Chapter 2
Thermodynamics

We know from experience that a macroscopic system behaves in a relatively simple manner. For example, when liquid water is heated under atmospheric pressure, it will boil at 100 °C. If the vapor so produced is cooled at the same pressure, it will condense at 100 °C. These statements hold true regardless of the initial conditions from which the body of water under consideration has evolved. This situation is in stark contrast to that in classical mechanics, in which initial conditions play a far more prominent role. In fact, our experience tells us that results of measurements we make of a macroscopic body are quite insensitive to the detailed microscopic state of the body. Thermodynamics is built on this empirical observation and systematically elucidates interconnections among these *insensitive observations*. In this chapter, we review the framework of thermodynamics before attempting to interpret it from the classical mechanical point of view in Chaps. 3 and 4.

2.1 The First Law of Thermodynamics

A macroscopic system, such as a glass of water, consists of many molecules. While behavior of molecules is subject to the laws of quantum mechanics rather than those of classical mechanics, the latter framework can still provide a useful approximation in many situations. On the basis of conservation of energy we saw in the previous chapter, we may conclude that the work W' done on the system, which is a collection of molecules in this case, is equal to the change ΔE in its total energy:

$$\Delta E = W' . \tag{2.1}$$

In writing this equation, it is assumed that the number of mechanical degrees of freedom remains fixed while the work is performed on the system. In thermodynamics, a system that does not exchange particles with the surroundings is called a **closed system** or a **body**. In contrast, an **open system** allows for particles to freely

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pass through its boundary, thereby changing its number of mechanical degrees of freedom. For a moment, we focus only on closed systems.

Our everyday experience tells us, however, that a change in the apparent state of the system can be brought about without exerting any work on it. For example, by immersing a piece of heated steel in a glass of cold water, we can cause the state of the water to change. It becomes warmer and, if the steel is sufficiently hot, the water may even start to boil. From this observation, we infer that its energy content has also changed. At the molecular scale, this may be understood as a result of kinetic energy being transferred from iron atoms to water molecules through collisions among them. The kinetic energy is also constantly redistributed within the piece of steel. It appears then that the process we are observing belongs to the realm of classical mechanics. While this is true aside from the abovementioned quantum nature of atomistic processes, a full description of the process from this mechanistic point of view demands that we be capable of knowing the position and velocity of each constituent particle in the system (a glass of water in this case) and in the surroundings (a block of steel) at some instant of time and that the equations of motion can be integrated from the initial conditions so determined. Even if this is somehow possible, it is not clear if the microscopic description we would obtain is particularly useful.

Thus, when we perform a macroscopic observation, which does not inquire into the molecular-level details of a process, we must acknowledge that there are two types of processes. Firstly, there are those processes for which the force and the resulting displacement can be identified at a macroscopic level. In this case, we can readily compute ΔE by means of (2.1). Then, there are other processes, such as those we have considered above, for which the relevant forces and displacements are detectable only at a microscopic level. In such a situation, we, as a macroscopic observer, cannot compute ΔE by means of (2.1).

It is then sensible to use separate notations and words referring to these two modes of affecting the energy content of the system. From this point on, we shall use the term **work** to mean the mode of energy transfer into a system in which the force and the resulting displacement are measurable at a macroscopic level. We use the symbol W to denote the work in this narrower sense of the word. The other mode of energy transfer is called **heat** and is denoted by the symbol Q. Thus, heat embraces all modes of energy transfer we cannot express in a form of a macroscopic force and the resulting macroscopic displacement. By means of the newly introduced quantities, (2.1) becomes

$$\Delta E = W + Q \,. \tag{2.2}$$

The principle of conservation of energy, when expressed in this form, is called the **first law of thermodynamics**.

Of course, (2.2) would not be very useful unless we can compute Q for a given process despite our inability to identify the relevant forces and displacements at the microscopic level. This question of quantifying Q will be taken up in the next section.

The state of a system defined in terms of the coordinates and momenta of all particles in the system is called the "microscopic state" or **microstate** of the system. In contrast, we use the phrase "macroscopic state," or **macrostate** for short, to refer to the state in which the system appears to us when making observations that are insensitive to the microscopic details. Thus, *the notion of heat arises when we describe the behavior of the system in terms of macrostates as opposed to microstates*.

In thermodynamics, we are primarily interested in the "internal state of the system" and not in its macroscopic motion in space or change in its position relative to an external field. Accordingly, the kinetic energy due to translational motion of the system as a whole and the potential energy due to an external field are subtracted off from E, and we focus only on what is left, which is called the **internal energy** of the system and is denoted by U.

If we consider a system enclosed by rigid walls that are fixed in space, the location of its center of mass fluctuates at a microscopic level as a result of interaction between the system and its surroundings. Because of this, the procedure just described is not well defined if applied within the context of microscopic description of the system. However, the change in the kinetic or the potential energy due to such fluctuation is generally too small to be detectable by *macroscopic measurements*. Within the accuracy of such measurements, the separation of E into U and the rest will be a well-defined procedure.

In Sect. 1.6, we saw that E is an additive quantity. Since both the kinetic and potential energies we are considering here are additive, U also is an **additive quantity**. For a homogeneous body, U is also an **extensive quantity**. That is, U is proportional to the size of the system. To see this, we may imagine dividing the homogeneous body into two equal parts. If each part is still macroscopic, the interaction between them makes a negligible contribution to U. By the additivity of the internal energy, U of the whole system is equal to twice the internal energy of one of the parts.

Provided that neither the heat nor the work affects the translational motion of the system as a whole or its position in the external field, we may rewrite (2.2) as

$$\Delta U = W + Q \,. \tag{2.3}$$

Given two macrostate A and B accessible to a system, there are many distinct ways of bringing it from one to the other. The amount of work W involved usually depends on exactly how the change is brought about. We express this fact by saying that W is path dependent. A path-dependent quantity is called a **path function**.

Based on the classical mechanical notion of energy, however, we expect that the energy of a system has a uniquely determined value for a given macrostate of the system. Such a quantity, the value of which is determined *only* by the macrostate in question, is called a **state function**. Consequently, the energy difference $\Delta U := U_b - U_a$ between the two states is path independent. According to (2.3), then Q must be a path function.

We note that the classical mechanical work W' is, as seen from (2.1), path independent. In defining W, we have focused only on macroscopic forces and macroscopic displacements and lost track of the processes occurring at the microscopic level. This is what makes W a path function.

We will often be concerned with infinitesimal changes, in which W and Q are infinitesimally small. Using $đW$ and $đQ$ to denote, respectively, the amount of work done on and heat added to the system, and replacing ΔU by $\mathrm{d}U$ to indicate that only the leading term of ΔU is retained, we write (2.3) as

$$\mathrm{d}U = đW + đQ \tag{2.4}$$

for an infinitesimal process. As with W and Q, and in contrast to $\mathrm{d}U$, both $đW$ and $đQ$ are path-dependent quantities. We use the notation đ to emphasize this fact.

Typically, the work term for an infinitesimal change is given by

$$đW = -P\mathrm{d}V\ , \tag{2.5}$$

where P and V are the pressure and volume of the system, respectively. In Sect. 2.3, we examine how this expression arises and under what conditions.

2.2 Quantifying Heat

The notion of heat was introduced as a result of our inability to track the detailed mechanism of energy transfer at the microscopic level. Therefore, it is not clear if heat can be quantified at all. How do we compute Q if it is defined as everything that cannot be expressed as force times displacement?

For expediency, we accept the following statement: Using a purely classical mechanical device, it is always possible to change the state of a system between two distinct macrostates A and B.

In other words, at least one of the two changes, from A to B *or* from B to A, can always be realized. By a purely **classical mechanical device**, we imply our ability to track all of its generalized coordinates and momenta. As a result, the device does not exchange heat with the system, but it can exchange work with the system. This means that the difference in energy between any two states can be measured in terms of force and the displacement. For example, if the change from A to B is achievable, we have

$$U_b - U_a = W_{\mathrm{cm}}\ , \tag{2.6}$$

where W_{cm} is the work done on the system by the purely classical mechanical device. Having determined the energy difference, we can compute the heat Q received by the system during *any* process that brings the system from A to B. In fact, from (2.3),

$$Q = (U_b - U_a) - W = W_{\mathrm{cm}} - W\ , \tag{2.7}$$

where W is the work done on the system during the process that involves an exchange of heat.

2.3 ‡A Typical Expression for $đW$

Suppose that an external body exerts a force $\boldsymbol{t}\mathrm{d}A$ on the system through a surface element of area $\mathrm{d}A$ on the boundary of the system. Further, let $\mathrm{d}\boldsymbol{l}$ denote the infinitesimal displacement experienced by the surface element. The work done by the force $\boldsymbol{t}\mathrm{d}A$ is then $\mathrm{d}\boldsymbol{l}\cdot(\boldsymbol{t}\mathrm{d}A)$. Repeating this computation for each of the surface elements, into which the system boundary A is divided, and adding together the results, we arrive at the total work done on the system:

$$đW = \int_A \mathrm{d}\boldsymbol{l}\cdot(\boldsymbol{t}\mathrm{d}A)\,, \tag{2.8}$$

where the integral is over the boundary A. If a part of the boundary is held fixed, then $\mathrm{d}\boldsymbol{l} = \boldsymbol{0}$ for that part of the boundary.

The stress vector $\boldsymbol{t}$ is given in terms of the stress tensor $\hat{T}$ as

$$\boldsymbol{t} = \boldsymbol{n}\cdot\hat{T}\,, \tag{2.9}$$

where $\boldsymbol{n}$, called the outward unit normal, is a unit vector perpendicular to $\mathrm{d}A$ and pointing away from the system. By definition,

$$\hat{T} = -P\hat{I} + \hat{T}_v\,, \tag{2.10}$$

where $\hat{I}$ is the unit tensor and $\hat{T}_v$ is referred to as the extra (or viscous) stress tensor.

We recall that $\hat{T}_v$ for Newtonian fluids is proportional to the *rate* of deformation. (The explicit expression for $\hat{T}_v$ is of no importance in the present discussion. For further details, consult Ref. [5], for example.) The key observation here is that, if any imbalance of force at any point on the system boundary is infinitesimally small, then the boundary moves very slowly and $\hat{T}_v$ will be negligibly small. Thus,

$$\hat{T} = -P\hat{I}\,. \tag{2.11}$$

Since $\boldsymbol{a}\cdot\hat{I} = \boldsymbol{a}$ for any vector $\boldsymbol{a}$, we have

$$\boldsymbol{n}\cdot\hat{T} = \boldsymbol{n}\cdot(-P\hat{I}) = -P\boldsymbol{n}\cdot\hat{I} = -P\boldsymbol{n}\,. \tag{2.12}$$

So,

$$đW = \int_A \mathrm{d}\boldsymbol{l}\cdot(-P\boldsymbol{n})\mathrm{d}A\,. \tag{2.13}$$

If P is uniform over the boundary A of the system, this may be written as

$$đW = -P\int_A \mathrm{d}\boldsymbol{l}\cdot\boldsymbol{n}\mathrm{d}A\,. \tag{2.14}$$

But, as seen from Fig. 2.1, $\mathrm{d}\boldsymbol{l}\cdot\boldsymbol{n}\mathrm{d}A$ is the volume swept out by the surface element $\mathrm{d}A$ as it moves by $\mathrm{d}\boldsymbol{l}$. When this quantity is added together for all such surface elements, the end result is the net change in the volume of the system. In this way, we arrive at (2.5).

We note that solids can sustain nonzero $\hat{T}_v$ even if the boundary does not move at all. This is because, according to Hooke's law, which is an excellent approximation

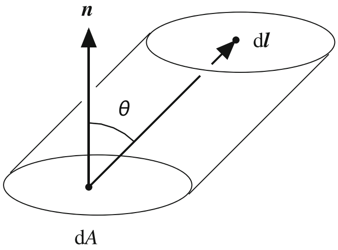

Fig. 2.1 The volume of the column swept out by the surface element dA as it moves by d$\boldsymbol{l}$ is given by $\mathrm{d}\boldsymbol{l}\cdot\boldsymbol{n}\mathrm{d}A = \mathrm{d}A\|\mathrm{d}\boldsymbol{l}\|\cos\theta$, in which $\boldsymbol{n}$ is the outward unit normal of dA and $\|\mathrm{d}\boldsymbol{l}\|\cos\theta$ is the height of the column.

for many solids as long as the deformation is sufficiently small, $\hat{T}_v$ in a solid is proportional *not* to the rate of deformation but to the size of deformation itself. We can still apply (2.5) to a solid under hydrostatic pressures, for which $\hat{T}_v \equiv 0$.

2.4 The Second Law of Thermodynamics

The content of the **second law of thermodynamics** is the following: There is a *state function* of a system called **entropy** S. The value of S can change as a result of both interactions with the surroundings and internal processes. Denoting the change associated with these processes by $đS_e$ and $đS_i$, respectively, we have

$$\mathrm{d}S = đS_e + đS_i \,. \tag{2.15}$$

For *closed* systems, $đS_e$ is given by

$$đS_e = \frac{đQ}{T} \tag{2.16}$$

where T is the **absolute temperature** and is a positive number. Thus, $đS_e$ can be positive, negative, or zero depending on the sign of $đQ$. A process for which $đQ \equiv 0$ is called an **adiabatic process**. In contrast,

$$đS_i \geq 0 \tag{2.17}$$

regardless of whether the system is closed or open. For processes occurring in a closed system, therefore, we have

$$\mathrm{d}S \geq \frac{đQ}{T} \,. \tag{2.18}$$

As shown more explicitly later in Example 2.1, the equality in (2.17) and (2.18) holds only for **reversible processes**. A process is called reversible if the sequence of states visited by the system can be traversed in an opposite direction by an infinitesimal change in the boundary conditions. As an example, we may think of a very slow expansion and compression of a gas enclosed in a thermally insulated cylinder fitted with a frictionless piston. The gas will expand if the external pressure is infinitesimally smaller than that of the gas. By an infinitesimal increase in the external pressure, the process can be reversed. Heat transfer due to an infinitesimal temperature difference is another example.

As is the case with the internal energy, entropy is an additive quantity. To see this, we may consider a composite system consisting of subsystems, each at its own uniform temperature. For each of them, we can assign a reference state at which its entropy is zero. Using a combination of reversible adiabatic processes and reversible heat transfer, we can bring a subsystem from its reference state to the actual state of interest and compute the change in its entropy by means of (2.18) with equality. The entire process in which this is done, one subsystem after another, may be regarded as a single process in which the composite system is brought to the state of interest from its reference state. As long as the interaction among subsystems can be ignored, the resulting change in entropy of the composite system is equal to the sum of the entropy change for each of the subsystems. **Additivity** of S, when applied to a homogeneous body implies that entropy of the body is proportional to its size. In other word, S is an **extensive quantity**. This property of S are in stark contrast with such quantities as T and P, which are independent of the size of the system and is said to be **intensive**.

As we shall see later, classification of thermodynamic quantities into extensive and intensive variables is of fundamental importance in thermodynamics. Without it, one cannot derive important equations such as the Euler relation and the Gibbs–Duhem relation. (See Sects. 2.10, 2.11, 6.4, and 6.5.)

We will be concerned primarily with the consequence of the second law and the properties of entropy as summarized above and will not inquire how the law can be established solely on the basis of macroscopic observations. An interested reader should consult Ref. [2].

2.5 Equilibrium of an Isolated System

When a system is isolated from the surroundings and thus left undisturbed, it eventually reaches a particularly simple state, in which no further change is observed in any *macroscopic* quantities we can measure of the system. This final state is called an **equilibrium state**. The second law of thermodynamics leads to a precise formulation of the condition of equilibrium of an isolated system in terms of entropy.

Since $đQ = 0$ for an isolated system, (2.18) reduces to

$$\mathrm{d}S \geq 0 \,. \tag{2.19}$$

That is, during a spontaneous internal process that brings the system eventually to a state of equilibrium, the entropy of the system does not decrease. At the same time, the internal energy of the system remains constant since $đW$ is also zero for an isolated system.

It seems unlikely that the entropy of a *finite* isolated system can increase indefinitely. Instead, we expect the entropy of the system to eventually reach the maximum possible value consistent with the given values of U, V, the total mass, and any other constraints that might be imposed on the system. Once the system reached this state of maximum entropy, any further change would require the entropy to decrease, which is impossible for an isolated system. Evidently, the same argument applies when S is only a local maximum. The entropy being (local) maximum is thus *sufficient* for an isolated system to be in equilibrium.

To establish its *necessity* for equilibrium, we may consider a system that is not at the state of maximum entropy under a given set of constraints. In this case, those processes that result in an increase of S are still possible while the processes in the opposite direction are not. Thus, we expect that the state of the system under consideration is not one of equilibrium.

In this way, we are led to accept the following formulation of the condition of equilibrium:

Condition of Equilibrium 1 *For the equilibrium of an isolated system, it is necessary and sufficient that the entropy of the system is (local) maximum under a set of constraints imposed on the system.*

For a more careful discussion aimed at establishing the necessity and the sufficiency of the condition, see pp. 58–61 of Ref. [3].

According to the second law, processes resulting in a decrease of the entropy are impossible for an isolated system. From a point of view of statistical mechanics, which provides a microscopic interpretation of the second law, this is not entirely accurate. In fact, the probability of finding the system with entropy S' which is less than the equilibrium value S is proportional to

$$e^{(S'-S)/k_B} , \tag{2.20}$$

where $k_B = 1.3806 \times 10^{-23}$ J/K is the **Boltzmann constant**. That the entropy of an isolated system can actually decrease by spontaneous fluctuation is directly responsible for the initial stage of the so-called first-order phase transition, the examples of which include freezing of a supercooled liquid, sudden boiling of superheated liquid, and condensation of supersaturated vapor. These phases of temporary existence, such as the supercooled liquid, superheated liquid, and supersaturated vapor, are said to be **metastable** and correspond to a *local* maximum of the entropy.

2.6 Fundamental Equations

The concept of fundamental equation is essential to thermodynamics. As we shall see, by merely accepting its existence and assuming that it meets some modest mathematical requirements, we can establish surprising interrelations among seemingly unrelated quantities almost effortlessly.

2.6.1 Closed System of Fixed Composition

For a moment, we restrict ourselves to reversible precesses occurring in a closed system. For simplicity, we also assume that there is no chemical reaction in the system so that the number of moles of species i, to be denoted by N_i, is constant for each species $(i = 1, \ldots, c)$. Under these conditions, we may rewrite (2.4) using (2.5) and (2.18) to obtain

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V\ . \tag{2.21}$$

As of now, we have accepted the validity of this equation only for reversible processes during which $N_1, \ldots, N_c$ of the system remain constant. We now argue that it applies to irreversible processes as well.

The key idea here is that, as long as we limit ourselves to an isolated system that is in *equilibrium* and *homogeneous*, its entropy S is a function only of U, V, and N_1, $\ldots$, N_c:

$$S = S(U, V, N_1, \ldots, N_c)\ . \tag{2.22}$$

This is so because the value of S, in the case of an isolated system in equilibrium, is determined by it being the maximum possible value for given values of U, V, and N_1, $\ldots$, N_c. Equation (2.22) is an example of **fundamental equations** of the system.

The restriction on homogeneity stems from our use of (2.5). In the case of an inhomogeneous system, there may be no single value of P. Thus, the work done on the system by an infinitesimal displacement of an infinitesimal portion of the system boundary depends on the position of this surface element. In order to specify the state of the system, then, one generally has to specify the shape of the system boundary, and not just its volume.

For the processes under consideration, N_1, $\ldots$, N_c are constant. Suppose now that we have changed the values of U and V by some infinitesimal amounts $\mathrm{d}U$ and $\mathrm{d}V$, respectively. The value of S in this new state is simply

$$S(U + \mathrm{d}U, V + \mathrm{d}V, N_1, \ldots, N_c)\ . \tag{2.23}$$

To the first order, therefore, the resulting change in S is given by

$$\mathrm{d}S = \left(\frac{\partial S}{\partial U}\right)_{V,N} \mathrm{d}U + \left(\frac{\partial S}{\partial V}\right)_{U,N} \mathrm{d}V\ , \tag{2.24}$$

where we used (B.16) and included N in the subscripts to remind us that the derivatives are taken while holding all of N_1, $\ldots$, N_c constant.

Note that (2.24) is obtained by applying (2.22) to the states before and after the infinitesimal change. Thus, so long as the system is in equilibrium and homogeneous both *before and after* the change and N_1, $\ldots$, N_c remain unaffected, (2.24) applies to *any* process including irreversible ones.

According to (2.21), however,

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V \tag{2.25}$$

for a reversible process. A comparison between (2.24) applied for a reversible process and (2.25) gives

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \quad \text{and} \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} . \tag{2.26}$$

The differential coefficients on the right-hand side are obtained by comparing the values of S for infinitesimally different two equilibrium states. Since S is a state function, the partial derivatives depend only on the values of $\mathrm{d}U$ or $\mathrm{d}V$, but not on how these changes are brought about. Therefore, (2.26) holds regardless of the nature of the process.

Combining (2.24) and (2.26) and noting that neither depends on the process being reversible, we conclude that (2.25), and hence (2.21), hold for *any* infinitesimal change that is occurring in a closed system without affecting $N_1, \ldots, N_c$.

We emphasize that, given a pair of initial and final states, values of $đQ$ and $đW$ do depend on the actual path taken, since they are path functions. In particular, $đQ \neq T\mathrm{d}S$ and $đW \neq -P\mathrm{d}V$ for irreversible processes. Only the sum of these two, $\mathrm{d}U = đW + đQ$, is independent of the path and is given by (2.21). We illustrate these points with the following example.

Example 2.1. Gas in a cylinder: Let us consider a gas enclosed in a cylinder that is fitted with a frictionless piston. We suppose that the gas is initially in equilibrium and has a uniform temperature T and pressure P. Then, we induce a change in the state of the gas by changing the external pressure acting on the piston to P_e and by changing the wall temperature of the cylinder to T_a.

The gas will expand if $P_e < P$ while it will be compressed if $P_e > P$. In both cases, the work $đW$ done *on* the system by the surroundings is given by

$$đW = -P_e\mathrm{d}V = -P\mathrm{d}V + (P - P_e)\mathrm{d}V . \tag{2.27}$$

Since temperature varies continuously across interfaces, T_a is also the temperature of the gas in the immediate vicinity of the wall. According to (2.16), the heat $đQ$ received by the system during this process is

$$đQ = T_a\, đS_e , \tag{2.28}$$

which is positive if $T_a > T$ and negative if $T_a < T$.

Unless $P_e = P$ *and* $T_a = T$, the process will momentarily make the system inhomogeneous. Nevertheless, after the process has completed and the system is left alone for a while, it will reach a new state of equilibrium and the state function S, and hence $\mathrm{d}S$, will have definite values. Let us introduce this $\mathrm{d}S$ in our expression for $đQ$. Using (2.15),

$$đQ = T\, đS_e + (T_a - T)\, đS_e = T(\mathrm{d}S - đS_i) + (T_a - T)\, đS_e . \tag{2.29}$$

We observe that the values of $đW$ and $đQ$ cannot be determined solely by those of T, P, $\mathrm{d}V$, and $\mathrm{d}S$. This is expected: $đW$ and $đQ$ are path functions. What we saw in this section is that their sum, $đW + đQ$, is nevertheless completely determined by these and is given by

$$đW + đQ = \mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \ . \tag{2.30}$$

It follows that

$$-P\mathrm{d}V + (P - P_e)\mathrm{d}V + T(\mathrm{d}S - đS_i) + (T_a - T)\,đS_e = T\mathrm{d}S - P\mathrm{d}V \ . \tag{2.31}$$

Thus,

$$T\,đS_i \equiv (T_a - T)\,đS_e + (P - P_e)\mathrm{d}V \ . \tag{2.32}$$

This result is entirely consistent with (2.17). If $T_a > T$, then $đS_e = đQ/T_a > 0$, while $đS_e < 0$ if $T_a < T$. Thus, the first term is positive unless $T = T_a$. Likewise, we see that the second term is positive unless $P = P_e$. The conclusion is that $đS_i = 0$ if and *only if* $T = T_a$ *and* $P_e = P$, that is, if and only if the process is reversible.

Finally, we note that (2.21) actually holds even when we allow for chemical reactions. This is to be expected since the equation is merely an expression of the first law of thermodynamics, that is, conservation of energy but applied to a system in equilibrium. An explicit demonstration, however, must wait until our formalism is fully developed. We shall visit this issue in Sect. 2.9.4.

2.6.2 Open System

Because an open system allows for particles of some of the species to freely pass through its boundary, some of $N_1, \ldots, N_c$ are no longer constant. Thus, the most general expression for $\mathrm{d}S$ is

$$\mathrm{d}S = \left(\frac{\partial S}{\partial U}\right)_{V,N} \mathrm{d}U + \left(\frac{\partial S}{\partial V}\right)_{U,N} \mathrm{d}V + \sum_{i=1}^{c} \left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_{j\neq i}} \mathrm{d}N_i \ , \tag{2.33}$$

where the first two partial derivatives are given by (2.26). In the last partial derivative, U, V, and all of $N_1, \ldots, N_c$ except for N_i are held constant. Following the convention, we write

$$-\frac{\mu_i}{T} := \left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_{j\neq i}} \tag{2.34}$$

and refer to μ_i as the **chemical potential** of species i. The quantity μ_i was first introduced by Gibbs, who referred to this quantity simply as potential. Combining

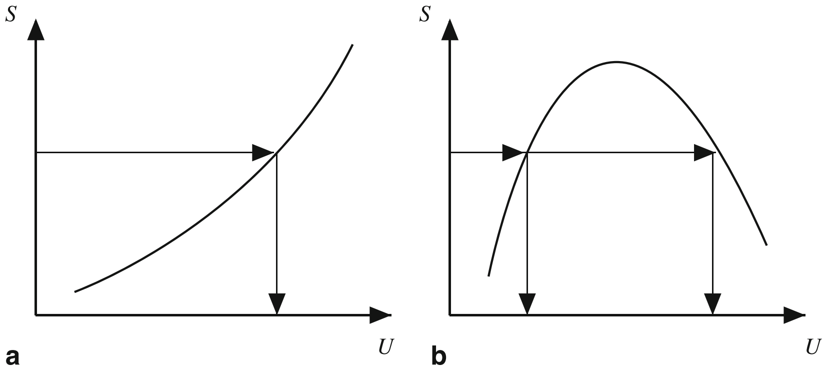

Fig. 2.2 The function $S = S(U)$, for some fixed values of $V, N_1, \ldots, N_c$, can be inverted to give $U = U(S)$ since $1/T = (\partial S/\partial U)_{V,N} > 0$, and hence the function is monotonic as indicated in **a**. If $1/T$ changes its sign as in **b**, there may be multiple values of U for a given value of S and the function $S = S(U)$ cannot be inverted.

everything, we arrive at

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V - \sum_{i=1}^{c} \frac{\mu_i}{T}\mathrm{d}N_i \,, \tag{2.35}$$

which is often referred to as the **fundamental property relation** or the fundamental equation in differential form.

Recall that T of a system is a positive quantity. Consequently, S increases monotonically with increasing U. As indicated in Fig. 2.2, this has an important implication that (2.22) can be solved for U, yielding

$$U = U(S, V, N_1, \ldots, N_c) \,. \tag{2.36}$$

It is graphically clear that the process can be reversed. That is, (2.22) and (2.36) are equivalent ways of expressing the same set of information regarding the thermodynamic behavior of the system. In view of this equivalence, the function in (2.36) is also a fundamental equation.

Solving (2.35) for dU, we obtain

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1}^{c} \mu_i \mathrm{d}N_i \,, \tag{2.37}$$

which is simply an alternative way of writing the fundamental property relation. From this, we obtain

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} , \quad -P = \left(\frac{\partial U}{\partial V}\right)_{S,N} , \quad \text{and} \quad \mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} , \; i = 1, \ldots, c \,. \tag{2.38}$$

Exercise 2.1. A pure gas is well described by the fundamental equation

$$S = aN + NR\ln\frac{U^{3/2}V}{N^{5/2}}\ . \tag{2.39}$$

a. Find the equation of state of the gas in the form of

$$P = P(T,V,N)\ . \tag{2.40}$$

b. Show that

$$U = \frac{3}{2}PV\ . \tag{2.41}$$

c. Show that

$$PV^{5/3} = \text{const.} \tag{2.42}$$

holds during an adiabatic reversible expansion of the gas.

d. An isolated cylinder made of adiabatic and rigid wall is divided into two compartments of equal volume by a frictionless piston. One of the compartments contains the gas well described by (2.39) and the other compartment is evacuated. If the piston is linked to an external work source and allowed to move very slowly until the gas fills the entire chamber, show that

$$U_2 = 2^{-2/3}U_1\ , \tag{2.43}$$

where the subscripts 1 and 2 refer to the initial and the final states, respectively.

///

Exercise 2.2. The fundamental equation of a pure system is given by

$$S = a(UVN)^b\ , \tag{2.44}$$

where a is a positive constant. The system is held at $P = 0.3$ MPa:

a. What is the value of b?
b. Find the value of U/V.
c. Find the value of μ in J/mol when $N/V = 0.1$ (mol/cm^3). ///

2.6.3 Heat Capacities

The **constant volume heat capacity** C_V is the ratio of the infinitesimal amount of heat $đQ$ injected into the system to the resulting infinitesimal increase $\mathrm{d}T$ in its temperature when the system is held at constant volume and $N_1, \ldots, N_c$:

$$C_V := \frac{đQ}{\mathrm{d}T}\ , \quad V, N_1, \ldots, N_c \text{ const.} \tag{2.45}$$

The heat capacity per mole of the material

$$\underline{C}_V := C_V \Bigg/ \sum_{i=1}^{c} N_i \tag{2.46}$$

is the **constant volume molar heat capacity**. Similarly, we define the **constant pressure heat capacity** C_P by

$$C_P := \frac{đQ}{\mathrm{d}T}\,, \quad P, N_1, \ldots, N_c \text{ const.} \tag{2.47}$$

and the **constant pressure molar heat capacity** $\underline{C}_P$ by

$$\underline{C}_P := C_P \Bigg/ \sum_{i=1}^{c} N_i \tag{2.48}$$

Heat capacity of a unit mass of the material is referred to as the **specific heat**.

Exercise 2.3.

a. Show that

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N} . \tag{2.49}$$

b. Show that

$$C_P = \left(\frac{\partial U}{\partial T}\right)_{P,N} + P\left(\frac{\partial V}{\partial T}\right)_{P,N} = \left(\frac{\partial H}{\partial T}\right)_{P,N} , \tag{2.50}$$

in which $H := U + PV$ is the **enthalpy**. The partial derivative $(\partial V/\partial T)_{P,N}$ is related to the **coefficient of thermal expansion** α by

$$\alpha := \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} . \tag{2.51}$$

///

2.6.4 ‡Ideal Gas

Later in optional sections, we require a few key results regarding properties of an ideal gas of fixed N_1, …, N_c. For convenience, we summarize them here while highlighting the key concepts we have introduced so far.

At the molecular level, an ideal gas is characterized by a lack of interaction among molecules. This is, of course, an idealization, which becomes increasingly more accurate with decreasing density and increasing temperature. Because a given molecule does not feel the presence of others, its energy is independent of density, and hence of V. Thus, the internal energy of an ideal gas of fixed N_1, …, N_c is a

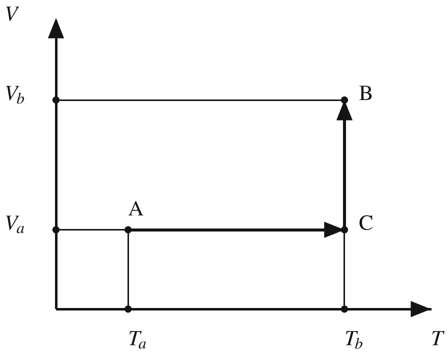

Fig. 2.3 A thermodynamic path bringing the system from state A to B.

function only of T. Exercise 2.23 provides a purely thermodynamic justification of this statement.

We wish to compute the changes U and S experience between states A and B that are specified by (T_a, V_a) and (T_b, V_b), respectively. For simplicity, we assume that C_V is constant in what follows.

To facilitate the computation, let us imagine bringing the system from A to B along the path shown in Fig. 2.3, in which we indicate the intermediate state C at (T_b, V_a). This does not affect the final answer since U and S are state functions.

For the constant volume process A→C, we can use (2.49) to write

$$\mathrm{d}U = C_V \mathrm{d}T \tag{2.52}$$

and hence

$$U_c - U_a = C_V (T_b - T_a) \,. \tag{2.53}$$

Applying (2.25) to a constant volume process,

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U = \frac{C_V}{T}\mathrm{d}T \,, \tag{2.54}$$

yielding

$$S_c - S_a = C_V \ln \frac{T_b}{T_a} \,. \tag{2.55}$$

For the constant temperature process C→B, U remains constant:

$$U_b - U_c = 0 \,. \tag{2.56}$$

Setting $\mathrm{d}U = 0$ in (2.25), we find

$$\mathrm{d}S = \frac{P}{T}\mathrm{d}V = \frac{NR}{V}\mathrm{d}V \tag{2.57}$$

and

$$S_b - S_c = NR \ln \frac{V_b}{V_a} \,, \tag{2.58}$$

where $R = 8.3145$ J/mol K is the **gas constant**. We also used the equation of state, $PV = NRT$, of the ideal gas, where N temporarily denotes $\sum_{i=1}^{c} N_i$.

Combining everything,

$$U_b - U_a = C_V (T_b - T_a) \tag{2.59}$$

and

$$S_b - S_a = C_V \ln \frac{T_b}{T_a} + NR \ln \frac{V_b}{V_a} \ . \tag{2.60}$$

We emphasize that (2.59) and (2.60) apply for any pair of states A and B and for any process regardless of whether the process goes through state C or not.

Now, let us suppose that the process A→B occurred adiabatically and reversibly. In this case, $\mathrm{d}S \equiv 0$ and (2.21) reduces to

$$\mathrm{d}U = -P\mathrm{d}V \ . \tag{2.61}$$

When this is combined with (2.52), we find

$$C_V \mathrm{d}T = -\frac{NRT}{V}\mathrm{d}V \ . \tag{2.62}$$

Integrating this equation from state A to state B,

$$C_V \ln \frac{T_b}{T_a} = -NR \ln \frac{V_b}{V_a} \ . \tag{2.63}$$

This is nothing but (2.60) applied to an adiabatic reversible process, for which $S_b = S_a$. Eliminating temperatures by means of the equation of state, we obtain

$$\frac{P_b}{P_a} = \left(\frac{V_b}{V_a}\right)^{-\gamma} , \tag{2.64}$$

where

$$\gamma := 1 + \frac{NR}{C_V} \ . \tag{2.65}$$

Exercise 2.4. Show that

$$C_P = C_V + NR \tag{2.66}$$

for an ideal gas. It follows that

$$\gamma = C_P / C_V \ . \tag{2.67}$$

///

Exercise 2.5. From (2.52) and the ideal gas equation of state, we see that

$$U = \frac{C_V}{NR} PV + \text{const.} \tag{2.68}$$

Applying this equation to an adiabatic reversible process, directly establish (2.64).

///

2.6.5 †Heat Flow into an Open System

Now that we have seen how (2.21) for a closed system generalizes to (2.37) for an open system, it is natural to ask how (2.4) and (2.18) written for a closed system should be generalized. There is no fundamental requirement imposing a unique solution to this question. Instead, it is a matter of convention. In this section, we shall limit ourselves to reversible processes and consider a few such conventions.

Convention 1: We can take a point of view that adding molecules to or extracting them from a system is a form of work and generalize (2.4) to read

$$\mathrm{d}U = đW_1 + đQ_1 + đW_{\text{mol}}\,, \tag{2.69}$$

where we use the subscript 1 to indicate the infinitesimal work and heat under the current convention. For reversible processes, $đW_{\text{mol}}$ is given by

$$đW_{\text{mol}} = \sum_{i=1}^{c} \mu_i \mathrm{d}N_i \tag{2.70}$$

and is called **quasi-static chemical work**. Under this convention, we retain the original meanings of work and heat, and write

$$đW_1 = -P\mathrm{d}V \quad \text{and} \quad đQ_1 = T\mathrm{d}S\,. \tag{2.71}$$

Convention 2: We recall that heat was defined as a mode of energy transfer that cannot be characterized as a macroscopic force times macroscopic displacement. Conduction of heat between bodies occurs when molecules moving about due to thermal motion exchange mechanical energy through collisions. Diffusive flux of molecules is also driven by thermal motion of molecules. That is, conduction and diffusion are both macroscopic manifestations of molecular level processes that do not involve macroscopic force or displacement. From this point of view, the concept of heat should be enlarged to include both heat conduction and diffusive molecular flux. That is, we retain (2.4):

$$\mathrm{d}U = đW_2 + đQ_2 \tag{2.72}$$

and write

$$đW_2 = -P\mathrm{d}V \quad \text{and} \quad đQ_2 = T\mathrm{d}S + \sum_{i=1}^{c} \mu_i \mathrm{d}N_i\,. \tag{2.73}$$

Convention 3: The second equation in (2.73) can be rewritten in a somewhat more illuminating manner using a thermodynamic identity to be established later in Exercise 2.24:

$$\mu_i = \overline{H}_i - T\overline{S}_i\,. \tag{2.74}$$

Here $\overline{H}_i$ and $\overline{S}_i$ are, respectively, the partial molar enthalpy and partial molar entropy to be introduced in Sect. 2.15. Using (2.74), we define heat as

$$
đQ_3 := đQ_2 - \sum_{i=1}^{c} \overline{H}_i \mathrm{d}N_i = T\mathrm{d}S - T\sum_{i=1}^{c} \overline{S}_i \mathrm{d}N_i \,. \tag{2.75}
$$

With this new definition of heat, (2.72) now reads

$$
\mathrm{d}U = đW_2 + đQ_3 + \sum_{i=1}^{c} \overline{H}_i \mathrm{d}N_i \,. \tag{2.76}
$$

Enthalpy is sometimes called the heat function. Thus, the last term of (2.76) may be interpreted as the heat brought into the system by the flow of molecules. Similarly, when (2.75) is written as

$$
\mathrm{d}S = \frac{đQ_3}{T} + \sum_{i=1}^{c} \overline{S}_i \mathrm{d}N_i \,, \tag{2.77}
$$

the last term suggests the flow of entropy associated with the flow of molecules. This is a very satisfying state of affair, at least psychologically.

Convention 1 is used in Ref. [1]. Conventions 3 is often adopted in textbooks on transport phenomena. Obviously, it is important to check which convention is being used in any given application. Any equation containing heat will have a different *appearance* depending on the convention.

2.7 Role of Additional Variables

In Sect. 2.5, we accepted the maximum of S under the existing constraints as both necessary and sufficient for equilibrium of an isolated system. Among other things, U and V of an isolated system are held constant. If we assume that c species in the system do not undergo chemical reactions, then the number of moles of each species, that is, all of $N_1, \ldots, N_c$, are fixed as well.

It is at this point that our formulation might appear inconsistent to you. In fact, according to (2.22), S is a function of U, V, and $N_1, \ldots, N_c$ only, all of which are fixed in an isolated system without chemical reactions. It is thus legitimate to wonder just what is meant by S being maximum when all of its arguments are fixed.

We need to remember, however, that (2.22) holds only for a homogeneous system in equilibrium. If the system is inhomogeneous or not in equilibrium, specification of its state may require not only those variables already listed but also some *additional variables*. Examples may include those variables characterizing spatial variation of composition, density, or temperature. If there is a macroscopic motion within the system, the velocity field throughout the system must also be given in order to fully specify the state of the system.

What the condition of equilibrium tells us is that *these additional variables, if allowed to vary, are determined so as to maximize S*. If a chemical reaction does take place in the system, then $N_1, \ldots, N_c$ can change in a manner that is consistent

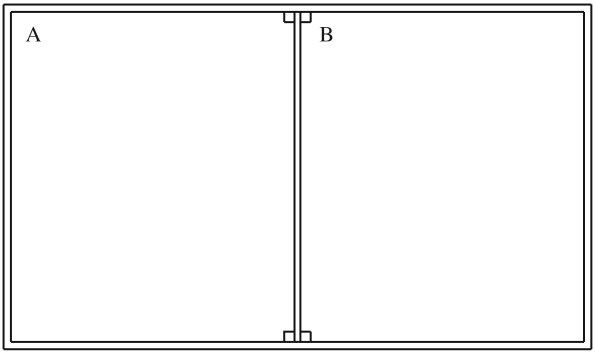

Fig. 2.4 A system consisting of two compartments. The system as a whole is isolated, while the properties of the wall separating the compartments can be modified as needed.

with the stoichiometry of the reaction. At equilibrium, the extent of reaction, once again, is determined by the condition that S is maximum.

To make the role of the additional variables clearer, we consider an example shown in Fig. 2.4. The system we consider is isolated from the surroundings by an adiabatic and rigid partition impermeable to all species. The interior of the box is divided into two compartments by a partition, whose property can be changed as needed. Initially, we suppose that the partition is adiabatic, rigid, impermeable to all species, and held fixed in place by stops. In this case, each compartment will eventually reach a state of equilibrium on its own independent of what is happening in the other compartment. When this final state of equilibrium is reached, the entropy of each compartment is a function of *its* U, V, N_1, …, N_c. Since entropy is an additive quantity, the total entropy S of the composite system is given by

$$S = S^a(U^a, V^a, N_1^a, \dots, N_c^a) + S^b(U^b, V^b, N_1^b, \dots, N_c^b) \,, \tag{2.78}$$

where the superscripts a and b label the respective compartment and we assumed that each compartment is homogeneous. Since the internal energy, volume, and the number of particles are all additive quantities, we have

$$U^a + U^b = U \,, \quad V^a + V^b = V \,, \quad \text{and} \quad N_1^a + N_1^b = N_1 \,,\ i = 1, \dots, c \,. \tag{2.79}$$

Using (2.79) in (2.78),

$$\begin{aligned} S &= S^a(U^a, V^a, N_1^a, \dots, N_c^a) + S^b(U - U^a, V - V^a, N_1 - N_1^a, \dots, N_c - N_c^a) \\ &= S(U, V, N_1, \dots, N_c; U^a, V^a, N_1^a, \dots, N_c^a) \,. \end{aligned} \tag{2.80}$$

The quantities U^a, V^a, and $N_1^a, \dots, N_c^a$ are examples of the additional variables. They are needed since the composite system taken as a whole, although in equilibrium, is not homogeneous.

Now, suppose that the partition suddenly became **diathermal**, allowing heat to pass from one compartment to the other. (The Greek prefix “dia” means “across”or “through.”) This implies that U^a is now free to change and, according to (2.80), S can change also even though $U, V, N_1, \dots, N_c, V^a$, and $N_1^a, \dots, N_c^a$ are all held constant. The content of the second law is that the equilibrium value of U^a is determined to maximize S for given values of $U, V, N_1, \dots, N_c, V^a$, and $N_1^a, \dots, N_c^a$. If the partition is made both movable and permeable to all species as well as being diathermal, all the quantities with superscript a in (2.80) can change. Their equilibrium values are again determined by the condition that S is maximum. (Such a partition is actually relevant in applications of thermodynamics. See Sect. 2.12.) The entire argument can be generalized to cases with more than two compartments.

2.8 Entropy Representation

We are now ready to formulate the condition of equilibrium in quantitative terms. The second law also tells us the direction of a spontaneous process as the system evolves toward the state of equilibrium.

2.8.1 Condition of Equilibrium

To proceed generally, let us suppose that r variables $X_1, \dots, X_r$ are required in addition to $U, V, N_1, \dots, N_c$ to fully specify the state of the system. Of these r variables, we assume that only the first m variables are free to change. In (2.80), for example, $r = c+2$. If the partition between the two compartments is diathermal, rigid, impermeable to all species, and is held fixed in place, then $m = 1$ and $X_1 = U^a$. On the other hand, if the partition is diathermal, movable, and permeable to all species, then $m = r = c+2$.

If an isolated system is in equilibrium, then its entropy S is maximum for given values of $U, V, N_1, \dots, N_c$, and $X_{m+1}, \dots, X_r$. This condition, in turn, determines the values of $X_1, \dots, X_m$ at equilibrium. Thus, if we denote the latter by $X_1^{\text{eq}}, \dots, X_m^{\text{eq}}$, then we may express the condition of equilibrium by saying that

$$\begin{aligned}\Delta S &= S(U,V,N_1,\dots,N_c;X_1^{\text{eq}}+\delta X_1,\dots,X_m^{\text{eq}}+\delta X_m;X_{m+1},\dots,X_r)\\ &\quad - S(U,V,N_1,\dots,N_c;X_1^{\text{eq}},\dots,X_m^{\text{eq}};X_{m+1},\dots,X_r) \leq 0\,. \end{aligned} \tag{2.81}$$

holds for any possible values of $\delta X_1, \dots, \delta X_m$.

We note that, after the infinitesimal changes denoted by $\delta X_1, \dots, \delta X_m$ are made, the system, in general, will no longer be in equilibrium. That is, unless we confine $X_1, \dots, X_m$ to their new values, they will simply return to their initial values $X_1^{\text{eq}}, \dots, X_m^{\text{eq}}$ to maximize S. The system may not be even homogeneous both before and after the change. This is to be contrasted with the situation considered in (2.35), in

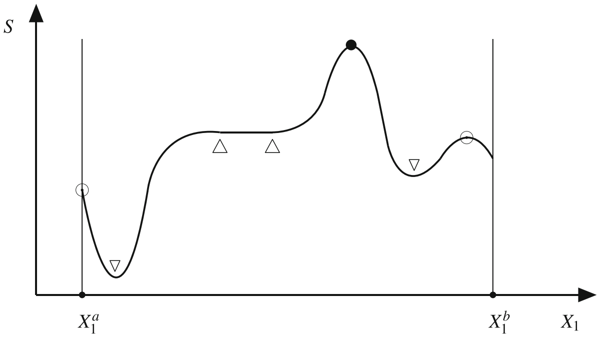

Fig. 2.5 Various possible states of equilibrium when X_1 is confined to the interval $\left[X_1^a, X_1^b\right]$. The system is in stable (●), metastable (⊙), unstable (▽), and neutral equilibrium (between the two △).

which the system was supposed to be homogeneous and in equilibrium *both* before and after the infinitesimal change. To make the distinction clear, we used the symbol δ for the infinitesimal changes occurring in (2.81) and refer to them as **variations**. We shall continue to use d as before to denote infinitesimal changes considered in writing (2.35) and refer to them as **differentiations**.

In what follows, we retain only up to the first-order terms in (2.81) and adopt the following statement as the condition of equilibrium:

Condition of Equilibrium 2 *For the equilibrium of an isolated system, it is necessary and sufficient that*

$$(\delta S)_{U,V,N_1,\ldots,N_c;X_{m+1},\ldots,X_r} \le 0 \tag{2.82}$$

for all possible variations of $X_1, \ldots, X_m$ *consistent with given constraints.*

The subscripts U, V, N_1, …, N_c, X_{m+1}, …, X_r remind us that the variations cannot affect the values of these (constrained) variables. However, the set of variables showing up in this list must be modified to suite the particular situation at hand. For example, if we allow for chemical reactions, N_1, …, N_c may change, but their variations must satisfy a set of equations expressing the constraint on the number of atoms of each element.

In practice, it may be very difficult to explore *all* possible variations and we will have to limit ourselves to a subset of all that are possible. The resulting conditions of equilibrium, therefore, will be *necessary but not sufficient* for equilibrium.

It is important, at least conceptually, to realize that both (2.81) and (2.82) allow for S to exhibit a kink (with a discontinuous first derivative) at the maximum. The maximum of S may also occur at an end point of the interval over which $X_1, \ldots, X_m$ can vary. In such cases, the system is in equilibrium even though $\delta S \neq 0$. According to (2.82), a minimum entropy state is also an equilibrium state as long as $\delta S = 0$. We illustrate these situations in Fig. 2.5 and classify them according to their stability with respect to perturbations.

Such perturbations may result due to outside influences which is so extremely minute that the system can otherwise be considered isolated. For example, your "isolated" system securely anchored to the floor of your building may experience small vibrations from time to time due to traffic outside. Even if the system is perfectly isolated from the rest of the universe, small inhomogeneity of density is constantly evolving throughout the system as the molecules move about. This is an example of spatially varying perturbation, which may be denoted as $\delta X_{\boldsymbol{r}}$ with $\boldsymbol{r}$ indicating the position dependence.

For simplicity, we let $m = 1$ in Fig. 2.5, that is, only X_1 is free to change. Then, • denotes a **stable equilibrium** state. This is because the system will return to this original state even after experiencing perturbations in X_1. States marked by ⊙ differ from the • state in that the system is stable only for small perturbations but not for sufficiently large perturbation in X_1. We call such a state **metastable**. The states marked by ▽ are in equilibrium. But the equilibrium is **unstable** because the system moves away from it as a result of even the slightest perturbation in X_1. Over the interval between the two △ where S is constant, the system is said to be in **neutral equilibrium**. In this case, there is no tendency for the system to return to the original state after an infinitesimal perturbation. But, there is not tendency to move away from it, either.

As we shall see shortly, there are other ways to express the condition of equilibrium. The current formulation, in which entropy plays a prominent role, is called the **entropy representation**.

2.8.2 Equality of Temperature

To illustrate the use of the condition of equilibrium, let us continue on the example in Sect. 2.7. We assume that the partition separating the two compartments is diathermal, rigid, impermeable to all species, and held in place by stops. Equations (2.80) and (2.82) provide a practical means of determining the value of the additional variable U^a at equilibrium.

According to (2.78), $S = S^a + S^b$, and hence

$$\delta S = \delta S^a + \delta S^b \, . \tag{2.83}$$

Using (2.35), we may rewrite this equation as

$$\delta S = \frac{1}{T^a}\delta U^a + \frac{1}{T^b}\delta U^b \, . \tag{2.84}$$

Since

$$U^a + U^b = U = \text{const.} \, , \tag{2.85}$$

and hence $\delta U^b = -\delta U^a$, (2.84) reduces to

$$\delta S = \left(\frac{1}{T^a} - \frac{1}{T^b}\right)\delta U^a \, . \tag{2.86}$$

Now, (2.82) demands that $\delta S \leq 0$ for any value of δU^a. Provided that δU^a can be either positive or negative, it follows that

$$T^a = T^b \,, \tag{2.87}$$

which is the condition of equilibrium of the composite system.

From (2.26), we see that T^a is a function of U^a, V^a, and $N_1^a, \ldots, N_c^a$. Likewise for T^b. Thus, (2.85) and (2.87) serve as the set of equations to determine U^a and U^b provided that the value of the constant U is known. Once U^a and U^b are found from these equations, then the temperature $T^a = T^b$ of the composite system in equilibrium can be computed from (2.26).

Strictly speaking, (2.87) is necessary for equilibrium but not sufficient since we have not considered *all* possible variations. For example, variations that disturbs homogeneity in either of the compartments were not considered. Such a concern is best addressed in terms of the stability of the equilibrium.

Finally, suppose that we remove the stops on the left of the partition but keep those on the right. In this case, V^a is incapable of a positive variation and $\delta V^a \leq 0$. From this, one can only deduce that $P^a/T^a \geq P^b/T^b$ at equilibrium. For a diathermal partition, we have $T^a = T^b$ and hence $P^a \geq P^b$. When this inequality is satisfied, clearly, the partition will not move to the left. It will not move to the right either because of the remaining stops. The composite system is thus in equilibrium even if P^a may differ from P^b.

Exercise 2.6. Suppose that the stops holding the partition are now removed and that the partition, besides being diathermal, just became permeable to species 1 while still impermeable to other species. Show that $T^a = T^b$, $P^a = P^b$, and $\mu_1^a = \mu_1^b$ hold at equilibrium. ///

Exercise 2.7. [7] The fundamental equation of a particular binary mixture is given by

$$S = aN + NR\ln\frac{U^{3/2}V}{N^{5/2}} - N_1R\ln\frac{N_1}{N} - N_2R\ln\frac{N_2}{N} \,, \quad N := N_1 + N_2 \,, \tag{2.88}$$

where a is an unspecified constant and R is the gas constant.

An isolated system is divided into two compartments A and B of equal volume by an adiabatic, rigid, and impermeable partition fixed in place by stops. Initially, compartment A is filled with $N_1 = 10$ mol of pure species 1 at $T^a = 300$ K while compartment B is filled with $N_2 = 4$ mol of pure species 2 at $T^b = 400$ K:

a. The partition suddenly became diathermal, while remaining rigid, impermeable, and held fixed in place by stops. After the system reached a new state of equilibrium, what is the temperature in each compartment?
b. The partition became permeable to species 1 in addition to being diathermal, while remaining rigid, impermeable to species 2, and held fixed in place by stops. After the system reached a new state of equilibrium, what is the final number of moles of species 1 in each compartment? What about the temperature? ///

2.8.3 Direction of a Spontaneous Process

In addition to identifying the state of equilibrium, the second law also determines the direction of a spontaneous process occurring in an isolated system.

In the example considered in Sect. 2.8.2, let us suppose that $T^a > T^b$ at the moment when the adiabatic partition became suddenly diathermal. Then we ask which of the two compartments receives heat as the composite system evolves toward a new state of equilibrium, at which $T^a = T^b$. You know the answer intuitively, of course. The purpose of this discussion is to make an argument based on the principle of thermodynamics.

From (2.86), we have

$$\mathrm{d}S = \left(\frac{1}{T^a} - \frac{1}{T^b}\right)\mathrm{d}U^a, \tag{2.89}$$

where we use "d" to indicate an infinitesimal change *without* implying that the *composite* system is in equilibrium either before or after the change. Instead, "d" in this equation denotes the infinitesimal change during a spontaneous process occurring in the system as it evolves toward equilibrium. Each compartment, taken separately, is assumed to be in equilibrium at all time. This assumption will be satisfactory if the change occurs very slowly.

By assumption, $T^a > T^b$ initially and the quantity in the brackets is negative. For a spontaneous process in the composite system that is isolated, $\mathrm{d}S$ must be positive. According to (2.89), $\mathrm{d}U^a < 0$ and hence $\mathrm{d}U^b = -\mathrm{d}U^a > 0$, that is, the heat flows from compartment A to B.

Just like a difference in temperature drives the heat flow between the two compartments, a difference in pressure drives the repartitioning of the volume between them. Similarly, a difference in the chemical potential of one of the species drives the flow of particles of that species. Chemical potentials also play a crucial role when chemical reactions can take place. You are invited to explore these remarks in detail in the following exercises.

Exercise 2.8. Consider an isolated system consisting of two compartments separated by a diathermal and rigid partition impermeable to all species and fixed by stops. Show that, when the stops are removed, the partition moves from the higher pressure compartment to the lower pressure compartment. You may assume that the temperatures of the two compartments are equal at all time. ///

Exercise 2.9. Consider an isolated system consisting of two compartments separated by a diathermal and rigid partition permeable to molecules of species 1 but not to the others. The partition is held fixed in place. Show that molecules of species 1 flow from the higher chemical potential compartment to the lower chemical potential compartment. You may assume that the temperatures of the two compartments are equal at all time. ///

Exercise 2.10. Consider an isolated and homogeneous ternary system ($c = 3$) consisting of species A_1, A_2, and A_3, in which the following chemical reaction can take place:

$$c_1A_1 + c_2A_2 \rightleftarrows c_3A_3 \ , \tag{2.90}$$

where c_1, c_2, and c_3 are some positive constants.

a. Show that

$$c_1\mu_1 + c_2\mu_2 = c_3\mu_3 \tag{2.91}$$

at equilibrium.

b. Show that the reaction proceeds from left to right if

$$c_1\mu_1 + c_2\mu_2 > c_3\mu_3 \; . \tag{2.92}$$

///

2.8.4 †*Very Short Remark on the Stability of Equilibrium*

In order for the composite system to eventually come to equilibrium through the spontaneous process considered in Sect. 2.8.3, the temperature must increase with an inflow of energy and decrease with an outflow of energy. This same condition is also necessary for the stability of a body with uniform temperature throughout. That is, if, by fluctuation, heat flows from one region to another, the temperature of a part receiving the heat must increase while the temperature of a region losing the heat must decrease. Otherwise, the ever-increasing inequality of temperature would drive the system further away from the original state. Thus, for the stability of any system, it is necessary that

$$\left(\frac{\partial T}{\partial U}\right)_{V,N} > 0 \, , \tag{2.93}$$

which, in view of (2.49), implies that

$$C_V > 0 \, . \tag{2.94}$$

We can develop a graphical approach to the question of stability. As an example, let us take an isolated homogeneous system and define the entropy density $s := S/V$ and the internal energy density $u := U/V$. Since S is an extensive quantity, we have

$$s = S(u, 1, N_1/V, \ldots, N_c/V) \, , \tag{2.95}$$

which simply states that the system containing U/V of the internal energy and N_i/V moles of species i in unit volume has $1/V$ times the entropy of the original system containing U of internal energy and N_i moles of species i in volume V. It follows that, for fixed values of V, and $N_1, \ldots, N_c$, the quantity s is a function only of u.

If $s = s(u)$ is concave up as shown in Fig. 2.6, the system is unstable with respect to separation into two homogeneous parts with distinct values of the internal energy density.

To see why, let us consider a homogeneous system having the internal energy U_0 and consisting of N_i moles of species i in volume V. We denote its entropy density by s_0 and its internal energy density by u_0. Then, the system is represented by the

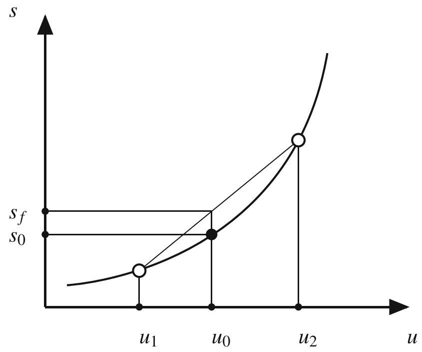

Fig. 2.6 If the curve $s = s(u)$ for a homogeneous body is concave up, the body is unstable with respect to the spontaneous separation into two homogeneous parts. Because of how the graph is drawn, the system can further increase its entropy by moving the *open circles* away from each other in such a way that the overall energy density remains at u_0.

filled circle in Fig. 2.6. Now, suppose that the system separated into two parts, one having the internal energy density u_1 and the other u_2 such that $u_1 < u_0 < u_2$ as represented by the open circles in Fig. 2.6. Then, the entropy density of the system at this final state is given by s_f in the figure. This is because the entropy density at the final state should be somewhere on the straight line connecting the two open circles, while the overall internal energy density must be u_0 because the system as a whole is isolated. If $s(u)$ is concave up, clearly, $S_f - S_0 = V(s_f - s_0) > 0$ and the process occurs spontaneously.

Exercise 2.11. Justify the graphical method given above for locating s_f through an explicit computation. ///

Exercise 2.12. By considering the sign of the second derivative:

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N}, \tag{2.96}$$

show that the constant volume heat capacity C_V defined by (2.49) is negative if $S = S(U)$ is concave up. Thus, $C_V > 0$ is necessary for the stability of a thermodynamic system. ///

2.9 Energy Representation

While the second law leads directly to the entropy representation of the condition of equilibrium, this is by no means the only possible formulation. Nor is it the most convenient. To explore alternatives, we begin by looking into the energy represen-

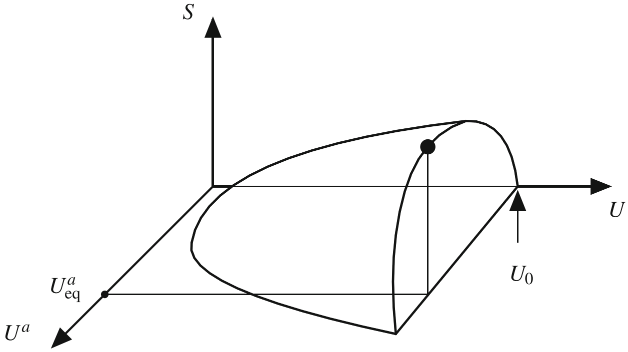

Fig. 2.7 Graphical representation of S of the composite system considered in Sect. 2.8.2. In drawing this graph, all the variables occurring in (2.80), except for U and U^a, are fixed. The equilibrium value of U^a, which we denote here by U^a_{eq}, is determined so that S takes the maximum possible value consistent with the given value, U_0, of the internal energy of the composite system. The equilibrium state is then indicated by the *filled circle*.

tation, in which the internal energy plays a central role in characterizing a state of equilibrium. Other possibilities are considered in Sect. 2.13.

2.9.1 Condition of Equilibrium

It is instructive to envision the approach to an equilibrium state graphically. For this purpose, let us revisit the example discussed in Sects. 2.8.2 and 2.8.3 and depict S of the composite system as a function of U and U^a as shown in Fig. 2.7.

Because the composite system is isolated, U is fixed at a constant value, say U_0. As the system evolves toward the equilibrium state, at which $T^a = T^b$ and $U^a = U^a_{\mathrm{eq}}$, its representative point moves along the curve defined by the intersection between the surface of S and the $U = U_0$ plane until it reaches the maximum S state indicated by • in Fig. 2.7. If this trajectory is projected onto the US-plane as shown in Fig. 2.8, the representative point is seen to move vertically upward until it meets the S versus U curve, at which $S = S_0$. From the latter figure, we observe that the same equilibrium state, that is, the point (U_0, S_0) can also be regarded as the state of *minimum* internal energy for a given value (S_0) of the entropy.

This suggests the following formulation, called the **energy representation**, of the condition of equilibrium as an alternative to the entropy representation:

Condition of Equilibrium 3 *For the equilibrium of an isolated system, it is necessary and sufficient that*

$$(\delta U)_{S,V,N_1,\ldots,N_c;X_{m+1},\ldots,X_r} \geq 0 \tag{2.97}$$

for all possible variations of $X_1, \ldots, X_m$ *consistent with given constraints.*

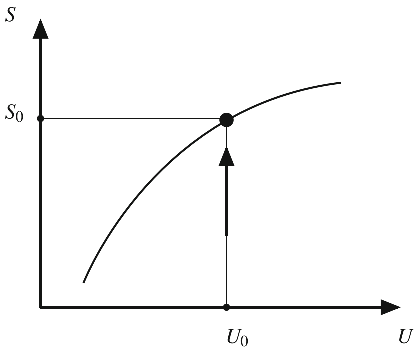

Fig. 2.8 Projection onto the US-plane of the locus of the maximum entropy as a function of U. The *vertical arrow* at U_0 indicates the trajectory of the system during evolution toward equilibrium as observed in the US-plane. The *filled circle* indicates the state of equilibrium after the partition became diathermal.

As is the case with *Condition of Equilibrium* 2, subscripts on δU must be modified according to the problem at hand. The same remark applies to all criteria of equilibrium we encounter later.

To illustrate the use of *Condition of Equilibrium 3* in a more concrete setting, we examine the same problem you considered in Exercise 2.6, that is, we deduce the equations that must be satisfied at equilibrium when the partition between the two subsystems is diathermal, movable, and permeable only to species 1.

Since the internal energy is an additive quantity, we have

$$U = U^a(S^a, V^a, N_1^a, \ldots, N_c^a) + U^b(S^b, V^b, N_1^b, \ldots, N_c^b) , \tag{2.98}$$

and hence

$$\delta U = \delta U^a + \delta U^b . \tag{2.99}$$

Applying (2.37) to each compartment, we can rewrite (2.99) as

$$\delta U = T^a \delta S^a - P^a \delta V^a + \mu_1^a \delta N_1^a + T^b \delta S^b - P^b \delta V^b + \mu_1^b \delta N_1^b , \tag{2.100}$$

where we note that $\delta N_2^a = \cdots = \delta N_c^b \equiv 0$ since the partition is impermeable to species 2, …, c.

Equation (2.97) requires that we minimize U for a given value of S, while allowing for S^a and S^b to change:

$$S^a + S^b = S = \text{const.} \tag{2.101}$$

Since the composite system is isolated, we also have

$$V^a + V^b = V = \text{const.} \quad \text{and} \quad N_1^a + N_1^b = N_1 = \text{const.} \tag{2.102}$$

Using (2.101) and (2.102), we rewrite (2.100) as

$$\delta U = (T^a - T^b)\delta S^a - (P^a - P^b)\delta V^a + (\mu_1^a - \mu_1^b)\delta N_1^a \ . \tag{2.103}$$

For equilibrium of the composite system, it is necessary that this quantity be nonnegative for *all* possible values of δS^a, δV^a, and δN_1^a, from which we deduce that $T^a = T^b$, $P^a = P^b$, and $\mu_1^a = \mu_1^b$. For example, (2.103) must be nonnegative even when δV^a and δN_1^a are both zero and δS^a takes an arbitrary value, which leads to the conclusion that $T^a = T^b$.

Suppose that the partition, besides being diathermal and movable, is now made permeable to all species. It is straightforward to show that, at equilibrium, $T^a = T^b$, $P^a = P^b$, and $\mu_i^a = \mu_i^b$ for $i = 1, \dots, c$.

2.9.2 Reversible Work Source

Looking at (2.97), you may object to the indicated increase of U because the system under consideration is isolated. Nevertheless, according to Fig. 2.8, *Condition of Equilibrium 3* is equivalent to *Condition of Equilibrium 2* in Sect. 2.8.1. We can give two distinct interpretations of (2.97).

In one interpretation, the variation is regarded as representing an act of comparing the values of U of many copies of the system, each having the same values of S, V, N_1, …, N_c, and X_{m+1}, …, X_r, but differing by the values of X_1, …, X_m. Equation (2.97) then identifies the system with minimum U as being in equilibrium.

An alternative, more physical, interpretation is possible. We may suppose that the increase in U is brought about by means of a purely classical mechanical device which is linked to the otherwise isolated system and induces changes in $X_1, \dots, X_m$. As discussed in Sect. 2.2, such a device does not exchange heat with the system. Since the variation is taken while maintaining S constant, the process must occur reversibly. The mechanical device capable of inducing the variation reversibly is called the **reversible work source**.

If we take the second view point, then from the conservation of energy, the reversible work imparted on the system by the reversible work source is given by

$$\delta W^{\text{rev}} = (\delta U)_{S,V,N_1,\dots,N_c;X_{m+1},\dots,X_r} \ . \tag{2.104}$$

This observation leads to yet another formulation of the condition of equilibrium:

Condition of Equilibrium 4 *For the equilibrium of an isolated system, it is necessary and sufficient that*

$$(\delta W^{\text{rev}})_{S,V,N_1,\dots,N_c;X_{m+1},\dots,X_r} \geq 0 \tag{2.105}$$

for all possible variations of X_1, …, X_m consistent with given constraints.

As we shall see later, this formulation applies not only to an isolated system but also to other kinds of systems, for example, a system held at a constant temperature by virtue of thermal contact with the surroundings.

Condition of Equilibrium 4 has a direct physical interpretation. To see if a system, isolated or otherwise, is in equilibrium, we connect it to a reversible work source and let the latter perturb the state of the system by varying the values of $X_1, \dots, X_m$. If, to the first order of variation, a nonnegative work is required for any such perturbation, then from this observation, we conclude that the initial unperturbed system was in equilibrium.[8]

We can now establish the equivalence of *Conditions of Equilibrium 2 and 3* without resorting to Fig. 2.8. Suppose that (2.97) holds and that we exerted work reversibly on the otherwise isolated system to induce a required change in $X_1, \dots, X_m$. This does not affect S but U may change. According to (2.97), however, U cannot decrease. If U remains unchanged, then the variation just considered satisfies (2.82) with equality. If U increases, it can be brought back to its initial value by removing the extra energy in the form of heat from the system while holding the values of $X_1, \dots, X_m$ at those in the varied state, that is, $X_1 + \delta X_1, \dots, X_m + \delta X_m$. The combined result of the two step process is a decrease of S without affecting U. Thus, if (2.97) holds for all possible variations, so does (2.82). To prove the converse, suppose that (2.97) is violated by some variation, that is, $\delta U < 0$ for this variation. The reversible work source then receives work, which can be converted to heat, using friction for example, and injected back into the system. This will restore U to its original value but will increase S. The combined result of the two step process is a variation that violates (2.82).

2.9.3 †Condition of Perfect Equilibrium

In the absence of any internal constraints $X_{m+1}, \dots, X_r$, the condition of equilibrium can be formulated as follows:

Condition of Equilibrium 5 *For the equilibrium of an isolated system subject to no internal constraint, it is necessary and sufficient that*

$$\delta U \geq T\delta S - P\delta V + \sum_{i=1}^{c} \mu_i \delta N_i \tag{2.106}$$

for all possible variations of S, V, $N_1, \dots, N_c$, and $X_1, \dots, X_m$.

This seems rather surprising since (2.106) looks very much like (2.37), which is essentially the first law of thermodynamics. The system we have in mind is a body that is homogeneous initially and enclosed in a container without any internal partitions. As an example of variations in $X_1, \dots, X_m$, one may consider fluctuations in local density that upset the homogeneity. A state of equilibrium that prevails when there is no internal constraints is called the **perfect equilibrium** state. With a slight modification to (2.106), this formulation of the condition of perfect equilibrium becomes an important starting point for thermodynamics of inhomogeneous systems as we shall see in Chap. 6.

To see that (2.106) is sufficient for equilibrium, suppose that (2.106) holds for any variations of S, V, $N_1, \dots, N_c$, and $X_1, \dots, X_m$. Then, $\delta U \geq 0$ for any variations of $X_1, \dots, X_m$ that *do not* affect the values of S, V, and $N_1, \dots, N_c$. This is just (2.97) written without $X_{m+1}, \dots, X_r$, which are absent for the situation under consideration.

The necessity of (2.106) takes a little more effort to establish. As in (2.80),

$$U = U(S,V,N_1,\dots,N_c;X_1,\dots,X_m) \, . \tag{2.107}$$

in general. Thus, when S, V, $N_1, \dots, N_c$, and $X_1, \dots, X_m$ are perturbed by infinitesimal amounts, the resulting variation in δU is given by

$$\begin{aligned} \delta U = {} & \left(\frac{\partial U}{\partial S}\right)_{V,N,X} \delta S + \left(\frac{\partial U}{\partial V}\right)_{S,N,X} \delta V + \sum_{i=1}^{c} \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j \neq i},X} \delta N_i \\ & + \sum_{i=1}^{m} \left(\frac{\partial U}{\partial X_i}\right)_{S,V,N,X_{j \neq i}} \delta X_i \, , \end{aligned} \tag{2.108}$$

where we abbreviated the subscripts $N_1, \dots, N_c$ and $X_1, \dots, X_m$ to just N and X, respectively.

Comparing (2.108) against (2.104), we see immediately that

$$\delta W^{\text{rev}} = \sum_{i=1}^{m} \left(\frac{\partial U}{\partial X_i}\right)_{S,V,N,X_{j \neq i}} \delta X_i \, . \tag{2.109}$$

If the system is initially in perfect equilibrium, this quantity is nonnegative as demanded by (2.105). Therefore, dropping the last term of (2.108), we arrive at

$$\delta U \geq \left(\frac{\partial U}{\partial S}\right)_{V,N,X} \delta S + \left(\frac{\partial U}{\partial V}\right)_{S,N,X} \delta V + \sum_{i=1}^{c} \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j \neq i},X} \delta N_i \, . \tag{2.110}$$

Now, can we say that

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N,X} ? \tag{2.111}$$

This looks very much like the expression for T in (2.38). In arriving at that expression, however, we considered a differentiation, that is, the system was assumed to be in equilibrium both before and after the change. In other words, $X_1, \dots, X_m$ were allowed to adjust themselves in order to maintain the equilibrium. This is why X does not show up as a subscript in (2.38). Going back to the definition of partial derivative, therefore, we can express T as given by (2.38) as

$$\begin{aligned} T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \lim_{\Delta S \to 0} \frac{1}{\Delta S} & \left[U(S+\Delta S,V,N_1,\dots,N_c;X_1+\Delta X_1,\dots,X_m+\Delta X_m) \right. \\ & \left. - \, U(S,V,N_1,\dots,N_c;X_1,\dots,X_m) \right] \, , \end{aligned} \tag{2.112}$$

where ΔX_i denotes the adjustment the system makes to X_i in order to maintain the equilibrium when S is changed by ΔS. Expanding the internal energy difference into the Taylor series,

$$T = \lim_{\Delta S \to 0} \frac{1}{\Delta S} \left[\left(\frac{\partial U}{\partial S} \right)_{V,N,X} \Delta S + \sum_{i=1}^{m} \left(\frac{\partial U}{\partial X_i} \right)_{S,V,N,X_{j\neq i}} \Delta X_i \right] , \tag{2.113}$$

where we dropped the higher order terms that vanish more rapidly than ΔS.

Now, suppose that the system is *initially* in equilibrium and that each X_i is capable of **reversible variation**, in the sense that both negative and positive values of δX_i are possible for each i. (Our usage of the word "reversible" in this context is due to Gibbs and differs from our earlier usage of the same word pertaining to processes.) Then, (2.105) and (2.109) lead to

$$\left(\frac{\partial U}{\partial X_i} \right)_{S,V,N,X_{j\neq i}} = 0 \, , \; i = 1, \ldots, m \, . \tag{2.114}$$

This is now introduced into (2.113) to give

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N,X} . \tag{2.115}$$

This proof is due to Ref. [4]. Similarly,

$$-P = \left(\frac{\partial U}{\partial V} \right)_{S,N,X} \quad \text{and} \quad \mu_i = \left(\frac{\partial U}{\partial N_i} \right)_{S,V,N_{j\neq i},X} , \quad i = 1, \ldots, m \, . \tag{2.116}$$

Because of (2.114), the last term of (2.108) is identically zero and (2.110) holds with equality. Therefore, by virtue of (2.115) and (2.116), we obtain

$$\delta U = T\delta S - P\delta V + \sum_{i=1}^{c} \mu_i \delta N_i \, , \tag{2.117}$$

which is a special case of (2.106).

What if one of ΔX_1, ..., ΔX_m, say ΔX_1, cannot take a positive value? Because the system is initially in equilibrium, the partial derivative

$$\left(\frac{\partial U}{\partial X_1} \right)_{S,V,N,X_{j\neq 1}} \tag{2.118}$$

cannot be positive. In fact, if it were positive, then the system could lower U by decreasing X_1, in contradiction to the assumption that the system was in equilibrium initially. It may be that the partial derivative, which is to be evaluated at the initial state, happens to be zero. In this case, we have (2.114) holding for all i including $i = 1$ and we once again obtain (2.117).

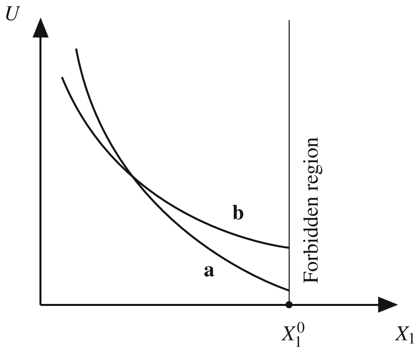

Fig. 2.9 The function $U = U(X_1)$. Suppose that X_1 cannot exceed X_1^0 and the slope of U at $X_1 = X_1^0$ is negative initially as indicated by curve **a**. As illustrated by curve **b**, the slope remains negative even after an infinitesimal change is made to S. Then, $X_1 = X_1^0$ at equilibrium both before and after the change. So, $\Delta X_1 = 0$.

On the other hand, if the partial derivative is negative, ΔX_1 occurring in (2.113), that is, the adjustment the system makes to X_1 in response to the change in S must be zero. This is because an infinitesimal change in S cannot induce a finite change in the value of the partial derivative, which thus remains negative even after the change. The underlying assumption here is that the partial derivative is a continuous function of S. Figure 2.9 illustrates the situation. In this way, we see that (2.115) and (2.116) hold in this case as well. When these equations are substituted into (2.110), we arrive at (2.106).

In this case, however, the inequality sign in (2.106) cannot be dropped. To see this, let us consider a variation of X_1. By assumption, δX_1 can only be negative. But, its coefficient $(\partial U/\partial X_1)_{S,V,N,X_{j\neq 1}}$ is also negative. Thus, the contribution to δU from any nonzero δX_1 is always positive. Note carefully the difference between ΔX_1 and δX_1 in this discussion. The former is the adjustment the *system* makes to maintain equilibrium, while the latter is the change in X_1 *we* impose on the system by means of the reversible work source.

2.9.4 †Closed System with a Chemical Reaction

We remarked in Sect. 2.6.1 that (2.21) holds even in the presence of chemical reactions provided that the system is homogeneous and in equilibrium both before and after the infinitesimal change, during which the system remains closed. We are now ready to see why this is so.

For simplicity, we allow only a single chemical reaction:

$$c_1A_1 + c_2A_2 \rightleftarrows c_3A_3 \tag{2.119}$$

among three species A_1, A_2, and A_3. The positive constants c_1, c_2, and c_3 are called the stoichiometric coefficients. There may be more species present in the system in addition to these three species. But, their numbers of moles are fixed. In contrast, N_1, N_2, and N_3 can change, but only in compliance with the stoichiometry of the reaction:

$$\delta N_1 = -\frac{c_1}{c_3}\delta N_3 \quad \text{and} \quad \delta N_2 = -\frac{c_2}{c_3}\delta N_3 \tag{2.120}$$

as you saw in Exercise 2.10.

If the system prior to variation is in equilibrium, (2.106) applies and

$$\delta U \geq T\delta S - P\delta V + \left(-\frac{c_1}{c_3}\mu_1 - \frac{c_2}{c_3}\mu_2 + \mu_3\right)\delta N_3 \tag{2.121}$$

must hold true for any possible values of δS, δV, and δN_3. In particular, it must hold even if $\delta S = 0$ and $\delta V = 0$. Provided that δN_3 is capable of assuming both positive and negative values, we find that

$$-\frac{c_1}{c_3}\mu_1 - \frac{c_2}{c_3}\mu_2 + \mu_3 = 0\,. \tag{2.122}$$

Thus,

$$c_1\mu_1 + c_2\mu_2 = c_3\mu_3\,, \tag{2.123}$$

which is the condition of equilibrium for the reaction under consideration. Substituting (2.123) back into (2.121), we find that

$$\delta U \geq T\delta S - P\delta V\,. \tag{2.124}$$

If we assume that $X_1, \ldots, X_m$ are all capable of reversible variations in the sense defined in the previous subsection, the inequality may be replaced by equality. Furthermore, if we restrict ourselves to such variations as to leave the system homogeneous and in equilibrium, δ can be replaced by d. Thus we finally arrive at

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V\,, \tag{2.125}$$

which is just (2.21).

2.9.5 †Maximum Work Principle

We can take advantage of the tendency of a system to evolve toward a state of equilibrium and extract a useful work. For this purpose, we connect the system to an external agency and suppose that the composite system, consisting of the system and the external agency attached to it, as a whole, is isolated. We show that, in this setting, the maximum amount of work is extracted by the external agency when the process is carried out reversibly.

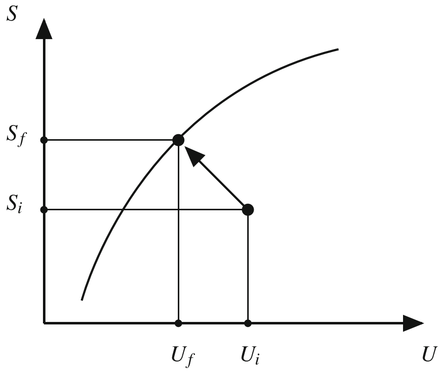

Fig. 2.10 Graphical illustration of the maximum work principle. The work extracted, $U_i - U_f$, is maximum when the arrow connecting the initial state to the final state points horizontally to the left so that $S_f - S_i = 0$. In the absence of the external agency, $U_f = U_i$ and the arrow would point vertically upward as in Fig. 2.8.

Let us first plot the equilibrium value of S of the system as a function of its U as shown in Fig. 2.10. If the system is not in equilibrium, its representative point lies below this curve because S of the system is not the maximum possible for a given value of U. Let us therefore suppose that the representative point is initially at (U_i, S_i).

If the system is allowed to relax toward equilibrium in the absence of the external agency, then as in Fig. 2.8, the representative point will simply move vertically upward until it hits the curve $S(U)$.

We now suppose instead that the system is linked to the external agency. From the conservation of energy, the work W extracted by the latter during the approach to equilibrium is given by

$$W = U_i - U_f \,, \tag{2.126}$$

where U_i and U_f denote the internal energy of the system at the beginning and the end of the equilibration process, respectively. *If the process is such as not to affect the entropy of the external agency*, we have

$$S_f - S_i \geq 0 \,. \tag{2.127}$$

Because the composite system, with the external agency attached, is isolated, this means that the process is spontaneous. From Fig. 2.10, it is evident that the maximum amount of work is extracted when the equality holds in (2.127), that is if the process occurred reversibly. This is the **maximum work principle**.

As an example of the external agency whose entropy remains unaffected, we may consider a purely classical mechanical device that can exchange energy with the system only in the form of work. A so-called **cycle**, which by definition, repeatedly returns to its original state is another example.

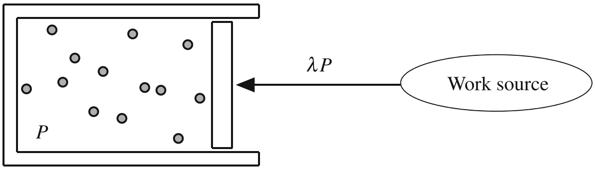

Fig. 2.11 The work source extracts work from an adiabatic expansion of an ideal gas. The expansion is reversible when $\lambda = 1$ and irreversible otherwise.

Example 2.2. Adiabatic expansion of an ideal gas: Suppose that an ideal gas is confined to a cylinder made of a rigid and adiabatic wall and is fitted with a piston. See Fig. 2.11. The space outside the cylinder is vacuum and our aim is to extract work using the tendency of the gas to expand. To do this, we connect the work source to the system so that it exerts a pressure λP on the piston. Here P is the pressure inside the cylinder and λ is a constant. In order for the expansion to occur, $\lambda < 1$.

For the process considered, $đQ = 0$, and hence

$$\mathrm{d}U = đW = -\lambda P \mathrm{d}V \ . \tag{2.128}$$

In order for this quantity to be negative so that we can extract positive work, $\lambda > 0$ and we assume that this is the case in what follows.

Using the equation of state of an ideal gas and recalling from Sect. 2.6.4 that $\mathrm{d}U = C_V \mathrm{d}T$,

$$C_V \mathrm{d}T = -\frac{\lambda NRT}{V}\mathrm{d}V \ , \tag{2.129}$$

which is now integrated to give

$$\ln \frac{T_f}{T_i} = -\frac{\lambda NR}{C_V} \ln \frac{V_f}{V_i} \ . \tag{2.130}$$

Applying (2.59), we find that the work extracted from the process is

$$U_i - U_f = C_V T_i \left[1 - \left(\frac{V_i}{V_f} \right)^{\lambda NR/C_V} \right] , \tag{2.131}$$

while it follows from (2.60) that

$$S_f - S_i = (1-\lambda) NR \ln \frac{V_f}{V_i} \ . \tag{2.132}$$

Remembering that $V_f/V_i > 1$ for an expansion, we see that $S_f - S_i$ is maximum at $\lambda = 0$ (free expansion) and decreases monotonically with increasing λ until it reaches the minimum value zero at $\lambda = 1$ (a reversible process). In contrast,

$U_i - U_f$ is zero for the free expansion and increases monotonically until it reaches the maximum value for the reversible expansion.

We can also extract work from the natural tendency for two bodies in thermal contact to reach a common temperature by means of a **heat engine**. This is a device that visits a given set of multiple states in a cyclic fashion and in so doing, it receives heat from the higher temperature body, converts a part of the energy into work, and expels the rest in the form of heat into the lower temperature body. After completing one cycle, the heat engine itself returns to the original state while the temperature difference between the bodies decreases. The heat engine is an example of a cycle.

Analogously, we can also operate what might be called a **material engine** between two bodies having the same temperature but different values of the chemical potentials for some of the species, say species 1. In this case, the engine receives heat and molecules of species 1 from higher chemical potential body and delivers them to the lower chemical potential body while extracting work from the process.

These possibilities are considered in the following two examples on the ground of the general principle. Each example is followed by an exercise, in which you are asked to consider the inner working of reversible engines in some detail.

Example 2.3. Heat engine: Consider two homogeneous bodies H and L at thermal contact that are initially at different temperatures T_h and T_l, respectively. To extract work, we break the thermal contact and insert a heat engine HE between H and L. The system now consists of H, L, and HE, and our goal is to figure out the amount of work this composite system delivers to a work source when the latter is linked to HE. We note that the work source is purely a classical mechanical device described in Sect. 2.2 and does not exchange heat with the composite system.

We restrict ourselves to processes occurring without affecting the volume of H or that of L. We also suppose that only a very small amount of heat and work are involved during a single cycle of HE so that T_h and T_l may be regarded as constant. Then, denoting by $đQ_h$ the amount per cycle of heat transferred from H to HE, we have

$$-đQ_h = \mathrm{d}U_h = T_h \mathrm{d}S_h \,, \tag{2.133}$$

and hence

$$\mathrm{d}S_h = -\frac{đQ_h}{T_h} \,. \tag{2.134}$$

Similarly, if $đQ_l$ is the amount per cycle of heat transferred from HE to L,

$$đQ_l = \mathrm{d}U_l = T_l \mathrm{d}S_l \,, \tag{2.135}$$

and hence

$$\mathrm{d}S_l = \frac{\text{đ}Q_l}{T_l}\ . \tag{2.136}$$

Since HE returns to its original state at the end of one cycle, $\mathrm{d}S_{he} = 0$. So, for the composite system, we have

$$\mathrm{d}S = \mathrm{d}S_h + \mathrm{d}S_l = -\frac{\text{đ}Q_h}{T_h} + \frac{\text{đ}Q_l}{T_l}\ . \tag{2.137}$$

According to the first law, the work $\text{đ}W$ delivered to the work source is

$$\text{đ}W = -(\mathrm{d}U_h + \mathrm{d}U_l) = \text{đ}Q_h - \text{đ}Q_l\ , \tag{2.138}$$

where we note that $\mathrm{d}U_{he} = 0$.

Now, let $\text{đ}Q_l := \lambda\, \text{đ}Q_h$ and rewrite these equations as

$$\mathrm{d}S = \left(\frac{\lambda}{T_l} - \frac{1}{T_h}\right)\text{đ}Q_h \quad \text{and} \quad \text{đ}W = (1-\lambda)\,\text{đ}Q_h\ . \tag{2.139}$$

For spontaneous processes, we have $\mathrm{d}S \geq 0$. Since we are interested in the amount of work that can be extracted from such processes, we demand that $\text{đ}W \geq 0$. These considerations lead to

$$\frac{T_l}{T_h} \leq \lambda \leq 1\ . \tag{2.140}$$

When $\lambda = 1$, $\text{đ}W = 0$ and $\text{đ}Q_h = \text{đ}Q_l$, and the process is seen to be identical to the direct heat conduction between H and L through a diathermal wall. In contrast, the maximum of $\text{đ}W$ occurs when $\lambda = T_l/T_h$, and is given by

$$\text{đ}W = \left(1 - \frac{T_l}{T_h}\right)\text{đ}Q_h\ . \tag{2.141}$$

In this case, $\mathrm{d}S = 0$ and the process is reversible.

This example demonstrates the existence of an upper limit of the **efficiency** η of *any* heat engines:

$$\eta := \frac{\text{đ}W}{\text{đ}Q_h} \leq 1 - \frac{T_l}{T_h}\ . \tag{2.142}$$

Exercise 2.13. As an example of reversible heat engines operating between the higher temperature body H at T_h and the lower temperature one L at T_l, consider a **Carnot cycle**. The engine uses a working fluid confined to a cylinder fitted with a frictionless piston. The wall of the cylinder is rigid and impermeable to all species. The wall is also adiabatic except that one side of the wall, denoted by Σ_T, can be made either adiabatic or diathermal as needed. The heat engine undergoes the following sequence of processes:

a. The engine containing the working fluid at T_h is brought to thermal contact with H through diathermal Σ_T and expands isothermally and reversibly at T_h while extracting heat Q_h from H.
b. The wall Σ_T becomes adiabatic and the fluid expands reversibly until its temperature reaches T_l.
c. The fluid is brought to thermal contact with L through diathermal Σ_T and is compressed isothermally and reversibly while rejecting heat Q_l to L.
d. The wall Σ_T becomes adiabatic again and the fluid is compressed reversibly until its temperature reaches T_h.

Assuming that the working fluid is an ideal gas, show that $W = (1 - T_l/T_h)Q$ by means of an explicit computation of work and heat involved in each step. ///

Example 2.4. Material engine: Consider two homogeneous mixtures H and L both at the same temperature T and suppose that the chemical potential of species 1 in H and that in L, denoted by μ_h and μ_l, respectively, satisfy $\mu_h > \mu_l$. If they are brought in contact through a wall permeable to species 1, molecules of 1 will flow from H to L. Instead of the permeable wall, we will insert a material engine ME in between. Once again, we are interested in the amount of work the composite system consisting of H, L, and ME delivers to the work source.

We suppose that only a very small amount of heat and material transfer is involved during one cycle of the engine, leaving T, μ_h, and μ_l constant. For the heat and material transfer from H to ME, we have

$$\mathrm{d}U_h = T\mathrm{d}S_h - \mu_h \mathrm{d}N \,, \tag{2.143}$$

where dN is the number of moles of species 1 being transferred to ME. Similarly,

$$\mathrm{d}U_l = T\mathrm{d}S_l + \mu_l \mathrm{d}N \,. \tag{2.144}$$

Note that ME gives up as many molecules of species 1 to L as it has received from H. Otherwise, there will be an accumulation or depletion of the molecules in ME and it will not qualify as a cycle.

Combining these equations,

$$đW = -(\mathrm{d}U_h + \mathrm{d}U_l) = -T\mathrm{d}S + (\mu_h - \mu_l)\mathrm{d}N \,, \tag{2.145}$$

where $\mathrm{d}S = \mathrm{d}S_h + \mathrm{d}S_l$ is the increment in entropy of the composite system per single cycle since $\mathrm{d}S_{mc} = 0$ as in the previous example. The maximum of $đW$ occurs when $\mathrm{d}S = 0$ and is given by $(\mu_h - \mu_l)\mathrm{d}N$.

Exercise 2.14. In analogy to Carnot cycle, let us consider a reversible material engine operating between two mixtures H and L. We suppose that they are at the same temperature T and denote the chemical potential of species 1 in H and that in L by μ_h and μ_l, respectively, where $\mu_h > \mu_l$. As the working fluid, we use a pure ideal gas of species 1 confined to a cylinder fitted with a frictionless piston. The cylinder is made of a rigid wall that is diathermal and impermeable to all species. However, one side of the wall, which we call Σ_μ, can be made either permeable or impermeable to species 1 as needed. In each of the following steps, expansion or compression is performed both isothermally and reversibly:

a. The engine containing the working fluid at μ_h is brought to thermal contact with H through the permeable Σ_μ and expands while extracting ΔN moles of species 1 from H.
b. The wall Σ_μ becomes impermeable and the fluid expands until the chemical potential of species 1 becomes μ_l.
c. The fluid is brought to thermal contact with L through Σ_μ, which now is made permeable to species 1. The fluid is compressed while rejecting ΔN moles of species 1 to L.
d. The wall Σ_μ is made impermeable again and the fluid is compressed until the chemical potential becomes μ_h.

Noting that

$$\mu(T,P) = \mu^\circ(T) + RT\ln P \tag{2.146}$$

for a pure ideal gas, show that $W = (\mu_h - \mu_l)\Delta N$. Not surprisingly, this is actually the work extracted from an isothermal and reversible expansion of ΔN moles of an ideal gas from the pressure P_h, at which $\mu = \mu_h$, to P_l at which $\mu = \mu_l$. ///

2.10 Euler Relation

We note that the variables occurring in (2.36) are all extensive quantities. That is, they are all proportional to the "size" of the system. This can be expressed more precisely as

$$U(\lambda S, \lambda V, \lambda N_1, \ldots, \lambda N_c) = \lambda U(S, V, N_1, \ldots, N_c)\ , \tag{2.147}$$

where λ is a positive constant. A function that satisfies such a relation is called a homogeneous function of degree one. This leads to the following important equation called the **Euler relation**:

$$U = TS - PV + \sum_{i=1}^{c} \mu_i N_i\ . \tag{2.148}$$

As we see in Sect. 2.15, (2.148) is a mathematical consequence of (2.147) and can be derived without making any further reference to the physical situation beyond what has been made so far. Nevertheless, it is of some interest to consider an alternative, physically more appealing, derivation of (2.148).

Let us consider a large homogeneous body. Within this body, we choose a small part enclosed by the smaller circle in Fig. 2.12 as our system. Note that this act of choosing the system is purely a thought process and does not involve us putting in any physical wall. In other words, the partition separating the system from the rest

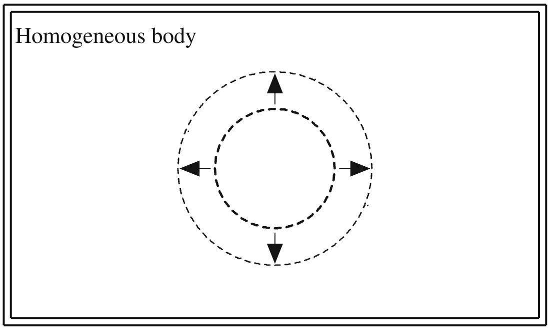

Fig. 2.12 A system taken inside a homogeneous body is indicated by the *smaller circle*. The *larger circle* represents the system after the infinitesimal change we considered in writing (2.150). Note that the expansion of the system boundary has no effect on the physical state of the matter anywhere in the homogeneous body.

of the homogeneous body is diathermal, permeable to all species, and has no effect either on the state or the property of the homogeneous body.[9]

Let u, s, and n_i denote, respectively, the densities of internal energy, the entropy, and the number of moles of species i in the homogeneous body. Then, U, S, and N_i of the system are given by

$$U = uV \,, \quad S = sV \,, \quad \text{and} \quad N_i = n_i V \,, \quad i = 1, \ldots, c \,, \tag{2.149}$$

where V is the volume of the system.

Now, let us consider a process in which the partition is enlarged to contain a larger part of the homogeneous body. Once again, this is a thought process and has no impact on the physical state of the body including the values of u, s, and n_1, …, n_c. But, U, S, and N_1, …, N_c of the system do change. If we denote by $V + \mathrm{d}V$ the volume of the system after the change, which is indicated in Fig. 2.12 by the larger circle, we have

$$\begin{aligned} U + \mathrm{d}U &= u(V + \mathrm{d}V) \,, \quad S + \mathrm{d}S = s(V + \mathrm{d}V) \,, \\ N_i + \mathrm{d}N_i &= n_i(V + \mathrm{d}V) \,, \quad i = 1, \ldots, c \,. \end{aligned} \tag{2.150}$$

Comparing (2.149) and (2.150), we find

$$\mathrm{d}U = u\mathrm{d}V \,, \quad \mathrm{d}S = s\mathrm{d}V \,, \quad \text{and} \quad \mathrm{d}N_i = n_i\mathrm{d}V \,, \quad i = 1, \ldots, c \,, \tag{2.151}$$

which is now substituted into (2.37) to yield

$$u\mathrm{d}V = Ts\mathrm{d}V - P\mathrm{d}V + \sum_{i=1}^{c} \mu_i n_i \mathrm{d}V \,. \tag{2.152}$$

Multiplying both sides by $V/\mathrm{d}V$, we arrive at (2.148).

2.11 Gibbs–Duhem Relation

Suppose that the state of the system is altered by infinitesimal changes made to the independent variables S, V, and $N_1, \ldots, N_c$. In general, this will be accompanied by the corresponding changes in the dependent variables U, T, P, and $\mu_1, \ldots, \mu_c$. If the system is homogeneous and in equilibrium both before and after the change is made, (2.148) must hold for both of these states. Thus, applying (2.148) to the system after the change, we write

$$U + \Delta U = (T + \Delta T)(S + \mathrm{d}S) - (P + \Delta P)(V + \mathrm{d}V) + \sum_{i=1}^{c} (\mu_i + \Delta\mu_i)(N_i + \mathrm{d}N_i) \;, \tag{2.153}$$

where U is the internal energy of the system before the change, and ΔU is the change in the internal energy due to the change in the independent variables. (As explained in Appendix B.1, $\Delta U = \mathrm{d}U + \mathrm{d}^2U/2 + \mathrm{d}^3U/6 + \cdots$, in which the first-order term $\mathrm{d}U$ dominates the remaining higher order terms.) Using (2.37) and (2.148) applied for the initial state, we obtain

$$\Delta U = \mathrm{d}U + S\Delta T - V\Delta P + \sum_{i=1}^{c} N_i\Delta\mu_i + \mathrm{d}S\Delta T - \mathrm{d}V\Delta P + \sum_{i=1}^{c} \mathrm{d}N_i\Delta\mu_i \;. \tag{2.154}$$

Retaining only the first-order terms, that is, ignoring such terms as $\mathrm{d}S\Delta T$ and replacing ΔU, ΔT, ΔP, and $\Delta\mu_i$, by $\mathrm{d}U$, $\mathrm{d}T$, $\mathrm{d}P$, and $\mathrm{d}\mu_i$, respectively, we find

$$S\mathrm{d}T - V\mathrm{d}P + \sum_{i=1}^{c} N_i\mathrm{d}\mu_i = 0 \;, \tag{2.155}$$

which is known as the **Gibbs–Duhem relation** and indicates that T, P, and $\mu_1, \ldots, \mu_c$ cannot be varied independently.

Dividing (2.155) by V,

$$\mathrm{d}P = s\mathrm{d}T + \sum_{i=1}^{c} n_i\mathrm{d}\mu_i \;, \tag{2.156}$$

from which we find

$$\left(\frac{\partial P}{\partial T}\right)_{\mu} = s \quad \text{and} \quad \left(\frac{\partial P}{\partial \mu_i}\right)_{T,\mu_{j\neq i}} = n_i \;. \tag{2.157}$$

The first equation, for example, is obtained by setting $\mathrm{d}\mu_1 = \cdots = \mathrm{d}\mu_c = 0$ in (2.156) and dividing both sides by $\mathrm{d}T$.

2.12 ‡Gibbs Phase Rule

In thermodynamics, the word **phase** refers to a homogeneous body without any regard to its size. Thermodynamic state of a phase can be specified once the values of s and $n_1, \ldots, n_c$ are fixed. Homogeneous bodies with identical values of these variables are the same phase regardless of their size. Those with distinct values of these variables constitute distinct phases.

Multiple phases can coexist at equilibrium. By heating water under atmospheric pressure, you can achieve liquid–vapor coexistence of water in a kettle at 100°C. If you pour enough sugar into a glass of water, you can observe the coexistence between aqueous sugar solution and sugar crystals.

Experience shows, however, that we cannot maintain the liquid–vapor coexistence of water if we fix the pressure and change the temperature from 100°C. You can certainly achieve the coexistence at temperatures other than 100°C, but only by properly adjusting the pressure. Why should this be?

The interface between coexisting phases may be regarded as a partition that is diathermal, movable, and permeable to all species. Continuing with the example of pure water, therefore, we have

$$T^l = T^v\,, \quad P^l = P^v\,, \quad \text{and} \quad \mu^l = \mu^v \tag{2.158}$$

as the condition of equilibrium, where the superscripts l and v refer to the liquid and the vapor phases, respectively. Now, suppose that we perturb the state of the system by changing its temperature, for example. If the phase coexistence is to subsist, (2.158) must hold after the change also:

$$T^l + \mathrm{d}T^l = T^v + \mathrm{d}T^v\,, \quad P^l + \mathrm{d}P^l = P^v + \mathrm{d}P^v\,, \quad \text{and} \quad \mu^l + \mathrm{d}\mu^l = \mu^v + \mathrm{d}\mu^v\,. \tag{2.159}$$

It follows that

$$\mathrm{d}T^l = \mathrm{d}T^v\,, \quad \mathrm{d}P^l = \mathrm{d}P^v\,, \quad \text{and} \quad \mathrm{d}\mu^l = \mathrm{d}\mu^v\,. \tag{2.160}$$

As we have seen in the previous section, these infinitesimal quantities are subject to the Gibbs–Duhem relation:

$$s^l\mathrm{d}T - \mathrm{d}P + n^l\mathrm{d}\mu = 0 \quad \text{and} \quad s^v\mathrm{d}T - \mathrm{d}P + n^v\mathrm{d}\mu = 0\,, \tag{2.161}$$

where we dropped the superscripts from $\mathrm{d}T$, $\mathrm{d}P$, and $\mathrm{d}\mu$ as they are common to both phases. If we hold P constant as we change T, (2.161) reduces to

$$s^l\mathrm{d}T + n^l\mathrm{d}\mu = 0 \quad \text{and} \quad s^v\mathrm{d}T + n^v\mathrm{d}\mu = 0\,. \tag{2.162}$$

Unless the ratio s^l/n^l happens to be equal to s^v/n^v, these equations demand that both $\mathrm{d}T$ and $\mathrm{d}\mu$ be zero. That is, if we want to perturb the state of the system while maintaining the vapor–liquid coexistence, we cannot possibly hold P constant. Instead, (2.161) uniquely determines the necessary change one must make to P for a given value of $\mathrm{d}T$. The same set of equations also determine the value of $\mathrm{d}\mu$.

In the case of sugar crystals in a glass of water, the condition of equilibrium is given by

$$T^c = T^l \,, \quad P^c = P^l \,, \quad \mu_s^c = \mu_s^l, \qquad \text{and} \quad \mu_w^c \geq \mu_w^l \,, \tag{2.163}$$

where the superscripts c and l refer to the crystal and liquid phases, respectively. The subscript s denotes sugar while w refers to water. The inequality in the last relation cannot be dropped since the crystal is, by assumption, pure sugar, and the number of water molecules in the crystal is incapable of a negative variation. Considering an infinitesimal change that maintains the coexistence, we have

$$\mathrm{d}T^c = \mathrm{d}T^l \,, \quad \mathrm{d}P^c = \mathrm{d}P^l \,, \quad \mathrm{d}\mu_s^c = \mathrm{d}\mu_s^l \,, \tag{2.164}$$

while

$$\mu_w^c + \mathrm{d}\mu_w^c \geq \mu_w^l + \mathrm{d}\mu_w^l \,, \tag{2.165}$$

which cannot be simplified further. The Gibbs–Duhem relations for the phases can then be written as

$$s^l \mathrm{d}T - \mathrm{d}P + n_s^l \mathrm{d}\mu_s + n_w^l \mathrm{d}\mu_w^l = 0 \quad \text{and} \quad s^c \mathrm{d}T - \mathrm{d}P + n_s^c \mathrm{d}\mu_s = 0 \,. \tag{2.166}$$

Thus, in order to maintain the coexistence, only two of the four infinitesimal quantities $\mathrm{d}T$, $\mathrm{d}P$, $\mathrm{d}\mu_s$, and $\mathrm{d}\mu_w^l$ can be specified independently and only within the confines of the inequality (2.165).

The above consideration can be generalized for coexistence among M phases of c component mixture, for which

$$s^I \mathrm{d}T - \mathrm{d}P + \sum_{i=1}^{c} n_i^I \mathrm{d}\mu_i = 0 \,, \quad I = 1, \ldots, M \,, \tag{2.167}$$

where the superscripts I labeling the phase should not be confused with exponents. We note that (2.167) provides M equations among $c+2$ infinitesimal quantities $\mathrm{d}T$, $\mathrm{d}P$, and $\mathrm{d}\mu_1, \ldots, \mathrm{d}\mu_c$. Thus, only $c+2-M$ of them can be specified independently. This result is known as the **Gibbs phase rule**.

The examples we considered above are consistent with the predictions of the Gibbs phase rule. In the case of vapor–liquid coexistence of water, $M = 2$, $c = 1$, and hence $c+2-M = 1$, indicating that only one of $\mathrm{d}T$, $\mathrm{d}P$, and $\mathrm{d}\mu$ can be specified as we please. For crystal–solution coexistence, $M = 2$, $c = 2$, and hence $c+2-M = 2$.

We note that the phase rule is obtained using the Gibbs–Duhem relation, which is a consequence of (2.37). The validity of the latter equation depends, among other things, on (2.5). But, this equation does not apply to a solid under a nonhydrostatic stress. Thus, when a solid phase is involved, the phase rule we derived applies only if the solid is under a hydrostatic pressure. During the initial stage of the first-order phase transition, the so-called critical nucleus, a small fragment of the new phase, forms in a bulk metastable phase. While the nucleus and the metastable phase are in (unstable) equilibrium, the phase rule does not apply here, either. This is because the nucleus is inhomogeneous and its fundamental equation cannot be written in the form of (2.37). (See Sect. 6.7.3.)

2.13 Free Energies

While isolated systems are conceptually the simplest to consider, rarely in our everyday life do we actually encounter such a system. Far more common is a system whose temperature, for example, is actively maintained through an interaction with some external body. It is therefore of practical importance to develop thermodynamics for systems that are not isolated.

In this section, we present the details only for a closed system held at constant temperature and volume. The analysis, however, can be generalized straightforwardly to other systems and you are invited to explore them in the exercises collected toward the end of this section.

2.13.1 Fixing Temperature

Before we proceed further, we need to know what exactly is meant by temperature being fixed. We recall that $1/T = (\partial S/\partial U)_{V,N}$, which is a function of U, V, N_1, …, N_c. Therefore, once the values of these independent variables are fixed, as is the case with any isolated system, the temperature is also fixed. This will be fine as far as we are concerned only with a state of equilibrium. In formulating condition of equilibrium, however, we must compare two states differing infinitesimally by the values of the additional variables as seen from (2.81). When the values of $X_1, \ldots, X_m$ are changed from the equilibrium values in an isolated system, there is no guarantee that the system temperature remain unchanged. Moreover, when we talk about a system held at a given temperature, we presume our ability to set that temperature as we please. Thus, we should demand that the temperature occur in our formulation not as a dependent variable but as an independent variable.

One simple way to fix the temperature of a system is to immerse it in a large body of liquid with uniform temperature and allow for exchange of heat between the two. If the body is much larger than the system itself, the temperature of the body will remain unchanged despite the energy exchange with the system. Such a body is called a **heat bath**.

2.13.2 Condition of Equilibrium

Because we are interested in the condition of equilibrium of the system but not that of the heat bath, we make a few simplifying assumptions about the bath. In addition to being sufficiently large, we assume that the relaxation time of the heat bath is extremely short. That is, the heat bath reestablishes equilibrium very quickly after it is disturbed by exchanging energy with the system. This allows us to assume that the heat bath is always in equilibrium.

Now, suppose that the composite system consisting of the heat bath and the system of interest, as a whole, is isolated. If the composite system is in equilibrium, then the system is evidently in equilibrium at the temperature T of the heat bath. Conversely, if the system is in equilibrium at T, the composite system is also in equilibrium by virtue of the assumptions made of the heat bath. Thus, for equilibrium of the system, it is necessary and sufficient that

$$\delta U^{\text{comp}} = \delta U + \delta U^B \geq 0 \tag{2.168}$$

for any possible variation of the state of the composite system. Here the superscripts comp and B denote the composite system and the heat bath, respectively.

Applying (2.37) to the heat bath,

$$\delta U^B = T\delta S^B \,. \tag{2.169}$$

Since $S^{\text{comp}} = S + S^B$ is constant as indicated in *Condition of Equilibrium 3*, $\delta S^B = -\delta S$, and hence

$$\delta U^B = -T\delta S \,, \tag{2.170}$$

which is now substituted into (2.168) to give

$$\delta U^{\text{comp}} = \delta U - T\delta S = \delta(U - TS) = \delta F \,, \tag{2.171}$$

where we used the fact that the variations considered do not affect T by virtue of the first assumptions made of the heat bath. We also introduced a new quantity called the **Helmholtz free energy** through the equation:

$$F := U - TS \,. \tag{2.172}$$

Note that, when considering all possible variations, the system temperature T was fixed through exchange of heat with the heat bath. Remembering that V and N_1, $\dots, N_c$ were also fixed and denoting, as before, any other constraints by means of the constant values of $X_{m+1}, \dots, X_r$, we arrive at the following condition of equilibrium:

Condition of Equilibrium 6 *For equilibrium of a closed system held at a given temperature T and volume V, it is necessary and sufficient that*

$$(\delta F)_{T,V,N_1,\dots,N_c;X_{m+1},\dots,X_r} \geq 0 \tag{2.173}$$

holds for any possible variation of the state of the system.

From (2.171) and the discussion in Sect. 2.9.2, we have

$$\delta F = \delta U^{\text{comp}} = \delta W^{\text{rev}} \,. \tag{2.174}$$

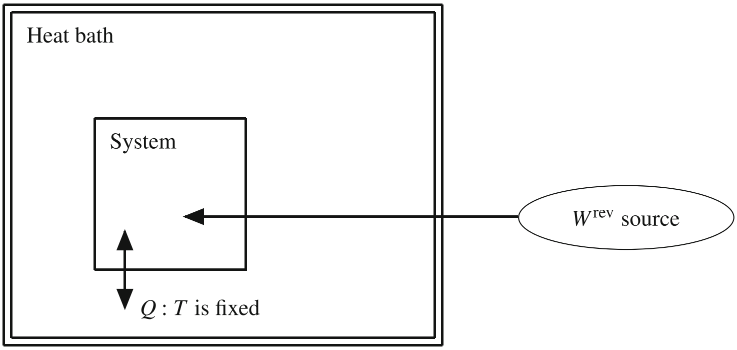

Fig. 2.13 The system of interest in contact with a heat bath. The reversible work source is connected only to the system and not to the heat bath.

Thus, *Condition of Equilibrium 4* applies also to the current situation provided that the subscript S is replaced by T in (2.105). We emphasize that the reversible work source is connected only to the system of interest and not to the heat bath as shown in Fig. 2.13. This is because the reversible work source does not exchange heat with other bodies. Thus, δW^{rev} in (2.174) is the work done on the system when it is allowed to exchange heat with the heat bath as needed in order to keep its temperature constant.

2.13.3 *Direction of a Spontaneous Process*

The Helmholtz free energy cannot increase for spontaneous processes occurring in the system. To see this, we start by noting that

$$\mathrm{d}S^{\mathrm{comp}} = \mathrm{d}S + \mathrm{d}S^B = \mathrm{d}S + \frac{1}{T}\mathrm{d}U^B \,. \tag{2.175}$$

Because the composite system is isolated, $\mathrm{d}U^B = -\mathrm{d}U$:

$$\mathrm{d}S^{\mathrm{comp}} = \mathrm{d}S - \frac{1}{T}\mathrm{d}U = \frac{\mathrm{d}(TS-U)}{T} = -\frac{\mathrm{d}F}{T} \,. \tag{2.176}$$

For spontaneous processes in the composite system, $\mathrm{d}S^{\mathrm{comp}} \geq 0$, and hence $\mathrm{d}F \leq 0$.

Applying (2.174) for a finite (as opposed to infinitesimal) constant temperature process, we have

$$\Delta F = W^{\mathrm{rev}} \,. \tag{2.177}$$

Likewise, (2.176) gives

$$\Delta S^{\mathrm{comp}} = -\frac{\Delta F}{T} \tag{2.178}$$

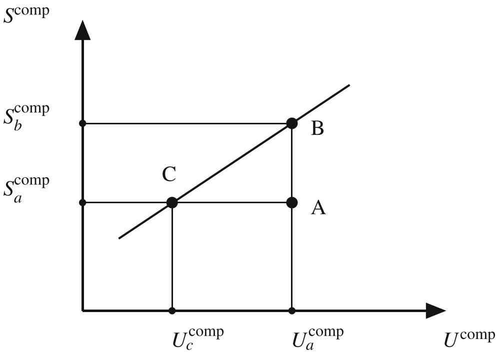

Fig. 2.14 The entropy change $\Delta S^{\text{comp}} = S_b^{\text{comp}} - S_a^{\text{comp}}$ for the spontaneous process A→B is related to the energy difference $W^{\text{rev}} = U_c^{\text{comp}} - U_a^{\text{comp}}$ by (2.179).

for a finite process of constant T. Combining (rather blindly) these equations, we obtain

$$\Delta S^{\text{comp}} = -\frac{W^{\text{rev}}}{T} \, . \tag{2.179}$$

We examine the validity of this equation closely in the next subsection. Accepting (2.179) for a moment, suppose that W^{rev} is positive so that ΔS^{comp} is negative. Identifying $S' - S$ in (2.20) with ΔS^{comp} and using (2.179), we conclude that the probability that the system undergoes the unfavorable finite change as a result of spontaneous fluctuation is given by

$$e^{-W^{\text{rev}}/k_B T} \, . \tag{2.180}$$

You will frequently encounter (2.180) when studying activated processes such as nucleation. If W^{rev} is negative, then ΔS^{comp} is positive and the process occurs spontaneously.

2.13.4 †W^{rev} and a Spontaneous Process

At this point, you may be feeling a little uncomfortable with (2.179). In fact, (2.176) pertains to a spontaneous process, while (2.174) is written for a process that is carried out reversibly by means of a reversible work source. So, δF in (2.174) and $\mathrm{d}F$ in (2.176) refer to *different processes*. Is it really admissible to combine these two equations to get (2.179)? How do we know that these two quantities have the same value when they refer to different processes?

Figure 2.14 helps us answer this question. Because of the first assumption regarding the heat bath, the slope $\partial S^{\text{comp}}/\partial U^{\text{comp}} = 1/T$ is constant and S^{comp} is a linear function of U^{comp}.

If we prepare the composite system in state A and simply let it evolve, it will eventually reach state B. The resulting change in entropy is

$$\Delta S^{\text{comp}} = S_b^{\text{comp}} - S_a^{\text{comp}} > 0 \,. \tag{2.181}$$

Since the slope of the line is $1/T$, this same quantity is given by

$$\Delta S^{\text{comp}} = \frac{U_a^{\text{comp}} - U_c^{\text{comp}}}{T} \,. \tag{2.182}$$

But, $U_a^{\text{comp}} - U_c^{\text{comp}} > 0$ is the reversible work we would be able to extract from the composite system during the spontaneous process *if* it were to be carried out reversibly, thus leaving the composite system in state C instead of B. Now, W^{rev} denotes the work done *on* the composite system, and hence

$$W^{\text{rev}} = U_c^{\text{comp}} - U_a^{\text{comp}} < 0 \,. \tag{2.183}$$

Combining the last two equations, we arrive at (2.179).

Conversely, if the composite system is initially at state B and a spontaneous fluctuation brings it to state A,

$$\Delta S^{\text{comp}} = S_a^{\text{comp}} - S_b^{\text{comp}} < 0 \,. \tag{2.184}$$

Using Fig. 2.14, we find that this same quantity is given by

$$\Delta S^{\text{comp}} = -\frac{U_a^{\text{comp}} - U_c^{\text{comp}}}{T} \,, \tag{2.185}$$

in which $U_a^{\text{comp}} - U_c^{\text{comp}} > 0$ is the reversible work required to bring the composite system to state A *but starting from state C instead of B*.

It is worth emphasizing that (2.179) holds only if B and C are equilibrium states and state A lies directly below B *and* directly to the right of C.

Fluctuations occurring in a stable system or those that initiate the eventual decay of a metastable system toward a more stable state are examples of process B→A. Using (2.179), we can, if desired, estimate ΔS^{comp} by means of a thought experiment in which the composite system is brought from C to A along a reversible path.[10]

Equation (2.179), when combined with (2.174) and (2.176), implies that

$$F_b - F_a = F_c - F_a \,, \tag{2.186}$$

leading us to expect that any difference between states B and C is confined solely to the heat bath. In fact, the composite system can be brought from state B to C by removing heat from the heat bath. Since the heat bath is extremely large, this has no impact on the state of the system of our interest. Disregarding the difference between states B and C, one may say that *a spontaneous process proceeds in such a direction as to deliver positive work to the reversible work source*.[11]

2.13.5 Fundamental Equation

We note that when F defined by (2.172) is expressed in terms of T, V, and $N_1, \dots, N_c$, the resulting function

$$F = F(T, V, N_1, \dots, N_c) \tag{2.187}$$

is the **Legendre transform** of the internal energy U expressed in terms of S, V, and $N_1, \dots, N_c$. Since the latter is a fundamental equation of the system, (2.187) also qualifies as a fundamental equation. (When the transformation is used in thermodynamics, the condition that $\mathrm{d}^2y/\mathrm{d}x^2$ be of a definite sign in the notation of Sect. C.1 is related to the stability of the system. See Exercises 2.3a and 2.12.)

To arrive at the differential form of the fundamental equation, consider infinitesimal changes in T, V, and $N_1, \dots, N_c$, which induce the corresponding changes in the quantities occurring in (2.172):

$$F + \Delta F = U + \Delta U - (T + \mathrm{d}T)(S + \Delta S) \; . \tag{2.188}$$

Using (2.172), we cancel F on the left-hand side and $U - TS$ on the right to obtain

$$\Delta F = \Delta U - T\Delta S - S\mathrm{d}T - \mathrm{d}T\Delta S \; . \tag{2.189}$$

Retaining the first-order terms only,

$$\mathrm{d}F = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T \; . \tag{2.190}$$

Now we use (2.37) and arrive at

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \sum_{i=1}^{c} \mu_i \mathrm{d}N_i \; , \tag{2.191}$$

which is the differential form of the fundamental equation we seek.

From (2.187), we have

$$\mathrm{d}F = \left(\frac{\partial F}{\partial T}\right)_{V,N} \mathrm{d}T + \left(\frac{\partial F}{\partial V}\right)_{T,N} \mathrm{d}V + \sum_{i=1}^{c} \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}} \mathrm{d}N_i \; . \tag{2.192}$$

Since the last two equations hold for any values of $\mathrm{d}T$, $\mathrm{d}V$, and $\mathrm{d}N_1, \dots, \mathrm{d}N_c$, we find

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,N} , \quad -P = \left(\frac{\partial F}{\partial V}\right)_{T,N} ,$$
$$\text{and} \quad \mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}} , \quad i = 1, \dots, c \; , \tag{2.193}$$

which are to be contrasted with (2.38).

Exercise 2.15. Show that

$$\left(\frac{\partial F/T}{\partial T}\right)_{V,N} = -\frac{U}{T^2} \ . \tag{2.194}$$

This identity is known as the **Gibbs–Helmholtz equation**. Following essentially the same approach, you can also show that

$$\left(\frac{\partial G/T}{\partial T}\right)_{P,N} = -\frac{H}{T^2} \ , \tag{2.195}$$

where G and H are, respectively, the Gibbs free energy and the enthalpy to be introduced in Sect. 2.13.6. This is also called the Gibbs–Helmholtz equation. ///

2.13.6 *Other Free Energies*

The relevant free energy when discussing equilibrium of a closed system held at constant temperature and pressure is the **Gibbs free energy** defined by

$$G := U - TS + PV \ . \tag{2.196}$$

To see why, attempt the following exercise.

Exercise 2.16. Formulate the condition of equilibrium for a closed system held at constant temperature and pressure. Then, using (2.196), obtain the equations corresponding to (2.176), (2.191), and (2.193). ///

Using (2.148) in (2.196), we find that

$$G = \sum_{i=1}^{c} \mu_i N_i \ . \tag{2.197}$$

One of the major goals in mixture thermodynamics is to predict μ_i as a function of T, P, and mole fractions $x_1, \ldots, x_{c-1}$, where

$$x_i := N_i \bigg/ \sum_{i=1}^{c} N_i \ . \tag{2.198}$$

Since

$$x_c = 1 - \sum_{i=1}^{c-1} x_i \ , \tag{2.199}$$

we do not include x_c in the list of independent variables. If functions

$$\mu_i = \mu_i(T,P,x_1,\ldots,x_{c-1}) \,, \quad i=1,\ldots,c \tag{2.200}$$

can be constructed for each species in a mixture, then G will be known as a function of T, P, and N_1, ..., N_c. But, this function is a fundamental equation of the mixture. From this point of view, various activity coefficient models, which are widely used for correlating phase equilibria data involving liquid phases, represent an effort to construct fundamental equations of mixtures. The following exercise explores the simplest example of such model mixtures.

Exercise 2.17. A mixture in which μ_i of each species is given by

$$\mu_i(T,P,x_1,\ldots,x_{c-1}) = \mu_i^\circ(T) + RT\left(\ln P + \ln x_i\right) \,, \quad i=1,\ldots,c \tag{2.201}$$

is called an **ideal gas mixture**. Suppose that a composite system made of two compartments, each containing the gas well described by (2.201), is held at some T and P by a heat bath and movable pistons.

a. Initially, compartment A contained 3 mol of species 1 and 1 mol of species 2, while compartment B contained no species 1 and 2 mol of species 2. Find the number of moles of species 1 in compartment B after they are brought into contact through the diathermal, rigid, and immovable partition permeable to the first but not to the second species and a new state of equilibrium is established.
b. Do the same when compartment A initially contained 3 mol of species 1 but no species 2. The initial numbers of moles in compartment B are the same as in part a.
c. In each case considered above, plot G/RT against the number of moles of species 1 in compartment B. ///

There are other commonly used free energies. For example, when

$$\Omega := U - TS - \sum_{i=1}^{c} \mu_i N_i \tag{2.202}$$

is expressed as a function of T, V, and μ_1, ..., μ_c, it is another fundamental equation. This is commonly known as the **grand potential**. The grand potential is particularly useful in describing open systems. If a system is open to species 1 but not to the others, the appropriate choice of the free energy is

$$\chi := U - TS - \mu_1 N_1 \tag{2.203}$$

to be expressed as a function of T, V, μ_1, and N_2, ..., N_c. A free energy of this type is often called a **semi-grand potential**. Finally, **enthalpy**, defined by

$$H := U + PV \,, \tag{2.204}$$

is also a fundamental equation when it is expressed as a function of S, P, and $N_1, \ldots, N_c$. Thus, enthalpy is a free energy characterizing a system held at constant entropy, pressure, and the number of moles of each species.

Exercise 2.18. Show that

$$\left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \left(\frac{\partial H}{\partial N_i}\right)_{S,P,N_{j\neq i}} . \tag{2.205}$$

///

Exercise 2.19. Use (2.202) as a starting point to derive (2.157). ///

The existence of a multitude of free energies prompts the following question: For a system consisting of c components, how many fundamental equations can we come up with? Let us start from the internal energy expressed in terms of S, V, and $N_1, \ldots, N_c$. A new free energy is constructed by replacing some of these variables by the corresponding intensive quantities, for example, S by T, V by $-P$, or, μ_i by N_i. (See Sect. 2.15 for an explicit demonstration that μ_i is an intensive quantity.) For each of the extensive variables, we may either choose to keep it or replace it. The choice we make for a given variable is independent of those we make for the others. Apparently, therefore, there are 2^{c+2} distinct free energies.

Of these, the choice of replacing every extensive quantity by the corresponding intensive variable does not work. The first sign of trouble is that the quantity defined by

$$\Upsilon := U - TS + PV - \sum_{i=1}^{c} \mu_i N_i \tag{2.206}$$

is, according to the Euler relation, identically zero. There are more convincing reasons why Υ does not qualify as a free energy. Firstly, when all the extensive quantities are replaced by the corresponding intensive quantities, information regarding the size of the system is permanently lost. Secondly, T, P, $\mu_1, \ldots, \mu_c$, which are to be used as the independent variables, are *not* independent of each other as seen from the Gibbs–Duhem relation.

In this way, we see that the total of $2^{c+2} - 1$ fundamental equations can be constructed. If we include those functions we obtain by starting from the entropy expressed as a function of U, V, and $N_1, \ldots, N_c$, we will find the same number of fundamental equations, known as **Massieu functions**, examples of which include $-F/T$, $-G/T$, and $-\Omega/T$. In total, therefore, there are $2(2^{c+2} - 1)$ fundamental equations all pertaining to the same system. Of course, only a few of them, such as those we have mentioned already, will be of any use in practice.

Exercise 2.20. You might still feel a slight discomfort with the above discussion of Υ. After all, we did follow the well-defined procedure of the Legendre transformation, did we not? Why should it ever fail? To put your mind at ease, attempt to find the Legendre transformation

$$\Upsilon := \Omega + PV \tag{2.207}$$

of the grand potential

$$\Omega = \Omega(T, V, \mu_1, \ldots, \mu_c) \,. \tag{2.208}$$

Exactly where does the procedure break down? ///

2.14 ‡Maxwell Relation

We recall the following result from calculus. Let $f = f(x,y)$ be a scalar-valued function of two variables x and y. If both

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) \quad \text{and} \quad \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) \tag{2.209}$$

are continuous in some domain, then

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) \tag{2.210}$$

in that same domain. For example, let $f = x^2y + x\ln y$. Then,

$$\frac{\partial f}{\partial x} = 2xy + \ln y \quad \text{and} \quad \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = 2x + \frac{1}{y} \,, \tag{2.211}$$

while

$$\frac{\partial f}{\partial y} = x^2 + \frac{x}{y} \quad \text{and} \quad \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = 2x + \frac{1}{y} \,. \tag{2.212}$$

As advertised, we ended up with the same function regardless of the order of taking the derivatives.

By applying this result from calculus to various free energies, we can obtain numerous **Maxwell relations**. Each Maxwell relation predicts an equality between a pair of seemingly unrelated partial derivatives, reflecting completely different physical situations. From the first two of (2.193), for example, we see that

$$-\left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{\partial^2 F}{\partial T \partial V} = -\left(\frac{\partial P}{\partial T}\right)_{V,N} \,, \tag{2.213}$$

and hence

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N} \,. \tag{2.214}$$

Since $T\mathrm{d}S = đQ$ for a reversible process, the left-hand side of this equation is related to the heat absorbed by the system upon expansion at constant T and $N_1, \ldots, N_c$. On the other hand, the right-hand side is related to the increase in P upon heating at constant V and $N_1, \ldots, N_c$. It will be difficult to anticipate that these quantities pertaining to these distinct physical processes are related in this simple manner. Yet, we have reached this conclusion by admitting only the existing of a fundamental equation and some basic mathematical properties about it. In particular, we made no reference to any specific material from which the system is made. Here lies the power of thermodynamics. Equation (2.214) holds for *any* homogeneous body in equilibrium.

Exercise 2.21. Derive the following Maxwell relations:

a.

$$-\left(\frac{\partial S}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial T}\right)_{V,N} . \tag{2.215}$$

b.

$$-\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial V}\right)_{T,N} . \tag{2.216}$$

c.

$$-\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{P,N} . \tag{2.217}$$

d.

$$-\left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} . \tag{2.218}$$

e.

$$\left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} . \tag{2.219}$$

///

Exercise 2.22. For a c component system, how many Maxwell relations are there? ///

Exercise 2.23. Using the ideal gas equation of state $PV = NRT$, show that

$$\left(\frac{\partial U}{\partial V}\right)_{T,N} = 0 , \tag{2.220}$$

that is U of an ideal gas is independent of its volume. ///

2.15 ‡Partial Molar Quantities

Let $\theta = \theta(T, P, N_1, \ldots, N_c)$ be an extensive quantity. That is

$$\theta(T, P, \lambda N_1, \ldots, \lambda N_c) = \lambda \theta(T, P, N_1, \ldots, N_c) , \tag{2.221}$$

where λ is a positive number. The **partial molar quantity** $\overline{\theta}_i$ is defined by

$$\overline{\theta}_i(T,P,N_1,\ldots,N_c) := \left(\frac{\partial\theta}{\partial N_i}\right)_{T,P,N_{j\neq i}} . \tag{2.222}$$

One particularly important example of $\overline{\theta}_i$ is the partial molar Gibbs free energy:

$$\overline{G}_i(T,P,N_1,\ldots,N_c) = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}} , \tag{2.223}$$

which is nothing but the chemical potential of species i. As other examples of partial molar quantities, we rewrite the last two equations in Exercise 2.21 as

$$\overline{S}_i = -\left(\frac{\partial\mu_i}{\partial T}\right)_{P,N} \quad \text{and} \quad \overline{V}_i = \left(\frac{\partial\mu_i}{\partial P}\right)_{T,N} , \tag{2.224}$$

respectively.

Partial molar quantities are intensive. To see why this might be so, we first recall the Gibbs–Duhem relation, (2.155), which reduces to

$$S\mathrm{d}T - V\mathrm{d}P + N\mathrm{d}\mu = 0 \tag{2.225}$$

for a single component system. Upon division by N, we find

$$\mathrm{d}\mu = -\underline{S}\mathrm{d}T + \underline{V}\mathrm{d}P , \tag{2.226}$$

where $\underline{S} := S/N$ and $\underline{V} := V/N$. For any changes in T and P, the corresponding change in μ is given by (2.226). Since neither $\underline{S}$ nor $\underline{V}$ depends on the size of the system, it follows that the chemical potential of a single component system is independent of the size of the system. Thus, it is an intensive quantity.

It seems natural to expect that the same conclusion hold when we move to a multicomponent system. But, because chemical potentials are just a particular example of partial molar quantities, we are lead to expect that the partial molar quantities are, in general, intensive quantities.

Now we verify this expectation. We start by noting that (2.221) holds for any positive value of N_i. Thus, when we take the partial derivative of (2.221) with respect to N_i, the equality still holds.[12] Thus,

$$\frac{\partial\theta(T,P,M_1,\ldots,M_c)}{\partial M_i}\frac{\partial M_i}{\partial N_i} = \lambda\frac{\partial\theta(T,P,N_1,\ldots,N_c)}{\partial N_i} , \tag{2.227}$$

where $M_i := \lambda N_i$, and hence $\partial M_i/\partial N_i = \lambda$. From (2.222), the partial derivative on the left-hand side of (2.227) is the partial molar quantity $\overline{\theta}_i$ of the system containing M_i moles of species i. Thus, we have

$$\overline{\theta}_i(T,P,M_1,\ldots,M_c) = \overline{\theta}_i(T,P,N_1,\ldots,N_c) . \tag{2.228}$$

Since λ is arbitrary, this equation holds even if we set $\lambda = 1/\sum_i N_i$:

$$\overline{\theta}_i(T,P,x_1,\ldots,x_{c-1}) = \overline{\theta}_i(T,P,N_1,\ldots,N_c) \,, \tag{2.229}$$

where $x_i = N_i/\sum_i N_i$ is the mole fraction of the ith species. Note that only $c-1$ of the mole fractions are independent because $\sum_i x_i \equiv 1$. *According to (2.229), $\overline{\theta}_i$ is an intensive quantity.*

Next, we consider the partial derivative of (2.221) with respect to λ:

$$\sum_{i=1}^{c} \frac{\partial \theta(T,P,M_1,\ldots,M_c)}{\partial M_i} \frac{\partial M_i}{\partial \lambda} = \theta(T,P,N_1,\ldots,N_c) \,. \tag{2.230}$$

Since $\partial M_i/\partial \lambda = N_i$, we find

$$\sum_{i=1}^{c} \overline{\theta}_i(T,P,x_1,\ldots,x_{c-1})N_i = \theta(T,P,N_1,\ldots,N_c) \,. \tag{2.231}$$

Essentially, the identical approach can be used to derive (2.148). In view of this, (2.231) is often referred to as the **generalized Euler relation** .

If we set $\theta = G$, (2.231) becomes

$$G(T,P,N_1,\ldots,N_c) = \sum_{i=1}^{c} \overline{G}_i(T,P,x_1,\ldots,x_{c-1})N_i \,, \tag{2.232}$$

which is just (2.197) since $\overline{G}_i = \mu_i$. To get something new, let $\theta = V$. Then,

$$V(T,P,N_1,\ldots,N_c) = \sum_{i=1}^{c} \overline{V}_i(T,P,x_1,\ldots,x_{c-1})N_i \,, \tag{2.233}$$

or dividing by $\sum_i N_i$,

$$\underline{V}(T,P,N_1,\ldots,N_c) = \sum_{i=1}^{c} \overline{V}_i(T,P,x_1,\ldots,x_{c-1})x_i \,. \tag{2.234}$$

Equations like this occur very often in mixture thermodynamics.

Just like the Gibbs–Duhem relation followed from the Euler relation in Sect. 2.11, we can derive the generalized Gibbs–Duhem relation from the generalized Euler relation using the identical approach. The only difference is in the symbols we use.

As in Sect. 2.11, suppose that the state of the system has changed as a result of infinitesimal changes of T, P, and $N_1, \ldots, N_c$. Both θ and $\overline{\theta}_1, \ldots, \overline{\theta}_c$ will change as a result. Applying (2.231) to the state after the change, we may write

$$\theta + \Delta\theta = \sum_{i=1}^{c} (\overline{\theta}_i + \Delta\overline{\theta}_i)(N_i + \mathrm{d}N_i) \,. \tag{2.235}$$

From this, we subtract (2.231) applied to the state prior to the infinitesimal change and obtain

$$\Delta\theta = \sum_{i=1}^{c} \overline{\theta}_i \mathrm{d}N_i + \sum_{i=1}^{c} N_i \Delta\overline{\theta}_i + \sum_{i=1}^{c} \Delta\overline{\theta}_i \mathrm{d}N_i \,. \tag{2.236}$$

Retaining the first-order terms only,

$$\mathrm{d}\theta = \sum_{i=1}^{c} \overline{\theta}_i \mathrm{d}N_i + \sum_{i=1}^{c} N_i \mathrm{d}\overline{\theta}_i \,. \tag{2.237}$$

But, since θ is a function of T, P, and $N_1, \ldots, N_c$,

$$\mathrm{d}\theta = \theta_T \mathrm{d}T + \theta_P \mathrm{d}P + \sum_{i=1}^{c} \overline{\theta}_i \mathrm{d}N_i \,, \tag{2.238}$$

where

$$\theta_T := \left(\frac{\partial\theta}{\partial T}\right)_{P,N} \quad \text{and} \quad \theta_P := \left(\frac{\partial\theta}{\partial P}\right)_{T,N} \,. \tag{2.239}$$

Combining (2.237) and (2.238), we finally arrive at

$$0 = -\theta_T \mathrm{d}T - \theta_P \mathrm{d}P + \sum_{i=1}^{c} N_i \mathrm{d}\overline{\theta}_i, \tag{2.240}$$

which is called the **generalized Gibbs–Duhem relation**.

Once again, let $\theta = G$. Then, (2.240) becomes

$$0 = -G_T \mathrm{d}T - G_P \mathrm{d}P + \sum_{i=1}^{c} N_i \mathrm{d}\mu_i \,. \tag{2.241}$$

But, since

$$G_T := \left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad \text{and} \quad G_P := \left(\frac{\partial G}{\partial P}\right)_{T,N} = V \,, \tag{2.242}$$

(2.241) is nothing but the usual Gibbs–Duhem relation.

Exercise 2.24. Establish (2.74). ///

2.16 Graphical Methods

In this section, we discuss a few graphical methods you will encounter in later chapters. From a computational point of view, the accuracy expected of such methods is not very high. Yet, they do have intuitive appeal and thus help us understand certain key concepts in thermodynamics. On occasion, they can also help diagnose difficulties that may arise in practical computations.

2.16.1 Pure Systems: $\underline{F}$ Versus $\underline{V}$ (Constant T)

Recall the definition of the Helmholtz free energy in (2.172). Using (2.148), we find

$$F := U - TS = -PV + \mu N\,. \tag{2.243}$$

for a single component system, where N is the number of moles in the system. Dividing both sides by N, we obtain

$$\underline{F} := \frac{F}{N} = -P\underline{V} + \mu\,, \tag{2.244}$$

where $\underline{V} := V/N$. We now show that

$$-P = \left(\frac{\partial \underline{F}}{\partial \underline{V}}\right)_T\,. \tag{2.245}$$

To see this, we apply (2.191) to a single component system and restricting our attention to processes in which T and N are held constant:

$$\mathrm{d}F = -P\mathrm{d}V\,. \tag{2.246}$$

Dividing both sides by N,

$$\mathrm{d}\underline{F} = -P\mathrm{d}\underline{V}\,, \tag{2.247}$$

where we note that $(\mathrm{d}V)/N = \mathrm{d}(V/N)$ since N is held fixed. Likewise for $(\mathrm{d}F)/N$. Dividing both sides of (2.247) by $\mathrm{d}\underline{V}$ and recalling that the equation holds only for constant T and N processes, we arrive at

$$-P = \left(\frac{\partial \underline{F}}{\partial \underline{V}}\right)_{T,N} = \left(\frac{\partial \underline{F}}{\partial \underline{V}}\right)_T\,. \tag{2.248}$$

In the last step, we used the fact that $\underline{F}$ is a molar quantity and hence is independent of N. Alternatively, we could proceed more mechanically as follows:

$$-P = \left(\frac{\partial F}{\partial V}\right)_{T,N} = \left(\frac{\partial F/N}{\partial V/N}\right)_{T,N} = \left(\frac{\partial \underline{F}}{\partial \underline{V}}\right)_{T,N} = \left(\frac{\partial \underline{F}}{\partial \underline{V}}\right)_T\,. \tag{2.249}$$

Equations (2.244) and (2.245) lead to the graphical construction illustrated in Fig. 2.15. Specifically, suppose that the isotherm is produced at some temperature T of interest. If we draw the tangent line at some particular value of $\underline{V}$, say $\underline{V}^*$, the negative of the slope is the pressure P^* at $(T,\underline{V}^*)$. The intercept of the tangent line on the $\underline{F}$-axis (on which $\underline{V} = 0$) is computed as

$$\underline{F}^* - \left(\frac{\partial \underline{F}}{\partial \underline{V}}\right)_T\bigg|_{\underline{V}=\underline{V}^*}\underline{V}^* = \underline{F}^* + P^*\underline{V}^* = \mu^*\,, \tag{2.250}$$

where we used (2.244). That is, the intercept is the chemical potential at $(T,\underline{V}^*)$.

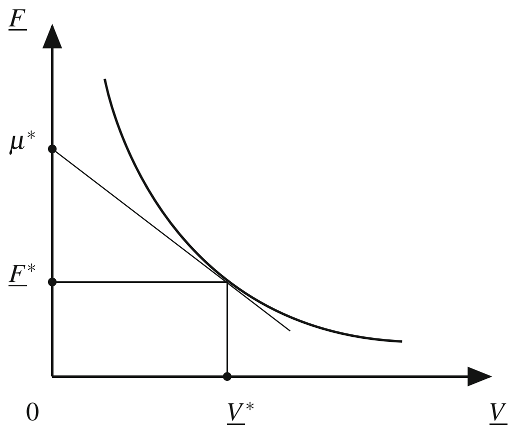

Fig. 2.15 Graphical construction involving an $\underline{F}$ versus $\underline{V}$ isotherm.

2.16.1.1 Gibbs–Duhem Relation at Constant T: Interpretation

Now, let us imagine what happens to the tangent line in Fig. 2.15 if we move $\underline{V}^*$ to the right. We see that, as the tangent line rolls on the curve, the intercept on the $\underline{F}$-axis (μ^*) decreases while the slope ($-P^*$) increases. In other words, at a given temperature, a decrease in μ is accompanied by a decrease in P. This is actually a consequence of the Gibbs–Duhem relation (2.155), which reduces to

$$d\mu = \underline{V} dP\,, \quad T \text{ const.} \tag{2.251}$$

for constant T processes in a pure system. In this way, the Gibbs–Duhem relation acquires a graphical interpretation.

2.16.1.2 †Gibbs–Duhem Relation at Constant T: Derivation

It is somewhat amusing to turn the above observation around and derive (2.251) graphically. Let us draw two tangent lines to the $\underline{F}$-$\underline{V}$ isotherm, one at $\underline{V}^*$ and the other at $\underline{V} = \underline{V}^* + d\underline{V}$ as shown in Fig. 2.16. The negative of the slope and the intercept on the $\underline{F}$-axis of the second tangent line are the pressure and the chemical potential at $(T, \underline{V}^* + d\underline{V})$, which we denote by $P^* + \Delta P$ and $\mu^* + \Delta\mu$, respectively.

If we shift this second tangent line vertically upward till it passes through the point of tangent (A_1) of the first tangent line at $\underline{V} = \underline{V}^*$, the intercept of the resulting line is

$$\mu^* + \Delta'\mu = \underline{F}^* + (P^* + \Delta P)\underline{V}^*\,. \tag{2.252}$$

Using (2.250), we find that

$$\Delta'\mu = \underline{V}^* \Delta P\,. \tag{2.253}$$

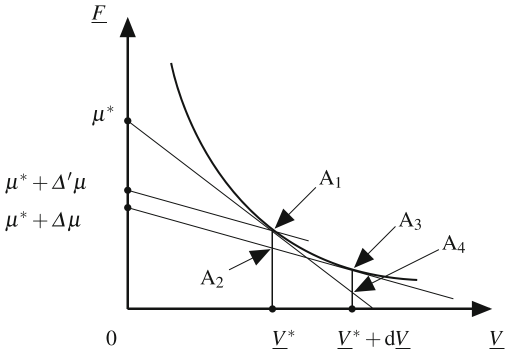

Fig. 2.16 Graphical derivation of the Gibbs–Duhem relation for a constant T process in a pure system.

We now show that the difference between $\Delta'\mu$ and $\Delta\mu$ is zero to the first order of $d\underline{V}$. In fact,

$$\Delta'\mu - \Delta\mu = (\mu^* + \Delta'\mu) - (\mu^* + \Delta\mu) = \mathrm{A}_1\mathrm{A}_2 \propto \mathrm{A}_3\mathrm{A}_4 \;, \tag{2.254}$$

where $\mathrm{A}_1\mathrm{A}_2$ is the length of the line segment connecting points A_1 and A_2. Likewise for $\mathrm{A}_3\mathrm{A}_4$. But,

$$\mathrm{A}_3\mathrm{A}_4 = \underline{F}(\underline{V}^* + d\underline{V}) - \left[\underline{F}(\underline{V}^*) + \left(\frac{\partial \underline{F}}{\partial \underline{V}} \right)_T \Bigg|_{\underline{V}=\underline{V}^*} d\underline{V} \right] = \text{h.o.} \tag{2.255}$$

Thus, retaining up to the first-order term in (2.253), we have

$$d\mu = \underline{V}^* dP \tag{2.256}$$

for a constant T process. Since the equality holds for any $\underline{V}^*$, (2.251) is now established.

2.16.2 Binary Mixtures: $\underline{G}$ Versus x_1 (Constant T and P)

From (2.148) and (2.196), we have

$$G := U - TS + PV = \mu_1 N_1 + \mu_2 N_2 \tag{2.257}$$

for a binary mixture. Dividing both sides by $N := N_1 + N_2$, we obtain

$$\underline{G} = \mu_1 x_1 + \mu_2 x_2 \;, \tag{2.258}$$

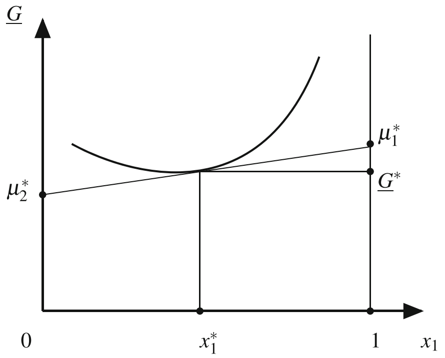

Fig. 2.17 Graphical construction involving a $\underline{G}$ versus x_1 plot at constant (T,P).

where $\underline{G} := G/N$ and $x_i := N_i/N$. To see the physical meaning of the slope of the $\underline{G}$ versus x_1 plot, we recall from Exercise 2.16 that

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mu_1\mathrm{d}N_1 + \mu_2\mathrm{d}N_2 \tag{2.259}$$

and consider constant T and P processes in which $N := N_1 + N_2$ is also held constant. This somewhat unusual constraint does not necessarily imply any chemical reaction between species 1 and 2. It simply states that, whenever species 1 enters the system, the equal number of moles of species 2 needs to be extracted from it. For such processes,

$$\mathrm{d}G = (\mu_1 - \mu_2)\mathrm{d}N_1\ , \quad T,P,N \text{ const.} \tag{2.260}$$

Dividing both sides by N,

$$\mathrm{d}\underline{G} = (\mu_1 - \mu_2)\mathrm{d}x_1\ , \quad T,P \text{ const.} \tag{2.261}$$

where $\underline{G} := G/N$ and $x_1 := N_1/N$. We also dropped the reference to N being constant since $\underline{G}$ is a molar quantity and hence, in this case, is a function of T, P, and x_1 only. Dividing (2.261) by $\mathrm{d}x_1$, we find

$$\left(\frac{\partial \underline{G}}{\partial x_1}\right)_{T,P} = \mu_1 - \mu_2\ . \tag{2.262}$$

This motivates the graphical method illustrated in Fig. 2.17. We draw a tangent line to the $\underline{G}$ versus x_1 curve for given (T,P) at the mole fraction $x_1 = x_1^*$. Its intercept on the $\underline{G}$-axis (at $x_1 = 0$) is μ_2 of the mixture at (T,P,x_1^*), which we denote by μ_2^*. In fact,

$$\underline{G}^* - \left(\frac{\partial \underline{G}}{\partial x_1}\right)_{T,P}\Bigg|_{x_1=x_1^*} x_1^* = \underline{G}^* - (\mu_1^* - \mu_2^*)x_1^* = \mu_2^*\ , \tag{2.263}$$

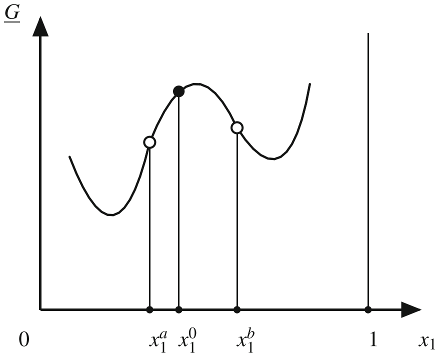

Fig. 2.18 $\underline{G}$ versus x_1 plot at constant (T,P) showing two inflection points indicated by the *open circles*.

where we used (2.258) and the identity $x_1 + x_2 \equiv 1$. Similarly, the intercept on the vertical line at $x_1 = 1$ is μ_1 of the same mixture:

$$\underline{G}^* + \left(\frac{\partial \underline{G}}{\partial x_1}\right)_{T,P}\bigg|_{x_1=x_1^*} (1-x_1^*) = \underline{G}^* + (\mu_1^* - \mu_2^*)x_2^* = \mu_1^* \,. \tag{2.264}$$

2.16.2.1 Gibbs–Duhem Relation at Constant T and P: Interpretation

As in Sect. 2.16.1.1, the above graphical method provides a graphical interpretation of the Gibbs–Duhem relation applied to constant (T,P) processes in a binary mixture:

$$x_1 \mathrm{d}\mu_1 + x_2 \mathrm{d}\mu_2 = 0 \,, \quad T,P \text{ const.} \tag{2.265}$$

In fact, imagine how the intercepts at $x_1 = 0$ and $x_1 = 1$ move as the tangent line rolls on the $\underline{G}$ versus x_1 plot with increasing x_1. From the figure, it is clear that μ_1 increases while μ_2 decreases. But, that is exactly what (2.265) indicates.

The $\underline{G}$ versus x_1 plot may contain inflection points as shown in Fig. 2.18. As x_1 passes through the inflection point at x_1^a in the figure, μ_1 goes through a local maximum, while μ_2 goes through a local minimum. Beyond this inflection point, the curve will be concave down, and μ_1 now decreases while μ_2 increases. In this way, we see that $\mathrm{d}\mu_1$ and $\mathrm{d}\mu_2$ either have opposite signs or they are simultaneously zero. Again, this behavior is consistent with (2.265).

As we shall see in Sect. 2.16.2.3, a binary mixture is unstable with respect to phase separation if its $\underline{G}$ versus x_1 curve is concave down. Thus, x_1^a marks the onset of instability. In Fig. 2.18, the curve develops another inflection point at x_1^b. For $x_1 > x_1^b$, the curve is concave up and the mixture regains its stability.

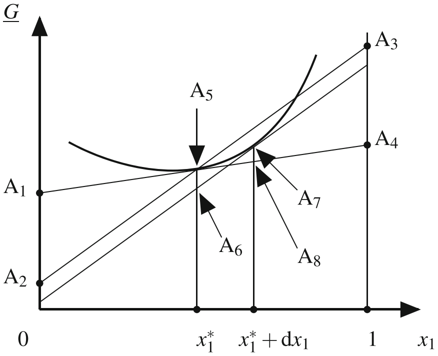

Fig. 2.19 Graphical derivation of the Gibbs–Duhem relation for a constant (T, P) process in a binary mixture.

2.16.2.2 †Gibbs–Duhem Relation at Constant T and P: Derivation

As in Sect. 2.16.1.2, let us derive (2.265) graphically. For this purpose, we draw another tangent line at $x_1 = x_1^* + \mathrm{d}x_1$ as illustrated in Fig. 2.19. Its intercepts on the $\underline{G}$-axis is the chemical potential of species 2 at $(T, P, x_1 + \mathrm{d}x_1^*)$, which we denote by $\mu_2^* + \Delta\mu_2$. The intercept on the vertical line $x_1 = 1$ is the chemical potential of species 1 at the same condition and is denoted by $\mu_1^* + \Delta\mu_1$.

Now, we shift the tangent line at $x_1 = x_1^* + \mathrm{d}x_1$ vertically upward so that it passes through the point of tangent (A_5 in Fig. 2.19) of the tangent line at $x_1 = x_1^*$. We denote the intercepts of this shifted tangent line at $x_1 = 0$ (A_2) and $x_1 = 1$ (A_3) by $\mu_2(x_1^*) + \Delta'\mu_2$ and $\mu_1(x_1^*) + \Delta'\mu_1$, respectively. From Fig. 2.19, we note that the two triangles $\triangle\mathrm{A}_1\mathrm{A}_2\mathrm{A}_5$ and $\triangle\mathrm{A}_4\mathrm{A}_3\mathrm{A}_5$ are similar. Thus,

$$\frac{\mathrm{A}_1\mathrm{A}_2}{\mathrm{A}_3\mathrm{A}_4} = \frac{\mu_2^* - (\mu_2^* + \Delta'\mu_2)}{(\mu_1^* + \Delta'\mu_1) - \mu_1^*} = \frac{x_1^*}{1 - x_1^*}\,, \tag{2.266}$$

from which we find

$$x_1^*\Delta'\mu_1 + x_2^*\Delta'\mu_2 = 0\,. \tag{2.267}$$

From the figure, we observe that

$$\Delta'\mu_i - \Delta\mu_i = \mathrm{A}_5\mathrm{A}_6 \propto \mathrm{A}_7\mathrm{A}_8\,, \quad i = 1, 2\,. \tag{2.268}$$

But,

$$\mathrm{A}_7\mathrm{A}_8 = \underline{G}(x_1^* + \mathrm{d}x_1) - \left[\underline{G}(x_1^*) + \left(\frac{\partial \underline{G}}{\partial x_1}\right)_{T,P}\bigg|_{x_1 = x_1^*} \mathrm{d}x_1\right] = \text{h.o.}\,, \tag{2.269}$$

and hence

$$\Delta'\mu_i = \Delta\mu_i + \text{h.o.}\,, \quad i = 1, 2\,, \tag{2.270}$$

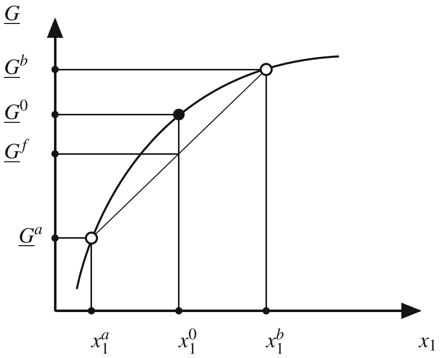

Fig. 2.20 $\underline{G}$ versus x_1 plot at constant T and P.

which in turn allows us to rewrite (2.267) as

$$x_1^* \Delta\mu_1 + x_2^* \Delta\mu_2 = \text{h.o.} \tag{2.271}$$

Retaining the first-order terms only, we obtain

$$x_1^* \mathrm{d}\mu_1 + x_2^* \mathrm{d}\mu_2 = 0\,. \tag{2.272}$$

Since this equality holds for any x_1^* as long as T and P are fixed, we finally arrive at (2.265).

2.16.2.3 Phase Separation

A binary mixture of a given mole fraction is unstable with respect to phase separation if $\underline{G}$ versus x_1 plot is concave down at that mole fraction. For example, the molar Gibbs free energy of a binary mixture at x_1^0 in Fig. 2.20 is $\underline{G}^0$. By separating into phase A with mole fraction x_1^a and phase B with x_1^b, the molar Gibbs free energy decreases to $\underline{G}^f$.

As you saw in Exercise 2.16, a closed system held at constant T and P evolves toward the direction of decreasing G. So, the phase separation we just considered is a spontaneous process and the initial phase is unstable.

As in Exercise 2.11, the graphical construction for $\underline{G}^f$ can be justified as follows. First, the Gibbs free energy G^f of the composite system consisting of phases A and B is given by

$$G^f = N\underline{G}^f = N^a\underline{G}^a + N^b\underline{G}^b\,, \tag{2.273}$$

where N is the total number of moles of molecules in the system and includes molecules of both species. We denote the total number of moles in phase A by N^a and that in phase B by N^b. Clearly,

$$N = N^a + N^b\,. \tag{2.274}$$

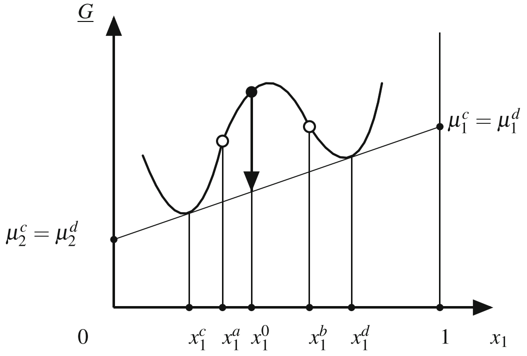

Fig. 2.21 The common tangent construction to find the mole fractions, x_1^c and x_1^d, at phase coexistence. The mixture is unstable between two inflection points (*open circles*) at x_1^a and x_1^b.

Considering the total number of moles of species 1 in the entire system, we obtain

$$x_1^0 N = x_1^a N^a + x_1^b N^b \; . \tag{2.275}$$

From (2.273) and (2.274), we find

$$\underline{G}^f = \frac{N^a}{N}\underline{G}^a + \frac{N^b}{N}\underline{G}^b = \underline{G}^a + (\underline{G}^b - \underline{G}^a)\frac{N^b}{N} \; , \tag{2.276}$$

while (2.274) and (2.275) gives

$$\frac{N^b}{N} = \frac{x_1^0 - x_1^a}{x_1^b - x_1^a} \; . \tag{2.277}$$

Thus,

$$\underline{G}^f = \underline{G}^a + \frac{\underline{G}^b - \underline{G}^a}{x_1^b - x_1^a}(x_1^0 - x_1^a) \tag{2.278}$$

in agreement with the graphical construction.

Because of the way the diagram is drawn, $\underline{G}$ versus x_1 plot is concave down at x_1^a and x_1^b. So, both phases A and B are still unstable. If $\underline{G}$ actually is concave down everywhere between $x_1 = 0$ and $x_1 = 1$, then the system will split into two pure phases. In reality, however, it is likely that the curve will eventually turn around and become concave up toward both ends of the x_1-axis (at $x_1 = 0$ and $x_1 = 1$).

2.16.2.4 Phase Coexistence

If the mole fraction x_1^0 of the system sits between two inflection points of the $\underline{G}$ versus x_1 plot as shown in Fig. 2.21, the mixture will separate into two phases. The mole fractions of these coexisting phases, which we denote by x_1^c and x_1^d, can be found by means of the **common tangent construction** illustrated in Fig. 2.21. According to this method, we draw a tangent line having two points of contact. The mole fractions of the coexisting phases are then given by those of the points of tangent.

Why? Recall that the intercept at $x_1 = 0$ of the tangent line gives you μ_2, while that at $x_1 = 1$ gives you μ_1. So, from the figure, we see that $\mu_1^c = \mu_1^d$ and $\mu_2^c = \mu_2^d$. Since the curve is for given T and P, clearly, $T^c = T^d$ and $P^c = P^d$. So, the composite system consisting of the two phases is in equilibrium. The equilibrium is stable because $\underline{G}$ is concave up at these mole fractions.

As indicated by the downward arrow in the Fig. 2.21, $\underline{G}$ decreases upon phase separation. The length of this arrow is the **driving force of phase separation**. As in (2.277),

$$\frac{N^d}{N} = \frac{x_1^0 - x_1^c}{x_1^d - x_1^c}\ , \tag{2.279}$$

where $N = N_c + N_d$ is the total number of moles in the system. Thus,

$$\frac{N^c}{N} = 1 - \frac{N_d}{N} = \frac{x_1^d - x_1^0}{x_1^d - x_1^c}\ . \tag{2.280}$$

Thus,

$$N^c(x_1^0 - x_1^c) = N^d(x_1^d - x_1^0)\ . \tag{2.281}$$

This result is known as the **lever rule**. The amount of each phase, as measured by the total number of moles, satisfies the condition of the mechanical balance of a lever with fulcrum at x_1^0 and loads N^c and N^d at x_1^c and x_1^d, respectively.

Between x_1^c and x_1^a, the phase is not unstable, but its free energy can be lowered by undergoing phase separation (into x_1^c and x_1^d). The phase is thus metastable. Likewise for a phase between x_1^b and x_1^d.

2.17 Frequently Used Symbols

c , the number of species.
k_B , Boltzmann constant, 1.3806×10^{-23} J/K.
n_i , N_i/V. We often drop the subscript for a pure system.
s , S/V.
u , U/V.
x_i , mole fraction of species i.

C_P , constant pressure heat capacity.
$\underline{C}_P$, constant pressure molar heat capacity.
C_V , constant volume heat capacity.
$\underline{C}_V$, constant volume molar heat capacity.
E , total energy.

F , Helmholtz free energy.
G , Gibbs free energy.
H , enthalpy.
N_i , the number of moles of species i. We often drop the subscript for a pure system.
P , pressure.
Q , heat.
R , gas constant. 8.3145 J/mol K
S , entropy.
T , absolute temperature.
U , internal energy.
V , volume.
W , work.
W^{rev} , work done by a reversible work source.
X_i , ith additional variable needed to specify the state of a system not in equilibrium.

α , coefficient of thermal expansion.
γ , C_P/C_V.
μ_i , chemical potential of species i. We often drop the subscript for a pure system.
θ , extensive quantity.
$\overline{\theta}$, partial molar quantity defined by $(\partial\theta/\partial N_i)_{T,P,N_{j\neq i}}$.
$\underline{\theta}$, molar quantity defined by $\theta/\sum_{i=1}^{c} N_i$.
Ω , grand potential.

References and Further Reading

1. Callen H B (1985) Thermodynamics and an Introduction to Thermostatistics, 2nd edn. John Wiley & Sons, New York
   Our exposition of thermodynamics is motivated, in part, by the axiomatic approach to thermodynamics by Callen. For a more detailed discussion on thermodynamics, this is probably the place to start. Chapters 1-6 should be sufficient for the first reading.
2. Fermi E (1956) Thermodynamics. Dover, New York
   One thing that is missing from Callen as well as from the current chapter is the concept of entropy introduced through purely macroscopic considerations. Fermi's book fills this gap very nicely. Entropy is covered in the first 60 pages or so. His definition of an adiabatic process differs from ours in that he demands the process to be reversible as well.
3. Gibbs J W (1993) The Scientific Papers of J. Willard Gibbs, Volume I. Thermodynamics. Ox Bow, Connecticut
   Contrary to some uninformed view, the original work by Gibbs still is among the most important resources on thermodynamics. This makes a notoriously difficult reading. However, the effort is more than justified by generality and rigor of the exposition.
4. Nishioka K (1987) An analysis of the Gibbs theory of infinitesimally discontinuous variation in thermodynamics of interface. Scripta Metallurgica 21:789–792
5. Whitaker S (1992) Introduction to Fluid Mechanics, Krieger Publishing Company, Florida
   Highly readable and thoughtfully written introduction to fluid mechanics.