolated system.

- If the system is not isolated, but gains an infinitesimal amount of heat q through a quasi-static process, the entropy of the system changes by $\Delta S = q / T$.

- The entropy has the limiting property that, as $T \to 0$, all systems have the same entropy, which we set to be zero.

- Entropy is an additive quantity. For a composite of several weakly interacting systems, the entropy of the composite is the sum of the entropies of the individual systems.

- If we dissect the set of all the states of an isolated system into a family of configurations, A, B, C… each configuration will have its own number of states, $\Omega_A, \Omega_B, \Omega_C, ...$, and its own value of entropy, $S_A = \log \Omega_A, S_B = \log \Omega_B, S_C = \log \Omega_C, ...$

- The entropy of a configuration is independent of how the isolated system reaches this configuration.

- The probability for an isolated system in equilibrium to be in configuration A is proportional to $\exp(S_A)$. The system is more likely to be in a configuration if the configuration has a larger value of entropy.

The entropy of a substance. A substance is a collection of a large number of molecules (or atoms), stable and homogeneous at a macroscopic scale. For example, diamond is a crystalline lattice of carbon atoms, water is a liquid of H_2O molecules, and oxygen is a gas of O_2 molecules. The entropy of a substance can be determined experimentally, just like the entropy of any other system.

For a substance composed of only one kind of molecules, the entropy of a piece of the substance is proportional to the number of molecules in the piece, so that we may report the entropy per molecule of the substance. At the room temperature and atmospheric pressure, the entropy of diamond, lead and water are 0.3, lead 7.8 and 22.70, respectively. A strong substance, such as diamond, has a small value of entropy, because individual atoms are held together by strong chemical bonds, which limit the number of the accessible quantum states.

Complex substances generally have larger entropies than simple substances; for example, the entropies for O, O_2 and O_3 are 19.4, 24.7, 28.6, respectively.

When a substance melts, the substance transforms from a crystal to a liquid. Associated with this transformation, more quantum states become accessible to the substance, and the entropy typically increases by a number between 1 to 1.5.