

CHAPTER 1

Thermostatistics

1. Context and origins

The object of thermodynamics is to describe “macroscopic” systems (systems that are extended in space) that vary slowly in time. Macroscopic systems are formed by a huge number of microscopic particles; for instance, a gallon of gas contains about 10^{23} molecules. But thermodynamics does not depend on the underlying nature of the system — it was actually pioneered before the atomic hypothesis was confirmed, and before quantum phenomena were discovered. The links between the micro- and the macroscopic worlds, and how the former determines the latter, are the subject of statistical mechanics. Within thermodynamics, *thermostatistics* is the physical theory that deals with equilibrium states, and with transformations where time is not an explicit variable; it ignores the *flows*, i.e. the time derivatives of quantities such as the energy or the number of particles.

The origins of thermodynamics go back to the XIXth century and the industrial revolution. This was the age of steam engines, which convert heat energy into work. The law of conservation of energy implies that no more work can be produced than heat is available. The challenge was to design an engine that could convert all the energy obtained by burning coal into work. But physicists came to realize that the efficiency of steam engines was not only limited by technical nuisances such as losses due to friction, but there were fundamental constraints as well. A new basic quantity emerged, that is hard to grasp although it is present in everyday life: the *entropy*.

The range of applicability of thermodynamics is enormous, so it makes sense to develop it as a general and abstract theory. It helps, however, to have in mind specific examples where the theory applies. The best example is a gas, where many particles occupy a certain domain in space and possess a certain energy. It is a remarkable fact, though common sense experience, that temperature characterizes the state of the gas. Temperature is a genuine thermodynamic quantity that does not occur in microscopic theories such as classical or quantum mechanics. The central part of thermodynamics is the “second law” that claims the existence of a notion: the entropy. It is a *concave function* and all thermodynamic quantities derive from it.

Everybody has thought about the following question: Why do we remember the past but cannot foretell the future? But did anyone think about this one: Why do we eat baked food rather than raw material? Thermodynamics provides important elements of answer.

Any process satisfies a principle of energy conservation: the gain of energy by the system is equal to the loss of energy by the environment, and conversely. But a cube of ice in a glass of martini will always melt and will not get bigger, although

conservation of energy allows it (with the martini getting hotter). Such empirical facts were formalized into the following two principles:

- Kelvin¹: *There exists no thermodynamic transformation whose sole result is to convert heat from a heat reservoir to work.*
- Clausius²: *There exists no thermodynamic transformation whose sole result is the transfer of heat from a cold reservoir to a hotter reservoir.*

These principles can be shown to be equivalent with one another, modulo a few reasonable assumptions. They constitute early versions of the second law of thermodynamics, which is much more precise.

2. Thermodynamic systems

We start with the notion of a *simple thermodynamic system*, such as a gas in equilibrium. It is characterized by a finite number of *extensive* parameters such as the energy U , the volume V , and the number of moles (or the number of particles) N . One can be more abstract and introduce the state space of a simple thermodynamic system to be a convex subset $\Sigma \subset \mathbb{R}^n$. Here, the number of parameters n is a small number, typically 1, 2, or 3. We choose to be more explicit here and consider (U, V, N) . In any case, generalizations are straightforward.

A composite system consists of several simple ones, and its state space is the cartesian product $\Sigma = \Sigma_1 \times \Sigma_2 \times \dots$. The subsystems can be made to interact, and to exchange energy (“thermal contact”), or volume (“through a piston”), or particles (“permeable membrane”). The total energy, total volume, or total number of particles is constant. In addition, systems can be brought into contact with “reservoirs”, that can be thought of as infinite simple systems. Systems interacting with reservoirs are called “open”. We shall see that a steam engine is an open system in contact with at least two different reservoirs. Thermostatistics does not attempt to describe how exchanges take place, but only what is exchanged.

Even though time is not an explicit variable in thermostatistics, we are interested in situations where the system goes through a succession of different equilibrium states. This is referred to as a “thermodynamical process”. A process is **quasistatic** if the transformation is so slow as to always leave the state in equilibrium. A quasistatic process is described by a continuous curve in Σ .

3. Laws of thermodynamics

History has endowed thermodynamics with four laws, numbered 0 to 3. The formulation of these laws varies according to the authors. The zeroth law claims the existence of equilibrium states. The first law states that thermodynamic systems have an *inner energy* that depends solely on the state of the system. As we will see in statistical mechanics, the inner energy may be equal to the sum of kinetic and interaction energies of atoms, but on the level of thermodynamics we should not discuss the microscopic nature of the system. The zeroth and first laws were implicitly used in the section above about parametrization of thermodynamic systems.

¹William Thomson, Lord Kelvin (1824–1907), an Irish-Scottish mathematical physicist. He suggested the absolute temperature scale. He also worked on electricity and on the transatlantic telegraph, and he used thermodynamics to estimate the age of the Earth (100 million years).

²The German *Rudolf Julius Emanuel Clausius* (1822-1888) was the first to propose, in 1854, that Q/T was a relevant physical quantity. He named it “entropy” in 1865, after the Greek work “trope” for “transformation”.

The third law is about properties of the entropy in the “ground state” (the state of lower energy). Its relevance is not too broad and it can be ignored here. The second law was pioneered by Gibbs³ and it can be formulated in modern language as follows.

*There exists a function S , called the **entropy**, with the following properties:*

- *In a simple thermodynamic system, the entropy is a differentiable, concave, extensive function of U, V, N ; it is increasing in U and V .*
- *The entropy of a composite system is the sum of entropies of each simple subsystem.*
- *A transformation is impossible if the entropy of the system decreases.*

For a simple system, extensivity means that $S(\alpha U, \alpha V, \alpha N) = \alpha S(U, V, N)$ for any $\alpha \geq 0$ — if the system is doubled, so is its entropy. The second claim is a more general form of extensivity. The differentiability property is important in view of phase transitions. Within thermodynamics the second law is an assumption; its derivation from the microscopic laws of motion is the subject of statistical mechanics. In summary, the entropy is concave and extensive, and it always increases in time.

It follows from the second law that $S(U, V, N)$ is invertible with respect to U , and that the inverse function $U(S, V, N)$ is differentiable, convex, extensive, increasing in S and decreasing in V . We introduce the following thermodynamic quantities:

- the **(absolute) temperature** $T = \left. \frac{\partial U}{\partial S} \right|_{V, N}$;
- the **pressure** $p = - \left. \frac{\partial U}{\partial V} \right|_{S, N}$;
- the **chemical potential** $\mu = \left. \frac{\partial U}{\partial N} \right|_{S, V}$.

This is elegantly written in differential form notation

$$\boxed{dU = T dS - p dV + \mu dN.} \quad (1.1)$$

Thus a simple system is entirely described by the function $S(U, V, N)$, or the function $U(S, V, N)$. Given U, V, N , the parameters T, p, μ are unambiguously determined. The converse is partly true. If U is *strictly* convex, then S may be replaced with T , V with p , and N with μ . But if U has a linear part with respect to S , temperature does not fully characterize the system; an example is H_2O at 0°C , that can be in the form of ice or water, or in a coexistence of both.

The definition for the pressure shows that it is related to the mechanical notion of force over area. We shall see below that the temperature has the well-known property that two systems are in thermal equilibrium iff their temperatures are equal. The meaning of the chemical potential may be best understood in the case

³Josiah Willard Gibbs (1839–1903), the first doctor in engineering in the United States. He got professorship in Yale in 1871 and wrote his first paper in 1873. According to Gibbs, “a mathematician may say anything he pleases, but a physicist must be at least partially sane”.

of electric devices, where particles are electrons; μ is then equal to the potential difference multiplied by the elementary charge. From (1.1) we also have the relation

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN.$$

Consider now a simple system where the amount of matter N is fixed; $dU = TdS - pdV$. Let γ be a (piecewise smooth) curve in Σ from (S_i, V_i) to (S_f, V_f) , thus corresponding to a quasistatic process. The **work** absorbed by the system is defined by

$$\Delta W = - \int_{\gamma} pdV. \quad (1.2)$$

To understand this notion, think of a piston compressing a gas. It almost matches the engineers' notion of work — up to the sign. For these practical persons, the work is the mechanical energy given by the system, that can be used. But we physicists do not fear the occurrence of a minus sign, and so the work is the mechanical energy given by the environment to the system. The integral in (1.2) depends not only on the initial and final states, but on the process γ as well. Besides work, energy is exchanged as **heat**, and we define

$$\Delta Q = \int_{\gamma} TdS. \quad (1.3)$$

The change of the total energy is thus given by

$$\Delta Q + \Delta W = \int_{\gamma} dU = U(S_f, V_f) - U(S_i, V_i). \quad (1.4)$$

The right side does not depend on γ . Definitions (1.2) and (1.3) remain valid for systems with varying amount of matter, but an extra term shows up in the left side of (1.4).

Full knowledge of a thermodynamic system is achieved only once $S(U, V, N)$ is given by an explicit expression. The second law claims that S exists and satisfies certain qualitative properties. Extra relations need to be provided that are specific to the system. We shall see the case of the ideal gas in Section 4. The job of the thermodynamicist is to use these relations and compute the entropy. The following quantities are usually well understood: energy, volume, temperature, pressure. So the work, then the heat, can be identified. One can use the following relation to compute the entropy:

$$S(U_f, V_f) - S(U_i, V_i) = \int_{\gamma} \frac{\delta Q}{T}. \quad (1.5)$$

Here, γ is any (piecewise smooth) curve between (U_i, V_i) and (U_f, V_f) . This formula follows from (1.3).

Suppose that two systems are brought in “thermal contact”: they can exchange heat, but geometric variables are held fixed and there is no exchange of work (we also suppose that numbers of particles in both systems are constant). By the extensivity of entropy, we have

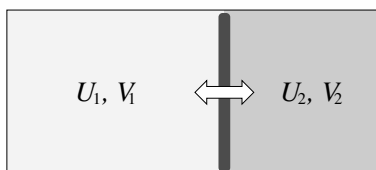
$$S(U_1, U_2) = S_1(U_1) + S_2(U_2).$$

The total energy $U = U_1 + U_2$ is constant. The maximum of S is given by $\frac{\partial S}{\partial U_1} = 0$, i.e.

$$\frac{\partial S_1}{\partial U_1}(U_1) - \frac{\partial S_2}{\partial U_2}(U - U_1) = 0.$$

In other words, the condition for equilibrium is $T_1 = T_2$! (We can easily check that it corresponds to a maximum; the second derivative is $\frac{\partial^2 S}{\partial U_1^2} = \frac{\partial^2 S_1}{\partial U_1^2} + \frac{\partial^2 S_2}{\partial U_2^2} \leq 0$ by concavity of S_1 and S_2 .)

Consider now a (composite) system that consists of two gases exchanging heat and work:



The total energy $U = U_1 + U_2$ and the total volume $V = V_1 + V_2$ are constant. What is the final equilibrium state? A method is to solve the evolution equation, and to look at the behavior of its solution as the time goes to infinity. It is usually impractical, however! Another method is provided by the second law. We maximize

$$S_1(U_1, V_1) + S_2(U_2, V_2) = S_1(U_1, V_1) + S_2(U - U_1, V - V_1).$$

Setting the derivative with respect to U_1 to zero yields $\frac{1}{T_1} - \frac{1}{T_2} = 0$: the temperatures are equal. Setting the derivative with respect to V_1 to zero yields $\frac{p_1}{T_1} - \frac{p_2}{T_2} = 0$: the pressures are equal. This solution is amazingly simple.

This can be generalized to arbitrary composite systems. Using Lagrange multipliers, we need to maximize the functional

$$\mathcal{S}(\{U_i\}, \{V_i\}, \alpha, \beta) = \sum_{i=1}^n S_i(U_i, V_i) - \alpha \sum_{i=1}^n U_i - \beta \sum_{i=1}^n V_i.$$

Then $\frac{\partial \mathcal{S}}{\partial U_i} = \frac{1}{T_i} - \alpha = 0$: all temperatures are equal; and $\frac{\partial \mathcal{S}}{\partial V_i} = \frac{p_i}{T_i} - \beta = 0$: all pressures are equal.

The same argument extends to systems that exchange particles. A further condition for equilibrium is that chemical potentials are equal.

Another important consequence of concavity of S is that equilibrium states are *stable*. Consider a system with energy U and volume V . Can it break into n pieces of energies U_1, \dots, U_n and volumes V_1, \dots, V_n ? It can only if the entropy increases. However, concavity means that

$$S\left(\frac{U_1 + \dots + U_n}{n}, \frac{V_1 + \dots + V_n}{n}\right) \geq \frac{1}{n} \sum_{i=1}^n S(U_i, V_i).$$

Extensivity implies that $S(\alpha U, \alpha V) = \alpha S(U, V)$. We find

$$S(U, V) \geq \sum_{i=1}^n S(U_i, V_i).$$

Breaking the system into pieces decreases the entropy, so this never happens!

4. The ideal gas

It was observed in the XIXth century that many gases display the same behavior. Experiments and educated guesses led to the following formulæ:

- The **ideal gas law**: $pV = nRT$, where n is the number of “moles” of gas and the *ideal gas constant* has value $R = 8.314 \text{ J/K}\cdot\text{mol}$. Only later was it realized that gases consist of atoms or molecules. The **Avogadro number** $N_0 = 6.022 \cdot 10^{23}$ is defined as the number of atoms with mass number M that weigh M grams (the relation being exact for ^{12}C , and approximate for other elements). Introducing **Boltzmann constant**

$$k_B = 1.3807 \cdot 10^{-23} \text{ J/K},$$

the ideal gas law can be rewritten $pV = Nk_B T$, where N denotes the number of particles.

- $U = C_V T$, where C_V is the heat capacity at constant volume. Its general definition is $C_V = \left. \frac{dQ}{dT} \right|_{V,N} = \left. \frac{\partial U}{\partial T} \right|_{V,N}$. It is due to Joule, who understood that the energy does not depend on V ; he then found that it is linear in T .
- $C_V = \frac{3}{2}nR$ for a monoatomic gas such as Ar, $C_V = \frac{5}{2}nR$ for a diatomic gas such as N_2 or O_2 . This the **law of Dulong and Petit**.

The entropy of the ideal gas is computed in the exercises. The result is

$$S(U, V, N) = C_V \log \frac{U}{N} + Nk_B \log \frac{V}{N} + S_0. \quad (1.6)$$

Since C_V is extensive, we see that S is extensive indeed.

This expression can be considered the fundamental equation for the ideal gas. The function $S(U, V, N)$ is consistent with the second law. We can compute the change of entropy for an ideal gas that expands from a volume V_1 to a bigger volume V_2 along an isotherm. We obtain $\Delta S = Nk_B \log \frac{V_2}{V_1}$ and it is positive indeed.

A process where no heat is exchanged is called **adiabatic**. In a simple system the entropy must be constant. From (1.6), we see that adiabats in the (p, V) diagram are described by curves where $U^{C_V} V^{Nk_B} = \text{const}$. This is equivalent to

$$pV^\alpha = \text{const} \quad \text{with} \quad \alpha = 1 + \frac{Nk_B}{C_V} > 1.$$

Notice that $\alpha = \frac{5}{3}$ for a monoatomic gas and $\alpha = \frac{7}{5}$ for a diatomic gas.

Finally, let us introduce the heat capacity at constant pressure, $C_p = \left. \frac{\delta Q}{dT} \right|_{p,N}$. Along a path with constant pressure, the change of work is

$$\Delta W = - \int_\gamma p dV = -p \Delta V = -Nk_B \Delta T. \quad (1.7)$$

By conservation of energy and the law of Dulong and Petit, we get

$$\Delta Q = \Delta U - \Delta W = (C_V + Nk_B) \Delta T. \quad (1.8)$$

It follows that $\frac{C_p}{C_V} = 1 + \frac{Nk_B}{C_V} = \alpha$.

5. Legendre transform

Convexity is a fundamental property of thermodynamic potentials and it is no surprise that the Legendre transform plays an important rôle, as it maps convex functions to convex functions. Recall that a function $f : D \rightarrow \mathbb{R}^d$ is **convex** if, for any $x, y \in D$ and any $\alpha \in [0, 1]$,

$$f(\alpha x + (1 - \alpha)y) \leq \alpha f(x) + (1 - \alpha)f(y). \quad (1.9)$$

Here, the domain D of f is assumed to be a convex set. We need to allow functions to take the value $+\infty$. Let $D_{\text{ess}}(f)$ be the **essential domain** of f ,

$$D_{\text{ess}}(f) = \{x \in \mathbb{R}^n : f(x) < \infty\}. \quad (1.10)$$

One can show that any convex function is continuous in the interior of its essential domain (exercise).

The **Legendre transform**⁴ of a function $f : \mathbb{R}^n \rightarrow \mathbb{R} \cup \{\infty\}$ is the function $f^* : \mathbb{R}^n \rightarrow \mathbb{R} \cup \{\infty\}$ defined by

$$f^*(y) = \sup_{x \in \mathbb{R}^n} [x \cdot y - f(x)]. \quad (1.11)$$

The geometric interpretation in one dimension is illustrated in Fig. 1.1.

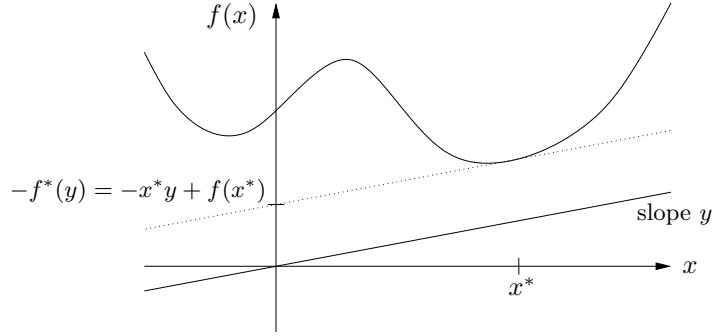


FIGURE 1.1. Geometric interpretation of the Legendre transform.

The Legendre transform of any function is convex:

$$\begin{aligned} f^*(\alpha y + (1 - \alpha)z) &= \sup_{x \in \mathbb{R}^n} [x \cdot (\alpha y + (1 - \alpha)z) - f(x)] \\ &= \sup_{x \in \mathbb{R}^n} [\alpha x \cdot y - \alpha f(x) + (1 - \alpha)x \cdot z - (1 - \alpha)f(x)] \\ &\leq \alpha \sup_{x \in \mathbb{R}^n} [x \cdot y - f(x)] + (1 - \alpha) \sup_{x \in \mathbb{R}^n} [x \cdot z - f(x)] \\ &= \alpha f^*(y) + (1 - \alpha)f^*(z). \end{aligned}$$

Further, we can check that $f^{**} = f$ whenever f is convex. f^{**} is the convex hull of f otherwise. Linear pieces become cusps and conversely; this is illustrated in Fig. 1.2.

Suppose that f is C^1 and that $x^* = x^*(y)$ is a maximizer for (1.11). It satisfies the equation $y = \nabla f(x^*)$, and we have $f^*(y) = (x^*, y) - f(x^*)$. Suppose that f^* is also C^1 ; it follows from this equation that

$$f'(x) = y \quad \iff \quad f^{*'}(y) = x.$$

⁴Adrien-Marie Legendre, 1752–1833. By the time the French revolution took away his wealth, he had established sufficient reputation in mathematics and he could carry on his work.

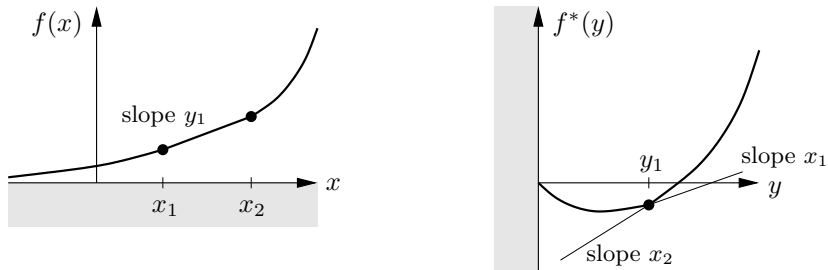


FIGURE 1.2. A convex function and its Legendre transform. f has an horizontal asymptote as $x \rightarrow -\infty$, and a linear piece with slope y_1 between x_1 and x_2 . $f^*(y) = \infty$ for $y < 0$ and it has a cusp at y_1 ; its derivative jumps from x_1 to x_2 .

6. Thermodynamic potentials

Functions $U(S, V, N)$ or $S(U, V, N)$ are two examples of **thermodynamic potentials**. They provide full knowledge of the physical system. However, a parameter such as the entropy is difficult to deal with. Temperature is more natural from an experimental point of view. As for statistical mechanics, we shall see that three thermodynamic potentials play an equally important role: the entropy S , the free energy F , and the grand-canonical potential G . While S is physically more justified, we shall see that F or G are much easier to deal with.

Thermodynamic potentials are related by Legendre transforms. Notice that any physical system is entirely determined by *one* potential.

The (**Helmholtz**) **free energy** $F(T, V, N)$ is defined by

$$F(T, V, N) = -\sup_S [TS - U(S, V, N)].$$

It is concave in T and convex in (V, N) . Technically, $F(T, V, N) = -\infty$ if $T < 0$ because $\frac{\partial U}{\partial S} \geq 0$, so negative T can be discarded. It follows from differentiability of U that the supremum is reached for $S = S(T, V, N)$ that satisfies

$$\left. \frac{\partial U}{\partial S}(S, V, N) \right|_{V, N} = T. \quad (1.12)$$

We then have $F(T, V, N) = U(S(T, V, N), V, N) - TS(T, V, N)$. It follows that whenever F is differentiable, we have

$$\left. \frac{\partial F}{\partial T} \right|_{V, N} = \left. \frac{\partial U}{\partial S} \right|_{V, N} \left. \frac{\partial S}{\partial T} \right|_{V, N} - S - T \left. \frac{\partial S}{\partial T} \right|_{V, N} = -S.$$

We used (1.12). Similarly,

$$\left. \frac{\partial F}{\partial V} \right|_{T, N} = -p, \quad \left. \frac{\partial F}{\partial N} \right|_{T, V} = \mu$$

This is best summarized with the differential form:

$$dF = -SdT - p dV + \mu dN.$$

The free energy is convenient for experiments where temperature is a natural parameter. Further, the change of free energy along *isotherms* is equal to the change

of work (assuming N to be constant as well). Let us mention three more formulæ for the record:

$$\begin{aligned} U(S, V, N) &= \sup_T [TS + F(T, V, N)], \\ F(T, V, N) &= \inf_U [U - TS(U, V, N)], \\ S(U, V, N) &= \inf_{T \neq 0} \frac{1}{T} [U - F(T, V, N)]. \end{aligned}$$

The **enthalpy** is defined by

$$H(S, p, N) = \inf_V [pV + U(S, V, N)].$$

It is concave in p and convex in (S, N) . We can check that

$$dH = T dS + V dp + \mu dN.$$

The enthalpy is useful in chemistry where chemical reactions often take place at constant pressure and constant temperature. The change in enthalpy is associated with the heat taken by or given to the system.

Mostly relevant to statistical mechanics, the **grand-canonical potential** is defined by

$$G(T, V, \mu) = - \sup_{S, N} [TS + \mu N - U(S, V, N)].$$

It is concave in (T, μ) and convex in V . It can be associated with the pressure thanks to an argument that is more intriguing than intuitive. Consider the densities $s = \frac{S}{N}$, $u = \frac{U}{N}$, $\rho = \frac{N}{V}$, $v = \frac{V}{N} = \rho^{-1}$. Inserting them in the equation above we obtain

$$\frac{G}{V} = - \sup_{s, \rho} \rho [Ts + \mu - u(s, \rho^{-1})]. \quad (1.13)$$

The equations for the maximum are $\frac{\partial u}{\partial s} = T$ and

$$Ts + \mu - u(s, \rho^{-1}) + \rho^{-1} \frac{\partial u}{\partial v} = 0. \quad (1.14)$$

Recall that $\frac{\partial u}{\partial v} = -p$. It follows from (1.13) and (1.14) that

$$\frac{G(T, V, \mu)}{V} = -p(T, \mu).$$

We also have

$$G(T, V, \mu) = \inf_N [F(T, V, N) - \mu N].$$

Notice that thermodynamic potentials are C^1 functions of extensive quantities, and they are strictly convex in terms of intensive quantities. This is the mathematical aspect of phase coexistence.

7. Phase transitions

A phase transition is a dramatic change in the state of the system under a tiny modification of the external conditions. Typical examples are the transitions from solid to liquid and liquid to gas. Others include magnetization, Bose-Einstein condensation, superconductivity, etc...

Let us discuss the melting of ice in some details. Let us start with ice below 0°C , and let us give it heat. The temperature of the system increases but it remains ice until 0°C . Now the temperature remains at 0°C while the system progressively turns into water. Once all ice has melted the temperature rises anew. Throughout this process the pressure and number of moles stay constant, so the natural thermodynamic potential is the enthalpy $H(S, p, N)$. Recall that $dS = \frac{\delta Q}{T}$. Then S increases as heat is pumped into the system.

Let H_1, H_2 be the enthalpy of ice and water at 0°C , respectively. The enthalpy for the system with αN moles in ice and $(1-\alpha)N$ moles in water is $\alpha H_1 + (1-\alpha)H_2$ by extensivity. The enthalpy therefore looks like the graph in Fig. 1.3.

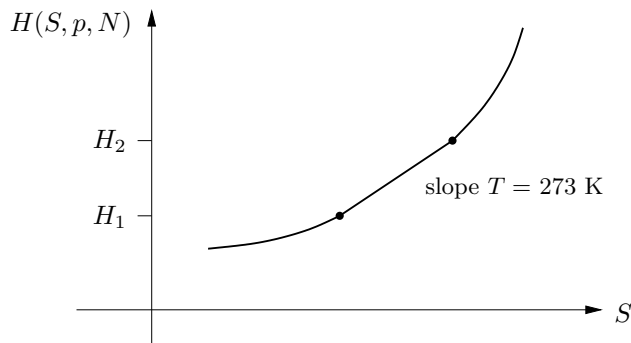


FIGURE 1.3. Qualitative graph for the enthalpy of H_2O at atmospheric pressure.

The flat piece in Fig. 1.3 signals *phase coexistence* of ice and water. The Legendre transform of H with respect to S is the Gibbs potential (it depends on T, p, N) and the phase transition is marked by a cusp.

It is a natural fact that almost all substances exist in three possible states — solid, liquid, and gas. Why Nature is so remains a mystery. Phase diagrams look similar and are sketched in Fig. 1.4.

8. Processes and engines

In words, a **process** or **transformation** is a succession of states ordered chronologically. A process is **quasistatic** if the system is in equilibrium throughout the whole process; mathematically, a quasistatic process is represented by a (piecewise smooth) curve $\gamma : I \rightarrow \Sigma$, where $I \subset \mathbb{R}$ is an interval. The parametrization of γ , which represents the speed of the process, is not relevant in thermostatics, where flows are not taken into account. If γ is a closed curve, the process is called a **cycle**.

We say that the process is **adiabatic** if there is no exchange of heat, i.e. if the entropy of each subsystem is constant. We say that the process is **reversible** if the total entropy is constant. Any adiabatic process is reversible, but the converse is

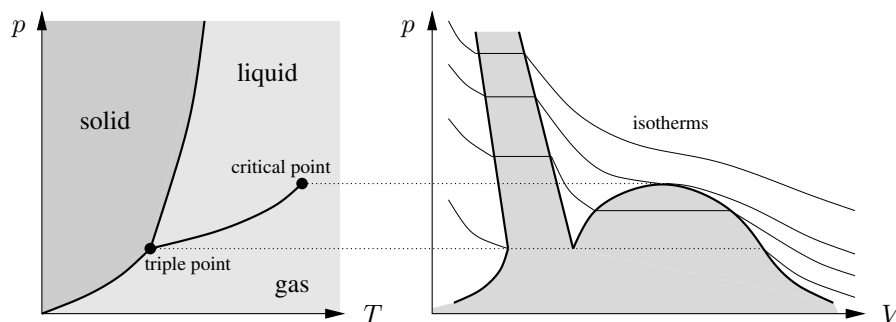


FIGURE 1.4. Qualitative phase diagram for most substances.

not true. For instance, consider the expansion of a gas in contact with a thermal reservoir; the process is not adiabatic because heat is exchanged. But the gain of entropy of the gas, $\frac{\Delta Q}{T}$, is just the negative of the loss of entropy of the reservoir, $-\frac{\Delta Q}{T}$. This process is then reversible.

Intuitively, an **engine** is a device that produces work out of heat. In thermostatics, an engine is a system that exchanges heat and work with reservoirs. We consider here a simple system connected to two thermal reservoirs, schematically depicted in Fig. 1.5 (a). One reservoir is the environment, and another reservoir is obtained by burning some material (coal, gas, nuclear fuel, etc...). The engine is described by a cycle γ in the state space of the simple system.

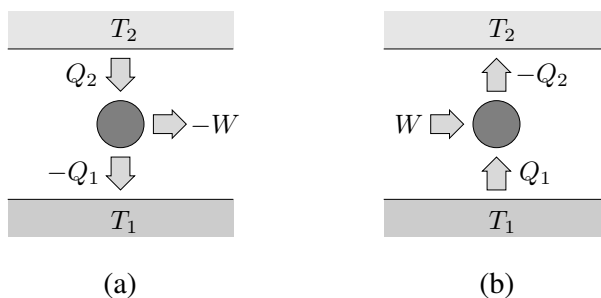


FIGURE 1.5. Schematic depiction of (a) an engine and (b) a heat pump. T_1 is usually the temperature of outside air. For the engine, $T_2 > T_1$ is the temperature obtained by burning some material. For the heat pump, T_2 may be the temperature inside the house.

In all applications, $Q_2 > 0$ is the heat that is given to the system in one cycle. $Q_1 < 0$ is the waste, so we ignore it. The work W is the useful form of energy. It is natural to define the **efficiency** of our engine by

$$\eta = \frac{-W}{Q_2}. \quad (1.15)$$

From conservation of energy, $-W = Q_2 + Q_1$, and we have $\eta \leq 1$ as expected. But the second law gives us more. Denoting T the temperature of the simple system,

that varies along the cycle, the gain in entropy in one cycle is

$$\Delta S = \underbrace{\int_{\gamma} \frac{\delta Q_1}{T} + \int_{\gamma} \frac{\delta Q_2}{T}}_{=0} - \frac{Q_1}{T_1} - \frac{Q_2}{T_2}. \quad (1.16)$$

The two integrals represent the change of entropy of the simple system; it is zero because the system is back to its initial state after a cycle. Now $\Delta S \geq 0$; then $-\frac{Q_1}{Q_2} \geq \frac{T_1}{T_2}$, and

$$\eta = 1 + \frac{Q_1}{Q_2} \leq 1 - \frac{T_1}{T_2}. \quad (1.17)$$

It is worth emphasizing that this limit for the efficiency does not arise from technological considerations, but from fundamental laws of physics! The limiting efficiency is reached in a reversible process where the total entropy is constant. At any given point in the cycle, the change of entropy is

$$dS = \left(\frac{1}{T} - \frac{1}{T_1}\right)\delta Q_1 + \left(\frac{1}{T} - \frac{1}{T_2}\right)\delta Q_2. \quad (1.18)$$

(Recall that $\delta Q_1 \leq 0$, since $T_1 \leq T$.) It is zero only if $\delta Q_i = 0$ (adiabat), or if $T = T_i$ (isotherm). The optimal cycle is called the **Carnot cycle** and consists of two adiabats and two isotherms, see Fig. 1.6 (a). It cannot be realized in practice, however, at least not in a finite time. The problem is with the isotherms, as a difference in temperature is necessary to get a heat flow — which results in a strictly positive entropy production.

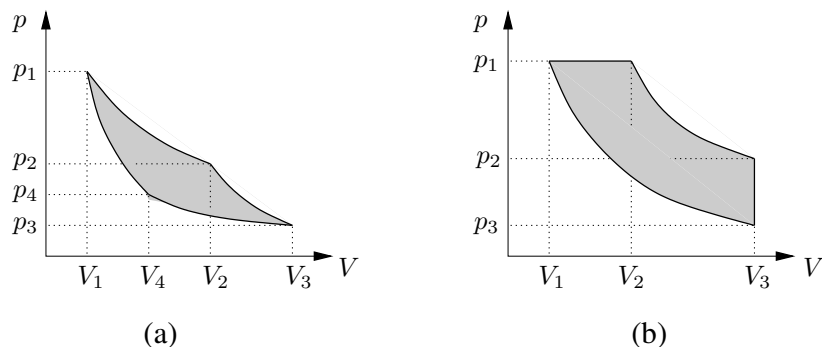


FIGURE 1.6. (a) The Carnot cycle has two adiabats and two isotherms. (b) The Diesel cycle has adiabats between a process at constant pressure and a process at constant volume.

An engine that can be realized is the Diesel engine, increasingly popular for powering cars. Its cycle is shown in Fig. 1.6 (b). Another interesting concept is the **heat pump**, schematically depicted in Fig. 1.5 (b). The idea is to provide work to the system so that heat is forced from the colder to the hotter reservoir. This process is used in refrigerators (where T_2 is the room temperature) or in heating systems (where T_1 is the outside temperature). A heat pump is a much better heating device than, say, a resistor that gets heat from an electric current: a heat pump has a *coefficient of performance* $\eta = \frac{-Q_2}{W}$ greater than 1, typically 3-4 in commercial realizations.

Exercise 1.1. Compute the entropy of the ideal gas. It helps to work with the densities $s = \frac{S}{N}$, $u = \frac{U}{N}$, $v = \frac{V}{N}$, $c_V = \frac{c_V}{N}$.

Exercise 1.2. Let f be a convex function. Show that f is continuous in the interior of its essential domain.

Exercise 1.3. Let f be a convex function in dimension $n = 1$. Show that, at every point x of the interior of $D_{\text{ess}}(f)$, the left and right derivatives exist, and satisfy

$$D_- f(x) \leq D_+ f(x).$$

Exercise 1.4. Generalize the result of the exercise above in higher dimension. Namely, define the directional derivative of f in the direction q by

$$D_q f(x) = \lim_{h \searrow 0} \frac{f(x + hq) - f(x)}{h}.$$

Suppose that f is convex and that $x \in D_{\text{ess}}(f)$. Show that $D_q f(x)$ exists for all q , and that

$$-D_{-q} f(x) \leq D_q f(x).$$

Exercise 1.5. The cycle of the Diesel engine is depicted in Fig. 1.6 (b). Explain why it goes clockwise. Show that the efficiency is given by the following formula, that depends solely on geometric variables of the engines:

$$\eta = 1 - \frac{1}{\alpha} \frac{\left(\frac{V_2}{V_3}\right)^\alpha - \left(\frac{V_1}{V_3}\right)^\alpha}{\frac{V_2}{V_3} - \frac{V_1}{V_3}}.$$

Here, α is the exponent for adiabatic compression; $\alpha = 1.4$ for air, which is essentially diatomic.

Exercise 1.6. Compute the optimum coefficient of performance of a heat pump. (Use a Carnot cycle.)