Chapter 2
Structure of Macroscopic Thermodynamics

Macroscopic thermodynamics deals with "energy" and materials stocked in and exchanged by the system. The system can be surrounded by environment(s) and external system(s). When the exchange of energy or materials takes place, several important constraints, i.e., the laws of thermodynamics are imposed. Thermodynamics allows for different point of views: view from the system, from the external system, or from the environment. Thermodynamics is also relevant for the study of (free) energy conversion, the thermal analysis of chemical reactions and phase transitions.

Stochastic energetics combines the description of stochastic processes and thermodynamic processes. In order to prepare for the main chapters (from Chap. 4) this chapter reminds the readers of the basic concepts and relations of thermodynamics and introduces the terminology and notations of thermodynamics. This chapter does not cover all the aspects of thermodynamics, but it focuses on those aspects of thermodynamics which will be relevant in later chapters. Those who know macroscopic equilibrium thermodynamics well may skip this chapter and come back when necessary.

2.1 Basic Concepts of Thermodynamics

2.1.1 * Terminology of Thermodynamics Includes System, Environments, and External System

The basis of thermodynamics is empirical. The definitions of elementary concepts rely on empirical or undefined notions. One can axiomatize it [1, 2] but cannot derive it. The framework of thermodynamics is supposed to be asymptotically exact for the large homogeneous system based on experiments.

> *System:* Of the whole world, a part which is properly cut out is called the system. In this chapter we suppose that a system contains a macroscopic number (say, $\sim 10^{23}$) of constituting elements of the same kind like particles, spins, etc. If a system is divided into more than one part by some criterion, each

part is called a subsystem. A system having no contact with any other system is called isolated system.

Internal energy of a system: If one can access the microscopic Hamiltonian of the system, or if one can observe or calculate the mechanical energy, either classical or quantum, then we naturally identify this energy as the internal energy of the macroscopic thermodynamics.

Extensive variables: When a system and its identical copy are combined to make a new system, certain variables take the values twice as large as the original ones before combining with its copy. Such variables are called extensive variables. For a system consisting of single-component particles, the internal energy, E, the volume, V, the number of particles, N (as well as the entropy, S, in the equilibrium states, see below), are extensive variables.

The other types of variables which do not change their values are called intensive variables of the system, but the latter refers to the equilibrium states (see below).

Environment: Those background systems to which the system of our interest is connected are called the environments, reservoirs, or baths. According to the entity that is exchanged with the system, the environment is called thermal environment or heat reservoir/bath (for energy exchange), particle environment or particle/chemical reservoir (for mass exchange) or pressure environment (for volume exchange).[1]

As an environment forms the background of a system and not the main object of study, they are considered to satisfy several simplifying assumptions.

(1)   We ignore the interaction energy between the system and its environments. (In case that it is not realistic assumption, we try to define the interface layer of interaction as a new system.)

(2)   Environments are big in the sense that the conservation laws for the total energy, mass, volume, or momentum have no effect on the state of the environment.

(3)   Environments return instantaneously to their equilibrium states (see below), and keep no memories of the system's action in the past. In other words, any action on the environments is supposed to be quasistatic from macroscopic point of view.[2]

Because of these simplifications, environments are characterized only by their intensive parameters, that is, temperature, chemical potential (or the density of particles), and pressure.

Heat exchange: It is the form of exchange of energy not through work, or involving mass exchange. This process occurs either between a system and its environment, or among different subsystems.

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[1] In this book we will use the words "heat bath" and "thermal environment" interchangeably.

[2] In other words, we do not discuss the irreversible entropy production proper to the environments.

Mass exchange: Mass is exchanged through the transport of particles between a system and its environment, or among different subsystems. Mass exchange can also take place through chemical reactions.[3]

External system: An agent which is capable of macroscopically controlling the system. The system can exchange energy and/or volume (and sometimes mass) with the external system. The role of external system and environment is somehow interchangeable in the sense that the definition of a system can include the environment through the Legendre transformation (see below). For example, the external system that controls the system's volume can be replaced by a pressure environment. In the latter case, the system's internal energy counts also as the potential energy of the pressing agent (a weight). The energy is then called enthalpy.

Work: The form of exchange of energy which is done by the control of external systems through the change of system's volume, external force, electric field, etc.

Macroscopic character of external system: The external system is allowed neither to make use of the microscopic information of a system nor to react adaptively to the microscopic change of the state of the system. This condition, on the one hand, excludes the intervention of the Maxwell's demon, a hypothetical agent which cools down the system by letting only rapidly moving particles to escape through a hole.[4] On the other hand, the above condition does not exclude certain devices having molecular selectivity of chemical species such as semipermeable membranes. The reason is that selectivity in the latter case is static with no adaptive functions to the particles which arrive at the membrane and also that the work is done only through the macroscopic displacement of the membrane as a whole.[5]

Sign conventions: Throughout this book, unless explicitly defined otherwise, we assign a positive sign to whatever quantities which the *system receives*.[6] For example, if an external system brings energy to a system through work, we say that a positive work, $W > 0$, is done. Also, if an environment brings energy to a system through heat, we say that positive heat ($Q > 0$) is transferred.

Some aspects of macroscopic thermodynamics are peculiar to the fact that the system is macroscopic.

1. When the system consists of several macroscopic subsystems, a subsystem can do work on the other subsystems as an external system.
2. The presence of extensive variables and the negligence of interaction energy between the system and environments suppose that the *surface* contributions

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[3] More about the macroscopic chemical thermodynamics will be described in the next chapter.

[4] For a review, see [3]. cf. Sect. 4.2.1.2

[5] The author acknowledges Izumi Ojima for his comment on this point.

[6] Note that certain textbooks of thermodynamics adopt the opposite sign convention.

to those variables are negligible compared with the *bulk* contributions. If the surface-to-volume ratio is larger than some inverse characteristic length (e.g., the interaction range of particles), this hypothesis is no more valid.

3. The extensive character implies the absence of fluctuations. It is related to the law of large numbers. It is often called the self-averaging property of macroscopic system. Entropy and temperature which are ensemble-based concept can be assigned to a single macroscopic system. Systems at critical point of phase transition, or with long-range interactions, cannot be described by usual thermodynamics.

2.1.2 * Some Laws of Macroscopic Thermodynamics Distinguish Thermodynamics from Mechanics

About the process of macroscopic thermodynamic systems, several universal laws apply independent of the details of interactions among the constituent materials. The laws deal with the relationship among the change of energy, the heat transferred, and the work done during a process of a system. We mention the four principal laws below. They do not constitute a complete set of axioms of the macroscopic thermodynamics, see [1, 2].

> *Zeroth law:* If a system is left isolated for sufficiently long time from any environment and from any external system, it will reach a state with no further macroscopic changes.[7] Such a state is said to be in an equilibrium state. For a single-component gas isolated in a single compartment, for example, the set of energy, volume, number of gas particles, (E, V, N), is sufficient to characterize its equilibrium state, and the entropy S is then a function of these variables. These variables are called thermodynamic variables, and the functions which relate the thermodynamic variables in an equilibrium system are called thermodynamic functions. If any process occurs slowly enough so that the system remains almost in equilibrium at each instant, the process is said to be quasistatic (or quasiequilibrium) process.
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> *First law:* We cannot realize a perpetual machine of the first kind, that is, there is no autonomous system, isolated from the environment, that produces work (i.e., $W < 0$) through a cyclic process. The inverse process is also not possible. More concretely, a balance of energy should always be established among the changes in the internal energy of the system, ΔE, the work, W, and a heat, Q, during any process:

$$\Delta E = W + Q. \tag{2.1}$$

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[7] Strictly speaking, there may remain global motions due to conserved total momentum or total angular momentum of the whole system.

Second law: One cannot realize a perpetual machine of the second kind, that is, being in contact with a single thermal environment at constant temperature, there is no autonomous cyclic engine which converts heat into work. The inverse process from work to heat is possible. More precisely, there is a thermodynamic function of equilibrium systems called entropy (S) which never decreases during processes of an isolated system. Entropy is an extensive variable.

Third law: This law, also called the Nernst–Planck's theorem, concerns the limit to absolute zero temperature. At absolute zero, the quantum interference is believed to impose a unique ground state at least in most cases, and the extensivity of the macroscopic thermodynamics should be carefully tested [4]. As quantum fluctuations are beyond the scope of this book, we will not go into the detail of this law.

"Fourth law" [8]: Any thermodynamic variable characterizing an equilibrium state is either extensive one or intensive one. For the system whose extensive variables are (E, V, N) and S, the intensive variables are temperature T, pressure p, and chemical potential μ. The intensive variables are the homogeneous function of the extensive variables of zeroth order. The intensive variables characterize the equivalence relationship "$\sim$" of equilibrium. If an equilibrium system A and another one B satisfy $A \sim B$, it means that the contact of these two systems cause no changes in their extensive variables. The system B can be an environment with which the system A is in contact.

The transitive property of this equivalence relationship, ($A \sim C$) $\wedge$ ($B \sim C$) $\Rightarrow A \sim B$, allows to compare, for example, the temperature T of two systems A and B using the "thermometer" C. The reflective property, A $\sim$ A, implies that the intensive variables remain unchanged upon combining the two identical systems A. The symmetric property, A $\sim$ B $\Leftrightarrow$ B $\sim$ A, implies that the assignment of the measuring system and the measured system is relative in the context of macroscopic equilibrium. Further properties of the extensive and intensive variables will be described below.

If the system is not macroscopic, the intensive variables can still be used to characterize the environment. But they are not the state variables of the small system.

2.1.3 Thermodynamic Relations Come from Several Different Aspects of Thermodynamic Systems

In this section we will describe several basic consequences of the laws of thermodynamics.

One important aspect of the thermodynamics, especially from the zeroth and fourth laws, is the presence of thermodynamic function by which various

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[8] There is no general consensus on which law should be put as the fourth law. Here we take up a version.

thermodynamics variables are derived. Its consequence is the fundamental relation and Maxwell relation.

Another important aspect, especially from the first and second laws, is the homogeneity of those thermodynamics function related to its extensive character. Its consequence is the Euler relations and Gibbs–Duhem relation.

2.1.3.1 Fundamental Relation

For a simple gas system, the equilibrium states are completely describable either by $\{S, V, N\}$ or by $E(S, V, N)$. In respective case, E or S are the functions of the first three extensive variables, i.e., $E=E(S, V, N)$ or $S=S(E, V, N)$. These are represented as a curved surface in 4D space coordinated by (S, E, V, N). Each point on this surface represents an equilibrium state. On a point on this surface, say (S, E, V, N), the equation of the tangent plane is written as

$$dE = T\,dS - p\,dV + \mu\,dN, \quad \text{or} \quad dS = \frac{1}{T}\,dE + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN, \qquad (2.2)$$

where "differentials," (dS, dE, dV, dN), are the local variables along (S, E, V, N), with the origin relocated to the tangent point, and the coefficients $(1/T, p/T, -\mu/T)$ are independent of these differentials. Thus we can have essentially all relations between the extensive variables and the intensive ones, such as $\frac{1}{T} = \frac{\partial S}{\partial E}_{V,N}$ for these equations. We call the relations (2.2) the fundamental relations. Those thermodynamic functions that generate the fundamental relations, such as $S(E, V, N)$ or $E(S, V, N)$, are called the complete thermodynamic functions. The pairs of thermodynamic derivatives associated with the partial derivative like $T(E, V, N)^{-1} = \frac{\partial S}{\partial E}_{V,N}$ are called conjugate variables. (T, S), $(-p, V)$, and (μ, N) are pairs of conjugate variables.[9]

Complete thermodynamic functions are not unique, and therefore, the fundamental relations are not either. However, all the fundamental relations of a system represent the same interdependencies. To obtain a new complete thermodynamic function, we must apply the Legendre transformation to the original complete thermodynamic function. For example, we can obtain the complete thermodynamic function, "Helmholtz free energy," $F(T, V, N)$ of a simple gas system by the Legendre transformation of $E(S, V, N)$: We solve $T = \partial E(S, V, N)/\partial S$ to find (formally) $S(T, V, N)$. (This function, $S(T, V, N)$, is not a complete thermodynamic function.) Then we substitute this into $E(S, V, N) - T(S, V, N)S$ to obtain $F(T, V, N) = E(S(T, V, N), V, N) - T(S(T, V, N), V, N)\,S(T, V, N)$. The variable S is now found through $(\partial F/\partial T)_{V,N} = -S$, instead of $(\partial E/\partial S)_{V,N} = T$. The exchange of the conjugate pair, (S, T), as independent–dependent variables

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[9] Incomplete thermodynamic functions can also be made. For example, we can solve $T(E, V, N)^{-1} = \frac{\partial S}{\partial E}_{V,N}$ for V and substitute the result in $S(E, V, N)$. Then we have a function $S = S(E, V(E, T, N), N)$. Such function, although correct, cannot generate all the other thermodynamic variables; there remains an undetermined additive constant.

requires the subtraction of the term TS from the original complete thermodynamic function.[10]

Physically, the subtraction of a product of conjugate thermodynamic variables (e.g., TS) in the transform (e.g., $E \mapsto F = E - TS$) implies the attachment or detachment of an environment. For example, suppose that an isolated simple gas system has the complete thermodynamic function, $S(E, V, N)$. We now attach a thermal environment to this system. Since the combined system is a new isolated system, we may use the entropy of the whole system $S(E, V, N) + S_{res}(E^{tot} - E)$ as a new thermodynamic function. Since the system can exchange energy with this environment satisfying the law of energy conservation, we control no more the energy E, but control the energy of the whole system, E^{tot}. Since the reservoir retains a constant temperature T_{res} by definition, we choose as a new independent thermodynamic variable T_{res} rather than E^{tot}, where T_{res} is given by $\partial S_{res}/\partial E^{tot} = 1/T_{res}$.[11] Then we have

$$S(E, V, N) + S_{res}(E^{tot} - E) \simeq S(E, V, N) + S_{res}(E^{tot}) - \frac{E}{T_{res}}$$

$$= -\frac{1}{T_{res}}(E - T_{res}S) + \text{const.} \qquad (2.3)$$

The repartitioning of the energy into E and $E^{tot} - E$ is self-adjusted so that the temperatures are equilibrated, $T = T_{res}$. The new complete thermodynamic function $F = E - TS$ then describes the combined system (the system and the thermal environment) with $\{T, V, N\}$ as independent variables.

As a consequence of the second law of thermodynamics, the work W done to the system through arbitrary isothermal system is bounded below by the change in the Helmholtz free energy, $\Delta F = \Delta E - T\Delta S$[12]:

$$W \geq \Delta F.$$

An ensemble of a very large number of identical copies of a small system obeys macroscopic thermodynamics. As there are no interactions among those copies, the

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[10] Mathematically the Legendre formulation is defined as follows: Take a fundamental relation, $df = \sum_{j=1}^{n} R_j dx_j$, where $f(x_1, \ldots, x_n)$ is the complete thermodynamic function and $R_j \equiv \partial f/\partial x_j$. In order to derive the new fundamental relation with $\{R_1, \ldots, R_k\}$ and $\{x_{k+1}, \ldots, x_n\}$ as the independent variables, where $0 < k < n$, we solve $R_j = \partial f/\partial x_j$ for $j = 1, \cdots, k$ to represent $\{x_1, \ldots, x_k\}$ as functions of $\{R_1, \ldots, R_k, x_{k+1}, \ldots, x_n\}$. Then the identity $d\left[f - \sum_{j=1}^{k} R_j x_j\right] = \sum_{j=1}^{k}(-x_j)dR_j + \sum_{j=k+1}^{n} R_j dx_j$ is the new fundamental relation which is generated by a new complete thermodynamic function $\tilde{f} \equiv f - \sum_{j=1}^{k} R_j x_j$ as function of new independent variables, $\{R_1, \ldots, R_k, x_{k+1}, \ldots, x_n\}$.

[11] Since we simplify the characterization of the environments, we do not explicitly take into account the volume and the particle number of the heat bath.

[12] The result is obtained from $\Delta S_{res} + \Delta S \geq 0$, $\Delta S_{res} = -Q$, and $\Delta E = W + Q$.

extensive character of the variables like E, V, and N is evident. By the law of large numbers (Sect. 1.1.2.3) we can define the energy, etc. *per* system. However, the results which we obtain from this macroscopic framework concern only the statistical average over the individual systems or the property characterizing the ensemble.

2.1.3.2 Maxwell Relation

If the equation of one plane (2.2) is the fundamental relation associated with a monovalent function, $S = S(E, V, N)$, the coefficients of the differentials, i.e., $(1/T, p/T, -\mu/T)$, should satisfy certain conditions.[13] For example, $(\partial\mu/\partial V)_{S,N} = -(\partial p/\partial N)_{S,V}$ is derived from (2.2) since

$$\left(\frac{\partial\mu}{\partial V}\right)_{S,N} = \frac{\partial^2 E}{\partial V \partial N} = \left(\frac{\partial(-p)}{\partial N}\right)_{S,V}.$$

These types of equations are called the Maxwell relation. Inversely, if the coefficients of the Eq. (2.2) satisfy the Maxwell relation, these local equations can be integrated to define a surface. See Appendix A.2.1 for a brief proof.

2.1.3.3 Euler Relations of Thermodynamic Variables

The complete thermodynamic potentials, $E = E(S, V, N)$ or $S = S(E, V, N)$, are the relations among the extensive thermodynamic variables. If a system in equilibrium and its copy is combined to make a new system, all of these variables should become twice as large as the original. In general, we expect

$$E(\lambda S, \lambda V, \lambda N) = \lambda\, E(S, V, N), \quad S(\lambda E, \lambda V, \lambda N) = \lambda\, S(E, V, N), \quad (2.4)$$

for $\lambda > 0$. This is a mathematical representation of the extensivity of the macroscopic thermodynamics. If we draw a graph, for example, of E as function of (S, V, N), the extensive character of the function $E(S, V, N)$ imposes a particular geometrical property on this graph: the graph consists only of the straight lines passing through the origin $(0, 0, 0, 0)$. Figure 2.1 illustrates such geometry for the case with three extensive variables. (One can imagine an umbrella cloth when it is folded loosely.)

An important consequence of this constraint is the following relationship among the thermodynamic variables:

$$TS - pV + \mu N = E. \quad (2.5)$$

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[13] In other words, if the continuous functions $(T(E, V, N), p(E, V, N), \mu(E, V, N))$ satisfy no mutual relations, a monovalent graph S vs. (E, V, N) cannot be constructed through the connection of the tangent planes (2.2).

Fig. 2.1 The graph of extensive thermodynamic function $z = f(x, y)$ as function of the two extensive thermodynamic variables, x and y
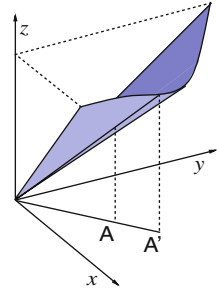
It is easily derived from either one of the relations in (2.4) by differentiating with respect to λ and then putting $\lambda = 1$. This type of identity is called the Euler's theorem.[14,15]

Euler's theorem applies also to the expressions of the intensive variables, e.g., $\mu = \partial E / \partial N = \mu(S, V, N)$. Since the value of μ should remain the same when the system and its copy is combined, we have

$$\mu(\lambda S, \lambda V, \lambda N) = \mu(S, V, N).$$

By the same token to the derivation of (2.5), we have

$$S\frac{\partial \mu}{\partial S} + V\frac{\partial \mu}{\partial V} + N\frac{\partial \mu}{\partial N} = 0 \tag{2.6}$$

and similar identities.

2.1.3.4 Gibbs–Duhem Relation

Extensivity of the complete thermodynamic function imposes further relationship among the intensive thermodynamic variables. Let us take the differential of (2.5), that is, $d(TS - pV + \mu N) = dE$. This expression imposes a linear relation among the first-order differentials of each variables when an equilibrium state, $(E(S, V, N), S, V, N)$, is displaced infinitesimally to another equilibrium state:

$$SdT + TdS - (pdV + Vdp) + \mu dN + Nd\mu = dE.$$

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[14] Mathematically, when the function $f(x_1, \ldots, x_n)$ has a homogeneity of kth order, i.e., $f(\lambda x_1, \ldots, \lambda x_n) = \lambda^k f(x_1, \ldots, x_n)$, the derivation of this equation by λ at $\lambda = 1$ yields an identity $\sum_{i=1}^{n} x_i R_i = kf$ valid for any $(x_1, \ldots, x_n)$, where $R_i = \partial f / \partial x_i$.

[15] Each new Legendre transformation on the complete thermodynamic function reduces by one of the independent extensive variables. We cannot have a complete thermodynamic function in which all the extensive variables are eliminated, since then the complete thermodynamic function would be $E - TS + pV - \mu N \equiv 0$ because of (2.5), or because the intensive variables along cannot fix the size of the system.

By subtracting the fundamental relation, (2.2), we obtain

$$SdT - Vdp + Nd\mu = 0. \tag{2.7}$$

This relation is called the Gibbs–Duhem relation.

When the macroscopic thermodynamic system consists of many copies of a small system, the Euler relations and Gibbs–Duhem relation may bring little constraint or information about the individual system.

2.1.4 * Heat of Macroscopic Open System Consists of Two Terms Both Including Entropic Parts

An open system exchanges not only heat but also particles with its environment. See Fig. 2.2.[16] Thermodynamics of open system is an important issue in biology since protein molecular motors are usually open systems which consume source molecules like ATP in the environment. The problem of organic or inorganic adsorption and diffusional transport across membranes are also the subject of open system. In this section and in Sects. 2.3.2 and 2.3.3, we deal explicitly with an open system.

For a closed system, we can identify the system with the particles, etc., that are therein. An open system, however, is rather a container of particles, and a particle belongs to the system while it is in the container.[17]
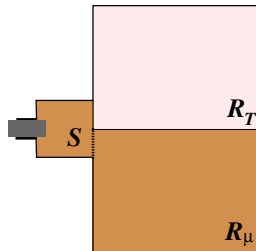

Fig. 2.2 An open system containing gas particles, S, in contact with a thermal environment, R_T, and a particle environment, R_μ. The *thick lines* and *filled rectangle* are isolating walls and piston, respectively, and the thin walls are thermally conducting walls. A *thick dashed line* is the wall permeable for the gas particle

2.1.4.1 Energetics of the Open System

The energy E of an open system can change not only due to heat and work but also due to the exchange of particles between the system and the particle environment.

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[16] In quantum physics, often the same word means the systems in contact with (only) a thermal environment.

[17] In the problem of adsorption, the container is the ensemble of adsorption sites. Those particles on the adsorption sites belong to the open system.

Let us consider a gas system in which work is done through the change of volume, $d'W = -pdV$. The first law of thermodynamics reads

$$dE = -pdV + d'Q^{\text{tot}}, \tag{2.8}$$

where $d'Q^{\text{tot}}$ denotes *all* the energy entering into the system except for the work $-pdV$.[18] We suppose that the system is in contact with a thermal environment of temperature T and also with a particle environment of chemical potential μ. Therefore, if a small number of particles, dN, have entered into the open system in keeping the equilibrium, and the volume is increased by dV, then the change in the internal energy is given by the fundamental relation, $dE=TdS - pdV + \mu dN$. The substitution of this expression for dE in (2.8) yields

$$d'Q^{\text{tot}} = TdS + \mu dN. \tag{2.9}$$

In general, both dN and dS are nonzero when a particle enters or leaves an open system. In other words, the chemical potential μ is not the (only) energy carried by a particle upon its migration across the system's border:[19] When the only change is the immigration of a single particle, $(dN)_1 = 1$, we will denote by $(dS)_1$ the associated change of entropy. The "heat" associated with this immigration is then the sum, $(d'Q^{\text{tot}})_1 = T(dS)_1 + \mu$. When the particle is an ideal gas particle, such energy changes should not involve the concentration of the particle in the particle environment simply by the definition of ideal particle. On the other hand, the particle concentration of the particle environment c enters in μ in entropic form, $k_B T \log c$. In order that the $(d'Q^{\text{tot}})_1$ is independent of the particle concentration of the environment, the last entropic term should be cancelled by a similar term in $T(dS)_1$.

2.1.4.2 Complete Thermodynamic Function for an Open System

When a system contains N_α particles of the species α, the pertinent complete thermodynamic function J is defined as follows:

$$J(T, a, \{\mu_\alpha\}) \equiv E - TS - \sum_\alpha \mu_\alpha N_\alpha, \tag{2.10}$$

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[18] Hereafter we will use d' to denote the infinitesimal transfer of work, $d'W$, and of (generalized) heat, $d'Q$ to distinguish from d which is related to the thermodynamic variables.

[19] Statistical mechanics shows that the chemical potential is related to the fugacity, i.e., the probability to escape, of *anonymous* particles. This is why μ depends on the concentration of the particles even if the particles do not interact among each other.

where μ_α is the chemical potential of the particle environment of the species α, and a denotes the extensive parameter that is controlled by an external system (e.g., $a = V$ if the volume is controlled). J gives rise to the following fundamental relation:

$$dJ = -SdT + \frac{\partial J}{\partial a}da - \sum_\alpha N_\alpha d\mu_\alpha. \tag{2.11}$$

The work done to the open system through the change of the parameter a is calculated from $\int (\partial J / \partial a)da$. When it is done quasistatically, the work, which we denote by $W|_{T,\{\mu_\alpha\}}$, is equal to the increment of J:

$$W|_{T,\{\mu_\alpha\}} = \Delta J|_{T,\{\mu_\alpha\}} \qquad \text{(quasistatic)}. \tag{2.12}$$

The chemical reaction is similar to the open system in the context that discrete atomic masses are transferred between one state to the other. For an open system the transfer is between a system and its particle environment, while for a chemical reaction it is between a molecular species and the another. These two processes can coexist. Typical examples are surface catalytic reactions and motor proteins[20] or the transport of molecules across a membrane channel. In the latter case, we can regard the transport as unimolecular reaction from one "species" to another "species," such as "cytoplasm"$\rightleftharpoons$ "nucleus." If both sides of a membrane are macroscopic, the channels on the membrane can be also described as an open system that exchanges particles with two particle environments.[21]

2.2 Free Energy as an Effective Potential Energy for the External System

In Sect. 2.1.3.1 we have shown that the complete thermodynamic function $F = E - TS$, i.e., the Helmholtz free energy, describes the combined system, the system and the thermal environment, with $\{T, V, N\}$ as independent variables. Here we describe another aspect of this thermodynamic function from the operational point of view. The Helmholtz free energy acts as an effective potential energy under the quasistatic operations by the external system. Figure 2.3 (top) shows a system of the gas confined in a cylinder with a piston, which an external system can move. When the external system pushes the piston, the first law of thermodynamics (2.1)

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[20] Different species of molecules can share the same space as distinct particle environments if the spontaneous reaction between these species is negligible.

[21] In the master equation formalism and related discrete Langevin equation discussed in the next chapter, the change in closed systems and the migration of particles in open systems are both described as a state transition of the whole system.
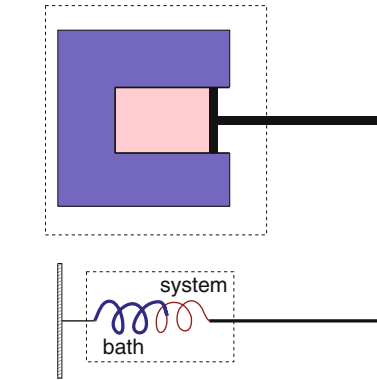
Fig. 2.3 Thermodynamic system viewed from the external system. Under quasistatic operations of the piston (*top figure*), the "black box" (*dashed rectangle*) which consists of a gas in the cylinder and the heat environment behaves like a spring (*bottom*). The temperature, instead of the force of spring, is equilibrated between the system and the thermal environment (heat bath)

tells us that the associated work W done onto the system is partitioned into the increment of the energy of the system, ΔE, and the heat released to the thermal environment, $(-Q)$.[22] For the external system, the system *and* the thermal environment, therefore, look like a single black box. The external system measures only the relation between the work W and the displacement of a piston.

To characterize this black box, let us denote by a the position of the piston and by $W(a_1; a_2)$ the work done through the displacement of the piston from a_1 to a_2. If this work can be described by a potential, $\phi(a)$, such that $W(a_1; a_2) = \phi(a_2) - \phi(a_1)$, then one might regard this black box as an elastic spring whose potential energy is $\phi(a)$ up to an additive constant (see Fig. 2.3 (bottom)). Macroscopic thermodynamics tells that (1) such $\phi(a)$ exists if the parameter a is changed quasistatically and (2) this potential energy, $\phi(a)$, is the Helmholtz free energy, $F = E - TS$, up to an arbitrary additive constant.[23] Thus the word "free energy" for F is justifiable because it behaves like a potential energy (for "energy"), and it is available as work (for "free"). A similar interpretation can be done for the free energies $G = E - TS + pV (= \mu N)$ or $J = E - TS - \mu N (= -pV)$ when the system undergoes a process keeping in contact with a pressure environment (for G) or with a particle environment (for J), respectively.

Let us summarize how the quasistatic operation of the piston in the Fig. 2.3 can be described differently according to the standpoint of the observer: the Ext who sees the system only through the parameter a, the Sys who has access to both E and

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[22] Note the sign convention about the work and heat, see Sect. 2.1.1.

[23] $dE = TdS - pdV + \mu dN$ under the constraints, $dT = dN = 0$, yields $d(E - TS) = dF = -pdV = d'W$.

S, and the Tot who regards the totality of the system and the thermal environment as an isolated system.

> Ext: The work W is apparently stored in the system as the increment of the potential energy, $\Delta F \,(= \Delta E - T \Delta S)$.[24] If the data of ΔF are accumulated at different temperatures, the change of the (internal) energy ΔE can be obtained by the following formula called the van't Hoff equation (see, e.g., [5]):
>
> $$\Delta E = \Delta F - T \, \Delta \left(\frac{\partial F}{\partial T} \right)_a , \qquad (2.13)$$
>
> where the suffix "a" indicates that the initial and final values of a should be fixed upon taking the derivative.[25] Equation (2.13) comes from the relation: $E = F + TS = F - T \partial F / \partial T$.
>
> Sys: The work W is partly stored in the system as ΔE, while the rest is transferred to the thermal environment as heat, $-T \Delta S$.[26] The actual partitioning of the work into ΔE and $(-T \Delta S)$ depends on the details of the system. For example, ΔF should be ΔE for a system made of metallic spring but it should be $(-T \Delta S)$ for a system of ideal gas or ideal polymer network.
>
> Tot: The work W is stored in the isolated system as the increment of (true) energy, $\Delta E + T \Delta S_{\mathrm{env}}$, where the entropy of the thermal environment, S_{env}, changes so that $\Delta S + \Delta S_{\mathrm{env}} = 0$.
>
> For nonquasistatic processes the second law of thermodynamics tells us that the entropy of the isolated system is nondecreasing: $\Delta S + \Delta S_{\mathrm{env}} \geq 0$. This inequality relates the work done to the system, $W = \Delta E - (-T \Delta S_{\mathrm{env}})$,[27] and the change of the Helmholtz free energy, $\Delta F = \Delta E - T \Delta S$, by the inequality,
>
> $$W \geq \Delta F. \qquad (2.14)$$
>
> In other words, the work obtainable from the system $(-W)$ is limited by the decrease of the free energy of the system $(-\Delta F)$:
>
> $$(-W) \leq (-\Delta F). \qquad (2.15)$$

---

[24] The quantities denoted like "ΔM" implies the increment of M through the change of the parameter a.

[25] Remember that the partial derivative can give different results depending on what variables are fixed: For example, $p = -(\partial U / \partial V)_S$ is rewritten as $p = -(\partial U / \partial V)_T + T(\partial p / \partial T)_V$. Generally, given the fundamental relation, $f(x_1, \ldots, x_n)$ and $R_j \equiv \partial f / \partial x_j$, we have a formula, $(\partial f / \partial x_i)_{R_j} = (\partial f / \partial x_i)_{x_j} - R_j (\partial R_i / \partial R_j)_{x_i}$.

[26] Remember the sign convention: the heat, $Q = T \Delta S$, is positive if the energy is transferred from the thermal environment to the system.

[27] Note that the thermal environment is supposed to be in equilibrium and, therefore, $Q = -T \Delta S_{\mathrm{env}}$ holds always.

Fig. 2.4 A gas in cylinder (*central rectangle*) in contact with two heat baths of the same temperature, T
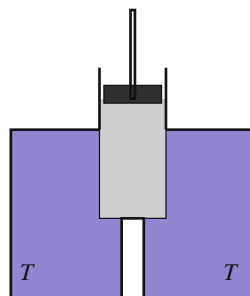
In the description of the energetics of fluctuating systems, the consciousness of the standpoint is as important as the macroscopic thermodynamics.

We should note that macroscopic thermodynamics cannot analyze the *kinetic* aspects of the quasistatic processes. First, thermodynamics gives no criterion for the quasistatic operation by an external system. Thermodynamics is not the framework to determine the characteristic timescale beyond which the excess work, i.e., the difference between the actual work and the quasistatic work, is sufficiently small. To answer such a question, we do not need a knowledge of the microscopic mechanics, but need an energetics of fluctuations in Chap. 4. Second, thermodynamics cannot access a slow kinetic process. Let us suppose a gas is confined in a cylinder and a piston, which is in contact with two thermal environments at the same temperature, T (Fig. 2.4). If we press down the piston quasistatically, the partition of the heat released to these environments could be experimentally observable.[28] The linear nonequilibrium thermodynamics [6, 7] incorporates the irreversible flux between the two equilibrium[29] systems when their intensive variables have a small gradient.

2.3 * Free-Energy Conversion

Free-energy conversion is one of the principal subjects of thermodynamics, since its advent by Carnot, until the recent interest in the context of molecular motor [7]. We, therefore, introduce several important notions and concepts related to the free-energy conversion.

2.3.1 Unused Work Is Not Released Heat

We here discuss reaction heat and the work produced by a heat engine.

A thermal environment is supposed to be an inexhaustible buffer of energy. Because of this character, the isothermal processes exhibit sometimes

---

[28] If the (almost) quasistatic process takes an extremely large time t, diffusive exchange of heat between the two thermal environments via the system will be of order $\sim t^{\frac{1}{2}}$. We neglect this as compared to the systematic part of $\sim t$.

[29] It is called "local equilibrium".

counterintuitive behaviors about their energetics. The rubber band mentioned above is an example: little heat is released from an ideal rubber band when it freely shrinks from a stretched state, while a quasistatic shrinkage can absorb heat. Free expansion of an ideal gas behaves similarly: although a quasistatic expansion from the volume V_{ini} to V_{fin} can do the reversible work of $k_B T \log(V_{\text{fin}}/V_{\text{ini}})$, the work-free expansion (Joule–Thomson process) absorbs no heat.

In the biochemical context, the hydrolysis reaction of an ATP (adenosine triphosphate) with a water molecule into an ADP (adenosine diphosphate) and an inorganic phosphate (Pi), ATP + $H_2O \to$ ADP + P_i, can do about $20k_B T$ of work under usual physiological conditions. It does not mean that we will observe this amount of dissipative heat when no work is extracted through this reaction. (See below.) We might also recall the existence of endothermic chemical reaction – while the reaction proceeds with consuming the relevant free energy (see below), the system absorbs heat, instead of absorbing heat. The point is that, for open systems, the heat released to the thermal environment, $(-Q)$, is not the total increase of entropy of the environment ΔS_{env}, that is $Q \neq -T\Delta S_{\text{env}}$: The total change ΔS_{env} generally includes a purely combinatorial part (mixing entropy change).

The chemomechanical coupling is a mechanism which converts a chemical free energy into work under constant temperature and pressure. We will see the interplay of heat and work in this mechanism. Figure 2.5 shows a schematic setup of chemomechanical coupling. In this setup, the material before the reaction (called the substrate) and the one after the reaction (called the product) are separated as subsystems in order to avoid a work-free reaction. As we are interested in the process under constant pressure p, the energy of the pressure environment is included in the energy of the system. That is, we use enthalpy, $H \equiv E + pV$, instead of E, where V is the volume. By adopting enthalpy as the energy of the system, the work due to volume change is not counted in W. Finally there is an engine that works between the substrate and the product subsystems. The two subsystems and the engine are immersed in a thermal environment (Fig. 2.5). The combined system, therefore, consists of four subsystems, i.e., the two particle subsystems, the pressure reservoir, and the chemical engine.
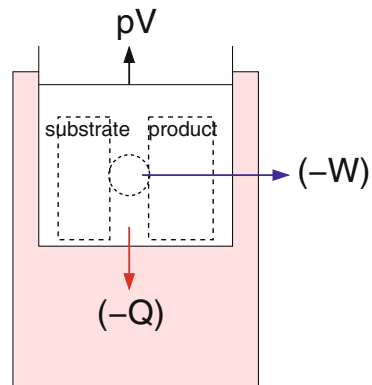

Fig. 2.5 Schematic setup of chemomechanical coupling. The system consists of the substrate subsystem, the product subsystem, the ambient pressure (*piston*), and the chemical engine (*circle*), all immersed in a thermal environment

In the case of the quasistatic process, the analysis is done by the aid of a thought experiment called a van't Hoff reaction box (see e.g., [5]). Here we include the general case of a nonquasistatic process and consider what occurs upon one cycle of operation of the engine. Let us denote by $(-Q)$ the heat released from the combined system to the thermal environment and by $(-W)$ the work done by the combined system to the external system. Let us also denote by ΔS, ΔV, and $\Delta H (= \Delta E + p\Delta V)$, the changes in the entropy, volume, and the enthalpy of the combined system.[30]

Application of the first law of thermodynamics: In the present context this law gives $\Delta E = W + (-p\Delta V) + Q$, or by noting that p is constant,

$$(-\Delta H) = (-W) + (-Q). \tag{2.16}$$

The minus signs are incorporated in the above equation so that we can use the extracted work, $(-W)$, and the released heat, $(-Q)$. There are two extreme cases:

Case where no work is extracted: We substitute $W = 0$ in (2.16) to have $(-Q) = (-\Delta H)$, which we shall call the heat of Joule–Thomson, $(-Q)_{JT}$. That is,

$$(-\Delta H) = (-Q)_{JT}, \qquad W = 0. \tag{2.17}$$

Therefore, this reaction is either exothermic or endothermic, depending on whether $(-\Delta H) > 0$ or $(-\Delta H) < 0$.

Case where the maximal work is extracted: The released heat, $(-Q) = T\Delta S_{env}$, is related to ΔS through $\Delta S + \Delta S_{env} = 0$. We shall call this the reversible extracted heat, $(-Q)_{rev} = -T\Delta S$. In this case, the extracted work $(-W)$ is the reversible work, $(-W)_{rev} = -\Delta H + T\Delta S$. Using the relation, $\Delta H = \Delta G + T\Delta S$, we have included the substrate and product subsystems as a part of the combined system. This justifies the Gibbs free energy as the fundamental function of the present problem:

$$(-\Delta H) - (-\Delta G) = (-Q)_{rev} : \text{reversible extracted heat}$$
$$(-\Delta G) = (-W)_{rev} : \text{reversible extracted work.} \tag{2.18}$$

In case where the particle environments are treated as environment, the chemical potentials should be the independent variables. See Sect. 2.1.4.2.

General case: In the general case, the total entropy is nondecreasing, $\Delta S + \Delta S_{env} \geq 0$, by the second law of thermodynamics. Therefore,

$$(-W) \leq (-W)_{rev}$$
$$(-Q) \geq (-Q)_{rev}. \tag{2.19}$$

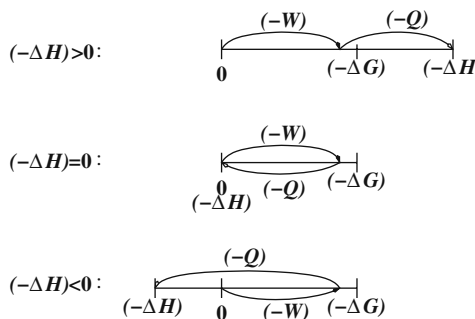[30] The changes associated to the engine are 0 by definition of the cycle.

Fig. 2.6 The partition of the extracted work, $(-W)$, (*filled arrows*) and the released heat, $(-Q)$, (*open arrows*) under constant temperature and pressure. They obey the first law; $(-\Delta H) = (-W) + (-Q)$. The reaction is either exothermic $((-\Delta H) > 0$, *top*), athermal $((-\Delta H) = 0$, *middle*), or endothermic $((-\Delta H) < 0$, *bottom*). The figures show only the case of "engine", i.e., $(-\Delta G) > 0$

Figure 2.6 summarizes the above relations for the cases with $(-\Delta H) > 0, (-\Delta H) = 0$, and $(-\Delta H) < 0$, respectively.[31]

Remark: We should avoid confusions like the following: "If the extracted work $(-W)$ is less than its maximum available value, $(-\Delta G)$, then the difference $(-\Delta G) - (-W)$ should be measured as the released heat." The correct statement is "..., then we have the irreversible heat, $(-\Delta G) - (-W) \geq 0$, in addition to the reversible one, $(-\Delta H) - (\Delta G)$."

Chemical pump: In the reverse case, that is, when the work is done to the system in order to drive the reaction or transport against the natural tendency, the Gibbs free energy increases, $\Delta G > 0$.

The equations and inequalities above are always valid with appropriate reinterpretation. For example, $(-W) \leq (-W)_{rev}$ of (2.19) should be read as $W \geq W_{rev}$, that is, the work done to achieve a cycle of engine is no less than the reversible one, W_{rev}, which in turn is ΔG according to (2.18).

Finally we note that the model of autonomous chemomechanical coupling is beyond the scope of macroscopic thermodynamics because it concerns the dynamics of the system.

2.3.2 Chemical Coupling Is a Transversal Downhill of a Gibbs Free-Energy Surface

We formulate the notion of chemical coupling (or conjugation) in the context of macroscopic thermodynamics. We will take up a very simple example: we suppose

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[31] If the volume, instead of the pressure, of the system is fixed, all the enthalpy H in the above formulas should simply be replaced by the energy E.
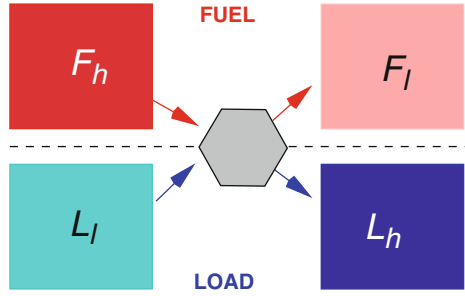
Fig. 2.7 Two reservoirs of the fuel (F) particles and two others of the load (L) particles with the high (h) and low (ℓ) chemical potentials. The passive diffusion of the fuel particles along their chemical potential gradient (*two arrows* in the *top layer*) is coupled by the chemical engine (*hexagon* at the *center*) to the active transport of the load particles against their chemical potential gradient (*two arrows* in the *bottom layer*)

two species of particles, the fuel (F) and the load (L) particles. For each species of particles, we prepare two particle reservoirs with high and low densities, which we distinguish by the suffixes, $_h$ and $_\ell$, respectively (see Fig. 2.7). For example, F_h denotes the high-density reservoir of fuel particles. We will denote the chemical potential of each reservoir by μ_{Fh}, etc. By definition, $\mu_{Fh} > \mu_{F\ell}$ and $\mu_{Lh} > \mu_{L\ell}$. A chemical engine (denoted by a hexagon at the center of Fig. 2.7) enables the active transport of the load particles from L_ℓ to L_h at the expense of the passive transport of the fuel particles from F_h to F_ℓ.

Gibbs free-energy surface: As in the previous section, we regard the four particle reservoirs and the chemical engine as a combined system working at a constant temperature and pressure. The relevant thermodynamic potential is then the Gibbs free energy,

$$G_{\text{tot}} = (\mu_{Fh} - \mu_{F\ell})N_{Fh} + (\mu_{Lh} - \mu_{L\ell})N_{Lh} + \text{const.}, \qquad (2.20)$$

where N_{Fh} [N_{Lh}] are the number of the fuel [load] particles in their respective high-density reservoirs, and we have used the fact that the total number of the fuel [load] particles are constant.[32] Equation (2.20) defines an inclined plane in the 3D space of ($N_{Lh}, N_{Fh}, G_{\text{tot}}$). See Fig. 2.8. We shall call this plane the Gibbs free-energy surface. The thermodynamically allowed processes are those which decrease this free energy, G_{tot}. Suppose that the reactions $L_\ell \rightarrow L_h$ and $F_h \rightarrow F_\ell$ are coupled at the ratio of $n_L{:}n_F$ particle transport on the average. This imposes a condition on (N_{Lh}, N_{Fh}) that

---

[32] After each cycle of the chemical engine, the number of the particles in the machinery returns to the same value. We then ignore the cyclically varying part of G_{tot}.

Fig. 2.8 Chemical coupling and Gibbs free energy. *The shaded plane shows the total Gibbs free-energy surface* (2.20) in the $(N_{Lh}, N_{Fh}, G_{tot})$. Chemical coupling is realized along the *thick arrowed line*, which satisfies (2.21) as well as (2.20). The process $A \rightarrow B$ consists of the downhill diffusion of the fuel, $A \rightarrow C$, and the uphill diffusion of the load, $C \rightarrow B$. The total Gibbs free energy G_{tot} decreases as a result. The $G_{tot} = \text{const.}$ line (*thick dashed line* on the Gibbs free-energy surface) is a visual guide
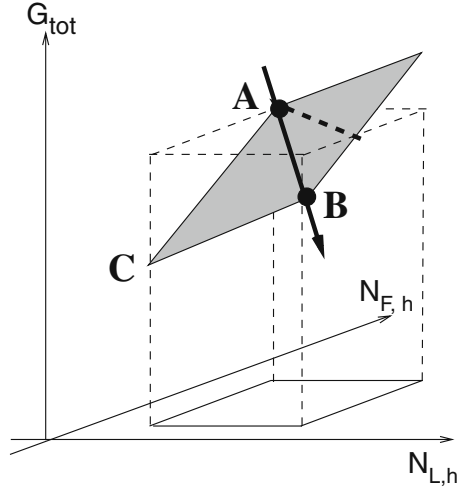
$$\frac{N_{Lh} - N_{Lh}^0}{N_{Fh} - N_{Fh}^0} = \frac{n_L}{n_F}, \tag{2.21}$$

where (N_{Lh}^0, N_{Fh}^0) are constants. While the chemical engine consumes the n_F fuel particles, decreasing the free energy by $\Delta G_F = (\mu_{Fh} - \mu_{F\ell})(-n_F) < 0$, it pumps up the n_L load particles, increasing the free energy by $\Delta G_L = (\mu_{Lh} - \mu_{L\ell})n_L > 0$. Figure 2.8 shows how the active transport, $\Delta G_L > 0$, is realized while satisfying the second law of thermodynamics, $\Delta G_{tot} \equiv \Delta G_F + \Delta G_L < 0$.

2.3.3 The Efficiencies of Heat Engine and Chemical Engine are Limited by the Second Law of Thermodynamics

In most cases, the phrase "efficiency of a heat engine" would refer to the Carnot cycle. When Carnot discussed his famous cycle, people had not yet recognized that heat can be transferred without transporting any material, nor had they discovered the second law of thermodynamics. It was, therefore, natural that the efficiency was defined so that it is unity when all the heat from the high-temperature environment is turned into a useful work. After thermodynamics was established, the efficiency of a heat engine was redefined in reference to the Carnot's theoretical maximum, allowed by the second law of thermodynamics.

For a single thermodynamic process, it is easy to introduce the efficiency of energy conversion in reference to the second law of thermodynamics. For example, for an isothermal process of changing the parameter a from a_1 to a_2, we can define the efficiency Θ as

$$\Theta = \frac{(-W)}{(-\Delta F)} \quad \text{(Isothermal process)}, \tag{2.22}$$

where $(-W)$ is the actually extracted work and $(-\Delta F) = F(a_1) - F(a_2)$ is the decrement in the Helmholtz free energy, that is, the maximally available work of this process (Sect. 2.1.2). By definition, Θ satisfies $(0 \leq)\Theta \leq 1$.

When a heat engine converts energy indefinitely, it must undergo a cycle of thermodynamic processes. The ideal cycle requires generally four quasistatic processes, as is the case with the ideal Carnot cycle: two processes in contact with the two thermal environments, respectively, one to absorb heat and the other to discard heat, and the other two processes for adjusting the system between these environments. The Carnot cycle is in this sense a minimal cyclic process to avoid irreversible losses. Below we derive the maximal work available from one cycle of Carnot heat engine. Later we will discuss the Carnot cycle on the fluctuating scale (Sect. 8.1.1).

When the cycle is ideal, each of the above mentioned thermodynamic processes must be reversible. Moreover, the attachment and detachment between the consecutive processes should cause no irreversibility. This requires that, at the end of each adiabatic process, the temperature of the system should be equal to the temperature of the thermal environment with which the system will be attached.[33] Let us denote the temperatures of the hot [cool] thermal environment by T_h [T_ℓ], respectively. For the isothermal process in contact with the hot environment the extracted work, $(-W_h)$, is the change of Helmholtz free energy of the system, $\Delta F_h = \Delta E_h - T_h \Delta S_h$, and similarly for the isothermal process with cool environment, i.e.,

$$(-W_h) = (-\Delta F_h) = (-\Delta E_h) + T_h \Delta S_h,$$
$$(-W_\ell) = (-\Delta F_\ell) = (-\Delta E_\ell) + T_\ell \Delta S_\ell.$$

During adiabatic processes the extracted work is equal to the change of the energy of the system:

$$(-W_{\text{ad}:h\ell}) = (-\Delta E_{\text{ad}:h\ell}), \qquad (-W_{\text{ad}:\ell h}) = (-\Delta E_{\text{ad}:\ell h}),$$

where the suffixes $_{\text{ad}:h\ell}$ and $_{\text{ad}:\ell h}$ indicate, respectively, the adiabatic cooling and heating processes. Because of the cyclicity of the processes, we impose

$$(-\Delta E_h) + (-\Delta E_{\text{ad}:h\ell}) + (-\Delta E_\ell) + (-\Delta E_{\text{ad}:\ell h}) = 0.$$

---

[33] We can assume the continuity of the temperature of the system from an isothermal process to the following adiabatic process.

Reversibility implies

$$(-\Delta S_h) + (-\Delta S_\ell) = 0.$$

The maximal available work per a cycle of the ideal heat engine, $(-W^{\text{tot}})_{\text{max}}$, is then

$$(-W^{\text{tot}})_{\text{max}} \equiv (-W_h) + (-W_\ell) + (-W_{\text{ad}:h\ell}) + (-W_{\text{ad}:\ell h}),$$
$$= (T_h - T_\ell)\Delta S_h. \tag{2.23}$$

The efficiency of an actual heat engine, which we denote by Θ, should be the ratio of the actual extracted work, $(-W^{\text{tot}})$, to the above maximum reversible value, $(-W^{\text{tot}})_{\text{max}}$:

$$\Theta \equiv \frac{(-W^{\text{tot}})}{(-W^{\text{tot}})_{\text{max}}} = \frac{(-W^{\text{tot}})}{(T_h - T_\ell)\Delta S_h} \leq 1. \tag{2.24}$$

The traditional definition of Carnot efficiency, η, as distinguished from our efficiency Θ, is $\eta = (-W^{\text{tot}})/(T_h \Delta S_h)$. For the reversible process, when $\Theta = 1$, the Carnot efficiency takes the well-known maximum, $\eta_{\text{rev}} = (T_h - T_\ell)/T_h$.

A similar argument can be applied to chemical engine consisting of an open system and two particle reservoirs, see Fig. 2.5.[34] In this case the system is in contact with a single thermal environment at temperature T throughout the cycle. Let us denote the chemical potentials of dense [dilute] particle reservoir by μ_h [μ_ℓ], respectively. An ideal cycle consists of two quasistatic processes under constant chemical potential and the intervening two quasistatic (closed) isothermal processes. The extracted work in the former processes reads $(-W_h) = (-\Delta E_h) + T\Delta S_h + \mu_h \Delta N_h$, etc.,[35] where ΔN_h, etc., denote the changes in the number of particles in the system in contact with a particle reservoir. The extracted work during the isothermal processes is $(-W_{\text{it}:h}) = (-\Delta E_{\text{it}:h}) + T\Delta S_{\text{it}:h}$, etc., where the suffix $_{\text{it}}$ stands for closed isothermal processes. The condition of the cyclicity is imposed on the energy of the system as above and the number of particles in the system; $\Delta N_h + \Delta N_\ell = 0$. The condition of reversible process imposes $\Delta S_h + \Delta S_{\text{it}:h} + \Delta S_\ell + \Delta S_{\text{it}:\ell} = 0$. The maximal extracted work, $(-W^{\text{tot}})_{\text{max}}$ then is

$$(-W^{\text{tot}})_{\text{max}} = (\mu_h - \mu_\ell)\Delta N_h. \tag{2.25}$$

This result can be rewritten in terms of the total Gibbs free energy G^{tot} defined by $G^{\text{tot}} = \mu_h N_h^{\text{res}} + \mu_\ell N_\ell^{\text{res}} + G^{\text{engine}}$, where N_h^{res}, etc., denote the number of particles

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[34] In the present context the substrate and product, Fig. 2.5, should be reread as high-density reservoir and low-density reservoir, respectively.

[35] "etc." implies the change of suffix, $_h \mapsto _\ell$.

in a particle reservoir and G^{engine} is that of the chemical engine. Since a balance of the number of particles transferred between a reservoir and the chemical engine imposes $\Delta N_h^{\text{res}} + \Delta N_h = 0$ and $\Delta N_\ell^{\text{res}} + \Delta N_\ell = 0$, and since the system undergoes a cycle, $\Delta G^{\text{engine}} = 0$, we arrive at $(\mu_h - \mu_\ell)\Delta N_h = -\Delta G^{\text{tot}}$. Therefore, the relevant definition of the efficiency of the chemical engine is

$$\Theta = \frac{(-W^{\text{tot}})}{(-\Delta G^{\text{tot}})}. \tag{2.26}$$

Remark: Any arbitrary positive quantity whose upper bound is unity does not necessarily deserve to be called efficiency: if we have an inequality in the form of $A - B - C \leq 0$ about the cycle of an energy converter, we might ask ourselves which of $A/(B + C)$, $(A - B)/C$, or $(A - C)/B$ is the most appropriate definition of the efficiency of energy conversion.

General remark: It is only the difference that the thermodynamic functions appeared in the thermodynamic efficiency Θ or in the Carnot efficiency η. It was so also in the heat and work of reversible reactions (2.18). It is because the thermodynamic functions have the arbitrariness of an additive constant and the experimentally observable results do not depend on that constant. So as to be compatible with the extensive character of these functions, this arbitrariness is reduced to the arbitrary additive constants in the molar [specific] energy and entropy. All the thermodynamic laws and relations are invariant under the change of these constants. See Appendix A.2.2.

The analysis of a Carnot cycle by conventional macroscopic thermodynamics is tautological, since macroscopic thermodynamics is constructed to explain the Carnot cycle. The above review will be still useful as a reference frame when a similar cycle is studied on the scale of thermal fluctuations.

The cost of the operations, i.e., of connecting or disconnecting with the environments, macroscopic thermodynamics is supposed to be negligible. For mesoscopic systems, irreversibilities associated to the operation on the system require attention. This issue will be discussed later (Chap. 7).

2.3.4 Discontinuous Phase Transition Accompanies the Compensation Between Enthalpy and Entropy

Phase transition can occur if a system takes two thermodynamically distinguishable equilibrium states (phases) at a temperature T and a pressure p of the environment. For a single-component system the transition occurs along a coexistence curve in the (T, p)-plane.[36] Typical examples are the boiling of water or precipitation of vapor.

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[36] The generalization to many component systems is known as the Gibbs phase rule.
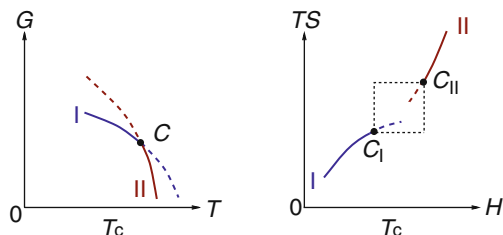
Fig. 2.9 (*Left*) Schematic representation of Gibbs free energy of two phases vs. T. From the gradient $\partial G/\partial T$ the entropy $S = -T\partial G/\partial T$ is estimated, while from the intersection at $T = 0$ of the tangent lines, the enthalpy, $H = G - T\partial G/\partial T$ is obtained. The smaller of G_I and G_{II} is realized; i.e., G_I for $T < T_c$ and G_{II} for $T > T_c$. (Right) The jump of H and of TS across the phase transition $C_I \leftrightarrow C_{II}$ on the (H, TS)-plane. The gradient of the jump C_I–C_{II} (a diagonal of the *dashed square*) is $45°$ because of the H–S compensation (2.28)

In thermodynamics this discontinuous transition, called the first-order phase transition, is characterized by the equality of the Gibbs free energy per mass of the two states, G_I and G_{II}:

$$G_I = G_{II} \qquad \text{(at transition)}, \qquad\qquad (2.27)$$

where we distinguish the two phases by I and II, see Fig. 2.9 (left), where the pressure p is fixed. Exactly at the transition point, either one of the states is realized or the two phases coexist macroscopically in the system.

Gibbs free energy consists of enthalpy (i.e., the internal energy of the system *plus* the pressure environment) H and the entropic term, $-TS$, that is $G = H - TS$. In the case of the liquid–vapor transition of water, the liquid phase (I) gains the enthalpic part of G_I by its cohesive energy, while the vapor phase (II) gains the entropic term $(-TS)$ by having a large specific volume per molecule. As a result, the enthalpy of these two phases satisfies $H_{II} - H_I > 0$, while their entropy obeys $T(S_{II} - S_I) > 0$. At the phase transition (2.27) tells that the differences of these two terms must balance (" Enthalpy–entropy (H–S) compensation"):

$$H_{II} - H_I = T(S_{II} - S_I) \qquad \text{(at transition)}. \qquad\qquad (2.28)$$

Figure 2.9 (right) shows schematically the condition (2.28).

When the system is infinitely large, the zeroth law of thermodynamics is compatible with the switching of two phases at the transition, because the "sufficiently longtime" at the transition point cannot be realized. By contrast, for a finite system, the equilibrium state is unique and there are no singularities in phase transition. Some proteins can take clearly distinguishable shapes ("conformations") over the timescale of msec. Upon the conformation transition, a phenomenon similar to the above mentioned H–S compensation has been observed [8]. The differences of enthalpy and, therefore, of the entropy between the two conformations are large when the conformation change accompanies the binding/release of the surround-

ing water molecules.[37] Biological molecules are thought to use such transition-like phenomena. Some soft materials often undergo the transition under physiological conditions.

The $H-S$ compensation has sometimes been an object of controversy because it can also arise as an experimental artifact [10]. In fact, if the term $-T\partial G/\partial T$ is predominant in the formula $H = G - T\partial G/\partial T$ over the magnitude of G, we have $TS = -T\partial G/\partial T \simeq H$. Therefore, we would have $\Delta H \simeq T\Delta S$ for any change of parameters, including T, within a relatively narrow range. The estimation of this artifact may be a good exercise for error analysis problems.[38]

2.4 Notes on the Extension of the Thermodynamics

It is being recognized that thermodynamics is an asymptotic mathematical structure where certain variables obey a set of universal relations. This structure appears in the phenomena consisting of a large number of similar objects. The conventional macroscopic thermodynamics, either classical or quantum mechanical, is not the only example. Thermodynamic relations that we will explore in this book from Chap. 4 are the another example. We mention below several extensions of the thermodynamics.

The geometrical aspect of thermodynamics has been studied under the name of *metric geometry of equilibrium thermodynamics* [11–13]. A framework to describe a large number of "thermodynamic elements" has been sought for by analogy to the theory of electric circuit, called *network thermodynamics* [14]. In linear nonequilibrium thermodynamics (see Sect. 2.2), subsystems are supposed to maintain local equilibrium within themselves and the transport and dissipation among the subsystems obey the Onsager (force–flux) relation [15, 16, 6, 7]. The Navier–Stokes equation [17] incorporates this framework.

More fundamental project has recently been proposed toward the *axiomatization of thermodynamics* [1, 2]. The latter [2] constructs a set of axioms for the conventional thermodynamics. The former [1] studies the axioms which are valid for any steady states including conventional thermodynamics. The subject is currently a hot topic [18–23].

In quantum information theory, people look for the *thermodynamics of quantum entanglement* [24]. The thermodynamic structure of chaotic systems has also been formulated [25, 26].

There are also attempts to remove some of the fundamental requirements of thermodynamic phenomena: in the *thermodynamics of small systems* [27], one does

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[37] Upon a principal conformation change of a myosin molecule (called the isomerization), about 120 water molecules leave from the surface, according to the analysis based on dielectric measurements [9]. There, the enthalpy changes of about $H = +51(\mathrm{kJ/mol})$ is mostly compensated, leaving little Gibbs energy difference between the conformations. (cf. $k_{\mathrm{B}}T = 2.4(\mathrm{kJ/mol})$.)

[38] [29] is a good introduction of error analysis.

without the extensivity of the system behavior. In the *theory of glass [transition]*, the lack of quasistatic processes gives rise to many interesting phenomena, such as memory effect, aging, and plasticity. The related issue will be addressed in Sects. 7.1.2 and A.7.2. The so-called effective temperature [28] of glassy states indicates the (decaying) memory of the initial preparation.

References

1. Y. Oono, M. Paniconi, Prog. Theor. Phys. Suppl. **130**, 29 (1998) 67, 70, 91
2. E. Lieb, J. Yngvanson, Phys. Rep. **310**, 1 (1999) 67, 70, 91
3. H.S. Leff, A.F. Rex, *Maxwell's Demon: Information, Entropy, Computing* (A Hilger (Europe) and Princeton U.P. (USA), 1990) 69
4. M. Toda, R. Kubo, N. Saitô, *Statistical Physics I: Equilibrium Statistical Mechanics*, 2nd edn. (Springer-Verlag, Berlin, 1992) 71
5. E. Fermi, *Thermodynamics*, 1st edn. (Dover Publications, New York, 1956) 80, 83
6. S.R. De Groot, P. Mazur, *Non-Equilibrium Thermodynamics* (Dover Publications, New York, 1984) 81, 91
7. T.L. Hill, *Free Energy Transduction and Biochemical Cycle Kinetics*, dummy edn. (Springer-Verlag, New York, 1989) 81, 91
8. E. Grunwald, L.L. Comeford, in *Protein-Solvent Interactions*, ed. by R.G. Gregory (Marcel Dekker, Inc., New York, 1995), Chap.10, p.421 90
9. M. Suzuki et al., Biophys. J. **72**, 18 (1997) 91
10. A. Cornish-Bowden, J. Biosci. **27**, 121 (2002) 91
11. F. Weinhold, J. Chem. Phys. **63**, 2479 (1975) 91
12. F. Weinhold, J. Chem. Phys. **63**, 2488 (1975) 91
13. F. Weinhold, J. Chem. Phys. **63**, 2495 (1975) 91
14. G. Oster, A. Perelson, A. Katchalsky, Nature **234**, 393 (1971) 91
15. L. Onsager, Phys. Rev. **37**, 405 (1931) 91
16. L. Onsager, Phys. Rev. **38**, 2265 (1931) 91
17. L.D. Landau, E.M. Lifshitz, *Fluid Mechanics (Course of Theoretical Physics, Volume 6)*, 2nd edn. (Reed Educational and Professional Publishing Ltd, Oxford, 2000) 91
18. M. Paniconi, Y. Oono, Phys. Rev. E **55**, 176 (1997) 91
19. K. Sekimoto, Prog. Theor. Phys. Suppl. **130**, 17 (1998) 91
20. T. Hatano, S. Sasa, Phys. Rev. Lett. **86**, 3463 (2001) 91
21. S. Sasa, H. Tasaki, J. Stat. Phys. **125**, 125 (2006) 91
22. T. Komatsu, N. Nakagawa, Phys. Rev. Lett. **100**, 030601 (2008) 91
23. T. Komatsu, N. Nakagawa, S. Sasa, H. Tasaki, Phys. Rev. Lett. **100**, 230602 (2008) 91
24. M. Horodecki, J. Oppenheim, R. Horodecki, Phys. Rev. Lett. **89**, 240403 (2002) 91
25. Y.G. Sinai, Sov. Math. Dokl. **4**, 1818 (1963) 91
26. D. Ruelle, *Thermodynamic Formalism* (Addison-Wesley, Reading, 1978) 91
27. T.L. Hill, *Thermodynamics of Small Systems, Parts I and II* (Dover Publications Inc., New York (Original: W.A. Benjamin, Inc. New York, 1963, 1964), 1994) 91
28. L.F. Cugliandolo, J. Kurchan, L. Peliti, Phys. Rev. E **55**, 3898 (1997) 92
29. J.R. Taylor, *An Introduction to Error Analysis*, (Sect. 8.5) 2nd edn. (University Science Books, California, 1997) 91