TEMPERATURE

Circular statements. What is temperature? We are told in kindergartens that temperature is the quantity measured by a thermometer. The answer begs for another question. What is a thermometer? We are then told that a thermometer is an instrument that measures temperature. These answers merely link temperature and thermometer. But what is temperature? What is a thermometer?

Another type of circular statements is found in some textbooks of thermodynamics.

- 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 nether define heat nor define temperature. They are correct and useful statements: they link heat and temperature.

Temperature and heat are distinct quantities. We will show that 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*.

What can we do for temperature? We will consider an everyday experience—*thermal contact*. We reach the concept of temperature in two ways: first from empirical observations of thermal contact, and then from analyzing thermal contact by combining two great principles of nature: an isolated system conserves energy and maximizes entropy.

An essential step to be a master—rather than a slave—of thermodynamics is to get to know temperature. How does temperature come down as an abstraction from everyday experience of thermal contact? How does temperature rise up as a consequence of conserving energy and maximizing entropy?

Let me borrow the language of a better-known Bostonian. And so, my fellow enthusiasts of thermodynamics: ask not what temperature can do for you—ask what you can do for temperature.

CALORIMETRY

Experimental determination of heat without the concept of temperature. To avoid circular statements, we now review previous lectures, and formulate the concept of heat without invoking temperature. We will also describe a method to measure heat without measuring temperature. The art of measuring heat is known as *calorimetry*. The art has so many variations that it is out of place here to describe them in detail. But all methods of calorimetry build on the concepts of thermodynamic states, internal energy, work, and heat. Here we are only interested in a method of calorimetry that does not require the concept of temperature.

Thermodynamic states and properties. To fix the idea, let us consider a closed system: a fixed number of water molecules, enclosed in a cylinder-piston setup, receiving energy from the weights placed over the piston and from the fire outside the cylinder. The water molecules can be in a liquid, or a gas, or a liquid-gas mixture.

At any time, we can temporarily make the water into an isolated system. Our experience indicates that a system isolated for a long time will reach a state of thermodynamic equilibrium. Our experience further indicates that the fixed amount of water can be in many *thermodynamic states*, capable of two and only two independent variations. We represent the two independent variations using two *thermodynamic properties*.

Here we name each thermodynamic state of the closed system by values of two thermodynamic properties: the pressure P in water, and the volume V occupied by the water. The two properties serve as the coordinates of a plane. Each point (P,V) in the plane represents a thermodynamic state. Often we also name a thermodynamic state by a letter, such as A, and give the values of the two properties, (P_A,V_A).

Adiabatic work. Consider an *adiabatic system*. We seal the system to prevent matter from leaking. We insulate the system to prevent energy from leaking by heat. But we can transfer energy to the system by work, known as *adiabatic work*, written as $W_{\text{adiabatic}}$. The process of changing the adiabatic system is called an *adiabatic process*.

How do we know whether we have sealed and insulated the system well enough to make it adiabatic? We may change the system from one thermodynamic state A to another thermodynamic state B by doing work in various ways, such as pushing the piston, passing an electric current through a resistor immersed in the water, and rotating a paddle immersed in the water. If we obtain the same work for all processes between state A and state B, the sealing and insulation are good enough, and the system is adiabatic.

Experimental determination of internal energy as a function of state. The internal energy U of the closed system is a thermodynamic property—that is, the internal energy is a function of the two independent properties, $U(P,V)$. We measure this function by insulating the closed system into an adiabatic system. We then record a process of changing the system from state A to state B, and call the work done by the external force the adiabatic work $W_{\text{adiabatic}}$. State A corresponds to pressure and volume (P_A,V_A), and state B corresponds to pressure and volume $\left(P_B,V_B\right)$. When the system changes adiabatically from state A to state B, the change in internal energy is

$$U\left(P_B,V_B\right)-U\left(P_A,V_A\right)=W_{\text{adiabatic}}.$$

Internal energy is a relative property; we can set the internal energy of any one state to be zero, and measure the internal energy of any other states if we can connect the two states with an adiabatic process.

If we limit ourselves to doing work to the closed system by a quasi-equilibrium process, then from a given state we can only form a single adiabatic path. To reach a state off this path by adiabatic process, we must do work to the closed system by some other means, such as passing an electric current through a resistor placed in water. This way we can do work to the closed system, for example, while keeping the volume of the system fixed. This procedure allows us to determine the function $U\left(P,V\right)$.

Heat. Suppose that we have discovered all modes of doing work to a closed system. We now block all these modes of doing work. The boundary of the system is rigid, so that the system and the rest of world do not exchange energy by mechanical work. The boundary of the system shields electric field, so that the system and the rest of the world do not exchange energy by electrical work. Indeed, we construct the closed system such that the system and the rest of the world do not exchange energy by any kind of work.

Thus, the system and the rest of the world do not exchange matter and do not exchange energy by work. But our experience indicates that the system and the rest of the world can still exchange energy. For example, we can change the thermodynamic state of the water by fire. We call such a system a *thermal system*, and call this mode of workless exchange of energy *heat*.

Experimental determination of heat. We now allow a closed system to exchange energy with the rest of the world by both work and heat. For this closed system, we have determined the function $U\left(P,V\right)$. We change the closed system via an arbitrary process, either a quasi-equilibrium or a non-equilibrium process, from one state of equilibrium to another. We identify the two thermodynamic states by recording the properties at the two states, $\left(P_A,V_A\right)$ and $\left(P_B,V_B\right)$. We record the work associated with the process, W. In general, $U\left(P_B,V_B\right)-U\left(P_A,V_A\right)\neq W$. The difference defines heat Q associated with the process:

$$U\left(P_B,V_B\right)-U\left(P_A,V_A\right)=W+Q.$$

We have just prescribed a method of calorimetry that measures heat for any process, either a quasi-equilibrium or a non-equilibrium process, without the concept of temperature.

A classification of systems. We classify systems according to how they interact with the rest of the world. Different authors may classify systems differently, and may name them differently. It is good to spell out the modes of interaction for each type of systems.

	exchange matter	exchange energy by work	exchange energy by heat
isolated system	no	no	no
adiabatic system	no	yes	no
thermal system	no	no	yes
closed system	no	yes	yes
open system	yes	yes	yes

EMPIRICAL OBSERVATIONS OF THERMAL CONTACT

Thermal contact. When we need an adjective to denote that a phenomenon concerns heat, we call it a *thermal* phenomenon. For example, on absorbing energy, a given quantity of material often increases its volume—a phenomenon known as thermal expansion.

When two systems exchange energy by heat, we say that they are in *thermal contact*. Often we idealize thermal contact as follows:

- The two systems together form an isolated system.
- The two systems interact in one mode: exchanging energy by heat only.

We make the transfer of energy by heat the only mode of interaction between the two systems. We block all other modes of interaction between them. The two systems do not exchange molecules, and do not exchange energy by work. That is, each of the two systems is a thermal system. The composite of the two systems as a whole is an isolated system.

Two systems can be in thermal contact without touching each other; for example, energy can transfer from one system to the other by electromagnetic radiation.

Experience of hotness. Temperature is synonymous to *hotness*. A value of temperature means a *place of hotness*. In this section of the notes, we will use the word “hotness” and the phrase “places of hotness”, so that we can focus on our own experience, without the interference of kindergarten teachers and international committees.

Our feeling of hotness comes from everyday experience. We use the adjectives hot, warm, cool and cold to indicate places of hotness. But the four words are insufficient to indicate all places of hotness. Everyday experience tells us that many places of hotness exist, and that all places of hotness map to a real variable.

Why is hotness so different from happiness? Most our feelings however, do not map to real variables. Think of happiness, love, and anxiety. It is remarkable that this particular type of feeling—hotness—does map to a real variable. What makes hotness so different from happiness? This question is hard to answer because we do not know happiness in the same way as we know hotness. What do we know about hotness?

We now form the concept of hotness from empirical observations of thermal contact. We will first describe these experimental phenomena without asking why they occur. These observations are milestones in a long march toward a profound discovery of humankind: we can name all places of hotness by a real variable.

Hotness is a child of entropy and energy. In the later part of the notes we will understand these observations in terms of two great principles of nature: an isolated system conserves energy and maximizes entropy. We describe another profound discovery of humankind: hotness is not an orphan; rather, hotness is a child of entropy and energy.

Places of Hotness

Observation 1: Two systems in thermal contact for a long time will stop transferring energy. The two systems are said to have reached *thermal equilibrium*.

For example, a glass of wine has been kept in a refrigerator for a long time and is then isolated, and a piece of cheese is kept in a room for a long time and is then isolated. When the glass of wine and the piece of cheese come into thermal contact, the vibration of the molecules in the wine will interact with the vibration of the molecules in the cheese, through the vibration of the molecules in the glass. After some time, energy re-allocates between the wine and the cheese, and stops transferring.

As another example, consider a tank of water, which we regard as an isolated system of many parts. Even when the system is isolated from the rest of the world, energy may flow from one part of the tank to another. But after some time, this transfer of energy will cease, and the isolated system is said to reach thermal equilibrium.

Observation 2: If two systems are separately in thermal equilibrium with a third system, the two systems are in thermal equilibrium with each other. This observation is known as *the zeroth law of thermodynamics*.

Places of hotness. Consider many isolated systems. Individually they have all reached thermal equilibrium—that is, within each isolated system, energy has stopped transferring from one part to another.

We discover places of hotness by experiments. We bring two systems into thermal contact, and check if they exchange energy by heat. If the two systems in thermal contact do not exchange energy by heat, we say that they are at the same place of hotness. If the two systems in thermal contact exchange energy by heat, we say that they are at different places of hotness.

Observation 3: For a fixed amount of a pure substance, once the pressure and volume are fixed, the hotness is fixed. This fact can be checked by the experiment of thermal contact. This empirical fact is familiar to us, but is unimportant to our effort to establish the concept of hotness. Nevertheless we have used this observation to illustrate a method of calorimetry above.

Observation 4: For a pure substance in a state of coexistent solid and liquid, the hotness remains fixed as the proportion of solid and liquid changes. This fixed place of hotness is specific to the substance, and is known as the *melting point* or *freezing point* of the substance. This empirical fact is also familiar to us, but is also unimportant to our effort to establish the concept of hotness. Nevertheless, we will use this empirical fact in some illustrations.

The hotness where ice and liquid water coexist has acquired many names: melting point of ice, freezing point of water, 0 C, 32 F, 273.15 K, etc. We will explain how various naming schemes work shortly.

So far we have talked about the melting point of ice as if it were a unique place of hotness. Upon further experiment of thermal contact, we discover that the melting point of a pure substance changes with variables such as pressure, electric field and magnetic field. These changes are typically small, and for the time being we neglect them.

Name places of hotness any way you like. Everyday experience indicates that many places of hotness exist. To talk about them individually, we need to give each place of hotness a name. Places of hotness are real: they exist in the experiment of thermal contact. How to name the places of hotness is our choice. The names exist between our lips, and in our ears and books. All naming schemes are arbitrary decisions of human beings (or committees), but some naming schemes are more convenient than others.

The situation is analogous to naming streets in a city. The streets are real: they exist regardless how we name them. We can name the streets by using names of presidents, or names of universities. We can use numbers. We can be inconsistent, naming streets in one part of the city by numbers, and those in another part of the city by names of presidents. We can even give the same street several names, using English, Chinese, and Spanish.

Name places of hotness after physical events. Let us consider one specific naming scheme. For a pure substance, its solid phase and liquid phase coexist at a place of hotness, known as the melting point of the substance. We can name this place of hotness after the substance.

Thus, a system is said to be at the place of hotness named "WATER" when the system is in thermal equilibrium with a mixture of ice and water at the melting point. Here are four distinct places of hotness: WATER, LEAD, ALUMINUM, GOLD. We can similarly name other places of hotness by using a large number of pure substances.

How does the above naming scheme differ from words used in everyday life, such as cold, cool, warm, and hot? When we say a system is at the place of hotness WATER, we mean a specific experimental observation: the system is in thermal equilibrium with an ice-water mixture. By contrast, when we use the word cold, we may not have a specific place of hotness in mind. Adjectives carry little weight in science and engineering. We need nouns, verbs and numbers.

Measurement of Hotness

Thermometry. Thermometry is the art of measuring hotness. The art has become sophisticated, but its foundation remains simple: thermometry relies on thermal equilibrium. By "measuring the hotness of system X" we mean matching system X in thermal equilibrium with a system of a known place of hotness.

We first build a library of known places of hotness. For example, we find a large number of pure substances, and use their melting points to locate various places of hotness. Name the places of hotness in the library as $\{A, B, C, ...\}$.

We then use the library to measure the hotness of system X. We bring system X in thermal contact with a system at hotness A, and observe if the two systems exchange energy by heat. If they do not exchange energy by heat, we have just measured the hotness of system X—it is at hotness A. If they do exchange energy by heat, we know system X is at a place of hotness different from A. We then bring system X in thermal contact with a system at hotness B. We repeat this procedure until we match system X in thermal equilibrium with a system of a place of hotness in the library.

What if we cannot match system X with any place of hotness in the library? We have just discovered a new place of hotness! We are the Columbus in the new world of hotness. We add this new place of hotness to the library, and name the place X.

Thermometry and calorimetry. To practice this art, we need to find a way to detect the exchange of energy by heat. We also need to ensure that, in each thermal contact, system X exchanges only negligible amount of energy with a system in the library, so that the procedure of measurement negligibly alters system X.

Incidentally, “detecting the exchange of energy” does not require us to measure the quantity of heat. For instance, in using a column of mercury as a thermometer, the exchange of energy is detected by the rise and fall of the column. In principle, thermometry (the art of measuring hotness) is independent of calorimetry (the art of measuring heat). In practice, however, the two types of measurement may mingle somewhat. Calorimetry determine both the direction and the quantity of heat. Thermometry only needs direction of heat.

Thermometer. A thermometer is an instrument that maps places of hotness to an observed variable. A set of pure substances, for example, serves as a thermometer. The melting point of each pure substance locates a place of hotness.

A material also serves as a thermometer. When energy is added to the material by heat, the material expands. The thermal expansion of the material acts as a *one-to-one function*. The domain of the function consists of various places of hotness. The range of the function consists of various volumes of the material. The function maps places of hotness to the volumes of the material.

Places of hotness are real, and have nothing to do with how humans measure them. Hotness is independent of the choice of thermometers. We can use one thermometer to *calibrate* any other thermometer. Let us calibrate a thermal-expansion thermometer using a melting-point thermometer. For example, the thermal-expansion thermometer is made of mercury. On the melting-point thermometer, we mark WATER is the place of hotness at which ice and water coexist. We bring a mixture of ice and water into thermal contact with the thermal-expansion thermometer. When the two systems are in thermal equilibrium, the thermal-expansion thermometer also reaches hotness WATER. We record that hotness WATER corresponds to the volume of the material.

Temperature affects everything, and everything is a thermometer. An electrical conductor serves as yet another thermometer. When energy is added to the electrical conductor, its electrical resistance changes. Thus, the electrical conductor maps places of hotness to values of electrical resistance. Other commonly used thermometers include bimetallic thermometers, pyrometers, and thermocouples.

Exercise. Describe practical considerations in constructing a thermometer using mercury.

Exercise. Describe practical advantages of a thermometer based on electrical resistance over a thermometer based on thermal expansion.

Scale of Hotness

Observation 5: When a system of hotness A and a system of hotness B are brought into thermal contact, if energy goes from the system of hotness B to the system of hotness A, energy will not go in

the opposite direction. This observation is a version of *the second law of thermodynamics*, known as the Clausius statement.

When the two systems of different places of hotness are in thermal contact, the flow of energy is *unidirectional* and *irreversible*. This observation does not violate the principle of the conservation of energy, but is not implied by the principle of the conservation of energy. Energy going either direction would be conserved.

When two systems at different places of hotness are brought into thermal contact, energy transfers by heat from the system at a high place of hotness to the system at a low place of hotness. That is, *in thermal contact, a difference in hotness gives heat a direction.*

Places of hotness are ordered. This observation allows us to order any two places of hotness. When two systems are brought into thermal contact, the system gaining energy is said to be at a lower place of hotness than the system losing energy.

For example, we say that hotness "LEAD" is lower than hotness "ALUMINUM" because, upon bringing melting lead and melting aluminum into thermal contact, we observe that the amount of solid lead decreases, whereas the amount solid aluminum increases.

In thermodynamics, the word "hot" is used strictly within the context of thermal contact. It makes no thermodynamic sense to say that one movie is hotter than the other, because the two movies cannot exchange energy.

Observation 6: If hotness A is lower than hotness B, and hotness B is lower than hotness C, then hotness A is lower than hotness C.

This observation generalizes the zeroth law of thermodynamics. By making thermal contact, we can order any library of places of hotness one after another. For example, experiments of thermal contact tell us the order of four places of hotness: WATER, LEAD, ALUMINUM, GOLD. We can order more places of hotness by using melting points of many pure substances. We call an ordered library of places of hotness a *scale of hotness*.

Exercise. Learn about a scale of earthquake, a scale of hurricane, a scale of happiness, and a scale of danger of terrorist attack. Compare these scales to a scale of hotness.

Numerical Scale of Hotness

Observation 7: Between any two places of hotness there exists another place of hotness. The experimental demonstration goes like this. We have two systems at hotness A and B, respectively, where hotness A is lower than hotness B. We can always find another system, which loses energy when in thermal contact with A, but gains energy when in thermal contact with B. This observation indicates that places of hotness are continuous.

Name all places of hotness by a real variable. All places of hotness are ordered, so that we can name them by using a set of numbers. Places of hotness are continuous, so that we cannot name them by using a set of integers, but we can name them by using a real variable. A map from places of hotness to a real variable is called a *numerical scale of hotness*.

Around 1720, Fahrenheit assigned the number 32 to the melting point of water, and the number 212 to the boiling point of water. What would he do for other places of hotness? Mercury is a liquid within this range of hotness and beyond, sufficient for most purposes for everyday life. When energy is added to mercury by heat, mercury expands. The various volumes of a given quantity of mercury could be used to name the places of hotness.

What would Fahrenheit do for a high place of hotness when mercury is a vapor, or a low place of hotness when mercury is a solid? He could switch to materials other than mercury; for example, he could use a flask of gas. He could also use phenomena other than thermal expansion, such as a change in electrical resistance of a metal due to heat.

Long march toward mapping hotness to a real variable. By now we have completed this long march. In the beginning of this long march, we have invoked the analogy of naming streets in a city. Now note two differences between naming streets and naming places of hotness. First, we do not have a useful way to name all streets by an ordered array. In what sense one street is higher than the other? Second, we do not need a real variable to name all the streets. A city has a finite number of streets.

By contrast, observations 6 and 7 enable us to name all places of hotness by a single, continuous variable. Most textbooks state that the zeroth law (observation 2) establishes the concept of hotness. This statement is wrong. Zeroth law does not enable us to name all places of hotness by a single, continuous variable.

Map one numerical scale of hotness to another. Once a numerical scale of hotness is set up, any monotonically increasing function maps this scale to 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) scale be linear in the Fahrenheit (F) scale. These prescriptions give a map from one scale of hotness to the other:

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

In general, the map from one numerical scale of hotness to another need not be linear. Any increasing function will preserve the order of the places of hotness. Any smooth function will preserve the continuity of the places of hotness.

Exercise. Learn about the Rankine scale of temperature. How does the Rankine scale map to the Fahrenheit scale?

Exercise. How do you calibrate a thermometer based on thermal expansion using a thermometer based on electrical resistance? Will the volume of the material in the thermal-expansion thermometer be linear in the electrical resistance of the resistive thermometer?

Non-numerical vs. numerical scales of hotness. As illustrated by the melting-point scale of hotness, a non-numerical scale of hotness perfectly captures all we care about hotness. By contrast, naming places of hotness by using numbers makes it easier to memorize that hotness 80 is hotter than hotness 60. Our preference to a numerical scale reveals more the nature of our brains than the nature of hotness.

Numerical values of hotness do not obey arithmetic rules. Using numbers to name places of hotness does not authorize us to apply arithmetic rules: adding two places of hotness has no empirical significance. It is as meaningless as adding the addresses of two houses on a street. House number 2 and house number 7 do not add up to become house number 9. Also, raising the temperature from 0C to 50C is a different process from raising temperature from 50C to 100C. For instance, for a given amount of water, raising the temperature from 0C to 50C takes different amount of energy from raising temperature from 50C to 100C.

Ideal-Gas Scale of Hotness

Observation 8: All places of hotness are hotter than a certain place of hotness, which can be approached, but not attained. So far as we know, all places of hotness hotter than this certain place can be attained. That is, there is a lower limit to the places of hotness, but no upper limit to the places of hotness.

Following this observation, we can name the lowest place of hotness *zero*, and name all other places of hotness by positive real numbers. Such a scale of hotness is called an *absolute scale*.

Under rare conditions, negative absolute temperature can be achieved. In this course we will not treat such conditions.

Observation 9: Thin gases obey the law of ideal gases. A flask contains a gas—a collection of flying molecules. Let P be the pressure, V the volume, and N the number of molecules. The gas is thin when V/N is large compared to the volume of an individual molecule.

Experiments indicate that, when two flasks of thin gases are brought into thermal contact, thermal equilibrium is attained when the two flasks of gases attain an equal value of PV/N. This observation holds regardless the identity of the gases, and is known as the *law of ideal gases*.

The law of ideal gas played significant role in the history of thermodynamics, but it is logically unimportant in establishing the concept of hotness.

Ideal-gas scale of temperature. According to the experimental observation, the values of PV/N define a scale of hotness, known as the ideal-gas scale of temperature. Denote this scale of temperature by τ, so that

$$PV/N = \tau .$$

This scale relates temperature to measurable quantities P, V and N.

The ideal-gas scale of temperature is an absolute scale of temperature. In the limit of an extremely thin gas, $PV/N \to 0$, this scale of temperature gives $\tau \to 0$. Because N is a pure number, and PV has the unit of energy, this scale of temperature has the same unit as energy.

Observation 10: For a pure substance, its solid phase, liquid phase and gaseous phase coexist at a specific hotness and a specific pressure. This point of coexistence of three phases of a pure substance is known as *triple point*. This empirical fact is familiar to us, but is unimportant in establishing the concept of hotness.

This observation is incidental in the development of the notion of temperature. Nonetheless an international committee has decided to use the triple point of pure water to set a scale of temperature.

Kelvin scale of temperature. An international convention specifies the unit of temperature by Kelvin (K). The Kelvin scale of temperature is defined as follows:

1. The Kelvin scale of temperature, T, is proportional to the ideal-gas scale of temperature, PV/N.
2. The unit of the Kelvin scale, K, is defined by marking the triple point of pure water as $T = 273.16\text{K}$ exactly.

Thus, we write

$$PV/N = kT .$$

Here k is the factor that converts the two units of temperature, $\tau = kT$. The factor k is known as the Boltzmann constant.

In the literature, the symbol T may denote temperature in both units. This practice is the same as using L to denote length, regardless whether the unit of length is meter or inch.

The conversion factor between the two units of temperature can be determined experimentally. For example, you can bring pure water in the state of triple point into thermal contact with a flask of an ideal gas. When they reach thermal equilibrium, a measurement of the pressure, volume and the number of molecules in the flask gives a reading of the temperature of the triple point of water in the unit of energy. Such experiments or more elaborate ones give the conversion factor between the two units of temperature:

$$k \approx 1.38 \times 10^{-23}\,\mathrm{J/K}\,.$$

Thus, the two units of energy convert as

$$1\mathrm{K} \approx 1.38 \times 10^{-23}\,\mathrm{J}\,.$$

It is hard to have much warm feeling for a numerical scale of temperature that just makes the triple point of water have an ugly reading. Boltzmann's constant k has no fundamental significance. For *any* result to have physical meaning, the product kT must appear together.

Often people call kT thermal energy. This designation is correct only for a few idealized systems, and is in general incorrect. There is no need to give any other interpretation: kT is simply temperature in the unit of energy.

Modern Celsius scale. Any scale of temperature can be mapped to any other scale of temperature. For example, the Celsius scale C relates to the Kelvin scale T by

$$C = T - 273.15\mathrm{K} \quad (T \text{ in the unit of Kelvin}).$$

This modern definition of the Celsius scale differs from the historical definition. Specifically, the melting point and the boiling point of water are not used to define the modern Celsius scale. Rather, these two places of hotness are determined by experimental measurements. The experimental values are as follows: water melts at $0^\circ\mathrm{C}$ and boils at $99.975^\circ\mathrm{C}$, according to the International Temperature Scale of 1990 (ITS-90).

The merit of using Celsius in everyday life is evident. It feels more pleasant to hear that today's temperature is 20C than 0.0253eV or 293K. It would be mouthful to say today's temperature is $404.34 \times 10^{-23}\,\mathrm{J}$. The hell would sound less hellish if we were told it burns at the temperature GOLD. Nevertheless, our melting-point scale of hotness can be mapped to the absolute temperature scale in either the Kelvin unit or the energy unit:

Melting-point scale	Kelvin scale	Ideal-gas scale
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

Exercise. What excuses the international committee might offer to assign the particular number to the triple point of water? If we accept this decision of the committee about the triple point of water, will the melting point of water be exactly zero degree Celsius? Will the boiling point of water be exactly hundred degree Celsius.

Exercise. The radius of the Earth is $6.4\times10^{6}\mathrm{m}$, and the mean atmospheric pressure at the surface of the Earth is $10^{5}\mathrm{Pa}$. What is the total mass of the atmosphere?

Exercise. The atmosphere is composed of a large number of molecules, mostly molecular nitrogen (78%), molecular oxygen (21%), and argon (0.093%). Other species of molecules make up the remainder of the atmosphere. The concentration of carbon dioxide has increased from 280 parts per million in preindustrial times to 365 parts per million today. Estimate the increase in the mass of carbon dioxide in the atmosphere.

Exercise. Calculate the number of oxygen molecules per unit volume in the atmosphere on the surface of the Earth. Assume that the atmospheric pressure is $10^{5}\mathrm{Pa}$ and the temperature is 20 degree Celsius.

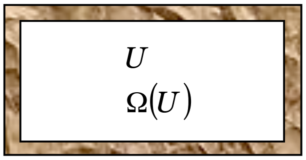
Exercise. You surround a piston-cylinder setup with a mixture of ice and water. The cylinder contains a gas. You move the piston slowly, do 1000-Joule work, and reduce the volume of the gas by a factor of ten. How many gas molecules are in the cylinder?

THEORY OF THERMAL CONTACT

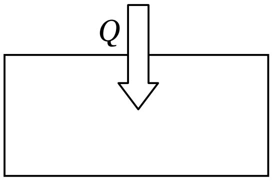
We now link the above empirical observations of thermal contact to two great principles of nature: an isolated system conserves energy and maximizes entropy.

System of Variable Energy

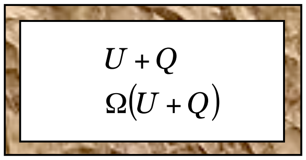
Consider a system interacting with the rest of the world in a single mode: exchanging energy by heat. We block all other modes of interaction between the system and the rest of the world. They do not exchange matter, and they do not exchange energy by work.



Isolate the system at energy U



Transfer energy to the system by a quantity of heat Q



Isolate the system at energy $U+Q$

When a quantity of heat Q transfers from the rest of the world to the system, according to the principle of the conservation of energy, the energy of the system increases from U to $U + Q$. Thus, the change in the energy of the system can be measured by the quantity of heat transferred to the system. The art of measuring the quantity of heat is known as calorimetry.

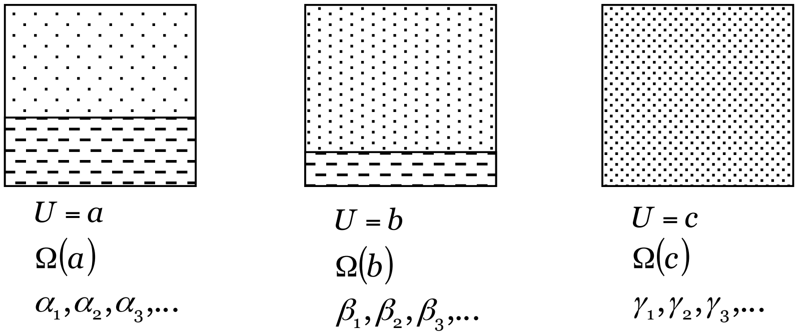
A system of variable energy is not an isolated system. However, when the energy of the system is fixed at any particular value U, the system is an isolated system. After being isolated for a long time, the system flips among a set of quantum states with equal probability. Denote the number of quantum states by Ω. Consequently, the system of variable energy is 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 system of variable energy is a thermodynamic system of a single independent variable—energy.

Hydrogen atom. A hydrogen atom changes its energy by absorbing photons. When isolated at a particular level of energy, the hydrogen atom has a set of quantum states. Each quantum state is characterized by a distinct electron cloud and spin.

The hydrogen atom is a system of variable energy, characterized by the function

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

The domain of the function $\Omega(U)$ is a set of discrete levels of energy: $-13.6\text{eV}, 3.39\text{eV}, 15.1\text{eV}, \ldots$ The range of the function is a set of integers: 2, 8, 18,.... For the hydrogen atom, the levels of energy have large gaps.

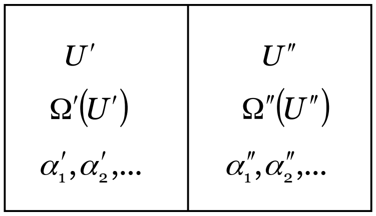


A bottle of water molecules. For a complex system like a bottle of water molecules, the levels of energy are so closely spaced that we regard the energy of the system as a continuous real variable. We can certainly heat up the bottle of water molecules, and make it a system of variable energy. The figure illustrates the system at three values of energy. When isolated at energy $U = a$, the system contains a mixture of liquid and vapor, and flips amount a total number of $\Omega(a)$ quantum states, labeled as $\alpha_1,\alpha_2,\alpha_3,\ldots$ When isolated at a higher energy, $U=b$, more liquid transforms into the vapor, and the system flips amount a total number of $\Omega(b)$ quantum states, labeled as $\beta_1,\beta_2,\beta_3,\ldots$ When isolated with at an even higher energy, $U=c$, the bottle contains vapor only, and the system flips amount a total number of $\Omega(c)$ quantum states, labeled as $\gamma_1,\gamma_2,\gamma_3,\ldots$

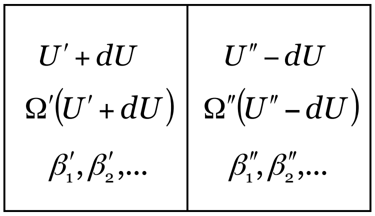
Thermal Contact Analyzed Using Basic Algorithm

Basic algorithm of thermodynamics. Recall the basic algorithm of thermodynamics in general terms:

1. Construct an isolated system with an internal variable, x.
2. Use the internal variable to dissect the whole set of the quantum states of the isolated system into subsets. Call each subset a configuration of the isolated system. When the internal variable takes value x, the isolated system flips among a subset of its quantum states. Obtain the number of the quantum states in this subset, $\Omega(x)$.
3. Maximize the function $\Omega(x)$ to determine the (most probable) value of the internal variable x after the constraint is lifted for a long time.



partition A



partition B

Thermal contact and the conservation of energy. When a glass of wine and a piece of cheese are in thermal contact—that is, the wine and the cheese interact in one mode: exchanging energy by heat. We make the composite of the wine and cheese an isolated system.

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, the composite has a fixed amount of total energy, which is designated as U_{total}. 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—that is, the flow of energy is unidirectional and irreversible. Furthermore, after some time, the flow of energy stops, and the wine and the cheese are said to have reached thermal equilibrium. In the state of equilibrium, the wine and the cheese partition the total energy into two definite amounts.

Isolated system with an internal variable. We have just constructed an isolated system of an internal variable. The isolated system is the composite of the two systems of variable energy. The internal variable is the partition of energy between the systems. To determine the partition of energy, we now analyze this isolated system using the basic algorithm of thermodynamics.

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

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

This is the number of quantum states in the subset of the quantum states of the composite. This subset corresponds to partition A, where energy is partitioned as U' and U'' between the wine and the cheese. 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 $\{\beta'_1, \beta'_2, ...,\}$. Isolated at energy $U' + dU$, the cheese has a total of $\Omega''(U'' - dU)$ number of quantum states, labeled as $\{\beta''_1, \beta''_2, ...,\}$. A quantum state of the composite can be any combination of a quantum state chosen from the set $\{\beta'_1, \beta'_2, ...,\}$ and a quantum state chosen from the $\{\beta''_1, \beta''_2, ...,\}$. The total number of all such combinations is

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

This is the number of quantum states in another subset of the quantum states of the composite. This subset corresponds to partition B, where energy partitioned as $U'+dU$ and $U''-dU$ between the wine and the cheese.

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 $\Omega'(U')$ and $\Omega''(U'')$ are differentiable. Consequently, the numbers of quantum states in the two partitions differ

$$\Omega'(U'+dU)\Omega''(U''-dU)-\Omega'(U')\Omega''(U'')$$
$$=\left[\frac{d\Omega'(U')}{dU'}\Omega''(U'')-\Omega'(U')\frac{d\Omega''(U'')}{dU''}\right]dU$$

We have retained only the terms up to the leading order in dU.

Thermodynamic inequality. The partition of energy is the 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—correspond to two subsets of quantum states of the composite. For partition B to happen *after* partition A in time, partition B must have is no less quantum states than partition A:

$$\left[\frac{d\Omega'(U')}{dU'}\Omega''(U'')-\Omega'(U')\frac{d\Omega''(U'')}{dU''}\right]dU\geq 0.$$

The fundamental postulate gives a direction of time, but not duration of time.

Divide the inequality by a positive number, $\Omega'(U')\Omega''(U'')$, and recall a formula in calculus,

$$\frac{d\log\Omega(U)}{dU}=\frac{1}{\Omega}\frac{d\Omega(U)}{dU}.$$

Re-write the above expression as

$$\left[\frac{d\log\Omega'(U')}{dU'}-\frac{d\log\Omega''(U'')}{dU''}\right]dU\geq 0.$$

This expression contains an inequality and an equation. We examine them in turn.

Thermal equilibrium. The equation is the condition of thermal equilibrium. Energy is equally probable to flow in either direction if

$$\frac{d\log\Omega'(U')}{dU'}=\frac{d\log\Omega''(U'')}{dU''}.$$

This condition of equilibrium, along with the conservation of energy $U' + U'' = U_{\text{total}}$ determines the partition of energy between the two systems in thermal equilibrium.

Irreversibility and direction of heat. The inequality dictates the direction of heat. Given the two thermal systems, the two functions $\Omega'(U')$ and $\Omega''(U'')$ are fixed. For a given partition of energy between the two systems, U' and U'', we can calculate the two numbers, $d\log\Omega'(U')/dU'$ and $d\log\Omega''(U'')/dU''$. We then compare the two numbers.

If $d\log\Omega'(U')/dU' > d\log\Omega''(U'')/dU''$, energy flows from the cheese to the wine, $dU > 0$.

If $d\log\Omega'(U')/dU' < d\log\Omega''(U'')/dU''$, energy flows from the wine to the cheese, $dU < 0$.

Thermodynamic Scale of Temperature

Thermodynamic scale of temperature. Given a system of variable energy, the function $\Omega(U)$ is specific to the system, so is the derivative $d\log\Omega(U)/dU$. The previous paragraph shows that the value $d\log\Omega(U)/dU$ is the same for all systems in thermal equilibrium, and therefore defines a scale of temperature. We will use a particular scale of temperature T set up by

$$\frac{1}{T} = \frac{d\log\Omega(U)}{dU}.$$

This scale of temperature is called the thermodynamic temperature. 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. In particular, the theory of thermal contact has named all places of hotness by a single, positive, continuous variable.

The function $\Omega(U)$ is 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.

But wait minute! Any monotonically decreasing function of $d\log\Omega(U)/dU$ will also serve as a scale of temperature. What is so special about the choice made above?

Thermodynamic scale of temperature coincides with the ideal-gas scale of temperature. Recall 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 scale of temperature set up by the law of ideal gases is the same as that set by $T^{-1} = d\log\Omega(U)/dU$. In a later lecture, we will derive the law of ideal gases theoretically and show that, indeed, the two scales of temperature are the same.

Experimental determination of thermodynamic scale of temperature. 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. Instead, she uses a thermometer. Let us say that she brings 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 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 thermodynamic scale of temperature follows these basic steps:

(1) For a simple system, formulate a theory that relates the thermodynamic scale of temperature to 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 thermodynamic 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 quantum state, and only for a very few idealized systems, such as an ideal gas.

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 contribute 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, or the Internet has become widely accessible). The new economic change will enable us to devise a new division of labor.

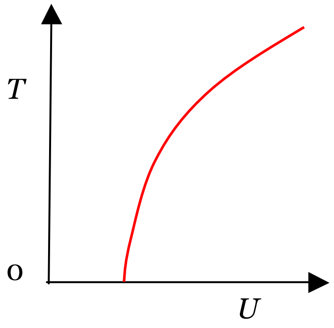
Range of temperatures. Usually we only measure temperature within some interval. Extremely low temperatures are studied in a science known as cryogenics. Extremely high temperatures are realized in stars, and other special conditions.

Energy-Temperature Curve

A system of variable energy. Consider a system of a single independent variable, the energy. The system and the rest of the world interact in a single mode: exchanging energy by heat. We block all other modes of interaction, so that the system and the rest of the world do not exchange matter, and do not exchange energy by work.

We add energy to the system by heat. We measure the change in energy U by calorimetry, and measure temperature T by thermometry. We add energy slowly: at each increment of energy, we wait until the system regains thermal equilibrium and reaches a uniform temperature. We then measure the temperature of the system.

The experimental data are plotted as the energy-temperature 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 energy-temperature curve represents the thermal system.



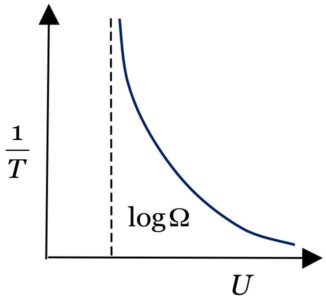
Experimental determination of the number of quantum states. When a small amount of energy dU is added to the system, the number of quantum states of the system changes according to

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

Once we have measured the function $T(U)$, this expression determines the function $\Omega(U)$ up to a multiplicative factor.

To fix the multiplication factor, we set $\Omega = 1$ as $T \to 0$. 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 $\log\Omega$.



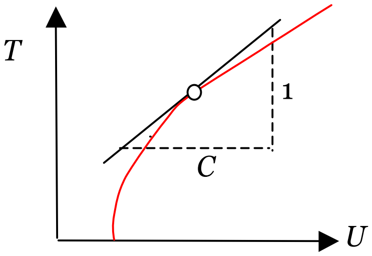
Often, the measurement only extends to a temperature much above absolute zero. Assume that the measurement gives the energy-temperature curve in the interval between U_0 and U. Upon integrating, we obtain that

$$\log\Omega(U) - \log\Omega(U_0) = \int_{U_0}^{U} \frac{dU}{T(U)}$$

The constant $\Omega(U_0)$ is undetermined.

Heat capacity. A system is in thermal contact with the rest of world, and 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, $C(U)$.

Entropy

The Clausius-Gibbs equation. Recall that we have abbreviated the phrase "logarithm of the number of quantum states" by a single word "entropy". The fundamental postulate gives us one property—entropy S, the principle of the conservation of energy gives us another property—internal energy U. A system of variable energy is characterized by a function, $S(U)$.

The combination of the two great principles gives us a third property—temperature T. The three properties obey a relation:

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

This relation defines thermodynamic scale of temperature. The relation shows that temperature is a child of entropy and energy. We will call this relation the Clausius-Gibbs equation.

Let us relate the Clausius-Gibbs equation back to an experimental setup. Consider a family of isolated systems of a single independent variable, the internal energy *U*. For example, the system can be a half bottle of wine—that is, a mixture of liquid and vapor, consisting of many species of molecules. Each member in the family is a system isolated at a particular value of the internal energy *U*. Each system has been isolated for a long time, has reached a state of thermodynamic equilibrium, and has the entropy *S*. We characterize this family of isolated system by a function $S(U)$.

For an isolated system in a state of thermodynamic equilibrium of internal energy *U*, the entropy relates to the internal energy by the function $S(U)$, and the temperature is given by the Clausius-Gibbs equation $T = \left[dS(U)/dU\right]^{-1}$.

Adding energy to a system. We can write the Clausius-Gibbs equation in another way

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

Start with a system in the family, a system isolated at energy *U*. We next transfer to the system a small amount of energy *dU*. How we transfer this amount of energy does not matter. We can place the system in an oven, or pass an electric current through a resistor immersed in the system, or rotate a paddle immersed in the system. What matters are that we do transfer a certain amount of energy *dU*, and that we do not add matter to the system and do not change the volume of the system.

Right after the transfer of energy, the system is not in a state of thermodynamic equilibrium. The liquid might be turbulent, and molecules might jump from the liquid to the vapor (evaporation). The system out of equilibrium does not belong to the family of isolated systems, and is not described by the function $S(U)$.

We then isolate the system at energy $U + dU$. Isolated for a long time, the system reaches a new state of thermodynamic equilibrium, and has entropy $S(U + dU)$. The Clausius-Gibbs equation says that

$$S(U + dU) - S(U) = \frac{dU}{T(U)}.$$

Thus, the Clausius-Gibbs equation applies to a family of isolated systems. We can change one member in the family to another member in the family by adding energy. But each member in the family has been isolated for a long time and has reached a state of thermodynamic equilibrium. The Clausius-Gibbs equation relates the change in entropy, $dS = S(U + dU) - S(U)$, to the change in internal energy, dU, through the temperature $T(U)$.

Needless complication. In describing the Clausius-Gibbs equation, textbooks of thermodynamics often restrict the change in internal energy dU to heat added to the system through a quasi-equilibrium (i.e., reversible) process. That's a lot of nebulous words for a simple idea: the Clausius-Gibbs equation applies to a family of isolated systems, and each member system has been isolated for a long time to reach a state of thermodynamic energy.

In changing from one member system to another, how we add energy does not matter, so long as we isolate the two systems for a long time and let each reach a state of thermodynamic equilibrium. We can add energy either reversibly (i.e., slowly), or irreversibly (i.e., violently). We can add energy either by heat (i.e., placing the system in an oven), or by work (i.e., by passing electric current through a resistor).

Yet another way to write the Clausius-Gibbs equation. The Clausius-Gibbs equation relates three thermodynamic properties: entropy, energy, and temperature. We can use the equation to express one property in terms of the other two. We have already written the Clausius-Gibbs equation in two ways:

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

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

Here is the third way to write the Clausius-Gibbs equation:

$$dU = T(S)dS.$$

Again, Clausius-Gibbs equation applies to the family of isolated systems, and each member in the family has been isolated for a long time and has reached state of thermodynamic equilibrium. We now regard the entropy as the independent variable, and describe the family of isolated systems collectively by the function $U(S)$. We regard temperature as a function of entropy, $T(S)$.

Irrational unit. 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

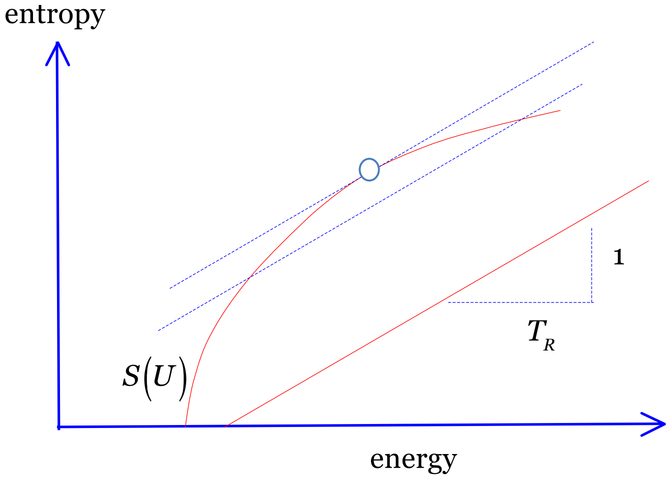
$$S = k \log \Omega .$$

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 sample points". The concept of entropy is independent of that of energy and of temperature. We happen to apply entropy to analyze thermal contact, where energy and temperature are involved.

At a more elementary level, entropy is a pure number associated with any distribution of probability, 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 ($S = \log 2$).

THEORY OF PHASES

Graphical derivation of the condition of equilibrium. Consider a plane with the energy as the horizontal axis and entropy as the vertical axis. The function $S_{\text{composite}}(U)$ consists of two parts. One part is the entropy of the small system, which is the nonlinear function $S(U)$, represented as a curve in the energy-entropy plane. The other part is the entropy of the reservoir, which is linear in energy, represented in the energy-entropy plane by an inclined line, with $1/T_R$ as the slope with respect to the horizontal axis.



The vertical distance between the curve $S(U)$ and the inclined line is the function U/T_R. Thermodynamics dictates that this vertical distance should maximize when the small system equilibrates with the reservoir.

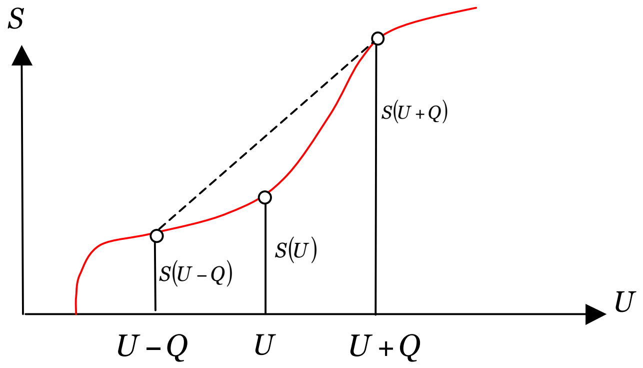
For a fixed T_R, the inclined line is fixed. A line parallel to the inclined line may intersect with the curve $S(U)$ at some points. All points give the equal value of the vertical distance $S_{\text{composite}}(U)$. The vertical distance between the two lines increases when we move upward the line parallel to the inclined line. From the geometry, the vertical distance $S_{\text{composite}}(U)$ is maximized when the line parallel to the inclined line becomes tangent to the curve $S(U)$. This geometric interpretation recovers the conditions of equilibrium:

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

As stated before, at a point on the curve $S(U)$, we can form a line tangent to the curve. The slope of the tangent line equals $1/T_R$.

When $1/T_R$ changes gradually, the inclined line rotates, and the associated tangent line rolls along the curve $S(U)$ with one degree of freedom.

The function $S(U)$ is usually convex. In the above discussion, we have assumed that the function $S(U)$ is convex. Recall the relation $1/T = dS(U)/dU$ and $1/C = dT(U)/dU$. The temperature is the slope of the entropy-energy curve. A convex entropy-energy curve means that the temperature is a monotonic increasing function of the energy, and that the heat capacity is positive.



Nonconvex $S(U)$ causes phase transition. Now consider a system with variable energy, characterized by a nonconvex function $S(U)$. Put two copies of the system together as two parts of a composite. The composite has a fixed amount of total energy $2U$, but the two parts can exchange energy. Let the energy be $U-Q$ in one part, and be $U+Q$ in the other part. Consequently, the composite is an isolated system with an internal variable Q. When a part has a fixed among of energy, the part itself is an isolated system, and has its own set of quantum states.

A quantum state of one part and a quantum state of the other part in combination constitute a quantum state of the composite. The set of quantum states of the composite with internal variable Q constitute a macrostate of the composite. The entropy of this macrostate is $S(U-Q)+S(U+Q)$. For another macrostate of the composite, each of the two parts has energy U, so that the entropy of this macrostate of the composite is $2S(U)$.

At a value of U where the function $S(U)$ is concave, we can find many values of Q to satisfy the following inequality:

$$S(U-Q)+S(U+Q)>2S(U).$$

Consequently, the composite is more likely to be in a macrostate where the two parts have unequal amounts of energy. The convex portion of the function $S(U)$ is never realized in the composite.

That we have used two copies of the system is not as artificial as it may appear. Most systems can redistribute energy internally, and effectively behave like a composite of multiple copies of a smaller system.

A pure substance in a single phase. A substance is an aggregate of a large number of a single species of molecules. The entropy and the energy of the piece of the substance, S and U, are proportional to the number of molecules in the piece, N. The entropy per molecule of the substance is $s=S/N$, and the energy per molecule is $u=U/N$. When we add energy to the aggregate, the entropy of the aggregate in increases. The function $s(u)$ is specific to the substance, and is independent of the size and shape of the piece.

When the substance is in a single phase, the function $s(u)$ is a smooth, convex curve. The temperature is given by

$$\frac{1}{T}=\frac{ds(u)}{du}.$$

Coexistent phases of a pure substance. Consider a mixture of ice and water at the melting temperature T_m. When energy is added to the mixture, the amount of water increases at the expense of the amount of ice, but the temperature remains constant. We would like to trace this empirical observation back to the fundamental postulate.

The substance can be in two phases, A' and A''. We regard the two phases as two systems, one characterized by function $s'(u')$, and the other by $s''(u'')$. Let N' be the number of molecule in one phase, and N'' be the number of molecules in the other phase. When the two phases coexist, molecules can detach from one phase and attach to the other. The total number of molecules in the mixture, N, remains unchanged:

$$N = N' + N''.$$

We neglect energy associated with the phase boundaries, so that the energy of the two-phase mixture is the sum of the energies of the two phases:

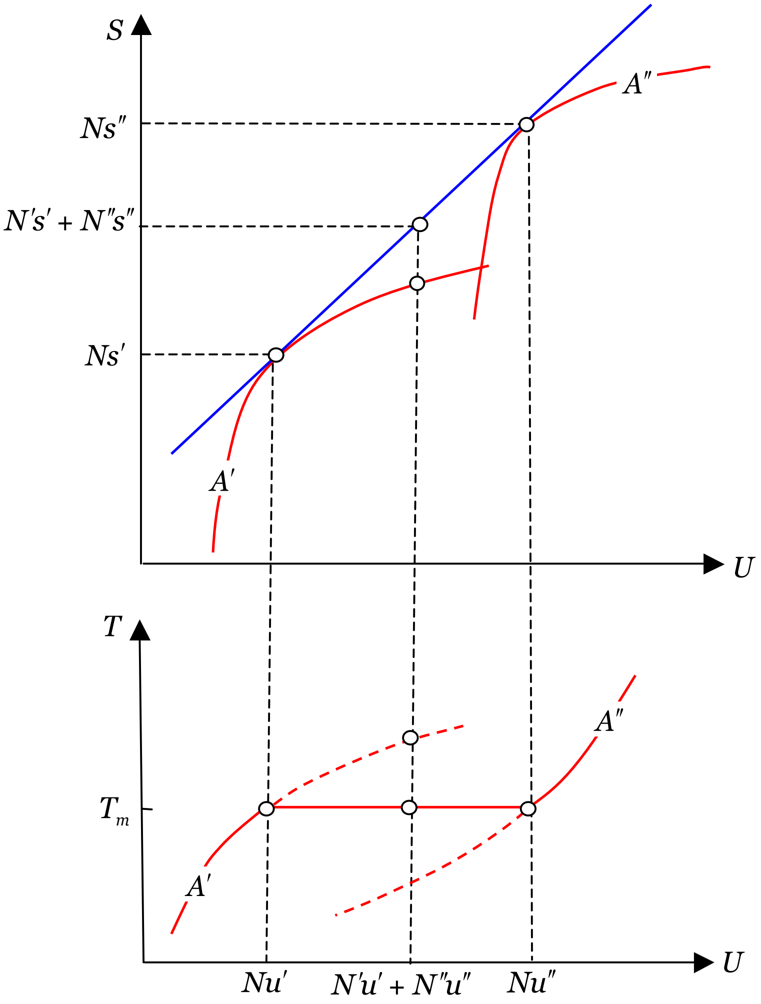
$$U = N'u' + N''u''.$$

Similarly, the entropy of the two-phase mixture is the sum of the entropies of the two phases:

$$S = N's' + N''s''.$$

The above equations are known as the *rules of mixture*.

When N and U are fixed, the mixture is an isolated system with internal variables: N', N'', u', u''. Of all values of the internal variables, the most probable ones maximize the entropy of the mixture, subject to the constraint of the fixed N and U.



Graphical representation of the condition for coexistent phases. This problem of maximization subject to constraints can be solved in a number of ways. Following Gibbs, we will solve this problem using a graph. Let S and U be the entropy and the energy of the mixture of two phases. In the plane (S,U), each point represents a particular mixture of the two phases.

Given a function $s'(u')$, the set of points (Nu',Ns') is a curve on the (S,U) plane, representing the substance when all molecules are in phase A'. Similarly, given a function $s''(u'')$, the set of points (Nu'',Ns'') is a curve on the (S,U) plane, representing the substance when all molecules are in phase A''.

Now pick one particular point (Nu',Ns') on one curve, and pick another particular point (Nu'',Ns'') on the other curve. Through the two points draw a straight line. Recall the rules of mixture:

$$N = N' + N'',$$

$$U = N'u' + N''u'',$$

$$S = N's' + N''s''.$$

The energy and the entropy of the mixture, U and S, are linear in the number of molecules in the two phases. Consequently, the energy and the entropy of the mixture is a point on the straight line.

When the energy of the mixture is fixed, the entropy of the mixture is maximized when the straight line is tangent to both curves. The line tangent to both curves determines two points, (u',s') and (u'',s''). The two points correspond two the states of the two phases in equilibrium. Reading off the graph, this condition of equilibrium corresponds to

$$\frac{s'-s''}{u'-u''} = \frac{\partial s'(u')}{\partial u'} = \frac{\partial s''(u'')}{\partial u''}.$$

The slope of the tangent defines the melting temperature:

$$\frac{s''-s'}{u''-u'} = \frac{1}{T_m}.$$

The latent heat is given by the difference in the energy of the two phases:

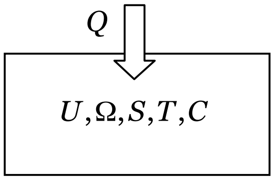
$$L = u'' - u'.$$

ALTERNATIVE INDEPENDENT VARIABLES

We have already introduced quite a few functions of state, or properties:

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

For a system of a single independent variation, we may choose one of the properties as the independent variable, and plot any one of the other properties as a function of the independent variable. We will describe several common choices of independent variable.

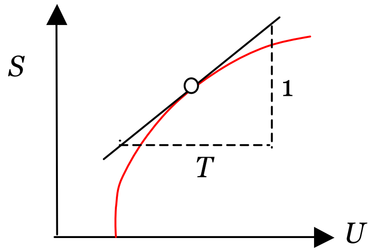


One difficulty in learning thermodynamics is to learn alternative choices of the independent variable, and what these choices mean in theory and experiment. So far we have been dealing systems with a single independent variable. The number of choices will proliferate when we look at systems with more independent variables.

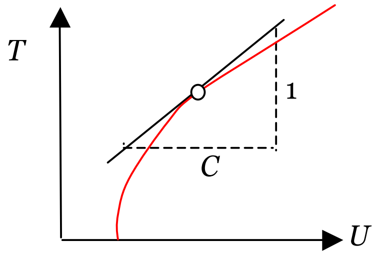
Energy as independent variable. Consider a plane with two coordinates S and U. On this plane, a system with variable energy is represented by a curve $S(U)$. A point on the curve represents the system isolated at energy U, flipping among $\exp(S)$ number of quantum states. The slope of the curve $S(U)$ 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 $T \to 0$.

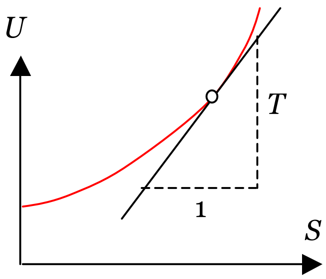
For many systems, the more energy the system has, the more quantum states the system has. That is, the function $S(U)$ is a monotonically increasing function. According to the Clausius-Gibbs equation, $T^{-1} = dS(U)/dU$, the temperature is positive. For some unusual systems, however, $S(U)$ is not a monotonically increasing function, and the absolute temperature is negative. We will not consider such systems in this course.

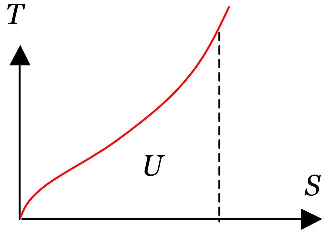


For may systems the function $S(U)$ is convex. A convex function $S(U)$ means that the function $T(U)$ is a monotonically increasing function. According to the definition, $C^{-1} = dT(U)/dU$, the heat capacity is positive $C > 0$. That is, the system must receive energy to increase its temperature. We will study non-convex $S(U)$ shortly.



Entropy as independent variable. One difficulty in learning thermodynamics is to learn alternative choices of the independent variable. So far we have been dealing with systems of 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 family of isolated systems. 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, whereas the energy is the area under the $T(S)$ curve.

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 independent variable. In everyday life, we almost always use temperature as the independent variable. Examples include thermal baths and thermostat.

Using temperature as an independent variable 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 $S(T)$.

Control of Temperature

Reservoir of energy. A reservoir of energy interacts with the rest of the world in only one manner: exchanging energy by heat. We further require that, upon gaining or losing energy by heat, the reservoir of energy should maintain a fixed temperature, which is constant within the reservoir and with respect to time. The reservoir of energy is also known as thermal bath or heat bath.

We use a reservoir of energy to control the temperature of a small system. The system is *small* in the sense that it has a much smaller heat capacity than the reservoir of energy. The small system and the reservoir exchange energy by heat. They do not exchange energy by work, and do not exchange matter. The small system and the reservoir together form an isolated system.

Coexistent solid and liquid of a pure substance. We can realize a reservoir of energy by using coexistent solid and liquid of a pure substance. The melting point of the substance sets the fixed temperature of the reservoir. As the reservoir and the rest of the world exchange energy by heat, the proportion of the solid and liquid changes, but the temperature of the mixture is held at the melting point.

We transfer energy by heat slowly into or out of the reservoir, so that energy has enough time to distribute in the reservoir, and keeps temperature uniform within the reservoir. We avoid heating the liquid above the melting point, or cooling the solid below the melting point.

When the solid melts or the liquid freezes, the volume of the substance changes. To avoid exchanging energy by work, we leave the substance unconstrained, so that the force is negligible.

Large amount of water. We can also realize a reservoir of energy by using a large tank of water. Water has large specific heat. When the water loses or gains a small amount of energy, the temperature is nearly unchanged. Water has modest thermal conductivity. We stir the water gently to keep temperature uniform within the reservoir, but do not heat it up.

Thermostat. A thermostat is a device that measures temperature and switches heating or cooling equipment on, so that the temperature is kept around a prescribed level.

Sous-vide (/suːˈviːd/; French for "under vacuum") is a method of cooking. Food (for example, a piece of meat) is sealed in an airtight plastic bag, and then placed in a water bath for a longer time and at a lower hotness than those used for normal cooking. The temperature is fixed by a feedback system. Because of the long time and low temperature, sous-vide cooking heats the food evenly; the inside is properly cooked without overcooking the outside. The airtight bag retains moisture in the food.

Isothermal process. Sous-vide cooking is an isothermal process, in which food is cooked at a fixed temperature. We have also described another isothermal process. At a fixed temperature, water can turn from liquid into gas as we increase volume. We describe this process by modeling a fixed number of water molecules as a system of two independent variations. We can vary thermodynamic state of the system by adding energy and increasing volume. To keep temperature constant, the change in energy and the change in volume will be related.

A small system in thermal equilibrium with a reservoir of energy. We model the reservoir of energy by prescribing its entropy as a function of its energy, $S_R(U_R)$. Denote the fixed temperature of the reservoir of energy by T_R. When the energy of the reservoir changes from U_o to $U_R = U_o - U$, the entropy of the reservoir changes by

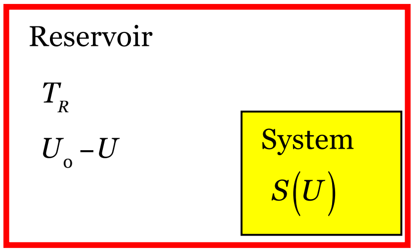
$$S_R(U_R) - S_R(U_o) = -\frac{U}{T_R}.$$

Because the reservoir maintains a fixed temperature, the change of entropy is proportional to the change of energy.

We model the small system by prescribing its entropy as a function of its energy, $S(U)$. We next analyze this thermal contact using the basic algorithm of thermodynamics.

The reservoir and the small system together form an isolated system. Denote the total energy of the composite by

$$U_{\text{composite}} = U_R + U.$$



As the reservoir and the small system changes energy, the total energy of the composite, $U_{\text{composite}}$, is fixed. Thus, the composite is an isolated system of a single internal variable, the energy of the small system U.

The entropy of the composite, $S_{\text{composite}}$, is the sum of the entropies of the two parts, the reservoir and the small system:

$$S_{\text{composite}} = S_R\left(U_{\text{composite}}\right) - \frac{U}{T_R} + S(U).$$

The energy of the composite $U_{composite}$ is fixed, so that $S_R\left(U_{\text{composite}}\right)$ is a constant. The reservoir maintains its temperature T_R. The entropy of the composite is a function of the internal variable, $S_{\text{composite}}(U)$.

The composite is an isolated system, flipping among a set of quantum states. When U is fixed at particular value, the composite flips among a particular subset of quantum states. The entropy $S_{\text{composite}}(U)$ is the logarithm of the number of quantum states in this subset. The fundamental postulate requires that, when the reservoir and the small system equilibrate, the value of the internal variable U maximizes the function $S_{\text{composite}}(U)$. This condition of equilibrium requires that the quantity in front of the variation to vanish, giving

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

This condition of equilibrium relates the temperature of the reservoir to the function characteristic of the small system, $S(U)$. Given the temperature T_R of the reservoir and the function $S(U)$ of the small system, the above equation determines the energy of the small system.

When the composite is in equilibrium, we can also speak of the temperature of the small system, T, and equate it to the temperature of the reservoir. We write

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

The equation recovers the definition of the temperature of the small system.

Free Energy

Legendre transform. A Legendre transform turns a derivative into an independent variable. The topic belongs to Calculus, but is seldom taught. As we will see, Legendre transform plays a significant role in thermodynamics.

Let $z(x)$ be a function of a single variable. The derivative of the function is

$$M = \frac{dz(x)}{dx}.$$

The derivative is a function $M(x)$. The increment of the function $z(x)$ is

$$dz = Mdx.$$

Define the Legendre transform of the function $z(x)$ by

$$L = z - Mx.$$

Note that

$$dL = dz - Mdx - xdM.$$

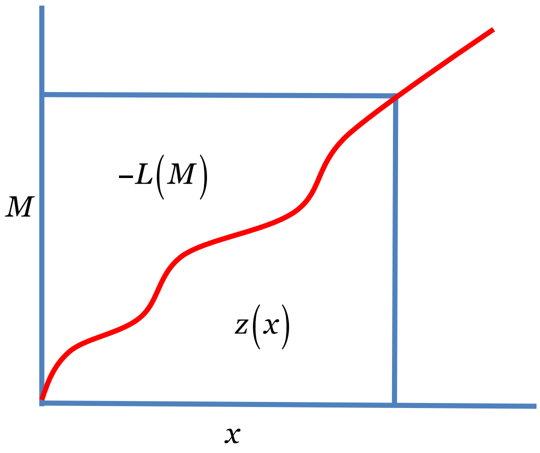
The first two terms cancel, so that

$$dL = -xdM$$

Provided $M(x)$ is a one-to-one function, the definition $L = z - Mx$ leads to a function $L(M)$. The relation $dL = -xdM$ gives that

$$-x = \frac{dL(M)}{dM}.$$

So long as the function $M(x)$ is one-to-one, the function $z(x)$ and its Legendre transform $L(M)$ act symmetrically.



A graphic representation of the Legendre transform. A relation between M and x corresponds to a curve in the plane with M and x as axes. The M-x relation is one-to-one if and only if the curve is *monotonic*. To simplify the description, we use a monotonically increasing curve, and place the origin of the coordinates on the curve. For given values of x and M, the relation $dz = Mdx$ indicates that the function $z(x)$ is the area between the curve and the x-axis. The relation $dL = -xdM$ indicates that the function $-L(M)$ is the area between the curve and the M-axis, and the product xM is the area of the rectangle. The Legendre transform means the obvious geometric relation between the three areas:

$$z(x) - L(M) = Mx .$$

Helmholtz Free energy. The Legendre of the function $U(S)$ is

$$F = U - TS .$$

This function is known as the free energy, the Helmholtz free energy, or the Helmholtz function.

The increment is

$$dF = dU - TdS - SdT$$

Recall the Clausius-Gibbs equation, $dU = TdS$. The above equation becomes that

$$dF = -SdT .$$

Consequently, the entropy relates to a partial differential coefficient of the free energy:

$$S = -\frac{dF(T)}{\partial T} .$$

Because entropy is a positive number, the free energy $F(T)$ is a monotonic decreasing function of T.

Debye model (1912). We have introduced three basic equations. The Clausius-Gibbs equation defines the thermodynamic scale of temperature:

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

Define the heat capacity C by

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

Define the Helmholtz function by

$$F = U - TS .$$

To illustrate these definitions, consider a model obtained by Debye (1912). Near absolute zero, the internal energy of a solid states the form

$$U = aT^4 ,$$

where a is a constant.

Write the Clausius-Gibbs equation in the form

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

Insert the Debye model $U = aT^4$, and we obtain that

$$S = \frac{4}{3}aT^3,$$

where we have used the condition $S = 0$ at $T = 0$.

Write the definition of the heat capacity as

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

Insert the Debye model $U = aT^4$, and we obtain that

$$C = 4aT^3.$$

The Helmholtz function is given by

$$F = U - TS = -\frac{1}{3}aT^4.$$

Up to this point we have used T as the independent variable. We can of course use U as the independent variable. Invert the Debye model $U = aT^4$, and we obtain that

$$T(U) = (U/a)^{1/4}.$$

Insert this expression into $S = \frac{4}{3}aT^3$, and we obtain that

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

Note that $S(U)$ is a convex function.

The Basic Algorithm of Thermodynamics in Terms of Free Energy

A system with variable energy and an internal variable. Once again consider the half bottle of water, now in thermal contact with the rest of the world. We are interested in two variables: the energy in the bottle, and the number of molecules in the gas phase. The bottle is sealed to prevent molecules from escaping the glass. The number of molecules in the gas phase is an internal variable in the system of variable energy.

We now formulate the idea in generic terms. A system is in thermal contact with the rest of the world, and we are interested in two variables: the energy of the system U, and an internal variable of the system Y. When both U and Y are fixed at specific values, the system is an isolated system. Denote the number of the quantum states of this isolated system by $\Omega(U,Y)$. The entropy of the isolated system is $S(U,Y) = \log \Omega(U,Y)$.

Thermal equilibrium. A system can be held at a constant temperature by a reservoir of energy, also known as a thermostat. We regard the system and the thermostat together as a composite. The composite is an isolated system with two internal variables: the energy U in the system, and the internal variable Y. A pair of values (U,Y) specifies a macrostate of the composite.

Let T_R be the temperature fixed by the reservoir. When the system draws energy U from the thermostat, the entropy of the thermostat reduces by U/T_R. Consequently, the entropy of the macrostate (U,Y) of the composite is

$$S_{\text{composite}} = S_R\left(U_{\text{composite}}\right) - \frac{U}{T_R} + S(U,Y).$$

Here we have dropped an additive constant.

According to the fundamental postulate, of all possible values of the internal variables, the most probable values maximize the above entropy of the macrostate. Setting the variation with respect to U to zero, we obtain that

$$\frac{\partial S(U,Y)}{\partial U} = \frac{1}{T_R}.$$

This equation recovers a fact we already know. When the internal variable Y is fixed, the system is a system of variable energy. When the system is in thermal equilibrium with the thermostat, the temperature of the system equals that of the thermostat. We will drop the subscript R in the following.

Assuming the function $S(U,Y)$ is known, the above condition of thermal equilibrium defines the function $U(T,Y)$.

Free energy. Now returning to the entropy of the composite. When the system and the reservoir are in thermal equilibrium, the energy of the system is given by the function $U(T,Y)$. Consequently, the entropy of the composite is to be maximized with the other independent variable: the internal variable Y. Temperature T is no longer a variable, but is fixed by the reservoir.

Maximizing the entropy of the composite is the same as minimizing the following function:

$$F = U - TS.$$

We now change variable U to T using the function $U(T,Y)$. The above function is written as $F(T,Y)$. This function contains quantities of the system alone, and is known as the *Helmholtz free energy* of the system.

When the system is held at a fixed temperature (i.e., in thermal equilibrium with the reservoir), of all values of the internal variable Y, the most probable value minimizes the free energy $F(T,Y)$. In this minimization, the temperature is not a variable, but is fixed by the reservoir.

Examine co-existent phases using the free energy. The use of free energy adds some mathematical convenience. Once we assume that temperature is held constant, we eliminate it from the list of independent variables in minimizing the free energy. We need to minimize the free energy by varying some other internal variables.

Consider a mixture of two phases held at a temperature T. Let the free energy of the two phases be $f'(T)$ and $f''(T)$. The free energy of the mixture is.

$$F = N'f'(T) + N''f''(T).$$

The number of molecules in one phase is the internal variable, to be selected to minimize the total free energy.

The equation

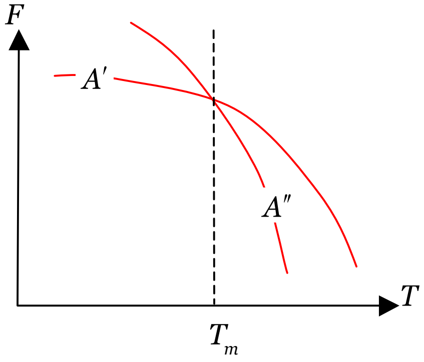
$$f'(T) = f''(T)$$

determines the phase-transition temperature T_m. When $T < T_m$, all molecules are in one phase. When $T > T_m$ all molecules are in the other phase.

Recall the definition of the free energy for each phase, $f = u - Ts$. The condition of coexistence $f'(T) = f''(T)$ gives

$$u' - T_m s' = u'' - T_m s''.$$

This expression recovers what we have obtained before.



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