

Chapter 2

Foundations of Thermodynamics

In Chapter 1 mathematical facts are dealt with exclusively. Now we are going to the physics of it. We may mention several important preliminaries, usually treated shabbily. We start to talk with the term energy and use the term system in this chapter without having it defined before. However, the term system is discussed soon afterward. Thus, we do not talk about the individual terms here in an axiomatic way. An axiomatic introduction into thermodynamics is, if it is possible at all, quite more difficult to understand. It is unnecessary to say that there are many impressive textbooks in thermodynamics [1–6].

2.1 Idealization

A few comments on idealization are in order here. We obtain physical laws by abstracting reality. Often, only the concept of simplification of the real world by abstraction allows a mathematical description of a physical phenomenon. On the other hand, problems and inconsistencies arise by the simplification procedure. Here we present some examples:

An ideal gas is abstracted as a couple of points that are moving freely in a confined space. The points have a zero extension in space. Further, they do not exert mutual forces. It is highly understandable that points with a zero extension would not be a source of forces. However, even when the points have zero extension, they carry mass. Therefore, applying common sense, we conclude that each point must have an infinite density. Moreover, these points show a heat capacity.

On first glance, this fact is also not understandable. However, if we are accustomed that the points have mass, then we could accept that the heat capacity is caused by the kinetic energy. This is in order again as we restrict ourselves to a translational energy.

We present still another example, Newton's law of motion. This law states that under the action of force a particle will undergo acceleration. The acceleration is inversely proportional to the mass. In the treatment, often the particles are considered as point masses, as in an ideal gas.

These innocently looking assumptions run into problems, if we extend the concept of force to the concept of energy. If we observe a particle at a short moment we do not know how much energy the particles are possessing. However, if we observe the path of a particle, then we can state how much energy it has gained or lost when moving along the path. The energy is the path integral, in one dimension, we find

$$U = - \int F(x) dx. \quad (2.1)$$

On the other hand, we can trace back the energy to the force:

$$F = - \frac{dU(x)}{dx}. \quad (2.2)$$

If we are approaching the concept of force from the energy view $U(x)$, we can state about the energy without knowing the force at all. If we are treating the energy as the basic quantity, the question arises as to how a point-shaped particle experiences that in a small distance; apart from the particle there exists a smaller energy and it could move to the position where the smaller energy is.

In other words, a point-shaped particle does not know about the gradient of the energy. We could introduce the concept that the point-shaped particle does not stand in its position, and the motion is fluctuating around a certain position. In this way, the particle could find out that besides its instantaneous position is a place where it would possess less energy. On the other hand, an extended particle in space could experience a gradient of the energy in space.

In common sense, we are accustomed to such gradients. If a drinking glass is positioned near the border of the table plate, a lot of people intuitively feel to place the glass more in the center of the table, to prevent it from falling down. This mental dictate emerges because it is believed that somebody could push the glass unintentionally and so cause the glass to reach the border and fall down eventually. If there would be nobody who could touch the glass unintentionally, then the habit to center a glass on the table is completely unnecessary. The glass would not fall down, no matter how high the table is.

2.2 Energy

Energy has the physical dimensions of $\text{kg m}^2\text{s}^{-2}$. From its nature, energy is a nonnegative quantity. From a thermodynamic system, we can withdraw all the energy available, but we cannot borrow energy that is not there. For this reason, the energy has an absolute zero. If we deal with the energy available, then we mean the energy that is accessible to us from a system. A system may still contain energy that is not accessible to us by the tools we have.

For example, if we have a gas in a container with a piston, we can access the energy of expansion. If the container is adiabatically insulated, we cannot access the

thermal energy directly. However, the gas is cooling down on adiabatic expansion. Therefore, we can access the thermal energy indirectly via the energy of expansion. After utmost expansion, the gas may still contain energy that could be set free by a chemical reaction or by a nuclear reaction. However, if we cannot initiate these reactions, we cannot access the energy. Therefore, we may set the energy, when all the energy of expansion is gathered as zero.

2.2.1 Extensive and Intensive Quantities

Energy can always be disassembled into two terms, one being extensive and the other being intensive. If we scale the system, then the extensive term will be scaled by the scale factor, but the intensive term does not change. Thus, the extensive term may contain the mass, the volume, the electric charge, and the like. We can distinguish several types of extensive variables. An extensive variable does not necessarily contain the mass in its physical dimension, for example, the volume of a system. On the other hand, the pressure is energy conjugated to the volume and contains the mass as basic unit.

We recall that in mechanics the energy is the negative integral of a force by the path. This concept holds ideally for masses that are concentrated in a mathematical point, so-called point masses:

$$U = - \int \mathbf{F} d\mathbf{s} + C, \quad (2.3)$$

where C is some constant of integration. If the mass is constant we can rewrite Eq. (2.3) as

$$U = - \int \frac{\mathbf{F}}{m} d(ms) + C = - \int \mathbf{F}_u d(ms) + C. \quad (2.4)$$

In Eq. (2.4) we have replaced the force \mathbf{F} by the force acting on the unit mass \mathbf{F}_u and the total mass we have pushed in the differential. The force and the path are vectors. If the point mass body is moving in the direction of the force then it is losing energy. If the body is moving against the force, it is accumulating energy. On the other hand, when the body loses mass at the same position, the energy also changes. We can address the intensive variable just as a specific force \mathbf{F}_u . The extensive variable is then a generalized mass path $m s$. This notation conforms more to the kinetic energy that is $v dP$, i.e., the energy-conjugated pair of velocity and momentum. The energy forms are close to a convenient description of the quantities in which a system may take up or release energy.

Since a macroscopic system has an extension in space, not all parts of the system can be at the same height. Therefore, the system is not homogeneous. In order to deal with a homogeneous system with gravitational energy, we must consider an infinitely thin shell where all parts of the system can be at the same height.

The way to create extensive and intensive variables, as exemplified in Eq. (2.4), does not work in general. For example, the volume is an extensive variable, but the mass is captured in the corresponding intensive variable, i.e., the pressure. Therefore, dividing the pressure by mass is not what we would expect. In the sense of thermodynamic homogeneity, scaling in the gravitational field is restricted to a direction in space where no field is actually acting.

Despite these problems, homogeneity is rather characterized by a certain portion of space where the properties are not changing. Thus, scaling the volume of a region in space where properties such as pressure, charge density, entropy density are constant seems to be a more fundamental process in order to identify extensive and intensive variables.

The volume is rather a basic concept of a region, as it appears in the derivation of all kinds of equations of continuity. For this reason, we introduce quantities that refer to the unit of volume. We will use the superscript \check{X} in order to indicate that this is X per volume. Remember that we are using \check{C}_v for the molar heat capacity (at constant volume), \hat{C}_v for the specific heat capacity, \tilde{C}_v for a reduced heat capacity, i.e., divided by a reference value, and now \check{C}_v for the heat capacity density. The quantities \check{X} are basically X densities, for example, the mass density or the molar density:

$$\check{m} = \frac{\partial m}{\partial V} = \rho; \quad \check{n} = \frac{\partial n}{\partial V} = c. \quad (2.5)$$

For the mass density and the molar density, we have common symbols available. Usually the molar density is referred to as concentration. However, there are other densities, such as the density of entropy, density of electrical charge, or density of momentum, which are

$$\check{S} = \frac{\partial S}{\partial V} = \rho_S; \quad \check{Q}_{el} = \frac{\partial Q_{el}}{\partial V} = \rho_{el}; \quad \check{P} = \frac{\partial P}{\partial V} = \rho_P. \quad (2.6)$$

For these quantities we have to introduce special symbols. The differentials in the definition indicate that we go to infinite small volume to get the property \check{X} . If \check{X} is not dependent on position, we have homogeneity in the system or region under consideration. In this case, we can extend the volume arbitrarily and the system will still remain homogeneous. As explained in Sect. 1.12, the energy of a homogeneous system can be written as

$$U = TS - pV + \mu n. \quad (2.7)$$

We are now coming into some detail to explain an intensive variable in the sense of thermodynamics. If we are forming the density of a system, the intensive variable will not be involved in the differential, since it is a constant. For this reason, in a homogeneous system described by Eq. (2.7) the energy density will emerge as

$$\check{U} = T\check{S} - p\check{V} + \mu\check{n} = T\check{S} - p + \mu c.$$

Note that $\check{V} = 1$. If the intensive variable varies in space, this is an indication that the system is not in equilibrium. When such a system equilibrates, it may but need not become a homogeneous system.

The concept of a homogeneous system will still hold in a system under gravity, or other fields, when we are changing the volume of the system only in a direction normal to the direction of gravity. Otherwise, in a more general case we must deal with an ensemble of infinitesimal small subsystems that make up the macroscopic system.

Intensive variables are independent on proper thermodynamic scaling, i.e., when all relevant extensive variables are multiplied by the same common factor, i.e., $S \rightarrow \lambda S$, $V \rightarrow \lambda V$, $\mu \rightarrow \lambda \mu$.

Extensive quantities cannot be essentially negative. This view is in opposition to the phlogiston theory that stated that weight increase by the oxidation reaction is caused by an escape of phlogiston that has a negative weight. Naturally, in modern science here we could think about the electric charge. We emphasize that the sign of the electric charge has been associated to the particle that it is bearing, initially completely arbitrary. We can deal with one charged particle, with two charged particles, and so on, but as such, we cannot deal with a vanished and thus minus one charged particle. A deficit in charge arises only by the interaction with other particles.

In fact, charges of opposite sign are neutralized, as they come close together only. If we are far away from the charges, we cannot identify them, but they are there. If the charge changes to opposite sign then this means that there is an excess of particles bearing the opposite charge.

It is a matter of the philosophical view, whether we treat a neutralization reaction like a chemical reaction and think that a new species has been formed or whether the particles are simply close together. Going one step further we may treat the reaction of an electron with a proton forming a neutron as a new species being formed or also that both species are close together only. However, from the properties exerted, it is more straightforward to deal with a new species.

Summarizing, we recall a common and simple definition of intensive and extensive variables. If two identical systems are gathered, the extensive term will double, whereas the intensive term will remain the same. Examples are the pairs (T, S) , $(-p, V)$, (μ, n) , (φ, q) ; i.e., (temperature, entropy), (pressure, volume), (chemical potential, mol number), (electrical potential, electrical charge). Often the extensive quantity may flow into or out of the system.

2.2.2 Change of Energy

We discuss again the topic of intensive and extensive variables in a formal way, namely in terms of exchange of energy. A change in energy form can be written in differential form, such as

$$dU = \xi dX. \quad (2.8)$$

In Eq. (2.8) we have two terms, one being before the differential, the other in the differential. The former ξ is addressed as the intensive variable, the latter X is the extensive variable. Thus the intensive variable ξ is, in fact, a function of the extensive variable, i.e., $\xi = \xi(X)$, and in general of other extensive variables that govern the system as shown in Eq. (2.9). The intensive variable is referred to as a thermodynamic potential, but only in certain cases:

$$dU(X_1, X_2, \dots) = \xi_1(X_1, X_2, \dots)dX_1 + \xi_2(X_1, X_2, \dots)dX_2 + \dots \quad (2.9)$$

From methodology, it seems to be advantageous to include all derivatives shown in a general way in Eq. (2.9) to the group of thermodynamic potentials.

2.2.3 Range of Energy

The energy of a system under consideration can be smaller in comparison to another system. Despite this fact, as such, as a standalone quantity, the absolute energy can never be negative. On the other hand, a finite system, i.e., a system composed of a finite number of particles n , cannot bear an infinite energy. In mathematical symbols we have,

$$0 \leq n < \infty \Rightarrow 0 \leq U < \infty,$$

i.e., the range of the energy is between zero and infinity in a finite system.

For this reason, if the intensive quantity bears a negative sign, such as the pressure, then

$$0 \leq U(\infty) - U(V_0) = - \int_{V=V_0}^{V \rightarrow \infty} p dV < \infty,$$

even when the volume approaches ∞ in the limit.

Conversely, at the other end of the scale the energy approaches zero if the number of particles in the system approaches zero. Obviously, the *nothing* bears no energy, thus

$$n \rightarrow 0 \Rightarrow U \rightarrow 0.$$

2.3 Energy Forms

We summarize in Table 2.1 the physical dimensions of various energy forms. We emphasize that the list is not complete. In square brackets the physical dimension of the extensive variable has been given. The intensive variable has the energy-conjugated physical dimension. In the following sections, we discuss briefly some issues of the energy forms detailed in Table 2.1.

Table 2.1 Physical dimensions of various energy forms

Energy name	Energy form	Physical dimension of intensive variable
Energy of compression (pressure \times volume)	$-p dV$	$\text{J}[\text{m}^3]^{-1}$
Thermal energy (temperature \times entropy)	$T dS$	$\text{J}[\text{JK}^{-1}]^{-1}$
Surface energy (surface tension \times area)	σdA	$\text{J}[\text{m}^2]^{-1}$
Gravitational energy (gravitational acceleration \times mass height)	$g d m h$	$\text{J}[\text{kg m}]^{-1}$
Kinetic energy (velocity \times momentum)	$v d P$	$\text{J}[\text{kg m}^2 \text{s}^{-2}]^{-1}$
Material energy ^a (chemical potential \times mol number)	$\mu d n$	$\text{J}[\text{mol}]^{-1}$
Electrical energy (electric potential \times charge)	$U_e d Q$	$\text{J}[\text{A s}]^{-1}$
Electric dipole energy (electrical field \times polarization)	$\mathbf{E}_e d \mathbf{P}$	$\text{J}[\text{m A s}]^{-1}$
Magnetic energy (magnetization \times auxiliary magnetic field)	$\mathbf{M} \cdot \mathbf{H}$	$\text{J}[\text{kg A}^{-1} \text{s}^{-2}]^{-1}$

Note: Acceleration, height, velocity, and momentum are vectors. Usually the acceleration is pointing down and height is pointing up. Therefore, the correct description would be $-\mathbf{g} d(\vec{m}h)$. The gravitational energy is related to the kinetic energy by $\frac{d(mh)}{dt} = dp$ and $\frac{dv}{dt} = g$.

^a The term chemical energy is misleading.

2.3.1 Energy of Compression

2.3.1.1 Energy

This energy form uses the volume V as extensive variable and the pressure p as intensive variable. It is associated with a negative sign. Elementary thermodynamics most often makes use of the energy of compression to demonstrate instructive examples. The energy of compression is often termed volume energy that includes both the energy of compression and the energy of expansion. These two types of energies are essentially the same. Compression means that $dV < 0$ whereas expansion means $dV > 0$.

We should not confuse the energy of volume with the energy of deformation. The energy of deformation plays a role for solids. It can change even when the volume does not change. The energy of volume changes only with the volume.

The following is valid for liquids and gases. We can interpret the pressure as a vector, pointing outward and normal to the surface border of the system. When the surface border of size A is moving by ds then the increase of volume is $dV = A ds$. Recall Eq. (2.3). If we modify this equation appropriately, we find immediately the explanation to why the volume energy has the negative sign:

$$U = - \int \mathbf{F} d\mathbf{s} + C = - \int \frac{\mathbf{F}}{A} d(As) + C = - \int p dV + C.$$

The pressure is not a force normalized by the mass, but normalized by some area. A closer look shows that in liquids or gases the pressure should not be a vector, because it is independent of the direction. The pressure acts not only at the border of a liquid

or gaseous system but also inside the system in any direction. However, we could argue that we can measure the pressure only by inserting a pressure-sensitive device. In this way, we have to create a surface. However, we observe that in a pressure gradient the motion of the material will occur. Therefore, the pressure gradient and also the pressure itself are basically inside the body.

From the view of energy, we can imagine the pressure as an energy density, namely the pressure has the physical unit of J m^{-3} .

We will show now that the pressure is in general a tensor. We consider a small surface area A and we establish the force in this region as $\mathbf{F} = \mathbf{T}\mathbf{A}$. \mathbf{A} is a vector normal to the surface, but the force could point in another direction, because \mathbf{T} is a tensor. The physical dimension of \mathbf{T} is just a pressure.

We can insert the expression into the basic equation of energy, but we have to follow a somehow modified procedure than in Eq. (2.3), because now the area is a vector that is mapped in the tensor. We can come back to the special case of Eq. (2.3) when the tensor \mathbf{T} has the same form as used in Eq. (1.76) and if the motion $d\mathbf{s}$ is normal to the area, i.e., the normal vector of the area \mathbf{A} and the motion $d\mathbf{s}$ are mutually parallel.

2.3.1.2 Volume as Thermodynamic Variable

Usually thermodynamic variables are as such that the energy has its low value, when the variable is approaching zero. For instance, the kinetic energy has the velocity v as intensive variable and the momentum $P = mv$ as extensive variable. As the momentum approaches zero, the velocity approaches zero, and thus the kinetic energy approaches zero. The same is true for the entropy, where the temperature is the intensive variable T and the entropy S is the extensive variable.

For the energy of compression the situation is different. If the volume for an ideal gas approaches infinity, then the energy approaches a minimum. We can see this also by the fact that in the differential the minus sign appears, i.e.,

$$dU = TdS - pdV + \mu dn.$$

However, we can reverse the situation. Similar to crystallography, we can move into the reciprocal space. We assign Υ as the reciprocal volume with the property $\Upsilon = 1/V$. We find immediately

$$\frac{d\Upsilon}{dV} = -V^{-2} = -\Upsilon^2. \quad (2.10)$$

Therefore, inserting for dV , the minus sign in the energy differential will cancel:

$$dU = TdS + p\Upsilon^{-2}d\Upsilon + \mu dn. \quad (2.11)$$

The form of Eq. (2.11) indicates that now the independent variables are Υ , S , and n , i.e., $U = U(S, \Upsilon, n)$, $T = T(S, \Upsilon, n)$, $p = p(S, \Upsilon, n)$.

We illustrate a simple case. For the isentropic expansion of an ideal gas we have $pV^\kappa = C(S, n)$, or in the new variables $p\Upsilon^{-\kappa} = C(S, n)$. We calculate the energy for the isentropic expansion to infinite volume as

$$U = C(S) \int_{x=\Upsilon}^{x=0} x^{\kappa-2} dx = \frac{C(S, n)}{\kappa - 1} (\Upsilon^{\kappa-1} - 0^{\kappa-1}) + C. \quad (2.12)$$

The expression for the energy will only be finite, if we have $\kappa - 1 > 0$. Observe that the Eulerian homogeneity relation still holds for an ideal gas, if V/n is replaced by n/Υ .

2.3.2 Thermal Energy

2.3.2.1 Energy

The inclusion of thermal energy into the theory of mechanics caused the success of thermodynamics. Originally and continuously until now thermal energy is noted as Q and the differential dQ . Then the increase of energy is subdivided into mechanical work dW and into thermal energy dQ :

$$dU = dQ + dW. \quad (2.13)$$

Equation (2.13) opposes the thermal energy to all other work in the system somewhat arbitrary and as such completely unjustified. The symbol d is used to show that dQ is not a total differential, but rather $dQ = TdS$ will be the appropriate notation.

We do not make use of these considerations, but we start directly with a statement valid in general for every energy form: The thermal energy has an extensive and an intensive part. The extensive variable of the thermal energy is the entropy S and the intensive variable is the thermodynamic temperature or absolute temperature T .

In common sense, the input of thermal energy into a system increases the temperature. In terms of entropy, the input of thermal energy means that entropy enters the system. A flow of entropy is basically a flow of heat consisting of a flow of entropy. When the temperature rises, then in the older literature this heat is also addressed as perceptible heat (in German: fühlbare Wärme). This results from the fact that we can detect it by our senses.

An increase of entropy in a system is not always accompanied with an increase of temperature. Similarly, an increase of temperature does not mean that the entropy increases.

Example 2.1. In the first step of the Carnot process, thermal energy will flow into a gas. This inflow is accompanied with an expansion of the gas, in order to run the process isothermal. In the last step of the Carnot process, the gas is compressed adiabatically. Strictly, we mean that the compression occurs at constant entropy, $dS = 0$. Here an increase of the temperature occurs, even when the entropy remains

constant. On the other hand, since

$$\frac{\partial T(S, V, n, \dots)}{\partial S} > 0, \quad (2.14)$$

we can safely expect that in a process, where S will increase, but all other variables V, n, \dots will remain constant, also the temperature T will increase. Equation (2.14) arises from the stability condition. \square

2.3.2.2 Entropy

The entropy is a mass-like quantity and cannot take negative values. It is often stressed that entropy does not follow a conservation law. Dealing with compression energy, it can be shown that it is possible to construct systems where the total volume is not conserved. Therefore, it should not be surprising that also entropy would not be conserved.

In fact, according to *Clausius*, the entropy tends to become a maximum $S \rightarrow \max$. When the entropy has reached the maximum we have $dS = 0$ or $S = C$. Therefore, all processes running in thermodynamic equilibrium, at $dS = 0$, are running with constant total entropy, even when the entropy in the subsystems may change.

Sometimes it is stated that entropy is not defined for a nonequilibrium process. We want to relativize this statement. Consider a pure mechanical process, e.g., a moving pendulum. Setting up the energy equation, we can clearly subdivide into kinetic and potential energy for the ideal pendulum. The ideal pendulum will never stop with motion. If we add a friction term, we can identify the total energy lost by the system to a gain of thermal energy and thus to the entropy gain. Thus, for the nonideal pendulum the entropy content is clearly defined even in the nonequilibrium state. However, in other thermodynamic systems it may cause problems to identify the kinetic energy clearly. In such situations, in addition to the content of kinetic energy the content of entropy of the system is not clearly defined.

2.3.2.3 Temperature

The thermodynamic temperature has its *zero*, when an input of entropy into a system will not cause an increase of energy, i.e., when $dU = T dS$, and

$$dS > 0; \quad T = 0 \quad \Rightarrow \quad dU = 0. \quad (2.15)$$

This definition is sound, but is not strictly applicable in practice. Note that in this case, even $dS < 0 \Rightarrow dU = 0$ holds. This behavior is in connection with the monotony of entropy with temperature. We will explain this issue elsewhere.

Nevertheless, even when the *zero* of T is fixed by Eq. (2.15), the scale is not fixed, because there is no freedom to insert a nonzero constant factor:

$$dU = (\beta T)d(S\beta^{-1}).$$

The absolute temperature is defined in that way that at the triple point of water $T = 273.16 \text{ K}$. If the physical unit of the temperature is K, then this means the unit of the entropy is J K^{-1} . Any other temperature can be accessed using the ideal gas thermometer.

Due to the relation $T = C pV$, where C is a unknown calibration constant, this calibration constant can be measured by bringing the ideal gas in contact with a body at triple temperature of water. Then, by measurement of pressure and volume of the ideal gas which is in contact with a body of unknown temperature, this temperature can be measured. Again, this prescription of measurement of the absolute temperature is highly impracticable and suffers from the fact that an ideal gas exists, as the name indicates only ideally.

Another possibility to access the ratio of two absolute temperatures is to measure the efficiency η of a *Carnot* process running between two temperatures T_h and T_l , a higher temperature and a lower temperature. If the process is running with one temperature at the triple point then via the efficiency the other temperature is known. The efficiency is independent of the working medium and is the ratio of work energy W withdrawn to the heat throughput Q into the working medium at the higher temperature T_h :

$$\eta = \frac{W}{Q} = \frac{T_h - T_l}{T_h}.$$

In this way, the temperatures are completely defined by a measurement of work and heat. Here the knowledge of the mechanical heat equivalent is necessary. Further, the practical implementation of the method faces problems with nonideal conditions, e.g., friction losses.

2.3.3 Surface Energy

The extensive variable of the surface energy is the area and the intensive variable is the surface tension. The surface energy is a typical example for an energy form, where the extensive variable can be increased and decreased nearly arbitrarily.

We first deal with a liquid in contact with vacuum. The surface tension σ is a vector that points into the inner region of the liquid. In static equilibrium, the vector points normal to the surface, whereas the surface vector $d\mathbf{A}$ which is also a normal vector points outward from the liquid. Since the two vectors are opposite in direction, the negative sign in the energy equation cancels.

If the liquid is not in contact with vacuum, but with a vapor or a liquid, then the above considerations hold. However, we must see the situation from both phases. The surface tension will be modified by the neighborhood of another phase, even in a different way for the individual phases. The particular change of the surface tension also governs the miscibility. Since both phases are coupled in the case by a

common interface, the areas of both will increase or decrease simultaneously. In the case of miscibility there is no longer a separating surface area.

2.3.4 Gravitational Energy

With the law of gravity, Newton was able to explain why Kepler's laws described the planetary motion. The law of gravity is an example of a central force. The force is directed along the center of mass of two bodies. The mathematical formulation is given as follows:

$$\mathbf{F} = G \frac{m_1 m_2}{r^2} \frac{\mathbf{r}}{r}. \quad (2.16)$$

Here \mathbf{F} is the force between two masses m_1 and m_2 separated by a distance \mathbf{r} . The last term \mathbf{r}/r builds the unit vector along the distance of the two masses. G is the gravitational constant. The gravitational constant is a constant number. A unit mass that is located on the surface of the earth is subject to an acceleration, i.e., force on the unit mass of $g = 9.8 \text{ m s}^{-2}$. We obtain this by inserting the numerical values of $G = 6.6726 \times 10^{-11} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-2}$, mass of earth $m_2 = 5.98 \times 10^{24} \text{ kg}$, and radius of earth $r = 6.37 \times 10^6 \text{ m}$.

Therefore, we obtain for the force of a mass m near the surface of the earth

$$\mathbf{F} = m\mathbf{g}. \quad (2.17)$$

This equation is commonly used to calculate the change in gravitational energy $\Delta U = -m\mathbf{g}\Delta\mathbf{h}$, if a mass is lifted by a distance of $\Delta\mathbf{h}$ against the earth acceleration \mathbf{g} . We emphasize that usually \mathbf{g} is pointing downward, say in z -direction, and \mathbf{h} is pointing upward. If Eq. (2.17) is written in scalar form, then the negative sign of the earth acceleration is pulled out and the minus sign cancels. Equation (2.17) is highly satisfactory under laboratory conditions. However, \mathbf{g} is slightly dependent on the altitude, as can be clearly seen by inspecting Eq. (2.16).

In thermodynamics, gravitational work has also been set up with gh as the gravitational potential and dm as the differential form of the extensive variable [7]. Here the preferred form is g as the gravitational potential and $d(mh)$ as the differential form of the extensive variable.

2.3.5 Kinetic Energy

The extensive variable for the kinetic energy is the momentum P and the intensive variable is the velocity \mathbf{v} . Since $\mathbf{P} = m\mathbf{v}$, the intensive and the extensive variables are highly coupled. In fact, both variables are vectors. Since the kinetic energy integrates to $U = m\mathbf{v}^2/2 + C$, from the consideration of the range of energy the integration

constant C should be zero to allow a zero energy and when not below zero, the mass m should be positive.

Example 2.2. Consider the free falling rigid body. The total energy U is

$$U = \frac{mv^2}{2} + mgh.$$

In differential form we obtain using $P = mv$ and $q = mh$

$$dU = v dP + g dq.$$

Now apply the law of Schwarz to get

$$\frac{\partial v}{\partial q} = \frac{\partial g}{\partial P}.$$

Note that we have dismissed the chemical potential and we deal with P and q as independent variables. The reader should discuss issues arising here. \square

2.3.6 Material Energy

We discuss now various forms of energy related to matter. We will see that this form of energy arises very naturally.

2.3.6.1 Chemical Potential

Charles *Kittel* states in his book *Introduction to Solid State Physics* [8] about the chemical potential:

A vague discomfort at the thought of the chemical potential is still characteristic of a physics education. This intellectual gap is due to the obscurity of the writings of *Gibbs*¹ who discovered and understood the matter 100 years ago.

Studying the scientific papers (*writings*) of J.W. Gibbs, the reader may find that Gibbs is a highly honest *writer*, in contrast to other contemporary *writers*.

The extensive variable for material energy is the number of moles n and the intensive variable is the chemical potential μ . We avoid the term chemical energy. The material energy is associated with chemical reactions, but it is more general. The material energy simply refers to an increase of the energy when a certain amount of material is put into the system, when all the other thermodynamic variables remain constant. There is no need that a chemical reaction occurs.

¹ Josiah Willard Gibbs, born Feb. 11, 1839, in New Haven, CN., USA, died Apr. 28, 1903, in New Haven, USA.

2.3.6.2 Electrochemical Potential

The electrochemical potential was introduced by *Guggenheim*.² The electrochemical potential μ_e is the sum of the chemical potential μ and the electric potential:

$$\mu_e = \mu + \tilde{Q}\varphi = \mu + zF\varphi, \quad (2.18)$$

where \tilde{Q} is the molar electrical charge, z is the elementary charge number, F is the *Faraday* constant, and φ is the electric potential. The Faraday constant refers to the electric charge of 1 mol of elementary charges.

The electrochemical potential is used to describe the equilibrium of charged particles. It arises naturally from the fact that when a charged particle enters or leaves the system, it takes its charge with it. Thus the molar charge \tilde{Q} in the system remains constant, and we have $U(S, V, Q, n)$ as the energy function, where $Q = n\tilde{Q}$.

According to the rules for forming partial differentials in functions with multiple arguments, $\partial U / \partial n$ yields Eq. (2.18). Actually, there is no need to *define* the electrochemical potential, as this potential is introduced in some textbooks. As pointed out above, the electrochemical potential emerges from the fact that the electric charge and thus the electric energy are coupled to matter in an unique manner. For related cases, refer to Example 5.2 on p. 186.

2.4 Energy Representation

We deal with a simple case of a homogeneous system of one component. The energy should be a function of entropy, volume, and mol number, $U = U(S, V, n)$. Recall that it is necessary to include the mol number as parameter for sake of homogeneity. In a homogeneous system, we can represent the energy as the sum of the terms

$$U(S, V, n) = TS - pV + \mu n. \quad (2.19)$$

We deal with the situation of constant energy, thus $U(S, V, n) = U$. Next, we substitute $TS \rightarrow y$, $-pV \rightarrow x$, and $\mu n \rightarrow z$. With these substitutions, Eq. (2.19) turns into

$$\frac{x}{U} + \frac{y}{U} + \frac{z}{U} = 1.$$

Recall that in cartesian coordinates [9]

$$\frac{x}{a} + \frac{y}{b} + \frac{z}{c} = 1,$$

² Edward Armand Guggenheim born 1901 at Manchester died 1970.

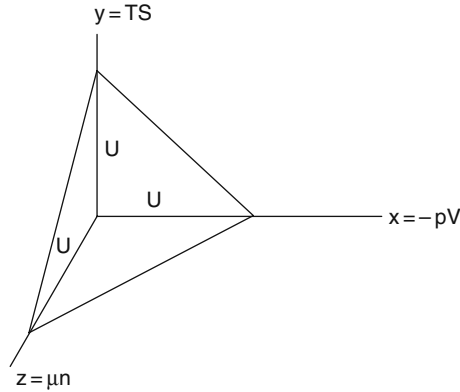


Fig. 2.1 Isodynamic path of a homogeneous one-component system

represents a plane that cuts the x -axis at a , the y -axis at b , and the z -axis at c . For this reason, the isodynamic path in an one component homogeneous system may be represented as the motion in a plane, with the coordinates TS , $-pV$, and μn . The situation is illustrated in Fig. 2.1. On the other hand, since the enthalpy H is $U + pV$, we get for isenthalpic processes

$$\frac{y}{H} + \frac{z}{H} = 1.$$

Next, we inspect the isentropic path for an ideal gas in terms of TS , $-pV$, and μn . Using the ideal gas equation, we find

$$\frac{pV}{TS} = \frac{nR}{S} = -\frac{x}{y}.$$

From the *Gibbs* form of the energy of an ideal gas, we get

$$\frac{z}{y} = -1 + n \frac{\tilde{C}_v + R}{S}.$$

Therefore, for an ideal gas, at constant entropy and mol number, the variables x , y , z are linearly dependent, as the motion is in a plane passing the origin.

There is still another way to substitute for the natural variables. By substitution of $S \rightarrow \exp(y)$, $V \rightarrow \exp(x)$, and $n \rightarrow \exp(z)$, we get

$$\frac{\partial U}{\partial y} = \frac{\partial U}{\partial S} \frac{\partial S}{\partial y} = TS.$$

Similar expressions hold for x and z . In a plot of x , y , z of constant energy, the distance of the isodynamic lines in the x , y , z directions represents the respective

energy forms. Thus, if TS becomes larger at some isodynamic path, the distance of certain adjacent isodynamic curves in the direction of the ordinate (y) shrinks.

2.5 System

A thermodynamic system is in general abstracted from a real object of interest. Issues not needed for a description in terms of thermodynamics are omitted. Moreover, the scientist is literally not interested in certain properties, often in the particular shape and other properties of the object of consideration. It is left to the skill of the scientist to map every issue of the real object properly into the thermodynamic system.

A system is a region in space confined by borders. We can obtain information of the properties of a system via its thermodynamic variables. To get the information we have to probe the variables by the exchange of certain energy forms. Thus, the system itself is a black box that outs itself by exchange processes. We can never be sure of what is really inside a system.

Example 2.3. Consider a system that is a container with a piston. But suppose that the container is closed and we can see only the plunger. By exchange of force onto the plunger, we can find out that the force F depends on the position of the plunger l according to

$$Fl^\alpha = C.$$

Now in the container there may be a gas adiabatically enclosed or a sophisticated gear mechanism connected to a spring that simulates this behavior. That is why the system is a black box. \square

In the thermodynamic sense a system is described by its extensive quantities. From these quantities, the energy can be calculated somehow. Basically, all energy forms must be taken into consideration. But most can be neglected. Those that never change can be safely neglected. In a laboratory, this may be the gravitational energy. Those that contribute very less to the energy may be neglected. In most chemical problems, surface energy does not play any role.

Note that the phase rule is based on the assumption that the description is governed by S , V , n_i for each phase. The thermodynamic description of a system is confined to quantities that belong, in fact, to the system. We can use this as definition of a system. If we are focusing on a reaction vessel in the hood, then the bottles in the refrigerator beside are not part of the description of the system and will never enter.

The energy of a system may be completely characterized by its extensive variables, such as S , V , n . If we would choose to replace some extensive variables by the corresponding intensive variables, then information is lost. On the other hand, certain functions of the energy, i.e., the *Legendre* transformations utilize intensive variables, but there is no loss of information, because the functions can be

transformed back into the original form. We have to clearly differentiate the variables of the system itself and the variables that exchange energy forms with the system.

Example 2.4. We allow a system to accept compression work $-pdV$, $dV < 0$. To make it more clear, we write $-p_{sys}dV_{sys}$. We mean that the pressure of the system is p_{sys} and that the volume shrinks by dV_{sys} . This does not necessarily mean that another system, say the environment, will lose just this energy. In particular, if the pressure of the environment is higher than the pressure of the system $p_{env} > p_{sys}$, $dV_{env} = -dV_{sys}$, then the environment will lose $-p_{env}dV_{env}$, $dV_{env} > 0$, which is more than the system gains. Of course, no energy is lost according to the first law of thermodynamics. The energy will be recovered most probably in the form of kinetic energy and eventually as thermal energy. \square

A system may exchange with the environment (in fact also a system) energy. It will never exchange any intensive quantity. This is basically a nonsense. However, the intensive quantity may change as a result of an exchange of any extensive quantity. The energy change of the system is exclusively governed by the parameters of the system itself.

Example 2.5. To a big gasometer a small piston is attached. When the piston is moving a small distance out to increase the volume by dV , the gasometer loses its energy, i.e., $-pdV$. It does not matter what is behind the piston.

There may be an engine that raises a weight, there may be a spring that takes up the energy, there may be gas that takes up the energy released. The energy that is taken up behind the piston can be zero in the worst case, if there is vacuum and $+pdV$ in the best case if the outer pressure is the same as in the gasometer itself. If the outer pressure is greater than the pressure in the gasometer, then the gas of the gasometer will not expand. The intended process is not possible at all. If the gas expands into vacuum, the interesting question arises of what will happen with the energy that is lost at the first glance. \square

We may not conclude, from the energy take up in any environment of the system, on how much energy the system has lost in fact. We can only conclude what is the minimum energy lost. Only in the case of an exchange of energy in an equilibrium state we can state that no particular energy form will be lost on exchange.

When a certain energy form is delivered into a system, we cannot state that the system bears this particular energy form. We can merely state that in the system some have changed by the input of an energy form.

Example 2.6. We can allow some entropy ΔS to flow in a gas at constant volume. In this case, the entropy of the system increases by ΔS . If the entropy before the process is S , then the new entropy is $S + \Delta S$. Now we can withdraw this entropy by thermal work, but we can also allow the energy that was introduced to be pulled out by mechanical work $-pdV$. \square

In this way, a system is a transformer of energy forms. This is not true in general. A necessary condition to transform energy forms is that the intensive variables are functions of the extensive variables. In order to transform thermal energy into energy of expansion we must have

$$p = p(S, V) \quad \text{and} \quad T = T(S, V).$$

If we would have

$$p = p(V) \quad \text{and} \quad T = T(S), \quad (2.20)$$

then the input of thermal energy could not cause an increase in pressure. However, such an action is necessary to transform the particular energy form. In the case of Eq. (2.20) we can withdraw thermal energy that has been put into the system only as thermal energy as such and the same is true for the volume energy.

2.5.1 Types of Systems

Several ways of classification of systems are possible. One classification refers to the way how energy forms can be exchanged and another more recent classification refers to the type of entropy.

2.5.1.1 Exchange of Energy Forms

Historically we differentiate between

1. Isolated systems.
 2. Closed systems.
 3. Open systems.
- The isolated system has no interaction with an environment. It cannot exchange any energy form with its environment.
 - The closed system cannot exchange matter, but it can exchange other energy forms with its environment.
 - The open system not only can exchange matter, but also can exchange other energy forms with its environment.

The reason for this classification arises from the various *Legendre* transformations of the energy. However, these transformations allow for a more subtle classification.

For example, when free exchange of entropy of the system at constant temperature ($dT = 0$) may occur, but no exchange of volume energy is allowed ($dV = 0$), we have for $dn = 0$, $d(U - TS) = -SdT - pdV + \mu dn = 0$. Thus, the Helmholtz energy is zero for this type of system. Other cases can be easily constructed in the same manner.

2.5.1.2 Entropy Behavior

We can define general properties of the entropy [10, 11]:

1. Super additivity: $S(x + y) \geq S(x) + S(y)$,
2. Homogeneity: $S(\lambda x) = \lambda S(x)$,
3. Concavity: $S(\lambda x) + (1 - \lambda)y \geq \lambda S(x) + (1 - \lambda)S(y)$.

Whether these three properties may, or may not, be independently fulfilled or not we can distinguish 2^3 different cases. These cases are shown in Table 2.2.

For example, the entropy of an ideal gas is

$$S = k \ln \left[\frac{aUV^g}{N^h} \right].$$

Here k , a , g , and h are positive constants. V is the volume, U is the internal energy, and N is the number of particles in the gas. Three classes of thermodynamics can be formed:

Type 1: $h = g + 1$

Type 4: $h < g + 1$

Type 6: $h > g + 1$.

Type 1 refers to ordinary thermodynamics, Type 4 is the classical analogue of the thermodynamics of the *Schwarzschild*³ black hole, it violates the property of concavity, however, it keeps the super additivity.

Table 2.2 Classes of thermodynamic systems

Number	Super additivity	Homogeneity	Concavity
1	+	+	+
2	+	—	+
3	+	+	—
4	+	—	—
5	—	+	+
6	—	—	+
7	—	+	—
8	—	—	—

+: fulfilled

—: not fulfilled

³ Karl Schwarzschild, born Oct. 9, 1873, in Frankfurt am Main, died May 11, 1916, in Potsdam.

2.6 Conservation Laws

There are several natural conservation laws. We have a natural feeling for some of these conservation laws. Distances in a distance table should follow certain conservation laws. Traveling from A to B directly should not show a longer distance than traveling from A to B via C . But in practice, some of these distance tables show this unexpected property – due to errors.

2.6.1 Heat of Reaction

In contrast to this is the law of *Heß*.⁴ The law of Heß states that the heat of reaction is independent of the reaction path. The law of Heß can be regarded as a precursor of the first law of thermodynamics.

2.6.2 Mass

The mass is constant. However, this is only true in a nonrelativistic situation. The equation of continuity expresses the conservation of mass. In relativity theory the mass m increases with its velocity v by

$$m = \frac{m_0}{\sqrt{1 - v^2/c^2}},$$

where m_0 is the mass at rest and c is the velocity of light.

2.6.3 Charge

The electric charge is constant. It is claimed that no exception has been observed. On the other hand, in the course of neutralization reactions, obviously charges disappear. A closer look into modern physics disguises the disappeared charges as being merely close together. So it is a matter of philosophy, the belief in modern physics, or the belief in illusion whether the charges after neutralization are there, not there, or merely disguised.

⁴ Heß, Germain Henri (Герман Иванович Гесс) born Aug. 7, 1802, in Geneva died Dec. 12, 1850, in St. Petersburg.

2.6.4 Momentum

The conservation of momentum and angular momentum is a fundamental law in mechanics. *Kepler's* second law can be easily justified by the conservation of angular momentum.

The momentum of a system remains constant if there are no external forces acting on the system. This is actually Newton's first law, the law of inertia. The conservation of momentum is valid in classical mechanics. However, *Heisenberg's*⁵ principle of uncertainty states that

$$\Delta x \Delta P \geq \frac{\hbar}{2}.$$

So, considering very small distances, a possible fluctuation of the momentum could occur that violates the conservation of momentum.

Note the laws of angular momentum and the laws of momentum are related by the operator $\nabla \times$ applied to the respective equations of momentum.

2.6.5 Volume

In science, the total volume of space is constant. The space is treated to have a constant extension. However, cosmology tells us that the space is expanding. Of course, we may ask what is behind the Schwarzschild radius and include a suspected space into consideration. The Schwarzschild radius r refers to the size of a black hole with a mass m . In a simplified treatment, it can be derived by setting the escape velocity v of a black hole equal to the velocity of light c . The velocity of light is $c = 2.99792458 \times 10^8 \text{ m s}^{-1}$. The escape velocity v is

$$v = c = \sqrt{\frac{2Gm}{r}},$$

where G is the gravitational constant which is $G = 6.672 \times 10^{-11} \text{ N m}^2\text{kg}^{-2}$.

On the other hand, even in a much simpler case the volume of a system may not be constant. Consider a system composed of two cylinders of different diameters with two pistons connected by a plunger. As the plunger moves the total volume of this system changes. Of course, the surrounding environment would compensate these changes.

⁵ Werner Karl Heisenberg, born Dec. 5, 1901, in Würzburg died Feb. 1, 1976, in Munich.

2.6.6 Surface Area

In contrast to volume, the surface area is definitely not constant. Surface area can be generated in an arbitrary way. Consider the formation of a foam.

2.6.7 Baryon Number

In a closed system, the baryon number remains constant. If a proton can decay, this conservation law is no longer valid. In particle physics there are also other conservation laws, e.g., the conservation of parity, the conservation of color, and others.

2.6.8 Energy

The first law of thermodynamics can be formulated as the conservation of energy.

2.6.9 Time Reversal

All time-dependent mechanical processes, such as a motion of a particle through the space, are still valid on time reversal. This means if we change the sign of time in a physical law, still a possible process will emerge. *Maxwell* observed that the second law of thermodynamics is not consistent on time reversal [12]. Time reversal plays a role in Loschmidt's paradox.

2.7 Process

A thermodynamic process is anything that changes the thermodynamic variables in the system or environment. A thermodynamic process can be effected in various ways. Note the difference between a thermodynamic process and the way to effect the process in practice, i.e., the realization of the thermodynamic process.

Example 2.7. We consider the isothermal expansion of a gas. Purposely we do not deal with an ideal gas, but with a real gas. At fixed mol number, the energy of the ideal gas is governed by two relevant variables, i.e., (S, V) . Before the expansion, at start, we mark the variables by the subscript s . At start, the energy is $U_s = U(S_s, V_s)$. After the isothermal expansion, the relevant variables have been changed by ΔS and ΔV . Therefore, at the end of expansion, which we indicate by the subscript e we have $S_e = S_s + \Delta S$ and $V_e = V_s + \Delta V$. In order to have an isothermal expansion we need the condition

$$\left. \frac{\partial U(S, V)}{\partial S} \right|_{S_s, V_s} = T = \left. \frac{\partial U(S, V)}{\partial S} \right|_{S_e, V_e}.$$

For the process as such, it is not important at which path we have reached $S_s \rightarrow S_e$ and $V_s \rightarrow V_e$.

On the other hand, for the realization of the particular process, it is important how we could reach this state. For example, the expansion could be achieved by allowing to expand against a certain pressure or to allow it to expand into vacuum. If the gas is doing work, then energy is lost, and thermal energy in the form of entropy has to be fed in a certain amount. Expanding into vacuum may change the internal energy and also some thermal energy is needed to maintain the temperature. \square

2.8 Transformers

We consider now a nonstandard exchange of an extensive variable. Two pistons may be connected with a gear or they may have simply different area so that $dV_1 \neq -dV_2$. But there may be a factor, not necessarily a constant, so that $dV_1 + \lambda dV_2 = 0$. So

$$dU(V_1, V_2) = -p_1 dV_1 - p_2 dV_2 = (-p_1 + p_2/\lambda) dV_1 \quad (2.21)$$

and to have the energy stationary, $dU(V_1, V_2) = 0$. The engine that effects $dV_1 + \lambda dV_2 = 0$ we will call a transformer for the respective variable. The factor λ is dimensionless. The experimental setup is very simple, it consists of two pistons with different areas connected by a common plunger as shown in Fig. 2.2. The factor λ is the ratio of the areas. If the piston associated to the volume V_1 has an area of A_1 and the piston associated to the volume V_2 has an area of A_2 , then $\lambda = A_1/A_2$.

The energy will become stationary when $-p_1 + p_2/\lambda = 0$. This means that when the energy becomes stationary, the pressures in the two subsystems need not be equal. To calculate the stationary value, we must have some information about the functional dependence of the pressure with the volume, i.e.,

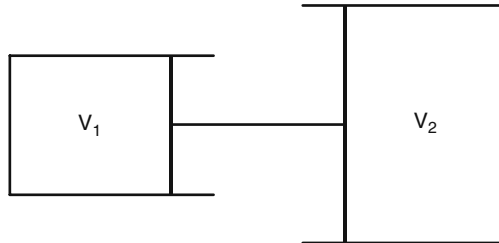


Fig. 2.2 Two pistons of different area connected with a common plunger

$$p_1 = p_1(V_1); \quad p_2 = p_2(V_2).$$

Another example for a transformer is a chemical equilibrium with dissociation, e.g.,

$$J_2 \rightleftharpoons 2J. \quad (2.22)$$

Here $dn_J = -2dn_{J_2}$. On the other hand, a simple sublimation $J_{2,s} \rightarrow J_{2,g}$ is a standard exchange with respect to the mol numbers.

Example 2.8. We can replace formally the variables p and V in Eq. (2.21) by T and S . In this way, we obtain the corresponding thermal problem to the volume energy as

$$dU(S_1, S_2) = -T_1 dS_1 - T_2 dS_2 = (-T_1 + T_2/\lambda) dS_1. \quad (2.23)$$

Equation (2.23) is completely analogous to Eq. (2.21), but there is some important difference. It is possible to conduct a thermodynamic process in which $dU = 0$ and $T_1 \neq T_2$. Setting $dS_1 + \lambda dS_2 = 0$, we get from the first equality in Eq. (2.23) $T_1 dS_1 + T_2 dS_2 = 0$, $\lambda = T_2/T_1$. Inserting this into the second equality of Eq. (2.23), we get the identity $T_1 = T_1$. Therefore, it is necessary to obtain the factor λ from an independent relation, if we want to calculate some specific values of S_1 and S_2 where the energy would be stationary. However, we can state that for stationary energy $dU = 0$, $T_1 \rightarrow T_2$ implies $dS_1 \rightarrow -dS_2$, which means the conservation of entropy. \square

Two systems (' and ''), not necessarily reservoirs, but big systems, can be thermally coupled by a Carnot cycle. This is in practice a heat pump, or if it runs in the reverse direction, a heat engine. In this case, we have $S' + S'' = 0$, thus if the systems are big, for one revolution of the Carnot cycle $dS' + dS'' = 0$. This constraint does not imply that $T' = T''$. Namely, the Carnot engine is an active device that releases or donates energy. In the Carnot engine, the change of entropy S' is not directly connected with the change of entropy S'' , even when the cross balance $dS' + dS'' = 0$ over a full turn holds.

In general, a transformer for an extensive variable X_1 is characterized by $X'_1 + \lambda X''_1 = C$ with $\lambda \neq 1$. This is in fact a constraint equation. The case of $\lambda = 1$ is the standard exchange.

There are still other types of transformers. A particular constraint equation could look like $dX'_1 + dX''_2 = 0$. In this case, the conversion of different energy forms occurs. For example, in the derivation of Kelvin's equation of surface tension such a constraint appears. The volume of a sphere $V = 4r^3\pi/3$ is connected to the area $A = 4r^2\pi$ via the differential equation

$$\frac{dV(r)}{dr} - A = 0.$$

2.9 Reservoir

A reservoir is a system that does not change its intensive variable when the corresponding energy-conjugated variable is changed. For example, for any man-made system that may change its volume, the atmosphere is a reservoir with respect to pressure. Here we idealize that the change of volume of this man-made system will be fast in comparison to the natural changes of pressure due to weather. The ocean is a reservoir with respect to the chemical potential. If we add a little bit of salt, then the chemical potentials of the components in the ocean will remain essentially constant.

It appears that a system is close to a reservoir if it is sufficiently big. Of course, there is a more subtle possibility to establish a reservoir if there is an engine that keeps the intensive variable under consideration somehow constant. We may think of a thermostat as a reservoir for temperature. In this case, the system is not standing alone, however, because the engine adds or removes entropy to keep the temperature of the system constant.

We may address the big systems as reservoirs of first order and the engine-controlled reservoirs as reservoirs of second order. However, dealing with the concept of a reservoir it is immaterial how the properties of a reservoir are achieved.

Example 2.9. A thermal reservoir is a system with the property

$$\frac{\partial T(S, \dots)}{\partial S} \rightarrow 0.$$

Thus, on input or output of entropy the temperature will remain utmost constant. \square

More general, a reservoir with respect to a thermodynamic variable X has the property of

$$\frac{\partial U^2(X, \dots)}{\partial^2 X} = 0.$$

The general method on how to couple a system of interest with a reservoir is shown in the literature [13].

2.10 Constraint Makers

A constraint maker is a system that is doing something in a rather mysterious way. Usually such a system is essential for the proper work of other thermodynamic systems, but only marginal attention is focussed to explain the properties of such a system. Thereby the obscure system is idealized in some way. Examples for constraint makers are the

- Rigid wall
- Diathermic wall in heat conduction
- Porous plug in the Joule – Thomson experiment
- Semipermeable membrane in osmometry
- Electrodes
- Interphase borders
- Filter membranes in general

2.10.1 Rigid Wall

The rigid wall is stiff. When pressure is applied, it does not change its shape and size. If a thermodynamic system is enclosed in a rigid wall, its volume remains constant, i.e., it ensures that $dV = 0$ under any change of the thermodynamic variables of the system.

2.10.2 Diathermic Border

The diathermic border has no volume. So it cannot take up volume energy. The diathermic border faces a temperature T_h from one surface and a temperature T_l from the other surface. Here $T_h > T_l$. When entropy $dS(T_h)$ passes into the border across a surface, the diathermic border ejects $-dS(T_l)$ at the opposite surface following the relation

$$T_h dS(T_h) + T_l dS(T_l) = 0.$$

In this way, the diathermic border is a generator for entropy, even when it cannot store entropy. Moreover, the diathermic border acts as a valve for entropy. If $T_h < T_l$ then it does not allow an inflow of entropy, $dS(T_h)$.

2.10.3 Porous Plug

Also, the porous plug in the *Joule – Thomson* experiment is an idealized device. It has certain properties, such as lack of volume, common to the diathermic border, but it does not allow a flow of entropy without flow of matter. When matter flows through the porous plug, the pressure and the temperature are reduced. This is associated with an increase of entropy.

2.10.4 Semipermeable Membrane

The semipermeable membrane in osmometry is a valve for the flow of certain kind of matter. It must be sufficiently stiff to withstand external forces resulting from a pressure difference on both sides.

2.10.5 Electrode

An ion may be imagined as a neutral matter that carries a charge. Of course, the charge has also some matter. So we will be more precise in the next sentence. An electrode serves as a separator for ions and the charge. It is permeable to the charge, but is not permeable to the neutral part of the ion. When an ion moves to the electrode, the charge is stripped off from the ion and the ion is discharged. Think about the similarity to the semipermeable membrane.

2.10.6 Interphase Border

When matter passes through an interphase border, e.g., through a liquid – gas interphase border, the matter evaporates and takes up thermal energy.

2.10.7 Filter Membrane

In the same way as for electrodes, we invent a filter membrane for entropy. When matter moves to this filter, the filter strips the entropy that the matter is carrying with it and leaves the entropy on the entrance side and the matter may move on the other side of the membrane. This device is an ideal cooler. To be in accordance with the second law of thermodynamics, a filter membrane for entropy must be an active device.

2.10.8 Examples of Constraints

In thermodynamics, often the extremum of a function of energy or the energy itself has to be found out to get an equilibrium state. This extremum is searched with certain additional conditions. These conditions are addressed as constraint equations. For example, the energy of a system $U(V', V'')$, consisting of two subsystems (' and ''), will become a minimum under the condition of constant volume $V_{\text{tot}} = V' + V''$.

It is important to verify that the constraint is in fact physically taking place at the process under consideration. If the total volume should be constant, both volumes

can be coupled by a plunger. The plunger ensures that if one volume expands by dV' the other volume will shrink by $dV'' = -dV'$.

Constraints are reflecting to some extent the process under consideration. The set $dV' = 0$ and $dV'' = 0$ implies $dV' + dV'' = 0$, but the first two constraints are stronger. Further, the constraint $dS' - \tilde{S}'dn' = 0$, which refers to a process at constant molar entropy, acts both on the entropy and on the mol number, when used in context with Lagrange multipliers.

In other words, the form of the constraint equations governs the intensive variables in equilibrium. If the volume of an individual system ($'$) is kept constant, then the pressure in a neighborhood coupled system ($''$) is not necessarily the same. However, if the wall is porous, then a gas will move through the porous wall to establish equal pressure. This process does not occur by an exchange of volume energy, but by an exchange of matter. However, if the wall is only semipermeable, again a pressure difference may be there in equilibrium in a multi-component system.

To illustrate the improper use of constraints, we deal with the Carnot cycle with an ideal gas as working system. In the isothermal expansion, the gas takes up thermal energy from the reservoir and does work of expansion to a further external system. Thus, the energy change of the working gas is

$$dU(T, V, n) = C_v dT + \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial n} dn = 0. \quad (2.24)$$

On the right-hand side of Eq. (2.24), the first and the third terms cancel because $dT = 0$ and $dn = 0$, and the second term cancels, because for an ideal gas, $\frac{\partial U(T, V, n)}{\partial V} = 0$. The statement $dU = 0$ remains still valid, if we change the variables from $(T, V, n) \rightarrow (S, V, n)$. With $dn = 0$ we have

$$dU(S, V, n) = T dS - p dV = 0. \quad (2.25)$$

In the Carnot cycle, the process indicated in Eq. (2.25) occurs twice. First, the gas is expanded isothermally in contact with the reservoir at high temperature (h) and after the adiabatic step, the gas is compressed isothermally in contact with the reservoir at lower temperature (l). We place now formally the indices to indicate the two steps and get

$$\begin{aligned} dU_h(S_h, V_h, n) &= T_h dS_h - p_h dV_h = 0 \\ dU_l(S_l, V_l, n) &= T_l dS_l - p_l dV_l = 0 \end{aligned} \quad (2.26)$$

We have now the constraint for a reversible process $dS_h + dS_l = 0$. However, we may not add up both equations (2.26) and conclude that $T_l = T_h$, etc. We would use the constraint in a wrong way.

In fact, even when the constraint $dS_h + dS_l = 0$ exists, this constraint does not appear actually in the process, because the entropy of the reservoir with lower temperature does not immediately increase when the entropy of the reservoir with higher temperature decreases. The process is conducted in a different way. Rather

the constraints appearing in Eq. (2.26) are valid as such. The increase of entropy under isothermal conditions in the working gas causes directly an expansion of the volume of the working gas, thus doing work to an external system and vice versa.

2.11 Fundamental Equations

The term *fundamental equation* as introduced by Gibbs is now also known as a Gibbs fundamental form [14, pp. 55–353]. It should not be confused with the Gibbs function, which is also addressed to as the Gibbs free energy or free enthalpy, but the Gibbs function. Gibbs himself had introduced what we here call Gibbs function in a different way.

First, we follow the ideas of Gibbs. A fundamental form is a relation of the energy, entropy, volume, and the masses or mol numbers, such as

$$\Phi(U, S, V, n_1, \dots, n_k) = 0. \quad (2.27)$$

There are $k + 3$ variables. From the property of homogeneity, the number of these variables can be reduced by one, by dividing by the volume. In this way, the densities of energy, entropy, and masses will emerge. If only one component is there, also the division by n_1 is useful. The function Φ relates now $k + 2$ variables, or totally there are $k + 1$ independent variables. Preferably Φ will be resolved to U , with the set of variables $S, V, n_1, n_2, \dots, n_k$ of independent variables. If the energy is a known function of these variables, then also the differential may be formed as

$$dU = T dS - p dV + \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_k dn_k. \quad (2.28)$$

$T, p, \mu_1, \mu_2, \dots, \mu_k$ are variables, but at the same time known functions of the independent variables $S, V, n_1, n_2, \dots, n_k$. We can obtain them by forming the partial derivatives

$$\begin{aligned} \frac{\partial U}{\partial S} &= T \\ \frac{\partial U}{\partial V} &= -p \\ \frac{\partial U}{\partial n_1} &= \mu_1 \\ &\dots = \dots \\ \frac{\partial U}{\partial n_k} &= \mu_k. \end{aligned} \quad (2.29)$$

So we have totally $2k + 5$ variables

$$U, S, V, n_1, n_2, \dots, n_k, T, p, \mu_1, \mu_2, \dots, \mu_k,$$

but of them only $k + 2$ are really independent. On the other hand, Eqs. (2.28) and (2.29) provide $k + 3$ relations.

A single equation from all these relations can be deduced called Gibbs fundamental equation. Not only the energy equation, but all Legendre transformations of the energy equation, such as enthalpy H , free energy F , free enthalpy G , the Massieu function, are fundamental equations. We summarize some types of fundamental equations in Table 2.3. As variables we use just those common in chemical thermodynamics. The fundamental equations shown in Table 2.3 are completely equivalent because they can be commuted one into another by the Legendre transformation without any loss of information. The variables given for the particular functions are addressed as the natural variables. For example, the energy U has the set of S, V, n_i, \dots as natural variables. If we want to use the temperature T instead of the entropy, we lose information, because the temperature is related to the entropy as the differential of the energy with entropy. Namely, the solution of the entropy from the temperature involves one unknown constant of integration.

The functions with the dimension of energy are sometimes addressed as thermodynamic potentials. This should not be confused with other thermodynamic functions that are also addressed as potential, such as the chemical potential or the electric potential.

There are basically two types of Legendre transformations, one type based on the energy and the other type based on the entropy. There are various other types of Massieu functions [15]. The Gibbs – Duhem equation is a very special type of Legendre transformation. It is a full transformation and is a relation of the intensive variables only.

To illustrate what is not a fundamental equation we compare a relation Eq. (2.27) with that given in Eq. (2.30).

$$\Psi(U, T, V, n_1, \dots, n_k) = 0. \quad (2.30)$$

Both relations differ only in that in Eq. (2.30), the temperature T appears instead of the entropy. From Eq. (2.27) we can deduce the temperature by $\partial U \partial S = T$. However, in Eq. (2.30) we are losing just this relation. So we cannot get back the

Table 2.3 Types of fundamental equations

Type	Differential		
Energy	$dU(S, V, n_i, \dots)$	$=$	$+T dS - p dV + \sum_{i=1}^{i=K} \mu_i dn_i$
Entropy	$dS(U, V, n_i, \dots)$	$=$	$+T^{-1} dU + p T^{-1} dV - \sum_{i=1}^{i=K} \mu_i T^{-1} dn_i$
Enthalpy	$dH(S, p, n_i, \dots)$	$=$	$+T dS + V dp + \sum_{i=1}^{i=K} \mu_i dn_i$
Free Energy	$dF(T, V, n_i, \dots)$	$=$	$-S dT - p dV + \sum_{i=1}^{i=K} \mu_i dn_i$
Free Enthalpy	$dG(S, p, n_i, \dots)$	$=$	$-S dT + V dp + \sum_{i=1}^{i=K} \mu_i dn_i$
Massieu	$d\Phi(T^{-1}, V, n_i, \dots)$	$=$	$-U dT^{-1} + p T^{-1} dV - \sum_{i=1}^{i=K} \mu_i T^{-1} dn_i$
Gibbs-Duhem Equation	0	$=$	$-S dT + V dp + \sum_{i=1}^{i=K} n_i d\mu_i$

entropy S . Note that the partial derivatives for $U(T, V, n_1, \dots, n_k)$, in general, are not the same as for $U(S, V, n_1, \dots, n_k)$ given in Eq. (2.29).

2.12 Partial Quantities

Here we exemplify the concept of partial quantities in terms of the volume in a system composed of two components. However, the concept is more general. We assume that the volume is a function of the mol numbers, $V = V(n_1, n_2)$. Then the total differential is

$$dV(n_1, n_2) = \frac{\partial V}{\partial n_1} dn_1 + \frac{\partial V}{\partial n_2} dn_2. \quad (2.31)$$

Because of the thermodynamic similarity, i.e., the volume is a homogeneous function of first order

$$V = V_1 n_1 + V_2 n_2.$$

By division by $n_1 + n_2$, thus introducing molar quantities, we obtain

$$\tilde{V} = V_1 x_1 + V_2 x_2 = V_1(1 - x_2) + V_2 x_2. \quad (2.32)$$

The partial volumes V_1 and V_2 do not need to be constant quantities, in particular in nonideal systems.

Obviously, in Eq. (2.32) the functional dependence changes now to x_1 or x_2 as independent variables, since the constraint $x_1 + x_2 = 1$ holds.

In Fig. 2.3, a plot of the total molar volume against the mole fraction is shown.

From Eq. (2.32), immediately the relation

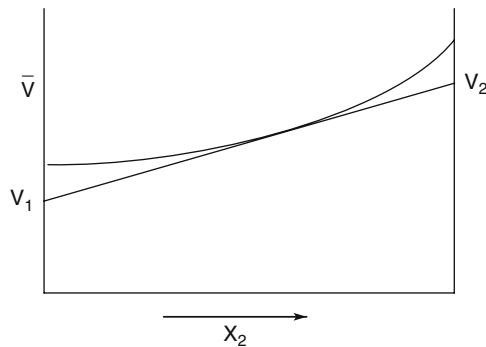


Fig. 2.3 Plot of molar volume against mole fraction

$$\frac{\partial \tilde{V}}{\partial x_2} = -V_1 + V_2 \quad (2.33)$$

is obtained. The tangent cuts the ordinate at $x_2 = 0$ at

$$\tilde{V} - \frac{\partial \tilde{V}}{\partial x_2} x_2,$$

where the molar volume and the slope have to be taken at the particular point x_2 , where the tangent touches the curve. From Eq. (1.23) follows that the tangent is some kind of the Legendre transformation.

Using Eqs. (2.32) and (2.32), we obtain finally the relation.

$$\tilde{V} - \frac{\partial \tilde{V}}{\partial x_2} x_2 = V_1.$$

2.13 Thermodynamic Derivatives

2.13.1 Potentials

The term potential originates from the Latin word *potentia* which means power. It is used in the sense of possibility in contrast to the term actual. There are several classes of thermodynamic derivatives of interest. Starting from the energy in natural variables, $U(S, V, n)$, the derivatives

$$\frac{\partial U(S, V, n)}{\partial S} = T; \quad \frac{\partial U(S, V, n)}{\partial V} = -p; \quad \frac{\partial U(S, V, n)}{\partial n} = \mu$$

are the common intensive variables, which are in general functions of the set S, V, n . The intensive variables are energy conjugated to their respective extensive variables. The quantity μ is addressed as chemical potential. Consequently, the other derivatives should be the thermal potential, the manal potential. Further, there should be the electric potential, the gravitational potential, the kinetic potential, etc. All these quantities should not be confused with the thermodynamic potentials that are basically energies themselves.

2.13.2 Capacities

The term capacity originates from the Latin words *capax* as able to hold much, or from *capere* as to take or to catch. In ordinary life we are talking, for example, of a vat that has the capacity of 101, which means that we can fill in a maximum of 101. The best-known capacity in thermodynamics is the heat capacity, either at constant volume or at constant pressure. Other terms concerning heat capacity appear in

the magnetocaloric effect, more commonly addressed as adiabatic demagnetization. However, there may also be a capacity with respect to compression energy. The heat capacity is defined as

$$C_v = \frac{\partial U(T, V, n)}{\partial T}; \quad C_p = \frac{\partial H(T, p, n)}{\partial T}.$$

Using Jacobian determinants, we can write

$$C_v = \frac{\partial(U, V, n)}{\partial(T, V, n)} = \frac{\partial(U, V, n)}{\partial(S, V, n)} \frac{\partial(S, V, n)}{\partial(T, V, n)} = T(S, V, n) \frac{\partial S(T, V, n)}{\partial T},$$

and in an analogous way for C_p

$$C_p = \frac{\partial(H, p, n)}{\partial(T, p, n)} = \frac{\partial(H, p, n)}{\partial(S, p, n)} \frac{\partial(S, p, n)}{\partial(T, p, n)} = T(S, p, n) \frac{\partial S(T, p, n)}{\partial T}.$$

Obviously, the general procedure to get a capacity is to formulate a thermodynamic function initially in its natural variables, say $U(S, V, n)$. Then a variable is replaced by its energy-conjugated variable, such as $U(T, V, n)$, and the partial differential with respect to this variable is formed to get the capacity, namely $\partial U(T, V, n)/\partial T$.

We try this procedure with the replacement of the volume by the negative pressure in the energy and in the Helmholtz energy

$$C_S = \frac{\partial U(S, -p, n)}{\partial(-p)}; \quad C_T = \frac{\partial F(T, -p, n)}{\partial(-p)}.$$

Thus, we are developing a capacity with respect to the energy of compression, rather than to heat energy. We arrive at

$$C_S = -p(S, V, n) \frac{\partial V(S, -p, n)}{\partial(-p)}; \quad C_T = -p(T, V, n) \frac{\partial V(T, -p, n)}{\partial(-p)}.$$

For example, for an ideal gas,

$$C_T = -p(T, V, n) \frac{\partial V(T, -p, n)}{\partial(-p)} = -\frac{nRT}{p} = -V.$$

In other words, if we would compress an ideal gas to zero volume, it can no longer store energy or free energy. In general, observe the following functional dependence of the capacities:

$$C_v(T, V, n); \quad C_p(T, p, n); \quad C_S(S, -p, n), \quad C_T(T, -p, n).$$

2.13.3 Susceptibilities

The term susceptibility originates from the Latin word *susceptus*, the past participle of *suscipere* in the sense of sustain or support. So we have not presented a real translation into basic English words.

Most common, the term susceptibility is used as electric susceptibility and magnetic susceptibility. In this connection, the susceptibility is the amount of dipole moment generated in a field and this per unit of volume. Dipole moment and field apply both to the electric and magnetic case. In physics, both electric and magnetic susceptibility are defined in a way so that they are dimensionless quantities.

2.13.3.1 Electric Susceptibility

The electric susceptibility χ_e is defined as

$$\chi_e = \frac{P}{\varepsilon_0 E}.$$

Here ε_0 is electric permittivity of vacuum, P is the dielectric polarization density, and E is the local electric field strength.

The dielectric polarization density has the units of $\text{m}^{-2} \text{s A}$ (dipole moment per volume) and the electric field strength has the units of $\text{V m}^{-1} = \text{m kg s}^{-3} \text{A}^{-1}$.

The electric permittivity is related to the permeability of vacuum μ_0 by

$$\varepsilon_0 \mu_0 = c^2.$$

In other words, the product of the electric permittivity of vacuum and the permeability of vacuum is the square of the velocity of light. The permeability is related to magnetism and has the units of $\text{m kg s}^{-2} \text{A}^{-2}$. It is magnetic induction per length. Thus, the electric permittivity has the units of $\text{m}^{-3} \text{kg}^{-1} \text{s}^4 \text{A}^2$. It is an electrical capacity per length. From these considerations, the electric susceptibility turns out as a dimensionless quantity.

2.13.3.2 Magnetic Susceptibility

The magnetic susceptibility χ_m is defined as

$$\chi_m = \frac{M}{\mathcal{H}}.$$

Here M is the magnetization and \mathcal{H} is the local magnetic field. Magnetization has the unit of A m^{-1} and the magnetic field has the same unit of A m^{-1} . Therefore, the magnetic susceptibility is a dimensionless quantity.

2.13.3.3 Generalized Susceptibilities

From the foregoing it is appealing to relate generalized susceptibilities χ_ξ as the differential of an arbitrary extensive variable X with respect to its energy-conjugated intensive variable ξ ,

$$\frac{\partial X}{\partial \xi}.$$

Examples are

$$\frac{C_v}{T} = \frac{\partial S(T, V)}{\partial T}; \quad \beta_T = -\frac{1}{V} \frac{\partial V(T, p)}{\partial p}; \quad \beta_S = -\frac{1}{V} \frac{\partial V(S, p)}{\partial p}.$$

Obviously, there is a relationship between the heat capacity and something like a susceptibility. β_T and β_S are the isothermal compressibility and the isentropic compressibility. The common definition of compressibility and electric and magnetic susceptibility suggests that susceptibility should be defined rather as

$$\chi_\xi = \frac{1}{V} \frac{\partial X}{\partial \xi} \quad \text{than} \quad \chi_\xi = \frac{1}{X} \frac{\partial X}{\partial \xi}.$$

It becomes now clear that the susceptibilities describe the response of the extensive variable on a change of the associated intensive variable. At first glance, it seems to be sufficient to place only one index, because the nature of the extensive variable can be found out. The generalized susceptibilities cannot be derived readily from the energy equation, but are accessible from the Legendre transformations of the energy. For instance, for

$$dG(T, p, n) = -S(T, p, n)dT + V(T, p, n)dp + \mu(T, p, n)dn,$$

a susceptibility can be derived as

$$\frac{\partial S(T, p, n)}{\partial T} = -\frac{\partial^2 G(T, p, n)}{\partial T^2}, \quad (2.34)$$

etc. Thus, the susceptibility appears to be a second-order derivative in terms of the natural variables of the energy-derived functions, the thermodynamic potentials.

Closer inspection of Eq. (2.34) indicates that it is possible to form also derivatives of the same kind, e.g., from the Helmholtz energy, so it is advisable to add the set of variables to the respective susceptibility.

Susceptibilities play a role in the theory of thermodynamic stability. Moreover, they can provide information useful for thermodynamic state functions.

2.13.4 Mixed Derivatives

There is a further class of important derivatives that can be traced neither back to a capacity nor a susceptibility. The most well known of these is the thermal expansion coefficient. Here the differential of an extensive variable with respect to a nonenergy-conjugated variable appears, such as

$$\alpha = \frac{1}{V} \frac{\partial V(T, p)}{\partial T}.$$

This type of differential can be converted into other expressions by using the Maxwell relations. The thermal expansion coefficient α originates naturally from the Gibbs free energy, since for the Gibbs free energy the set (T, p, n) are the natural variables.

2.14 Thermodynamic Similarity

Imagine a gas consisting of a single component in a big vessel. There should not be any external forces acting on the gas, such as gravity. It should be sufficient to describe the gas in the thermodynamic sense completely by three variables, i.e., the entropy, the volume, and the number of particles.

To find out the state of the gas, we probe a small, but still macroscopic, region within the vessel with the volume V . We will find a certain mol number of particles n and we will find a certain content of entropy S in this particular probed volume. If we probe in another region a volume of the same size, we will find the same values of entropy and mol number. Thus, from the thermodynamic data afterward we cannot find out from which region we had probed.

We address the two regions from where we had probed as two subsystems of the gas in the vessel. If we combine the two subsystems into a single one, it is intuitively obvious that in the combined subsystem the volume, the number of particles, and further the entropy will be additive. Also, the energy will be additive. This is the condition of a homogeneous system, which is also addressed as a phase.

If the vessel contains both liquid and gas, then the additivity will no longer hold in general, but is, if at all, restricted to carefully selected regions. In particular, it must be probed along an interphase border, in a certain position to catch equal amounts of the phases and surface.

The mathematical formulation of homogeneity of a phase occurs by the theorem of *Euler* on homogeneous functions. The theorem of *Euler* and the postulate that the energy is a homogeneous function of first order implies a property that resembles similarity. However, this is not a geometrical similarity, as we may see, and the energy function involving the volume V and a surface A , e.g., $U(S, V, A, n)$. The homogeneity demands that both volume and surface should grow by the same factor λ to result in

$$\lambda U(S, V, A, n) = U(\lambda S, \lambda V, \lambda A, \lambda n). \quad (2.35)$$

Note that on choosing $\lambda = 1/n$ will make n to disappear as independent variable in the argument list. The right-hand side of Eq. (2.35) turns into

$$U\left(\frac{S}{n}, \frac{V}{n}, \frac{A}{n}, 1\right) = U(\tilde{S}, \tilde{V}, \tilde{A}),$$

in that the respective molar quantities emerge. Therefore, also the energy will refer to molar quantities. The left-hand side of Eq. (2.35) tells us that the energy of an arbitrary-sized system can be converted into the molar energy by dividing the energy by the mol number n .

On the other hand, geometric similarity wants a growth like

$$\begin{aligned} V &\propto \lambda^3 \\ S &\propto \lambda^3 \\ n &\propto \lambda^3 \\ A &\propto \lambda^{2/3} \end{aligned} \quad (2.36)$$

In Eq. (2.36), l is a length. The situation becomes still more puzzling, when gravitation is in effect. In the case of gravitational energy we could think that the extensive variable is $gd(mh)$, where m is the mass and h is the height (position) in the gravitational field. An increase of the system by a factor of λ would cause the mass to increase by a factor of λ^1 , since it runs like the mol number. If we treat the gravitational energy as $(mg)dh$ as usual then only the height has to be increased.

We will address the homogeneity according to Eq. (2.35) as thermodynamic similarity. This similarity tells itself that an enlargement of the whole system is effective, when two systems of the same kind are put into one system. For instance, with regard to kinetic energy, if we consider two particles with the same velocity, we may integrate these two particles into one system to double the momentum, but having the same velocity.

2.15 Gibbs – Duhem Equations

If we use $dU(S, V) = TdS - pdV$, the Gibbs – Duhem equations demand $-SdT + Vdp = 0$. However, this application of the Gibbs – Duhem equations is wrong. In fact, a similarity of the system is relying, i.e.,

$$U(\alpha S, \alpha V, \alpha n) = \alpha U(S, V, n). \quad (2.37)$$

Forming the differential of Eq. (2.37) with respect to α and evaluating at $\alpha = 1$ results in

$$TS - pV + \mu n = U(S, V, n). \quad (2.38)$$

Forming the total differential from Eq. (2.38) results in

$$T dS + S dT - p dV - V dp + \mu dn + n d\mu = dU(S, V, n)$$

and from the form of dU

$$S dT - V dp + n d\mu = 0. \quad (2.39)$$

We must include all variables that contribute to similarity. For instance, if in a system the surface energy is relevant, the surface does not increase linearly with the volume of a similar system and a Gibbs – Duhem equation does not hold longer.

Example 2.10. We illustrate the Gibbs – Duhem equation for a two-component system. Equation (2.39) turns now into

$$S dT - V dp + n_1 d\mu_1 + n_2 d\mu_2 = 0. \quad (2.40)$$

We expand the chemical potential in a Taylor series:

$$\begin{aligned} d\mu_1 &= \frac{\partial \mu_1}{\partial T} dT + \frac{\partial \mu_1}{\partial p} dp + \frac{\partial \mu_1}{\partial n_1} dn_1 + \frac{\partial \mu_1}{\partial n_2} dn_2 \\ d\mu_2 &= \frac{\partial \mu_2}{\partial T} dT + \frac{\partial \mu_2}{\partial p} dp + \frac{\partial \mu_2}{\partial n_1} dn_1 + \frac{\partial \mu_2}{\partial n_2} dn_2. \end{aligned} \quad (2.41)$$

Observe that by the law of *Schwarz*:

$$\begin{aligned} \frac{\partial \mu_1}{\partial T} &= -\frac{\partial S}{\partial n_1} = -\tilde{S}_1, \\ \frac{\partial \mu_1}{\partial p} &= +\frac{\partial V}{\partial n_1} = +\tilde{V}_1. \end{aligned}$$

Inserting these relations into Eq. (2.41) results in

$$\left(n_1 \frac{\partial \mu_1}{\partial n_1} + n_2 \frac{\partial \mu_2}{\partial n_1} \right) dn_1 + \left(n_1 \frac{\partial \mu_1}{\partial n_2} + n_2 \frac{\partial \mu_2}{\partial n_2} \right) dn_2 = 0 \quad (2.42)$$

since both entropy and volume will cancel. For example, the total entropy of the system is $S = n_1 \tilde{S}_1 + n_2 \tilde{S}_2$ and similarly holds for the volume. Further, dn_1 and dn_2 can be varied independently so that both terms in brackets in Eq. (2.42) will equate to zero. \square

Often it is advantageous to divide Eq. (2.39) by the sum of the mol numbers, here $\sum_i n_i = n$. In this case, the molar quantities appear

$$\tilde{S}dT - \tilde{V}dp + d\mu = 0. \quad (2.43)$$

On dividing Eq. (2.40) by $\sum_i n_i = n_1 + n_2$, the mole fractions and the average molar quantities per total moles of mixture, $S \rightarrow S/(n_1 + n_2) = \tilde{S}$ and $V \rightarrow V/(n_1 + n_2) = \tilde{V}$, will emerge:

$$\tilde{S}dT - \tilde{V}dp + x_1d\mu_1 + x_2d\mu_2 = 0. \quad (2.44)$$

Equations (2.43) and (2.44) no longer contain terms that are dependent on the size of the system. A similar procedure as above results in

$$\begin{aligned} x_1 \frac{\partial \mu_1}{\partial x_1} + x_2 \frac{\partial \mu_2}{\partial x_1} &= 0 \\ x_1 \frac{\partial \mu_1}{\partial x_2} + x_2 \frac{\partial \mu_2}{\partial x_2} &= 0. \end{aligned} \quad (2.45)$$

2.16 The Principle of Finite Energy

We consider the isothermal expansion of an ideal gas. Expanding the gas loses the energy:

$$- \int_{V_{Start}}^{V_{End}} p dV = - \int_{V_{Start}}^{V_{End}} \frac{RT}{V} dV. \quad (2.46)$$

If we expand to infinite volume, we can extract infinite energy. On the other hand, the amount of gas is not infinite. We presume that a finite amount of substance may contain only a finite amount of energy. Therefore, the ideal gas law cannot be valid in this case. We should have a relation like $p = V^{-\kappa}$ with $\kappa \geq 1$.

Actually, the ideal gas law in Eq. (2.46) is sound when the gas is in contact with a thermal reservoir. The thermal reservoir has by definition an infinite capacity. Here, we want to focus that interest to the case of finite entropy and the consequences for heat capacity, when the absolute temperature approaches zero, as important in statements on the third law of thermodynamics.

For historical reasons we emphasize the following:

- In the derivation of the speed of sound, originally the ideal gas law was inserted, before it was recognized that the process is adiabatic.
- Although it should be clear, we may emphasize that an isothermal expansion may occur only if heat is delivered from a thermal reservoir.

Next, we consider another example for the principle of finite energy. According to Newton's law of gravitation, Eq. (2.16), the potential gravitational energy is $U_g = -Gm_1m_2/r$. G is the gravitational constant, m_1 and m_2 are the masses involved, and r is the mutual distance of the masses. Now, the potential gravitational energy turns to infinity, if the distance approaches zero. In order to avoid infinite energy, we

must not allow a zero distance. Thus, the principle of finite energy suggests that the masses have a finite extension so that they cannot approach zero distance. In other words, the principle of finite energy rejects the concept of point masses.

2.17 The Minimum Energy Principle

The principle of conservation of energy says that in the universe or more abstract in a closed system the energy is constant. This statement is different that the energy is tending to a minimum. We experience this principle in everyday mechanics.

For example, if we raise a body and allow it to fall down, we would feel that due to the action of gravity the body will search a state where its energy is a minimum. However, here we are considering only the potential energy of the body. We will not take into account that the potential energy is meanwhile transformed into kinetic energy and that the floor where the body is coming at rest would warm up in the course of the crash.

Further, we have withdrawn gravitational energy from the system that provides the gravitational energy. Therefore, in summary we have balanced the energy only for a part of the actors that are important to a body that is falling down.

We deal now with the statement of minimum of energy in detail and somewhat heuristically. Since the energy of a closed system is a real constant, we cannot speak strictly of a minimum in the sense that a neighboring state would have more energy than the state under consideration. However, since the energy is constant for such a system, every process that changes the thermodynamic variables X, Y, \dots of the energy $U(X, Y, \dots)$ as function of them must proceed that the energy would not change, i.e., $dU(X, Y, \dots) = 0$. This does not mean that the energy is a minimum in the sense that

$$U(X + \Delta X, Y + \Delta Y, \dots + \Delta \dots) > U(X, Y, \dots). \quad (2.47)$$

Instead, $U(X + \Delta X, Y + \Delta Y, \dots + \Delta \dots) = U(X, Y, \dots) = C_1$. We divide now the system under consideration into two subsystems U_1 and U_2 . Since the original system was chosen arbitrarily, we expect the same property of attaining a minimum energy also for the subsystems. However, the subsystems now can exchange energy among them.

The statement that the energy would tend to a minimum means that the system would give or release energy. In contrary, if we postulate that the energy should tend to a maximum this would mean that the system would like to take or to catch energy. So, if both subsystems have the property to release energy as far as possible then we intuitively feel that there would be a state of minimum energy in that way that the energy is somewhat equally distributed among the two subsystems.

On the other hand, if there should be a maximum of energy, than the tendency is reverse. Each subsystem would like to catch energy at the cost of the other subsystem. So, the particular subsystem that is stronger would accumulate energy, as long as it can suck energy from the other system. In the limiting case in one system a zero

energy would remain. For these reasons we could feel that in general the postulate of minimum energy is more sound than the postulate of maximum energy.

Nevertheless, the principle of minimum energy is not always reasonable. Astronomers have found black holes. These systems are accumulating energy from other systems in their neighborhood and would never release energy. Also, the atom is a system related to this type. Here we use the term atom rather in the original sense than in the nowadays chemical or physical sense, i.e., we mean a system that may not further be subdivided. Therefore, it can release neither energy nor mass. We annotate that mass could also be interpreted as energy. The situation is still more complicated. A black hole should emit radiation. We will discuss this issue in detail in Sect. 10.7.

2.18 Energy of a Quadratic Form

2.18.1 Energy

We will point out here the difference of constant energy and the minimum of energy. We exemplify the consideration by a spring, which is a quadratic form in terms of the variables. However, there are a lot of other examples for that the energy is a quadratic form. For example, the kinetic energy is quadratic in terms of the momentum. Further, the electric energy of a plate condenser is a quadratic form in terms of the electric charge.

2.18.2 Energy of a Spring

The energy of a spring is

$$U = \frac{k}{2} (x - x_0)^2. \quad (2.48)$$

Here $x - x_0$ is the extension of the spring apart from its equilibrium position and k is the force constant. This means that when the spring extends to its equilibrium position, its energy U equals zero. We consider this spring as an ideal spring. We can see easily, if we form the derivative with respect to the position, Hooke's law will emerge:

$$-\frac{dU}{dx} = F = -k(x - x_0).$$

We transform Eq. (2.48) now to dimensionless variables by putting $\xi = (x/x_0 - 1)$ and $\Upsilon = 2U/(kx_0^2)$ and we arrive at

$$\Upsilon = \xi^2.$$

If we have more than one identical spring with equal force constants k and equal equilibrium position x_0 , we insert an index

$$\Upsilon_{tot} = \Upsilon_1 + \Upsilon_2 + \dots = \xi_1^2 + \xi_2^2 + \dots$$

The total length of the springs when switched in series is $x = x_1 + x_2 + \dots$. In dimensionless variables we find

$$\xi_{tot} = \frac{x_1 - x_0 + x_2 - x_0 + \dots}{x_0} = \xi_1 + \xi_2 + \dots$$

2.18.3 Constant Energy and Length

We demand now that the dimensionless total energy Υ_{tot} and the dimensionless total length ξ_{tot} should be constant. Further, we deal with two springs only. In this case, we have now the following two equations:

$$\begin{aligned}\Upsilon_{tot} &= \xi_1^2 + \xi_2^2 \\ \xi_{tot} &= \xi_1 + \xi_2\end{aligned}\tag{2.49}$$

We have only two variables ξ_1 and ξ_2 in these two equations. Therefore, we could have one unique solution in a linear set of equations and since one of the equations is quadratic and the equations are completely symmetric with respect to ξ_1, ξ_2 we obtain a set of solutions:

$$\begin{aligned}\xi_1 &= \frac{\xi_{tot} \pm \sqrt{2\Upsilon - \xi_{tot}^2}}{2} \\ \xi_2 &= \frac{\xi_{tot} \mp \sqrt{2\Upsilon - \xi_{tot}^2}}{2}.\end{aligned}$$

We show the situation in Fig. 2.4. The isodynamic curves are forming circles around the origin, whereas the curves of equal dimensionless length are straight lines with a slope of -1 .

When we extend Eq. (2.49) for three springs, we get

$$\begin{aligned}\Upsilon_{tot} &= \xi_1^2 + \xi_2^2 + \xi_3^2, \\ \xi_{tot} &= \xi_1 + \xi_2 + \xi_3,\end{aligned}\tag{2.50}$$

and we easily see that we have now one variable, say ξ_3 , for free adjustment. In other words, we have under favorite selection of the energy and the total length a continuous path along which we can change one of the variables $\xi_i, i = 1, 2, 3$ and can still fulfill Eq. (2.50).

The graphical representation of Fig. 2.4 can be easily extended in three dimensions. In three dimensions, the dimensionless isodynamic curves are now spheres

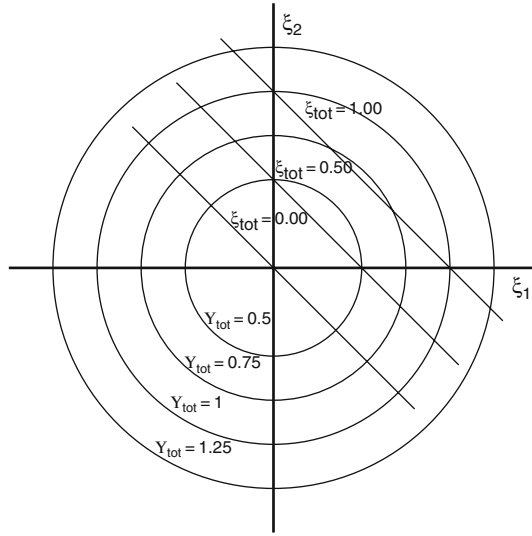


Fig. 2.4 Graphical representation of the dimensionless energy and the dimensional length

around the origin, whereas the curves of equal dimensionless length are straight planes. The planes are cutting the spheres as a spherical segment. The intersecting curve is then a cycle, which is the graphical solution.

2.18.4 Minimum of Energy

The situation becomes completely different when we ask for the energy to be an extremum at a given length.

2.18.4.1 Two Coupled Springs

For two coupled springs $\Upsilon_{tot}(\xi_1, \xi_2)$ as a function of the energy of the springs under consideration, Υ is no longer a constant. If the other condition regarding the length remains still the same, the total length will be a constant. Therefore, we have the equations:

$$\begin{aligned}\Upsilon_{tot}(\xi_1, \xi_2) &= \xi_1^2 + \xi_2^2 \\ \xi_{tot} &= \xi_1 + \xi_2.\end{aligned}\tag{2.51}$$

For the first equation we want to find a minimum. The second equation in Eq. (2.51) is a constraint equation. We can easily insert the second equation of Eq. (2.51) in the first equation to obtain

$$\Upsilon_{tot}(\xi_1, \xi_2) = \xi_1^2 + (\xi_{tot} - \xi_1)^2.$$

By substitution, we have now reduced the problem to a function of one variable, ξ_1 , find the extremum under the constraint, form the derivative as usual and obtain

$$\frac{d\Upsilon_{tot}}{d\xi_1} = 4\xi_1 - 2\xi_{tot}.$$

Therefore, the dimensionless elongation is $\xi_1 = \xi_2 = \xi_{tot}/2$. Eventually we from the second derivative which is $d^2\Upsilon_{tot}/d\xi_1^2 = 4$. This indicates that basically only a minimum energy is possible.

In the representation of Fig. 2.4 we move along a line of constant length and look for the curve of minimum energy.

2.18.4.2 Three Coupled Springs

The dimensionless total energy becomes $\Upsilon_{tot}(\xi_1, \xi_2, \xi_3)$ for three coupled springs. Further, the total length should again be a constant. We set up the constraint equation now as

$$\xi_{tot} - \xi_1 - \xi_2 - \xi_3 = \Phi(\xi_1, \xi_2, \xi_3) \equiv 0. \quad (2.52)$$

In the argument set Φ , only ξ_1, ξ_2, ξ_3 appear, indicating that ξ_{tot} is not a variable. We introduce now the more convenient method of undetermined multipliers by Lagrange. In the differential form this equation reads as

$$-d\xi_1 - d\xi_2 - d\xi_3 = 0.$$

To find the extremum under the constraint, we will multiply Eq. (2.52) with an undetermined multiplier λ and add a zero valued function $\Phi(\xi_1, \xi_2, \xi_3)$ to the expression for $\Upsilon(\xi_1, \xi_2, \xi_3)$. In detail, we form a function

$$\Psi(\xi_1, \xi_2, \xi_3) = \Upsilon(\xi_1, \xi_2, \xi_3) + \lambda\Phi(\xi_1, \xi_2, \xi_3).$$

Forming now the differential of Ψ we get

$$d\Psi(\xi_1, \xi_2, \xi_3) = (2\xi_1 - \lambda)d\xi_1 + (2\xi_2 - \lambda)d\xi_2 + (2\xi_3 - \lambda)d\xi_3. \quad (2.53)$$

Therefore, we have to equate the set of equations

$$2\xi_1 - \lambda = 0; \quad 2\xi_2 - \lambda = 0; \quad 2\xi_3 - \lambda = 0$$

to zero which means that $\xi_1 = \xi_2 = \xi_3$. This means that also the energy of each individual spring is the same. We observe here that the energy distributes itself in same amounts in a system of equal subsystems, or in other words, the energy follows an equipartition law.

We carefully point out the difference between the meaning of Eq. (2.50) where we are dealing with a constant energy and Eq. (2.53) where we are searching for a minimum or more generally for an extremum of the energy. We now make use of Eq. (2.52) and find

$$\xi_1 = \xi_2 = \xi_3 = \frac{\xi}{3}. \quad (2.54)$$

Depending on whether the springs are pulled or pushed, or left freely corresponding to $\xi > 0$, $\xi < 0$, or $\xi = 0$ also the individual elongations ξ_1, ξ_2, ξ_3 reflect the state.

Finally, we should always inspect the second derivative of the energy $d^2\Upsilon$ to obtain information about the type of stationarity. The second total differential is simply

$$d^2\Upsilon(\xi_1, \xi_2, \xi_3) = 2(d\xi_1^2 + d\xi_2^2 + d\xi_3^2),$$

since the mixed terms cancel.

We return now again to the condition of constant energy. However, we set now the total length as a variable. We have now

$$\xi_{tot}(\xi_1, \xi_2, \xi_3) = \xi_1 + \xi_2 + \xi_3$$

and $\Upsilon_{tot} - \xi_1^2 + \xi_2^2 + \xi_3^2 = 0$. To find an extremum of the dimensionless length at constant energy we proceed in the same way as we found the minimum of the energy in Eq. (2.53). We form the function $\Phi(\xi_1, \xi_2, \xi_3) = \Upsilon - \xi_1^2 - \xi_2^2 - \xi_3^2$ and further $\Psi(\xi_1, \xi_2, \xi_3) = \lambda\Phi(\xi_1, \xi_2, \xi_3) + \xi_{tot}(\xi_1, \xi_2, \xi_3)$. Then the equation in question will turn out as

$$d\Psi(\xi_1, \xi_2, \xi_3) = (-2\xi_1\lambda + 1)d\xi_1 + (-2\xi_2\lambda + 1)d\xi_2 + (-2\xi_3\lambda + 1)d\xi_3. \quad (2.55)$$

Obviously, Eq. (2.55) gives the same result as the treatment where we searched for a minimum energy. Again, we find the result of Eq. (2.54).

2.18.5 Spring Coupled with Two Gases

Consider the system shown in Fig. 2.5. Here, two gases (1) and (2) are separated by a freely movable piston. Further the gas (2) is coupled by a movable piston with a spring. The spring is fixed on the other end. The total volume V_{tot} of both gases is the sum of their individual volumes V_1 and V_2

$$V_{tot} = V_1 + V_2. \quad (2.56)$$



Fig. 2.5 Two ideal gases (1) and (2) coupled by a spring

The energy of the spring is related exclusively to the total volume in some way, $U_s = U_s(V_{tot})$. We could calculate the dependence of the energy of the spring on the length of the spring and relate the energy of the spring to the total volume, but we will not do this in detail.

The energy of the gas is a function of entropy S , volume V , and mol number n . Since we have two gases we will provide the indices (1) and (2). Thus

$$U_1 = U_1(S_1, V_1, n_1); \quad U_2 = U_2(S_2, V_2, n_2).$$

The total energy of the system is

$$U_{tot} = U_1 + U_2 + U_s.$$

We assume now that the walls of the systems are impermeable to entropy and matter. Further we consider a state of equilibrium. This assumption implies the constraints $dS_1 = 0$, $dS_2 = 0$, $dn_1 = 0$, $dn_2 = 0$. For this reason we may express the total energy merely as a function of the volumes, i.e.,

$$U_{tot}(V_{tot}, V_1, V_2) = U_1(V_1) + U_2(V_2) + U_s(V_{tot}). \quad (2.57)$$

Using the constraint equation (2.56) together with the method of undetermined multipliers,

$$(-V_{tot} + V_1 + V_2)\lambda = 0,$$

we get immediately

$$dU_{tot} = \left(\frac{\partial U_s}{\partial V_{tot}} - \lambda \right) dV_{tot} - (p_1 - \lambda) dV_1 - (p_2 - \lambda) dV_2. \quad (2.58)$$

Thus, without knowing the special form of the energy of the spring, we come to the conclusion that in equilibrium the pressures of the gases must be equal, i.e., $p_1 = p_2$.

The constraints with respect to entropy and mol number allow different temperatures and different chemical potentials for the gases (1) and (2). The spring, of course, ideally does not have entropy, mol number, and volume. The dependence of the energy of the spring on the total volume arises, because the length of the spring is coupled with the total volume of both gases.

We may point out a special case in that the energy of the spring does not change with length at all. Then $\lambda = 0$ from the first term on the right-hand side of Eq. (2.58) and the gases will expand to zero pressure.

2.19 Maximum of Entropy

We examine now the entropy of two subsystems under the constraint of constant volume and constant energy. We have two systems with the energies $U_1(S_1, V_1)$ and $U_2(S_2, V_2)$. These energies are functions of their entropies denoted as S_1, S_2 and their volumes V_1, V_2 . The total energy and the total volume should be constant:

$$\begin{aligned} U_{\text{tot}} - U_1(S_1, V_1) - U_2(S_2, V_2) &= 0 \\ V_{\text{tot}} - V_1 - V_2 &= 0 \end{aligned} \quad (2.59)$$

We form now the total entropy and add the constraint equations (2.59) multiplied with undetermined coefficients λ_U, λ_V :

$$\begin{aligned} \Psi_S(S_1, S_2, V_1, V_2) = & \\ & S_1 + S_2 + \\ & \lambda_U(U_{\text{tot}} - U_1(S_1, V_1) - U_2(S_2, V_2)) + \\ & \lambda_V(V_{\text{tot}} - V_1 - V_2). \end{aligned} \quad (2.60)$$

To find the extremum we form in Eq. (2.60) the partial differentials and we substitute also $\partial U(S, V)/\partial S = T(S, V)$ and $\partial U(S, V)/\partial V = -p(S, V)$ introducing the appropriate index 1 or 2:

$$\begin{aligned} d\Psi_S(S_1, S_2, V_1, V_2) = & \\ & (1 - \lambda_U T_1(S_1, V_1)) dS_1 + \\ & (1 - \lambda_U T_2(S_2, V_2)) dS_2 + \\ & (\lambda_U p_1(S_1, V_1) - \lambda_V) dV_1 + \\ & (\lambda_U p_2(S_2, V_2) - \lambda_V) dV_2. \end{aligned} \quad (2.61)$$

Equating all differentials in Eq. (2.61) to zero and eliminating λ_U, λ_V results in

$$\begin{aligned} T_1(S_1, V_1) &= T_2(S_2, V_2) \\ p_1(S_1, V_1) &= p_2(S_2, V_2) \end{aligned} \quad (2.62)$$

In this procedure we do not search for an extremum for the total energy. Instead, we assume the total energy to be constant. We do not use a condition of constant entropy but we search an extremum of the entropy under the constraint of constant energy and constant volume. Nevertheless, it turns out that under these constraints not only the pressures of the two systems are equal but also the temperatures.

However, if we search for an extremum of the energy under the constraint of constant total volume $V_{\text{tot}} - V_1 - V_2 = 0$ and of constant total entropy $S_{\text{tot}} - S_1 - S_2 = 0$, the same result would be obtained. In fact, we would have to evaluate an expression like

$$\begin{aligned}\Psi_U(S_1, S_2, V_1, V_2) = \\ U(S_1, S_2, V_1, V_2) + \\ \lambda_S(S_{\text{tot}} - S_1 - S_2) + \\ \lambda_V(V_{\text{tot}} - V_1 - V_2)\end{aligned}$$

in a similar manner like Eq. (2.61).

2.19.1 Entropy Gain in an Ideal Gas

It could be that Eq. (2.62) is not satisfactory by inspection and common sense. We consider a system as shown in Fig. 2.6. Here the total volume V_{tot} is constant and is the sum of the individual volumes V_1 of gas (1) and V_2 of gas (2), i.e., $V_{\text{tot}} - V_1 - V_2 = 0$. When we start with equal amounts of gas with the volume at the left side V_1 smaller than the volume at the right side V_2 , it is suggestive that the pressure on the left side is higher than the pressure on the right side. In general, this may not be true, because the pressure is dependent also on the temperature of the respective gas. However, we assume $p_1 > p_2$.

When we allow the plunger to move freely the volume at the left side will increase and the volume at the right side will decrease correspondingly. Therefore, we naturally feel that the process will continue until both pressures become equal. This means that the condition $p_1(S_1, V_1) = p_2(S_2, V_2)$ from Eq. (2.62) is fulfilled, but not necessarily the condition of equal temperature.

In fact, the calculation of maximum entropy finds the most possible maximum entropy. We have not given a constraint for the entropy in Eqs. (2.60) and (2.61). However, in a nonequilibrium process the entropy should increase. Thermodynamics does not provide an answer as to which way the entropy would increase. We

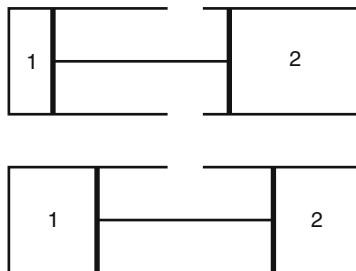


Fig. 2.6 Two ideal gases (1) and (2) coupled by a piston

could obtain an answer, if we are dealing with one gas only in the way as the experiment of *Gay-Lussac*⁶ runs. This means that a single gas is expanding into vacuum. In the case of two gases, the situation is already more complicated and we must state additional constraints to find the way in which the gases would equilibrate.

2.20 Coupled Energy Forms

We inspect now an arbitrary system together with an environment system. The arbitrary system should have a certain energy dependent on the entropy, the volume, and the mol number, as usual $U_{sys}(S_{sys}, V_{sys}, n_{sys})$. The environment should have an energy dependent on certain variable that we will specify later as $U_{env}(X_1, X_2, \dots)$. The energy of both systems should be constant, i.e.,

$$U_{\text{tot}} = U_{sys}(S_{sys}, V_{sys}, n_{sys}) + U_{env}(X_1, X_2, \dots). \quad (2.63)$$

For illustration we may think that the system consists of an ideal gas. The system and its environment is presented schematically in Fig. 2.7.

The energy of the systems as can be deduced easily from the mathematical form of $U(S, V, n)$ is solely dependent on the entropy S , the volume V , and the mol number n of the system. In fact, when we know the entropy and the volume we can find out the energy. We recall that for an ideal gas the energy is something like

$$U_{sys}(S_{sys}, V_{sys}, n_{sys}) = n \left(C_1 \exp \left(\frac{S_{sys}}{\tilde{C}_v n_{sys}} \right) \left(\frac{V_{sys}}{n_{sys}} \right)^{-R/\tilde{C}_v} + C_2 \right). \quad (2.64)$$

The adiabatic coefficient κ is defined as $\kappa = \tilde{C}_p / \tilde{C}_v$. Since $R = \tilde{C}_p - \tilde{C}_v$, $R/\tilde{C}_v = \kappa - 1$. For a monoatomic gas $\kappa = 5/3$ and for a diatomic gas $\kappa = 7/3$. This can be concluded from the equipartition theorem.

Further, we could express the entropy in a dimensionless quantity, in units of C_v , i.e., $\check{S}_{sys} = S_{sys}/C_v$. We can adjust a dimensionless energy as $\check{U}_{sys}(\check{S}_{sys}, \check{V}_{sys}) = \exp(\check{S}_{sys}) \check{V}_{sys}^{-2/3}$. We will discuss now certain possibilities of changing the energy of the system.

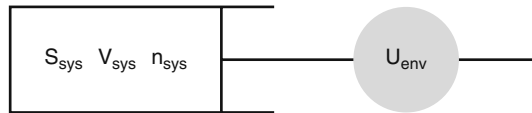


Fig. 2.7 An ideal gas as system and its environment

⁶ Joseph Louis Gay-Lussac, born Dec. 6, 1778, in Saint-Léonard-de-Noblat, died May 9, 1850, in Paris.

2.20.1 Environment Takes Up Volume Energy

We construct the environment as an engine that can take up volume energy, $U_{env} = U_{env}(V_{sys})$. In particular, the environment knows about the volume of the system, thus

$$U_{env} = f(V_{sys}). \quad (2.65)$$

Without elaborating the nature of engine of the environment in detail we can imagine that the energy storage of the environment can be a spring coupled with a gear that has a variable gear transmission ratio depending on the volume of the system. In this way, a variable pressure can be transduced to the system depending on the volume, as shown schematically in Fig. 2.7.

We now make a closer assumption on the nature of $f(V_{sys})$ given in Eq. 2.65. We assume that

$$U_{env} = f(V_{sys}) = U_{tot} - C_3 V_{sys}^{-R/C_v} V_{sys}^\beta.$$

Inserting this expression into Eqs. (2.63) and (2.64) we find:

$$n \left(C_1 \exp \left(\frac{S_{sys}}{\tilde{C}_v n_{sys}} \right) \left(\frac{V_{sys}}{n_{sys}} \right)^{-R/\tilde{C}_v} + C_2 \right) - C_3 V_{sys}^{-R/C_v} V_{sys}^\beta = 0.$$

We adjust $C_2 = 0$ and find, introducing a new (positive) constant C that gathers all the former constants,

$$S_{sys} = C\beta \ln V_{sys}.$$

We can discuss now the following cases:

1. If $\beta = 0$, then the entropy of the system will not change provided that the volume of the system changes. This is a reversible change of the state. This does not mean that the temperature will be constant in this case, because the temperature is also a function of the volume. The temperature will decrease with expanding volume according to energy equation of the ideal gas.
2. If $\beta > 0$, then the entropy of the system will increase provided that the volume of the system increases. This is an irreversible change of the state.
3. If $\beta < 0$, then the entropy of the system will decrease provided that the volume of the system increases. This case is an impossible change of the state, since the second law of thermodynamics does not allow a spontaneous process where the overall entropy decreases. We emphasize that the environment according to the model does not bear any entropy.

2.21 Dimensionless Relative Variables

We inspect now the thermodynamic variables and functions of the various energy forms by making the respective extensive variable dimensionless.

We illustrate the principle first with the kinetic energy. The kinetic energy U of a mass point with mass m expressed in terms of the momentum P is $U(P) = P^2/(2m)$, which is well known in classical mechanics. We form the differential, thinking that the mass is constant and obtain

$$dU(P) = \frac{P}{m} dP. \quad (2.66)$$

We can rearrange Eq. (2.66) to obtain

$$dU(P) = \frac{P^2}{m} \frac{dP}{P} = \frac{P^2}{m} d \ln P. \quad (2.67)$$

Here dP/P is a dimensionless increase of the momentum, the relative increase of the momentum. Consequently, the first term P^2/m on the right-hand side of Eq. (2.67) is an energy. Formally P^2/m is the increase of the kinetic energy when the relative increase of the momentum dP/P equals 1.

We could further substitute $\ln P = z$ and further $P = \exp z$ into Eq. (2.67) but we will leave it as is. However, we can state that the differential is of the order P^2 .

We may repeat the same procedure for other energy forms. We collect some energy forms in Table 2.4. For the volume energy in Table 2.4 we have converted the volume V into its reciprocal $1/V$ to eliminate the negative sign in the differential. Further, in Table 2.4 functions of the extensive variables appear. This is the pressure p now as a function of the logarithm of the reciprocal volume $1/V$ or the temperature as a function of the logarithm of the entropy for the thermal energy. We can resolve these functions under certain conditions, i.e., the pressure as a function of volume at constant entropy or the temperature as a function of entropy at constant volume, etc. For the isentropic expansion of an ideal gas we have $pV^\kappa = C_1(S)$ and for the temperature change at constant volume we have $T = \exp(S/C_v)$ when C_v is a constant. We can insert these dependencies for the special cases as done in the third column of Table 2.4.

Inspecting Table 2.4 we find that the kinetic energy runs with the order p^2/m , the gravitational energy runs with the order mgh , the volume energy runs with the order $C(S)/V^{\kappa-1}$, and finally the thermal energy runs with the order $\exp(S/C_v)S$.

Table 2.4 Energy forms with relative dimensionless argument

Energy form	Differential	Special case
Kinetic energy	$P^2/m \, d \ln(P)$	
Gravitational energy	$mgh \, d \ln(mh)$	
Volume energy	$pV \, d \ln(1/V)$	$C(S)/V^{\kappa-1} \, d \ln(1/V)$
Thermal energy	$TS \, d \ln(S)$	$\exp(S/C_v)S \, d \ln(S)$

This means among the energy forms considered here, the thermal energy runs in the highest order.

We make a little bit more precise of what and how we understand the order discussed here. In the case of a polynomial, we deal with the exponents. For example, the polynomial $x^2 + x + 1$ has the highest exponent x^2 and thus the order of 2. Here we mean which function is growing faster with increasing argument. If we have two functions $f(x)$ and $g(x)$ both being real positive then $f(x)$ has a higher order if $f(x) - g(x) > 0$ for some range in x .

2.22 Stability

In this section, we anticipate the problem of stability of a thermodynamic system briefly, which needs understanding of equilibrium and the second law. We may start from the equilibrium instead from the inequalities for entropy, which are discussed in Sect. 3.3 and vice versa. Say, we have free exchange of a certain extensive variable of state and we ask why it will not happen that an exchange will not occur in a certain direction.

Example 2.11. There are two systems $U_1(S_1)$ and $U_2(S_2)$ that can freely exchange S . Suppose $T_1 = T_2$. Why it does not happen that entropy will flow from one to the other on a small disturbance so that one system will release entropy and the other will catch it. Note that in the case of two soap bubbles of equal radi in fact this will occur. The soap bubble system is not stable. \square

Imagine a system composed of two subsystems with fixed volume, etc. Only entropy can be varied. Therefore, we suppress variables other than entropy in the variable list. We emphasize that the consideration can be extended to more than one variable. The energy is a function of the entropies of the individual subsystems. The total energy is additive with respect to the energies of the subsystems

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

Think about a change of energy in such a way that the total entropy remains constant. We will exchange a small amount of entropy ΔS . Initially the energy is $U(S_1, S_2)$. Moreover, we start from an equilibrium position which means that $T_1 = T_2 = T$. After varying the energy we have $U(S_1 + \Delta S, S_2 - \Delta S)$. Inspect the first total differential:

$$\begin{aligned} dU_1(S_1 + \Delta S) &= + \frac{\partial U(S_1)}{\partial S_1} \Delta S = T \Delta S \\ dU_2(S_2 - \Delta S) &= - \frac{\partial U(S_2)}{\partial S_2} \Delta S = -T \Delta S. \end{aligned} \tag{2.68}$$

Thus, the first derivative $dU = dU_1 + dU_2$ equals zero. Now inspect the second total differential:

$$\begin{aligned}
d^2U_1(S_1 + \Delta S) &= \frac{1}{2} \frac{\partial^2 U(S_1)}{\partial S_1^2} \Delta S^2 \\
d^2U_2(S_2 - \Delta S) &= \frac{1}{2} \frac{\partial^2 U(S_1)}{\partial S_1^2} \Delta S^2.
\end{aligned} \tag{2.69}$$

The second total differential d^2U will be positive if $dT/dS > 0$. In this case, the total energy will be a minimum with respect to an exchange of entropy. This is the condition of stability. A process that varies the entropy will not take place, if

$$\frac{\partial T}{\partial S} > 0. \tag{2.70}$$

Otherwise, the world would collapse or disproportionate to an infinitely cold state and to an infinitely hot state. We emphasize, if the material condition

$$\frac{\partial S}{\partial T} > 0 \tag{2.71}$$

is not valid we would not exist at all, nor our world could exist. This is more fundamental than the statement of *Clausius* on the second law.

We generalize now stability to more variables.

Example 2.12. Consider the function

$$f(x, y) = ax^2 + bxy + cy^2.$$

The function has an extremum at $x = 0, y = 0$. We show a plot of the function with $a = 1, c = 1, b = 3$ in Fig. 2.8. If the discriminant $D \equiv 4ac - b^2 > 0$, the contour plot will show ellipses, with a definite maximum, otherwise a saddle point emerges. In fact, we are dealing with a binary quadratic form in two real variables. The binary quadratic form is positive definite if its discriminant is positive. \square

Now, we assume that the internal energy is a function of the extensive variables X_1, X_2, \dots, X_n , i.e., $U = U(X_1, X_2, \dots, X_n)$. We normalize the energy that in the minimum, indexed by m with $X_1 = X_{1,m}, X_2 = X_{2,m}, \dots, X_n = X_{n,m}$ it reaches zero. We can now expand the energy around the minimum into a Taylor series. The result is

$$\begin{aligned}
U(X_1, X_2, \dots, X_n) &= U(X_{1,m}, X_{2,m}, \dots, X_{n,m}) \\
&+ \frac{\partial U}{\partial X_1}(X_1 - X_{1,m}) + \frac{\partial U}{\partial X_2}(X_2 - X_{2,m}) + \dots + \frac{\partial U}{\partial X_n}(X_n - X_{n,m}) \\
&+ \frac{\partial^2 U}{\partial X_1^2}(X_1 - X_{1,m})^2 + \frac{\partial^2 U}{\partial X_1 X_2}(X_1 - X_{1,m})(X_2 - X_{2,m}) + \dots \\
&+ \frac{\partial^2 U}{\partial X_n^2}(X_n - X_{n,m})^2. \tag{2.72}
\end{aligned}$$

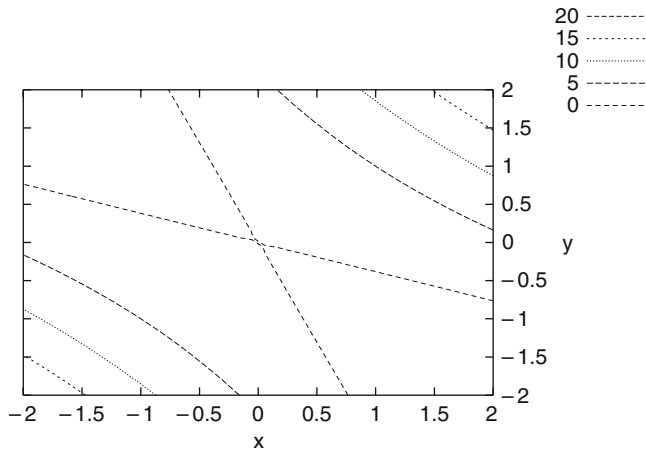


Fig. 2.8 Plot of $f(x, y) = x^2 + 3xy + y^2$

The first line on the right-hand side of Eq. (2.72) is zero. The second line is the total differential of first order, which is zero when the function is stationary. The further terms are the total differential of second order. This differential must be positive in order that the function provides a minimum.

From the theory of positive definite bilinear forms it has been shown that all the coefficients must be positive, for the condition of a minimum [2, Appendix G, pp. 361–366]. From the view of mathematics, we are dealing with definite positive quadratic forms.

We point out still another formal issue of Eq. (2.70) and (2.70). The natural variables of the energy are the set (S, V, n, \dots) . These variables are extensive in nature. Now Eq. (2.71) deals with the reciprocal of Eq. (2.70). Forming the reciprocal, the independent variables change. In particular, writing the independent variables explicitly, when we use $\partial T(S, V, \dots)/\partial S$, the reciprocal turns into $\partial S(T, V, \dots)/\partial T = C_v(T, V, \dots)/T$. This is not very exciting.

However, observe that the corresponding pressure changes from $\partial p(S, V, \dots)/\partial V$ into $\partial V(S, p, \dots)/\partial p$. Thus, keep in mind that the entropy is still the dependent variable. As an exercise, we change the variables using Jacobian determinants. For simplicity, we are using two independent variables in the list of variables:

$$\begin{aligned}
 \frac{\partial p(S, V)}{\partial V} &= \frac{\partial(p, S)}{\partial(V, S)} = \frac{\partial(p, S)/\partial(V, T)}{\partial(V, S)/\partial(V, T)} = \\
 &= \frac{\frac{\partial p(T, V)}{\partial V} \frac{\partial S(T, V)}{\partial T} - \frac{\partial p(T, V)}{\partial T} \frac{\partial S(T, V)}{\partial V}}{\frac{\partial S(T, V)}{\partial T}} = \\
 &= \frac{\partial p(T, V)}{\partial V} - \frac{T}{C_v(T, V)} \left(\frac{\partial p(T, V)}{\partial T} \right)^2. \quad (2.73)
 \end{aligned}$$

Observe the square in the last term of Eq. (2.73). It effects that the squared term is always positive.

2.23 Phases

Commonly, in a system with multiple phases, the phase is defined as a region; when moving into this region an abrupt change in the physical properties is observed. Thus, the phase is rather characterized by its sharp border.

As well known, in equilibrium of a PVT system, the intensive variables such as temperature T , pressure p , and the chemical potentials of the individual components μ_i in each phase are equal. This is the starting point of the derivation of the phase rule.

One important prerequisite for the derivation of the phase rule is that the phases are distinguishable. Obviously, the phases cannot be distinguished by their intensive parameters, except composition. Therefore, other properties must hold in order to characterize a phase. In order to detect a phase, at least one property, either a direct thermodynamic property such as the extensive properties or a property that is dependent on these properties, such as diffraction, must differ in each phase. Here we annotate that there is agreement that a thermodynamic potential contains the complete information in order to describe a thermodynamic system unambiguously. Among the extensive variables of a phase, the mol numbers just tell about the size of the phase. In contrast, the mole fractions give information about the constitution of the components in the phase.

If all direct and indirect properties in each region of a system are equal, then it does not make sense to talk about multiple phases. In particular, the properties in a liquid – gas system approach one another at the critical point. At the critical point the two phases disappear.

It is somehow suggestive to postulate that if the direct extensive properties are equal, also the derived properties are equal. For example, in a two-component system, if the molar entropy, the molar volume, and the mole fraction are the same, also other properties that are functions of these parameters should be the same. We are talking about properties that are beyond the equations of state. For example, the refractive index should be the same for each phase and different phases will no longer be detectable.

Likewise, we may state that a proper handling of the phase rule requires a complete set of thermodynamic variables. Properties derived from this complete set allow unambiguously to state whether there are two or more phases present or not. This postulate does not appear directly in the thermodynamic laws.

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