Lecture 4 The Algorithm of Thermodynamics

I have taught this course four times before, but have never devoted lectures on basic thermodynamics. It is a subject I'm not good at, but I have used it often in research, in a loose way. One can ride a bicycle without knowing Newton's laws, even though bicycle-riding is governed by Newton's law. If thermodynamics gives me so much trouble, perhaps it also gives my students a lot of trouble. I have taken lectures from many teachers on the subject. None have really made me feel comfortable with it. Now I'm trying to teach you. I hope that I can help you become comfortable with the subject. Maybe you already are. Maybe you never will. I have no evidence that I can be more effective than these other teachers, but I have the enthusiasm of an amateur.

To understand thermodynamics, one has to understand its algorithm, a large sample of phenomena, as well as techniques of computation and measurement. This lecture focuses on the algorithm.

When my older son was very young, perhaps three or four, I began to tell him about electrons and protons and molecules. I'd like to see my son grow up comfortable about things that he had no direct evidence of. I grew up during the Cultural Revolution in China, and knew how effective propaganda could be. Radical ideas seem to become reasonable after one says them a lot of times. This method of persuasion can be used to a good end. When I was a child, people kept telling me that the earth circles around the sun, and I became comfortable with the idea, despite that daily evidence seemed to suggest the opposite. So a bombardment of ideas can be effective, and even noble if the ideas are true. If I keep telling my son about molecules, he might grow up as familiar with molecules as with his younger brother. That will prepare him for the Age of Molecules.

System, Environment, and Their Interactions

A glass of wine is a system, and the rest of the world its environment. The system interacts with the rest of the world in many ways. The wine is composed of molecules: water alcohol, and others. When you smell the wine, it is because some of the molecules escape from the wine and reach your nostrils. When your hand warms the wine, it is because the molecules of your hand vibrate more violently than the molecules in the wine. We say that your hand adds heat to the wine. When the wine is placed in an electric field, the electron clouds of the molecules change shape somewhat, and the electric dipoles of the molecules orient more along the electric field direction. We say that the electric field does work to the wine.

Quantum States (or Microstates)

A system has many quantum states. Each quantum state has a definite energy. Different quantum states may have the same value of energy. Consider, for example, a system composed of a proton and an electron. We call this system the hydrogen atom. Because the proton is much heavier than the electron, we may assume that the proton is stationary, and allow the electron to move. At the ground energy level, the wavefunction of the electron has a spherical symmetry. This energy level corresponds to two quantum states, because the electron can have two spin orientations. At the second energy level, 13.6 eV above the ground level, the system has 8 quantum states, 2 having spherical symmetric wavefunctions, and 6 having dumbbell-shaped wavefunctions. At higher energy levels, the system has even more quantum states.

For a large system, such as the glass of wine, with many electrons and protons and neutrons, we may not be certain of the exact value of the energy. It will suffice to know energy within some narrow range.

In many model systems, such as vacancies in a crystal lattice, quantum mechanics does not enter explicitly. In this example, each configuration of the vacancies in a lattice is described in classical terms. Each configuration of the system is called a **microstate**. Since the quantum mechanics governs our world, the existence of atoms and vacancies is consequences of the quantum mechanics. In this lecture, we use the terms microstate and quantum state interchangeably.

Closed System

We quantify the interactions between a system and the rest of the world by a set of variables: the energy of the system, the number of particles in the system, the volume of the system, the amount of electric charge in the system, etc. How many modes of interaction do we need to account for? The answer has to be pragmatic. We'll account for as many modes as our instruments can detect.

A system is said to be a **closed system** if it has *no* interaction with the rest of the world. (Both Callen and Kittel-Kroemer use the closed system in this sense. Some other people call such a system an *isolated system*, and reserve the name closed system for something else. I like the name closed system, because I'll talk a lot about *opening* the system in one way or another. When a system is closed, it is closed to any interaction. When a system is open, it is open to one specific interaction or another, as specified.)

By definition, a closed system has constant values of energy, of number of particles, and of *all* other variables that would register the interactions with the rest of the world, should we open the system. The closed system has a specific set of quantum states. Which quantum state will the system be in?

The Fundamental Assumption

A closed system is equally likely to be in any one of its quantum states. This assumption sounds so wrong if you read it quickly. Well, "quickly" is precise the origin of confusion. Let's say we have prepared the system in a specific quantum state. For example, we drop a drop of water molecules in the glass of wine, and then close the system. Momentarily, the fresh water molecules have no time to visit everywhere in the wine. For the fundamental assumption to make sense, we have to wait long enough for the closed system to reach **equilibrium**. Only in equilibrium, the closed system is equally likely to be in any one of its quantum states.

Let g be the number of quantum states of a closed system. Every quantum state has the same values of the variables that characterize the interactions between the system and its environment. According to the fundamental assumption, the probability for the closed system to be in any one of its quantum states is $1/g$.

Ink Particles Suspended in Water

It's difficult to observe water molecules in a glass of wine. Let's talk about an experience we all have. Say we drop a tiny amount of ink into a full glass of water. The ink contains tiny solid particles (e.g., carbon black) that give the color. Why do the ink particles tend to disperse in the water? A given configuration of the locations of all ink particles defines a microstate of the system. There is negligible interaction between any two ink particles, so that each every particle is free to explore everywhere in the water. All configurations are equally likely. For example, the configuration that all ink particles are in a small region in the glass is just as likely as a configuration that the ink particles are dispersed in the entire glass. However, there are much more configurations that ink particles disperse in the entire glass than the configurations that ink particles are in a small region. Consequently, dispersion is more likely than localization.

Let's make this idea quantitative. Let *V* be the volume of the full glass of water. The number of microstates of each ink particle is proportional to *V*. We have a dilute concentration of ink particles suspended in water, so that the number of microstates for *N* ink particles is proportional to V^N. If the *N* particles are confined in a small region in the glass, say of volume V/10, the number of microstates is proportional to $(V/10)^N$. Thus,

$$\frac{\text{probability for N particles in volume V}}{\text{probability for N particles in volume V/10}} = \frac{V^N}{(V/10)^N} = 10^N$$

This ratio is huge if we have more than a few particles suspended in the glass of water.

An event like "*N* particles dispersed in a glass of water" is such a vague description at the levels of each particle, that many microstates fit this description. Consequently, one such event is represented by a **set** of larger number of microstates. *In a closed system, all microstates have the same probability to occur. An event represented by a set of microstates is more likely to occur because the set has more member microstates.*

The Multiplicity Function

We now *open* a system in just one way: the system can exchange energy with its environment, but still retains constant values of the number of particles, the volume, etc. That is, of all variables that characterize the interactions between the system and its environment, only the energy of the system, *U*, is actually allowed to vary. We call this mode of energy transfer the **heat**. The practice of registering the heat is known as the **colorimetry**.

When the system is held at one value of energy, the system is in effect a closed system and has one specific set of quantum states. When the system is held at another value of energy, the system has another specific set of quantum states. The number of quantum states of the system is a function of its energy, $g(U)$, known as the **multiplicity function**. This function is a fundamental characteristic of the system.

Thermal Contact: Systems That Can Exchange Energy

Consider two systems. System 1 has $g_1(U_1)$ quantum states when it has energy U_1. System 2 has $g_2(U_2)$ quantum states when it has energy U_2. The two systems can be totally different, like a glass of wine and a piece of cheese, so that the two multiplicity functions can be different. The two systems exchange energy with each other, but do not exchange particles, or volumes, etc. That is why the numbers of quantum states are the functions of only energy. The composite of the two systems is insulated from the rest of the world, and forms a closed system. Consequently, the composite is a closed system, and the combined energy, $U_1 + U_2$, is constant. The two systems are said to be in **thermal contact**. After some time, the energy flow stops, and the composite system is said to have reached **thermal equilibrium**. When the two systems are brought into thermal contact, will energy flow from system 1 to system 2, or in the opposite direction? How do the two systems partition the energy at thermal equilibrium?

We are careful, so that the act of thermal contact does not alter the two systems in their fundamental characteristics. For example, if the contact creates some additional interface states, the number of such states is taken to be negligible for the time being. When the energy in system 1 changes to a new value U_1, the number of the quantum states of system 1 is still given by the same multiplicity function $g_1(U_1)$, just evaluated at the new value of the energy. The same is true for system 2.

Here comes the crux of thermodynamic thinking. For a given energy partition, U_1 and U_2, system 1 has $g_1(U_1)$ quantum states, and system 2 has $g_2(U_2)$ quantum states. This energy partition grants the composite system

$$g = g_1(U_1)g_2(U_2)$$

quantum states. The number g depends on energy partition: a different energy partition grants the composite system a different number of quantum states. The sum of the number of quantum states over all energy partitions gives the total number of quantum states accessible to the composite system. According to the fundamental assumption, the composite system is equally likely to be in any one of the accessible quantum states, time permitting. One energy partition may grant the composite system more quantum states than another energy partition. The more quantum states an energy partition grants the composite system, the more likely this energy partition will occur. The most likely energy partition grants the composite system the most quantum states. We identify this most likely energy partition as the **equilibrium state** of the two systems in thermal contact.

Let's determine this most likely energy partition. This is a standard calculus problem. When a small amount of energy, δU, flows from system 2 to system 1, system 1 has energy $U_1 + \delta U$, and $g_1(U_1 + \delta U) \approx g_1(U_1) + \frac{\partial g_1}{\partial U_1}\delta U$ quantum states. We retain the Taylor series up to the first order in δU. Similarly, system 2 has energy $U_2 - \delta U$, and $g_2(U_2 - \delta U) \approx g_2(U_2) - \frac{\partial g_2}{\partial U_2}\delta U$ quantum states. Consequently, when a small amount of energy δU flows from system 2 to system 1, the composite changes its number of quantum states by $\delta g = g_1(U_1 + \delta U)g_2(U_2 - \delta U) - g_1(U_1)g_2(U_2)$, namely,

$$\delta g = \left(\frac{\partial g_1}{\partial U_1} g_2 - g_1 \frac{\partial g_2}{\partial U_2} \right) \delta U \ .$$

Divide the above equation by $g_1(U_1)g_2(U_2)$, and we obtain that

$$\delta \ln g = \left(\frac{\partial \ln g_1}{\partial U_1} - \frac{\partial \ln g_2}{\partial U_2} \right) \delta U \ .$$

A given energy partition grants g quantum states to the composite system. The larger the number g, the more likely this energy partition will occur. Consequently, energy flows in the direction to increase the number of the quantum states of the composite system, making $\delta \ln g > 0$. For example, for energy to flow from system 2 to system 1, namely, $\delta U > 0$, we require that

$$\frac{\partial \ln g_1}{\partial U_1} > \frac{\partial \ln g_2}{\partial U_2} \ .$$

The two systems reach equilibrium when

$$\frac{\partial \ln g_1}{\partial U_1} = \frac{\partial \ln g_2}{\partial U_2} \ .$$

If we know the two systems, i.e., know the two characteristic functions $g_1(U_1)$ and $g_2(U_2)$, we can determine how the two systems partition the energy when they reach thermal equilibrium.

The Entropy and The Temperature

If you are tired of the phrase "the logarithm of the number of quantum states", you just join the crowd and use a cryptic word. You call the quantity

$$\sigma = \ln g$$

the entropy. The entropy is also a function of the energy. The entropy increases if the energy increases. In this definition, the entropy is a dimensionless number. The entropy is just an abbreviation for the phase “the logarithm of the number of quantum states”. Nothing more or less.

As another abbreviation, define the temperature of a system, τ , as

$$\frac{1}{\tau}=\frac{\partial\sigma}{\partial U}.$$

The temperature is a function of the energy. Because the number of quantum states increases with the energy, and so does the entropy, the temperature is positive. The temperature defined this way has the unit of energy.

Now we can paraphrase the analysis of thermal contact in terms of entropy and temperature. When the two systems are in thermal contact and the composite system is closed to the rest of the universe, the following things happen.

- For a given energy partition, U_1 and U_2, the entropy of the composite system is the sum of the two systems: $\sigma=\sigma_1(U_1)+\sigma_2(U_2)$.
- A different energy partition gives a different entropy to the composite system. The most likely energy partition maximizes the entropy.
- To increase the entropy of the composite system, energy flows from the system with high temperature to the system with low temperature.
- The two systems reach thermal equilibrium when their temperatures equal.
- Of all energy partitions, the energy partition in thermal equilibrium maximizes the entropy of the composite system.

The Second Law

Let us analyze the thermal contact experiment again. During the experiment, the two systems together form a closed system. Before the two systems are in thermal contact, they are insulated from each other, and each system maintains a constant energy. The insulation between the two systems provides a **constraint**, preventing energy from flowing from one system to the other. Now we remove the insulation between the two systems, so that energy flows from one system to the other. For a given energy partition U_1 and U_2, the number of quantum states of the composite system is $g = g_1(U_1)g_2(U_2)$, which is the probability for this energy partition to occur. Entropy of the composite system is defined as $\sigma = \ln g$. *When an internal constraint is lifted, the number of quantum states of a closed system increases, and so does the entropy.* This is the content of the second law of thermodynamics.

A System Exchanging Energy with a Reservoir: The Free Energy

A system can exchange energy with a reservoir. The combination of the system and the reservoir is a closed system, with constant energy U_0. The reservoir is so large that the change in its energy does not change its temperature. Denote the constant temperature of the reservoir by τ. In equilibrium, how much energy does the system have?

Assume that the system itself has energy U and entropy $\sigma(U)$. The reservoir has energy $U_R = U_0 - U$ and entropy $\sigma_R(U_0 - U)$. The composite system has entropy

$$\sigma_R(U_0 - U) + \sigma(U).$$

Expand the entropy of the reservoir into the Taylor series,

$$\sigma_R(U_0 - U) = \sigma_R(U_0) - \frac{\partial \sigma_R}{\partial U_0} U = \sigma_R(U_0) - \frac{U}{\tau}$$

We rewrite the entropy of the composite system as

$$\sigma_R(U_0) - \frac{U - \tau\sigma(U)}{\tau}.$$

The composite system is a closed system. In equilibrium, the composite has the maximum entropy. Because $\sigma_R(U_0)$ is constant, equilibrium requires that $U - \tau\sigma(U)$ reach minimum.

The quantity

$$F = U - \tau\sigma$$

is known as the free energy. We have used it in determining the equilibrium vacancy concentration. In generic terms, the free energy is useful for any system held at a constant temperature (by allowing it to exchange energy with a reservoir). Thus the system is not closed any more. When an internal constraint is removed, the system reaches equilibrium by minimizing the free energy.

The Boltzmann Distribution

Once again consider the system in thermal contact with the reservoir held at the constant temperature τ. The combination of the system and the reservoir is a closed system. Their combined energy is fixed at U_0. Energy can flow between the system and the reservoir. Now the system is no longer closed. Because the energy of the system can take many values, quantum states of all energy levels are assessable to the system. What is the probability to find the system in a particular quantum state?

Consider *one particular quantum state* of the system. In this quantum sate, the system has energy ε. The reservoir has the energy $U_0 - \varepsilon$ and the entropy $\sigma_R(U_0 - \varepsilon)$. When the system is in this quantum state, the reservoir can be in many quantum states. The number of the quantum states of the reservoir is $\exp[\sigma_R(U_0 - \varepsilon)]$. This is also the number of quantum states of the composite of the system and the reservoir, when the system is in the particular state. The probability of finding the system in this quantum state, P, is proportional to the number of quantum states of the composite system:

$$P \propto \exp\left[\sigma_R\left(U_0 - \varepsilon\right)\right].$$

Expand the entropy of the environment into the Taylor series as before:

$$\sigma_R\left(U_0 - \varepsilon\right) = \sigma_R\left(U_0\right) - \varepsilon / \tau .$$

Consequently, the probability is

$$P \propto \exp\left(-\varepsilon / \tau\right).$$

We have dropped the factor $\exp\left[\sigma_R\left(U_0\right)\right]$, which is a constant independent of the system.

The probability of finding a system in a state with energy ε in thermal contact with a reservoir at constant temperature τ is proportional to $\exp\left(-\varepsilon / \tau\right)$. The higher the energy of a quantum state, the less likely the system will be in this state. This is the Boltzmann factor. Of course, the system may have many other quantum states with the same amount of energy, ε. The system is equally likely to be in any one of these quantum states.

Denote $P(0)$ as the probability for the system to be in a ground state (with zero energy), and $P(\varepsilon)$ as the probability for the system to be in a quantum state with energy ε. The ratio of the two probabilities is

$$\frac{P(\varepsilon)}{P(0)} = \exp\left(-\frac{\varepsilon}{\tau}\right).$$

In contact with the reservoir with a constant temperature, the system is unlikely to be in a quantum state with energy much above the temperature.

The Partition Function

The function

$$Z(\tau) = \sum_s \exp(-\varepsilon_s / \tau)$$

is called the partition function. The summation is over all quantum states *s* of the system (having all possible values of energy). When the system is in contact with the reservoir with a constant temperature τ, the probability of the system in a particular state with energy ε_i is

$$P(\varepsilon_i) = \frac{\exp(-\varepsilon_i / \tau)}{Z}.$$

The sum of probabilities over all states is unity.

Ensemble Average

Once more consider the system in thermal contact with the reservoir held at the constant temperature τ. Because the system can exchange energy with the reservoir, the system can be in any one of the quantum states having the energy ε_1, of the quantum states having the energy ε_2, etc. If we measure the energy of the system, what value should we get?

We should get ε_1 sometime, ε_2 sometime, etc. If we take many measurements, or most likely, if our instrument is so slow that a reading takes a long time, we will get an average value, given by

$$\langle \varepsilon \rangle = \sum_s \varepsilon_s P(\varepsilon_s).$$

This is known as the **ensemble average**. A direct calculation confirms that, when the system is in thermal contact with the reservoir held at the constant temperature τ, the ensemble average of the energy of the system relates to the partition function as

$$\langle \varepsilon \rangle = \tau^2 \frac{\partial \ln Z}{\partial \tau}.$$

(Carry out the calculation.)

Averaged Square Fluctuation

Once more consider the system in thermal contact with the reservoir held at the constant temperature τ. How much energy fluctuation will we measure? Of cause, sometimes we measure an energy higher than the average, and sometimes we measure an energy lower than the average. Define the **averaged square fluctuation** by

$$(\Delta\varepsilon)^2 = \left\langle \left(\varepsilon - \langle\varepsilon\rangle\right)^2 \right\rangle .$$

A direct calculation confirms that

$$(\Delta\varepsilon)^2 = \tau^2 \frac{\partial\langle\varepsilon\rangle}{\partial\tau} .$$

(Carry out the calculation.)

For a system containing a large number N of identical particles, the average energy of the system is proportional to the number of particles, $\langle\varepsilon\rangle \propto N$. A good measure of the energy fluctuation is

$$\frac{\sqrt{(\Delta\varepsilon)^2}}{\langle\varepsilon\rangle} \propto \frac{1}{\sqrt{N}} .$$

Consequently, the fluctuation is extremely small if the system contains a large number of particles, say $N \approx 10^{24}$ particles.

The Multiplicity Function Extended

It is straightforward to extend the above algorithm by including other modes of interactions between the system and its environment. For example, a system can be opened in two ways, exchanging both energy and particles with its environment. The number of quantum states of the system, g, is a function of both its energy U and the number of particles N, $g(U, N)$. For example, the glass of wine can both warm up and evaporate. *The way we open the system determines the variables to use. The content of the system determines the multiplicity function.*

Systems That Can Exchange Both Energy and Particles

Consider two systems, each having its own multiplicity function, $g_1(U_1, N_1)$ and $g_2(U_2, N_2)$. Allow both energy and particles to exchange between the two systems. Make the composite system a closed system, so that $U_1 + U_2$ and $N_1 + N_2$ remain constant. Our wine-and-cheese example may still be helpful. Seal a glass of wine and a piece of cheese in a bag, which isolates the wine-cheese composite from the rest of the universe. We allow both energy and water molecules to transfer between the wine and the cheese, and neglect the transfer of any other molecules. What will be the energy and water content in the wine and the cheese when equilibrium is reached?

For a given partition of energy and particles, (U_1, N_1) for system 1 and (U_2, N_2) for system 2, the number of quantum states of the composite system is

$$g = g_1(U_1, N_1) g_2(U_2, N_2)$$

The probability for this partition to occur is proportional to the number g. The most likely partition maximizes the number of quantum states of the composite system. We have learned the beauty of the logarithm before, and will now use it from start. Take the logarithm on the both sides of the above equation, and we use the abbreviation $\sigma_1(U_1, N_1) = \ln g(U_1, N_1)$, etc. The above becomes

$$\sigma = \sigma_1(U_1, N_1) + \sigma_2(U_2, N_2)$$

For given partition in the energy and the number of particles, the entropy of the composite is the sum of the entropies of the two systems.

Imagine a slightly different partition: $(U_1 + \delta U, N_1 + \delta N)$ for system 1 and $(U_2 - \delta U, N_2 - \delta N)$ for system 2. The difference in the partition charges the entropy of the composite system by

$$\delta\sigma = \left(\frac{\partial\sigma_1}{\partial U_1} - \frac{\partial\sigma_2}{\partial U_2}\right)\delta U + \left(\frac{\partial\sigma_1}{\partial N_1} - \frac{\partial\sigma_2}{\partial N_2}\right)\delta N$$

We can change the partition of energy and partition of particles independently. Consequently, each change in partition must be in the direction to increase the number of quantum states of the composite system, making $\delta\sigma > 0$. For example, when $\delta U > 0$ and $\delta N = 0$, to increase *g*, we require that

$$\frac{\partial\sigma_1}{\partial U_1} > \frac{\partial\sigma_2}{\partial U_2}$$

Similarly, when $\delta U = 0$ and $\delta N > 0$, to increase *g*, we require that

$$\frac{\partial\sigma_1}{\partial N_1} > \frac{\partial\sigma_2}{\partial N_2}$$

The two systems reach both thermal and diffusive equilibrium when

$$\frac{\partial\sigma_1}{\partial U_1} = \frac{\partial\sigma_2}{\partial U_2}, \frac{\partial\sigma_1}{\partial N_1} = \frac{\partial\sigma_2}{\partial N_2}$$

The Chemical Potential

Once again define the temperature τ by

$$\frac{1}{\tau} = \frac{\partial\sigma}{\partial U}.$$

Define the chemical potential μ by

$$-\frac{\mu}{\tau} = \frac{\partial \sigma}{\partial N}.$$

Entropy of a system is a function of two variables, $\sigma(U, N)$. When the energy varies by dU and the number of particles varies by dN, the entropy varies by

$$d\sigma = \frac{1}{\tau} dU - \frac{\mu}{\tau} dN .$$

One can also regard the energy as a function of two variables, $U(\sigma, N)$. When the entropy varies by $d\sigma$ and the number of particles varies by dN, the energy varies by

$$dU = \tau d\sigma + \mu dN .$$

Now the independent variables are σ and N. The temperature and the chemical potential are differential coefficients:

$$\tau = \frac{\partial U(\sigma, N)}{\partial \sigma}, \quad \mu = \frac{\partial U(\sigma, N)}{\partial N}.$$

When two systems can exchange both energy and particles, equilibrium is reached when the two systems have the identical temperature and the identical chemical potential.

Thermodynamics of Fluids

A fluid is characterized by a multiplicity function of two variables, $g(U,V)$. For example, one can increase the number of quantum states of a gas by increasing either its energy or its volume. We consider bulk properties of the fluid, so that the number of molecules in the fluid scale things proportionally. For example, we can talk about energy per unit mass or per molecule. The shape of the container does not affect the number of the quantum states of the fluid.

Following the same algorithm, we define the entropy by

$$\sigma(U,V) = \ln g ,$$

the temperature τ by

$$\frac{1}{\tau} = \frac{\partial \sigma(U,V)}{\partial U} ,$$

and the pressure p by

$$\frac{p}{\tau} = \frac{\partial \sigma(U,V)}{\partial V} .$$

The motivation for this definition will be clear shortly.

Consider two systems in contact, exchanging both energy and volume, but with the total energy and volume held constant. The two systems reach equilibrium when they have the identical temperature and the identical pressure. An example can be a liquid and its vapor in a sealed container.

The combination of the above two definitions gives the differential expression for the entropy function $\sigma(U,V)$:

$$d\sigma = \frac{1}{\tau} dU + \frac{p}{\tau} dV .$$

Rearranging, we obtain the differential expression for the energy function $U(\sigma,V)$:

$$dU = \tau d\sigma - pdV .$$

This recovers the familiar work term pdV. Of course this consideration motivates our definition of the pressure.

The multiplicity function $g(U,V)$, the entropy function $\sigma(U,V)$, and the energy function $U(\sigma,V)$ contain the same information. All thermodynamic properties can be deduced from any one of these functions. For example, if the energy function $U(\sigma,V)$ is known, the temperature and the pressure are differential coefficients:

$$\tau = \frac{\partial U(\sigma, V)}{\partial \sigma}, \qquad p = -\frac{\partial U(\sigma, V)}{\partial V}.$$

Gibbs described a geometric representation. The function $U(\sigma, V)$ is a surface in the three dimensional space with axes σ, V, and U. Each point on the surface represents a thermodynamic state. The tangent plane of the surface at the point defines the temperature and the pressure. Gibbs went on to use this representation to discuss phase equilibrium.

The Ideal Gas

A container of volume V contains N molecules. If distance between the molecules are sufficiently large, i.e., if V/N is large, the probability of finding a molecule is independent of the location in the container, and of the presence of other molecules. The total number of ways in which the N molecules can be distributed equals the product of the numbers of ways in which the individual molecules be independently distributed. With N and U fixed, each of these numbers will be proportional to V. The total number of ways is proportional to the Nth power of V:

$$g(U, V, N) = \text{constant} \times V^N.$$

The constant is independent of V. Recall that

$$\frac{p}{\tau} = \frac{\partial \ln g}{\partial V}.$$

Evaluate the partial differentiation, and we obtain that

$$pV = N\tau.$$

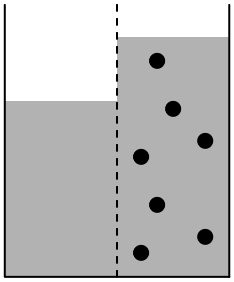
This is the familiar equation of state of the ideal gas.

A bag of air acts like a spring. The volume decreases as the pressure increases. The volume recovers when the pressure drops. This elasticity clearly does *not* result from bond stretching. It is known as **entropic elasticity**. If you detest any cryptic word as I do, just remember that air molecules will have more microstates if the volume is large. To confine the molecules in a small volume, you press.

Osmosis

A bag contains a liquid of volume *V*, with *N* particles dispersed in the liquid. The particles can be of any size. When the particles are molecules, we call them solutes. When the particles are somewhat larger, say from 10 nm to 10 μm, we call them colloids. The bag is immersed in a reservoir of the same liquid but without any such particles. The liquid is incompressible, but we can change the volume of the liquid inside the bag by allowing the molecules of the liquid to permeate through the skin of the bag. The particles dispersed in the bag, however, cannot permeate through the skin. Such a skin is **semi-permeable**.

Our glass of whine now has a rigid, semi-permeable wall in it. Water is on both sides of the wall, but alcohol is only on one side. Water molecules can diffuse across the wall, but not alcohol molecules. For the alcohol molecules to explore more volume, pure water has to diffuse into the solution. If this experiment were carried out the in the zero-gravity environment, infusion would continue until the pure water is depleted. In the gravitation field, the infusion stops when the pressure in the solution balances the tendency of the infusion. This pressure is known as the **osmotic pressure**.



The physics of this situation is analogous to the ideal gas, provided that the concentration of the particles is dilute. Every particle is free to explore the entire volume in the bag. The multiplicity function of the *N* particles in volume *V* scales as $g \propto V^N$. The liquid molecules permeate through the skin to drive the composite system (the bag and the reservoir) to reach equilibrium. Consequently, V is variable that enters the multiplicity function. Recall once again that

$$\frac{p}{\tau} = \frac{\partial \ln g}{\partial V}$$

Inserting the expression $g \propto V^N$, we obtain that

$$pV = N\tau$$

The particles insert on the skin of the bag the pressure p, known as the osmotic pressure.

In equilibrium, the pressure can be balanced in several ways. For example, for a spherical bag, the membrane tension can balances the osmosis pressure. One can also disperse particles in the reservoir, and make sure that the particles do not permeate into the bag. The pressures in the reservoir balances that in bag provided the concentrations of the particles are equal.

Thermometry

Appendix B of Kittel-Kroemer gives the basic information on thermometry, or the practice of registering temperature. An entry point to the literature is the proceedings of an international symposium held every few years under the title *Temperature, Its Measurement and Control in Science and Industry* (The Gordon McKay Library Call Number: QC 271. A6). Once we know how to measure the temperature, assuming that we know how to measure the change in the energy, we will know how to measure the change in the entropy. Recall that

$$\frac{1}{\tau} = \frac{\partial \sigma}{\partial U} \ .$$

The thermodynamics is thus placed on an experimental basis.

Conventional Wisdom about the Temperature. Bring two systems together and insulate them from the rest of the world. Make sure that the two systems interact with each other in only one way: energy can flow from one system to the other. Each system retains constant values of its volume, particles, and any other parameters that we may find to characterize its interaction with environment. The two systems are said to be in thermal contact. Note the following experimental observations:

If when two systems are in thermal contact, one system gives energy, and the other system gains energy, the system giving energy is said to have a higher temperature than the system gaining energy.

If when two systems are in thermal contact, neither of them gives or gains energy, the two systems are said to have equal temperatures. The two systems are said to be in thermal equilibrium.

Systems in thermal equilibrium with the same system are themselves in thermal equilibrium.

Empirical Temperature Scales. These ancient observations are sufficient to establish the concept of the temperature, and allow us to order the temperatures. These observations, however, leave the scale of the temperature arbitrary. One method to *define* a temperature scale is to list a sequence of phenomena that occur at different temperatures. For example, we could list, in the order of their melting points, a collection of pure substances: nitrogen, water, lead, aluminum, gold, etc. We could register a particular temperature by the name of the substance. We would know that the temperature “nitrogen” is lower than the temperature “water” because of the following experiments. We would first make system A in thermal equilibrium with the melting nitrogen, and system B in thermal equilibrium with the melting water. Upon bringing system A into thermal contact with system B, we would observe that system A gains energy, and system B loses energy. Similar experiments would convince us that the temperature “water” is lower than the temperature “lead”, “lead” is lower than “aluminum”, and “aluminum” is lower than “gold”.

All empirical temperature scales are variations of this basic theme. Some empirical temperature scale gives an air of scientific sophistication. But it’s just an air. There is no substance to such a claim. 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 would we do for other temperatures? Mercury is a liquid for this temperature range and beyond, sufficient for most purposes for our ancestors. Mercury expands as the temperature increases. We could define the change in the temperature to be proportional to the change in the volume of mercury. What would we do for high temperatures when mercury is a vapor, or low temperatures when mercury is a solid? We would switch to materials other than mercury, or phenomena other than thermal expansion.

The procedure would be cumbersome, acceptance of any empirical temperature scale would be slow, and patriotism may come into play. Where science is weak, politics is strong. However, there would be nothing inherently wrong with the practice; we would still communicate to each other about temperatures, once we had agreed on a scale, or on the conversion between scales. The practice was merely untidy.

The Thermodynamic Temperatures in Theory. Thermodynamics provides a far more elegant temperature scale. Let g be the number of quantum states of a closed system having energy U. The thermodynamic temperature τ is defined as

$$\frac{1}{\tau} = \frac{\partial \ln g}{\partial U} .$$

As we have seen, this definition conforms to the conventional wisdom about the temperature.

The Thermodynamic Temperatures in Practice. One method is to establish the thermodynamic temperature scale with the aid of model systems that are simple enough that one can count the number of quantum states. For example, an ideal gas obeys $pV = N\tau$. Say we want to know the temperature when water melts. We can use a container with a gas. Allow thermal contact between the freezing water and the gas container. When heat transfer stops between the water and the gas container, the measured value of pV / N is the temperature of the melting point of water. At very low and very high temperatures, the ideal gas thermometer is inapplicable. One can use other simple model systems, such as spins and black body radiation, to establish the thermodynamic temperatures.

Other Temperature Scales. All other temperature scales are defined by the thermodynamic temperature scale.

The Kelvin temperature scale *T* is defined by (1) *T* is proportional to τ, namely, $\tau = kT$, and (2) the triple point of pure water is *assigned* the number $T_t = 273.16\mathrm{K}$, exactly. The Boltzmann constant *k* converts the two temperature scales. Its experimental determination amounts to measuring the fundamental temperature of the triple point of pure water. The experimental value of the Boltzmann constant is $k = 1.38 \times 10^{-23}\ \mathrm{J/K}$. The conventional entropy relates to the fundamental entropy as $S = k\sigma$. This recovers the commonly used relations: $S = k \ln g$ and $1/T = \partial S / \partial U$. The conversion factor: the temperature 1K corresponds to $0.863 \times 10^{-4}\ \mathrm{eV}$.

It is hard to have any respect for a temperature scale that just make the triple point of water have an ugly reading. The pretentious name “absolute temperature” is such an abuse of language. It makes George W. Bush sound sincere. The Boltzmann constant *k* has no fundamental significance. For *any* result to have physical meaning, the product *kT* must appear together, and the ratio *S/k* must appear together. The world will be rid of the clutter if we simply call $\tau = \left(\partial \ln g / \partial U\right)^{-1}$ the temperature, and $\sigma = \ln g$ the entropy. But, then, an engineer has to be a team player. I'll live with a piece of clutter if it makes the team happy. A question still remains. Why is the team happy with it?

The Celsius temperature scale, *C*, relates to the Kelvin scale by $C = T - T_0$, where T_0 is the freezing point of water. The experimental value is $T_0 = 273.15\mathrm{K}$. I can see the merit to use a temperature scale like the Celsius temperature in daily life. It feels so much more pleasant to hear that today's temperature is 20 C than 0.0253 eV.

The Fahrenheit temperature scale, *F*, relates to the Celsius scale by $F = \frac{180}{100}C + 32$.

Our melting-point temperature scale can be mapped to the Kelvin scale or the fundamental scale as follows:

Melting-point scale	Kelvin scale	Fundamental 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

References

Kittel C, Kroemer H: *Thermal Physics*. W.H. Freeman and Company, San Francisco, 1980. This lecture follows the initial chapters of the book. The book develops the algorithm of thermodynamics more clearly than other books I've looked at. It also describes a collection of classical thermodynamic phenomena. One complaint one might have about this book is that it gives no indication how people today analyze thermodynamic phenomena by a combination of experiments and computation, i.e., how the labor is

divided. The book may give you an impression that the subject is mostly theoretical, and all you do is to calculate the multiplicity function or the partition function for various systems. For example, after reading this book, you may still be clueless about how people today develop phase diagrams for multicomponent systems. Then, thermodynamics is a big subject, and a book can only cover so much.

Gibbs, J.W.: *The Collected Works of J. Willard Gibbs*. Longmans, Green and Co., New York, 1928. Gordon McKay Library call number: TJ 265.57. Article II is a gem (A method of geometric representation of the thermodynamic properties of substances by means of surfaces, published in 1873. 20 pages). Here Gibbs accepted basic thermodynamics, and went on to develop its consequences. I wonder why I cannot find his thermodynamic surface anywhere in today's textbooks. It was recounted (on p. xvi) that Maxwell, in the last years of his life, spent considerable time in carefully constructing, with his own hands, a model of this surface, a cast of which, very shortly before his death, he sent to Professor Gibbs. Reading Gibbs's Article II was a revelation to me. I have also tried to read his Article III (On the equilibrium of heterogeneous substances, published in 1878. 300 pages), but have never been successful. For a topic attributed to him, I have to learn it elsewhere, and return to Article III only to see what he wrote about it. For example, on page 315, Gibbs distinguished the surface energy and the superficial tension (now known as the surface stress).

Maxwell, J.C.: *Theory of Heat*. The book is reissued recently by Dover. The beginning chapters gave a lucid account of how to register temperature and heat. Maxwell wrote this book for evening schools. There are few equations, but many helpful discussions.

Callen, H.B., *Thermodynamics and Introduction to Thermostatistics*. John Wiley & Sons, 1985.

I liked this book in my late twenties, but not any more. You may be at the right age to like it now.