Chapter 2
Postulates of Thermodynamics

Thermodynamics is a general theory; it deals with the properties of all kinds of matter where the behavior of a large number of *microscopic* particles (such as molecules, atoms, ions, etc.) determines the *macroscopic* properties. It is stated sometimes that this branch of science deals with the transformation of the *thermal energy* hidden in the internal structure and modes of movements of the enormously large number of particles that build up macroscopic bodies, into other forms of energy. As the microscopic structure of matter, the modes of movements and the interactions of particles have further consequences than simply determining the energy of a macroscopic body; thermodynamics has a more general relevance to describe the behavior of matter.

The number of particles in a macroscopic piece of matter is in the order of magnitude of the Avogadro constant ($6.022\,141\,79 \times 10^{23}$/mol). Obviously, there is no question of describing the movement of individual particles; we should content ourselves with the description of the average behavior of this large population. Based on our actual knowledge on probability theory, we would naturally use a statistical description of the large population to get the average properties. By comparing the calculated averages – more precisely, the *expected values* – with macroscopic measurements, we could determine properties that "survive" averaging and manifest at the macroscopic level. There are not many such properties; thus, this treatment of the ensemble of particles would lead to practically useful results. This probabilistic approach is called *statistical thermodynamics* or, in a broader sense, *statistical physics*.

However, as it has been mentioned before (and is described in details in Appendix 3), thermodynamics had been developed in the middle of the nineteenth century while attempting to theoretically solve the problem of efficiency of transforming heat into mechanical work. The "atomistic" theory of matter was of very little interest in those days, thus thermodynamics developed only by inspection and thorough investigation of macroscopic properties. This is reflected in the term *phenomenological thermodynamics*, which is related to the Latin word of Greek origin *phenomenon* (an observable event). This "classical" thermodynamics used terms relevant to heat engines to formulate a few "laws" from which relations

useful to solve problems were derived. After more than half a century later, *postulational thermodynamics* has been developed where the basic principles are formulated not in terms of heat engines but useful relations of general validity ready to use for solving problems. In this chapter, these postulates are introduced and discussed. As it is also important to know the treatment based on the classical "laws" partly to understand scientists who learnt thermodynamics this way, partly to understand traditional thermodynamic tables and articles, classical laws are discussed in details in the Appendix.

2.1   Thermodynamic Systems: Postulate 1

Objects studied by thermodynamics are called *thermodynamic systems*. These are not simply "the part of the world under consideration"; rather physical bodies having a special property: they are in *equilibrium*. It is not straightforward to determine if a piece of matter is in equilibrium. Putting this piece of matter into a "container," it would come to rest sooner or later and its properties would not depend on time and typically not on the spatial position either. However, this temporal and spatial independence could allow for stationary flow inside the container, which cannot be considered as rest. Another approach could be to assure that, besides keeping the piece of matter within the container, no other external influence is allowed. Again, we cannot be quite sure that this system would be in equilibrium. A better formulation was that thermodynamics is valid for those bodies at rest, for which the predictions based on thermodynamic relations coincide with reality (i.e., with experimental results). This is an *a posteriori* definition; the validity of thermodynamic description can be verified after its actual application. However peculiar, this is common practice in science. We can often encounter statements that, to describe a phenomenon or solve a problem, classical mechanics is valid (or not valid). As we will see further in the book, thermodynamics offers a valid description for an astonishingly wide variety of matter and phenomena.

In the light of the above considerations, it is not surprising that the first postulate of thermodynamics declares the existence of equilibrium and states its important properties. Before announcing the postulate, let us limit the variety of the physical bodies under consideration for practical reasons. Let us restrict our attention to *simple systems*, defined as follows. *Simple systems* are pieces of matter that are macroscopically *homogeneous and isotropic*, electrically *uncharged*, chemically *inert*, large enough so that *surface effects can be neglected*, and they are *not acted on by electric, magnetic, or gravitational fields*. These restrictions largely facilitate thermodynamic description without limitations to apply it later to more complicated systems where these limitations are not obeyed. We can conclude from the above description that the postulates will be formulated for physical bodies that are homogeneous and isotropic, and their only possibility to interact with the surroundings is mechanical work exerted by volume change, plus thermal and chemical interactions. (It is important to note here that chemical interactions are still possible

even for chemically inert systems, for we consider as chemical interaction the transport of chemical species from or into the system.) Now we are in a position to formulate *Postulate 1* of thermodynamics:

> There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy U, the volume V, and the amounts of the K chemical components $n_1, n_2, \ldots, n_K$.

An important consequence of this postulate is that the equilibrium state of simple systems consisting of K chemical components can completely be described by $K + 2$ data. In other words, a simple system has $K + 2$ *degrees of freedom*. This means that if we know the amounts of substances of the K components – the *composition vector* $\boldsymbol{n} = (n_1, n_2, \ldots, n_K)$ – along with the internal energy[1] U and the volume V, we know everything from a thermodynamic point of view of the simple system; any other (thermodynamic) quantities are well defined as functions of the variables $U, V, n_1, n_2, \ldots, n_K$. This is the reason to call these variables as *state variables* or *thermodynamic coordinates*. Functions that are completely determined by these variables are called *state functions*. We shall introduce several state functions later in the book.

Another important consequence is that the state of a thermodynamic system cannot depend on the past history of the system. There exist materials (e.g., glass and steel) which do not obey this condition; their properties depend on the cooling rate, heat treatment, etc., during their manufacturing procedure, not only on the actual values of $U, V, n_1, n_2, \ldots, n_K$. If such systems are characterized on the basis of thermodynamic formalism, predicted results are usually different from experimental observations. This failure of the theoretical description can be used *a posteriori* to detect nonequilibrium states.

It is worth considering another aspect of the thermodynamic equilibrium. From the properties of mechanical equilibria we know that the equilibrium state can be different depending on different conditions. The condition of mechanical equilibrium is the minimum of energy. A rigid body at rest on a desktop shelf is in mechanical equilibrium. The same body placed lower on the top of the desk is in a "more stable" equilibrium state. We can place it even lower, say, on the floor, where its stability is further increased. This lowering could be continued down to the deepest point achievable below the earth's surface. If the body has an elongated shape, it has at least two different equilibrium states already on the desktop; a standing and a lying position. Obviously, the lying position has lower energy; thus,

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[1]The term *internal energy* refers to the energy content of the thermodynamic system which does not include either the kinetic energy or the potential energy acting on the whole system. In other words, it is the energy of the system if the entire system as a whole has zero velocity, zero angular momentum and there is no field acting on the system as a whole. It can be considered as the sum of the energy of the particles in their microscopic modes of motion without the above mentioned contributions. However, as the scale of the energy is not absolute (we can determine it only up to an additive constant), we can restrict the microscopic modes to contribute to the internal energy. Nuclear energy is usually not included in the summation to get the internal energy as it does not change in typical everyday applications of thermodynamics.

it is more stable than the standing position. Similarly, we can consider thermodynamic systems also to be in a less stable or more stable state. If the particles of a thermodynamic system can "explore" all the possible microstates, the system is in its most stable (macroscopic) state. If the particles are hindered to access all the possible microstates, the system can be "stuck" in a less stable state we call *metastable* state. These metastable states are more common in the solid state than in a gas or a liquid, where particles do not "freeze" into the solid structure. However, chemical reactions that do not occur (as for example in a mixture of H_2 and O_2 at room temperature) result in metastable equilibria even in a gas or a liquid. Until the conditions leading to the metastable state would persist, thermodynamic description can be applied; thus, Postulate 1 is also valid. It is worth noting that metastable equilibria are much more frequent within earthly conditions than stable equilibria. Thinking over that stable equilibrium on Earth would necessitate winds to stand still, waters to cease rolling, all chemical and nuclear reactions to run to completion, etc., we can easily see that the majority of earthly equilibria should be metastable. To maintain a metastable equilibrium, different *constraints* play a crucial role. We shell explore some of these constraints in the next section.

2.1.1 Constrained Systems and the Measurability of Energy via Mechanical Work

As it was mentioned before, thermodynamic systems are typically enclosed in a container. This container can also be a common everyday device. Wine is a thermodynamic body having several pleasant properties which we can keep in a barrel, a bottle, a glass, along with several other containers. In case of solid bodies, the container is usually only virtual, not a physical device. Despite this, a solid body lying on the tabletop is within well defined constraints. It is at constant pressure (equal to the pressure of the surrounding air), or at constant temperature if the temperature of the tabletop and the air are equal and would not change. If the volume of the body does not change, the constraint of constant volume also applies. This is equivalent to a real container whose walls would ensure constant temperature, pressure and volume. In thermodynamics, walls having the properties shown in Table 2.1 are usually distinguished. Systems enclosed within walls of given properties are usually named after the according constraints.

To solve thermodynamic problems, the choice of appropriate container properties could help a lot. As an example, let us consider (simple) adiabatic systems where changes of the internal energy U can easily be measured and calculated. Let us consider a simple system having internal energy U_1, volume V_1, and composition $\boldsymbol{n}_1$ in a closed adiabatic enclosure having flexible walls. (As an example, we can think of a gas inside a thermally insulating cylinder with a freely moving piston.) These constraints only allow for volume change as interaction between the system and the surroundings.

Table 2.1 Container types and enclosed systems

Container wall	Enclosed system
Completely isolating	Isolated
Diathermal[a]	Diabatic[a]
Thermally insulating	Adiabatic[a]
Rigid	Rigid
Flexible	Flexible
Permeable (to chemical components)	Open
Impermeable	Closed
Semi-permeable	Partly closed (partly open)

[a]The words *diabatic*, *adiabatic* and *diathermal* have Greek origin. The Greek noun $\delta\iota\alpha\beta\alpha\sigma\iota\varsigma$ [diabasis] designates a pass through, e.g., a river, and its derivative $\delta\iota\alpha\beta\alpha\tau\iota\kappa\sigma\varsigma$ [diabatikos] means the possibility that something can be passed through. Adding the prefix α- expressing negation, we get the adjective $\alpha\delta\iota\alpha\beta\alpha\tau\iota\kappa\sigma\varsigma$ [adiabatikos] meaning non-passability. In thermodynamic context, diabatic means the possibility for *heat* to cross the wall of the container, while adiabatic has the opposite meaning, i.e., the impossibility for heat to cross. In a similar manner, *diathermal* can be derived from the Greek word $\theta\varepsilon\rho\mu\eta$ [therme] = heat, thus it refers more directly to a heat-conducting wall. (Note that the terms diabatic and adiabatic are also used in quantum mechanics with the difference that they do not refer to heat but for a particle (e.g., electron) that can (or cannot) pass from one potential surface onto the other.) Avoid using the double-negation form nonadiabatic instead the correct form diabatic

It is easy to calculate the work associated to the volume change. Mechanical work during linear displacement can be calculated by integrating the force F parallel to the direction of the movement with respect to the displacement s:

$$W = \int_{s_1}^{s_2} F \, ds. \tag{2.1}$$

The work during volume change can be calculated considering displacements in the three independent directions of the three-dimensional space. As a result we should replace in (2.1) the one-dimensional force F by the three-dimensional *pressure P*, and the one-dimensional displacement s by the three-dimensional *volume V*. This way we get the so called *volume work*, referred to hereinafter simply as *mechanical work*. (Other types of mechanical work are related to, e.g., a rotating shaft, a lifted weight, or jet propulsion; but we will not consider them in this book.) Calculation of the volume work can easily be formulated thinking in terms of the displacement of a piston in a cylinder. The force F in (2.1) acting on the piston of surface A is PA, which is multiplied by the infinitesimal displacement ds. The product Ads yields the infinitesimal volume change dV, which should be multiplied by the pressure P to give the volume work:

$$W = -\int_{V_1}^{V_2} P \, dV. \tag{2.2}$$

Changing the position of the piston, we can transform the system having internal energy U_1, volume V_1 and composition $\boldsymbol{n}_1$ into a system having internal energy U_2, volume V_2, and composition $\boldsymbol{n}_2$. (As the system is closed, its composition cannot

change but the work associated to the volume change can change the internal energy as well.) Being adiabatic, the internal energy of the system could have changed only as a result of the mechanical work. The minus sign in (2.2) is due to the fact that work done against the pressure (compression) increases the energy of the system, while in the opposite direction (expansion) it decreases the energy of the system.

Consequently, in a closed adiabatic system the following statement (expressing the conservation of energy) is valid:

$$\Delta_1^2 U = W_{\text{adiabatic}} = - \int_{V_1}^{V_2} P \, dV. \tag{2.3}$$

In this equation, $\Delta_1^2 U$ refers to the change of energy when changing the state of the system from the state $(U_1, V_1, \boldsymbol{n}_1)$ to the state $(U_2, V_2, \boldsymbol{n}_2)$. (We know that, in this special case, $\boldsymbol{n}_1 = \boldsymbol{n}_2$) As we have seen, this energy change can easily be calculated for an adiabatic system. Let us change the state of the system by replacing the adiabatic wall by a diathermal wall. (We may do this by removing the heat insulator from the cylinder.) In this case, not only work but also heat can be exchanged with the surroundings during the change of the state. The work exchanged can be calculated again using (2.2). The heat exchanged can be calculated based on Postulate 1:

$$Q = \Delta_1^2 U - W. \tag{2.4}$$

Based on the above considerations we can conclude that the change in internal energy of thermodynamic systems is not only *determined* completely – as stated by Postulate 1 – but it can also be *measured* making use of the adiabatic enclosure. This statement can also be formulated in a general way saying that the change in internal energy (of a closed simple system) can be given as the sum of the work done on the system and the heat absorbed from the surroundings:

$$\Delta U = Q + W. \tag{2.5}$$

As already mentioned before, Postulate 1 thus expresses the conservation of energy including its change by heat transfer. It can also be seen from (2.5) that only *changes* in internal energy can be measured, not its absolute value. Similarly to mechanics, the absolute value of energy cannot be determined, thus its zero point is a matter of convention. We shall see later that this zero point will be given by fixing the scale of *enthalpy*, introduced in Sect. 8.3.

2.2   The Conditions of Equilibrium: Postulates 2, 3 and 4

Postulate 1 guarantees that the (equilibrium) state of a thermodynamic system is completely determined by fixing its relevant state variables $(U, V, \boldsymbol{n})$. It would be useful to know how these variables would change when changing conditions

resulting in a new (equilibrium) state of the system. To specify this problem, let us consider a simple system consisting of two subsystems that we shall call a *composite system*. In addition to the walls of the entire composite system, the wall dividing it into two subsystems determines what consequences eventual changes will have on the system. As it will turn out, this arrangement provides a general insight into the basic problem of thermodynamics concerning the calculation of the properties of a new equilibrium state upon changes of conditions, and actual calculations can be traced back to it.

Before discussing the problem, let us explore an important property of the state variables U, V, and $\boldsymbol{n}$. To calculate the variables characterizing the entire composite system using the data $(U^{\alpha}, V^{\alpha}, \boldsymbol{n}^{\alpha})$ and $(U^{\beta}, V^{\beta}, \boldsymbol{n}^{\beta})$ of the constituent subsystems, we have to add the energies, volumes and the amounts of components of the subsystems. In mathematical terms, these variables are *additive* over the constituent subsystems. In thermodynamics, they are called *extensive variables*. When solving the problem of finding a new equilibrium state, we shall make use of this property and calculate U, V, n_1, n_2, ..., n_K as sums of the corresponding variables of the subsystems α and β.

We can restrict ourselves to discuss the problem considering as example a closed cylinder inside which a piston divides the two subsystems (see Fig. 2.1).

The overall system (the cylinder) is rigid, impermeable and adiabatic; in one word, isolated. In the initial state, the piston is also rigid (i.e., its position is fixed in the cylinder), impermeable and adiabatic. Let U^{α}, V^{α}, $\boldsymbol{n}^{\alpha}$ and U^{β}, V^{β}, $\boldsymbol{n}^{\beta}$ denote the state variables of the subsystems in equilibrium within these conditions. This equilibrium can be changed in different ways. Releasing the fixing device of the piston (making the rigid wall flexible), it can move in one of the two possible directions which results in volume changes in both subsystems and, as a consequence, in a change of the internal energies U^{α} and U^{β}. Stripping the adiabatic coating from the fixed piston, heat can flow between the two systems, also changing the internal energies of the subsystems. Punching holes in the piston, a redistribution of chemical species can occur, resulting also in a change of the internal energy. Parts of the piston can also be changed for a semipermeable membrane allowing some chemical components to pass but not all of them. All of these changes result in
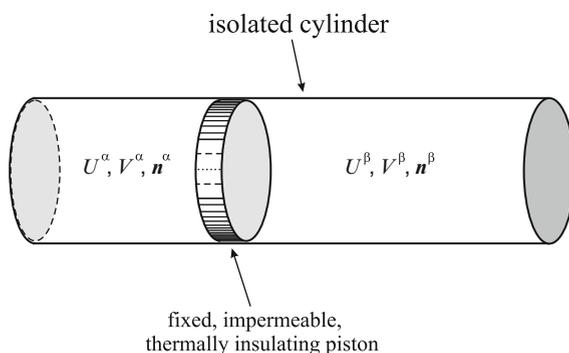

isolated cylinder

Fig. 2.1 Variables to describe a composite system consisting of two subsystems

fixed, impermeable, thermally insulating piston

changing U^{α} and U^{β}. However, as the overall system (the cylinder) is isolated, its energy cannot change during the changes described above.

From our studies in physics we might expect that an economical form of the equilibrium criterion would be in terms of an extremum principle. In mechanics it is the minimum of energy, which can be used in case of electric or magnetic interactions as well. It is easy to see that using the energy but multiplied by –1 would lead to the maximum as a criterion indicating equilibrium. The criterion of thermodynamic equilibrium can also be formulated using an extremum principle. This principle is formulated in *Postulate 2* of thermodynamics.

> There exists a function (called the entropy and denoted by S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

2.2.1 Properties of the Entropy Function

Let us examine the meaning of Postulate 2 concerning the properties of the entropy function. Its first important property is that it is defined only for equilibrium states. If there is no equilibrium, there exists no entropy function. The maximum principle can be interpreted the following way. In the absence of a given constraint, there could be many states of the system imagined, all of which could be realized keeping the constraint. If, for example, we consider states that could be realized by moving the impermeable adiabatic piston, there are as many possibilities as different (fixed) positions of the piston. (The position of the piston is *in principle* a continuous variable, so it could be fixed in an infinity of positions. *In practice*, we can only realize finite displacements, but the number of these finite displacements is also very large.) At every position, the values of $U, V, n_1, n_2, \ldots, n_K$ are unique, and they determine the unique value of the entropy function. Releasing the constraint (removing the fixing device of the piston), the equilibrium state will be the one from the manifold mentioned above which has the maximum of entropy.

Postulate 2 assigns valuable properties to the entropy function. If we know the form of this function and an initial set of the state variables in a given (equilibrium) state, we can calculate the state variables in any other state. Consequently, the entropy function contains all information of the system from a thermodynamic point of view. That's the reason that the equation

$$S = S(U, V, n_1, n_2, \ldots, n_K) \tag{2.6}$$

is called a *fundamental equation*. It is worth to note that the actual form of the entropy function is different from one system to another; an entropy function of wider validity is rare to find. For practical systems (materials), there cannot be usually given an entropy function in a closed form. Instead, a table of the entropy as a function of different values of its variables is given for many systems.

Further properties of the entropy function are stated by two other postulates. *Postulate 3* states the following:

> The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a strictly increasing function of the internal energy.

Several properties of the entropy function follow from Postulate 3. Its *additivity* means that it is an *extensive property*. All the variables of the entropy function are also extensive. Therefore, if we have to increase a part of the system λ-fold to get the entire volume λV of the system, then its other variables (U, n_1, n_2, ..., n_K) as well as the value of the entropy function will also increase λ-fold. Putting this in a mathematical form, we get

$$S(\lambda U, \lambda V, \lambda n_1, \lambda n_2, \ldots, \lambda n_K) = \lambda S(U, V, n_1, n_2, \ldots, n_K). \tag{2.7}$$

In mathematics, functions of this property are said to be *homogeneous first order functions* which have other special properties we shall make use of later on. There exists a particular value of λ which has special importance in chemical thermodynamics. Let us denote the sum of the amounts of components n_1, n_2, ..., n_K constituting the system by n and call it the *total amount* of the system. Any extensive quantity divided by n will be called the respective *molar quantity* of the system. These properties will be denoted by the lower case Latin letters corresponding to the upper case symbols denoting the extensive quantity. An exception is the symbol of the amount of a component n_i which is already a lower case letter; its molar value is denoted by x_i and called the *mole fraction* of the i-th component:

$$x_i = \frac{n_i}{\sum\limits_{j=1}^{K} n_j} = \frac{n_i}{n}. \tag{2.8}$$

Writing (2.7) using the factor $\lambda = 1/n$ we get the transformed function

$$S(U/n, V/n, n_1/n, n_2/n, \ldots, n_k/n) = S(U, V, n_1, n_2, \ldots, n_k)/n \tag{2.9}$$

that can be considered as the definition of $s(u, v, x_1, x_2, \ldots, x_K)$, the *molar entropy*. However, its variables ($u, v, x_1, x_2, \ldots, x_K$) are no more independent as the relation

$$\sum_{i=1}^{K} x_i = 1 \tag{2.10}$$

between the mole fractions x_i holds, following from the definition (2.8). Consequently, the number of degrees of freedom of the molar entropy function is less by one, i.e., only $K + 1$. This is in accordance with the fact that – knowing only the molar value of an extensive quantity – we do not know the extent of the system; it should be given additionally, using the missing degree of freedom. For this reason, molar quantities are not extensive, which is reflected by their name; they are called

intensive variables or *intensive quantities*. Coming back to the intensive entropy function; the equation specifying this function contains *all information* (except for the extent) of the thermodynamic system. Therefore, the equation

$$s = s(u, v, x_1, x_2, \ldots, x_K) \tag{2.11}$$

is called the *entropy-based intensive fundamental equation*.

Applying (2.7) for functions whose value is a molar quantity, we get the result that they remain unchanged when multiplying each of their extensive variables by a factor λ:

$$s(\lambda U, \lambda V, \lambda n_1, \lambda n_2, \ldots, \lambda n_K) = s(U, V, n_1, n_2, \ldots, n_K). \tag{2.12}$$

We can put a factor λ^0 in front of the left-hand side function. This is the reason to call the functions having the above property as *homogeneous zero order functions*.

Postulate 3 states that entropy is a strictly increasing function of energy, differentiable and continuous; thus it can also be inverted to give the internal energy function

$$U = U(S, V, n_1, n_2, \ldots, n_K). \tag{2.13}$$

This function can of course also be inverted to provide the entropy function again. We can conclude that specifying the above energy function is equivalent to specifying the entropy function $S(U, V, n_1, n_2, \ldots, n_K)$ from which we know that its knowledge makes it possible to describe all equilibrium states of a system. Consequently, (2.13) is also a fundamental equation that we call the *energy-based fundamental equation* to distinguish it from the *entropy-based fundamental equation* given in (2.6).

If entropy is a strictly increasing function of energy, it follows from this property that its inverse function, energy is also a strictly increasing function of the entropy. We can formulate these conditions using partial derivatives of the functions:

$$\left(\frac{\partial S}{\partial U}\right)_{V,\boldsymbol{n}} > 0 \quad \text{and} \quad \left(\frac{\partial U}{\partial S}\right)_{V,\boldsymbol{n}} = \frac{1}{\left(\frac{\partial S}{\partial U}\right)_{V,\boldsymbol{n}}} > 0. \tag{2.14}$$

As we shall see later, the derivative $\left(\frac{\partial U}{\partial S}\right)_{V,\boldsymbol{n}}$ can be identified as the temperature.

Keeping this in mind we can conclude that Postulate 3 also specifies that temperature can only be positive. *Postulate 4* – the last one – is also related to this derivative:

The entropy of any system is non-negative and vanishes in the state for which $\left(\frac{\partial U}{\partial S}\right)_{V,\boldsymbol{n}} = 0$ (that is, at zero temperature).

(This condition is not always fulfilled in practice, as an equilibrium state at zero temperature is often not possible to reach. We shall discuss further this topic in Chap. 10.) It is worth noting here that the zero of the entropy scale is completely determined, similarly to that of the volume V or of the amount of substances

n_1, n_2, ..., n_K. Internal energy is the only quantity mentioned whose zero point is not determined, but it has this property already in mechanics. Consequently, the zero point of energy is arbitrarily fixed according to some convention. The state of a system where the energy is zero is usually called a *reference state*.

2.2.2 Properties of the Differential Fundamental Equation

The differential form of a fundamental equation is called the *differential fundamental equation*. Let us differentiate both sides of (2.13). This results in the *total differential* dU on the left side and its expression as a function of the infinitesimal increments of the variables S, V, n_1, n_2, ..., n_K:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,\boldsymbol{n}} dS + \left(\frac{\partial U}{\partial V}\right)_{S,\boldsymbol{n}} dV + \sum_{i=1}^{K} \left(\frac{\partial U}{\partial n_i}\right)_{S,V,\,n_{j\neq i}} dn_i. \qquad (2.15)$$

Variables of the function different from the one with respect of which we differentiate it are shown as subscripts of the parenthesis enclosing the derivative. The reason is that we can see from this notation what the variables of the function we differentiate are, without additionally specifying them. It is important to note that the variables written as subscripts are constant only from the point of view of the differentiation, but of course they are the variables of the partial derivative as well, so they can change. In the subscripts, we only show the composition vector $\boldsymbol{n} = (n_1, n_2, ..., n_K)$ for the sake of brevity. The symbol $n_{j\neq i}$ in the subscript of the derivative with respect to n_i expresses that the variable n_i should not be listed among the "constant" variables during derivation. We shall keep using this notation throughout the book.

Let us examine the meaning of terms on the right side of the equation. Each one contributes to the increment of the energy; thus, they must have energy dimension. The first term

$$(dU)_{V,\boldsymbol{n}} = \left(\frac{\partial U}{\partial S}\right)_{V,\boldsymbol{n}} dS \qquad (2.16)$$

is the partial differential of the energy if volume and composition are constant; thus, it is in a closed, rigid but diathermal system. In simple systems, this change is only possible via heat transfer, so $(dU)_{V,\boldsymbol{n}}$ is the *heat absorbed from the surroundings*. In a similar way, the term

$$(dU)_{S,\boldsymbol{n}} = \left(\frac{\partial U}{\partial V}\right)_{S,\boldsymbol{n}} dV \qquad (2.17)$$

is the infinitesimal energy change as a result of volume change; i.e., the volume work – or mechanical work in simple systems. At constant entropy and volume, the contribution to the change of energy is proportional to dn_i for the change of each of

the components. This energy contribution associated to the change of composition is called *chemical work* or *chemical energy*. An interesting property of this energy increment is that it should be calculated separately for all the components and summed to give the chemical work:

$$(\mathrm{d}U)_{S,V} = \sum_{i=1}^{K} \left(\frac{\partial U}{\partial n_i} \right)_{S,V,\, n_{j \neq i}} \mathrm{d}n_i. \tag{2.18}$$

Let us examine the partial derivatives of the above three equations. It is readily seen that all of them are quotients resulting from the division of two extensive quantities. They are energies relative to entropy, volume, and amount of substance; consequently, they are intensive quantities similar to molar quantities introduced before. Comparing (2.2) and (2.17) we can see that the partial derivative of the energy function $U(S, V, \boldsymbol{n})$ with respect to volume is the negative pressure, $-P$:

$$\left(\frac{\partial U}{\partial V} \right)_{S,\boldsymbol{n}} \equiv -P. \tag{2.19}$$

The partial derivative of the energy function $U(S, V, \boldsymbol{n})$ with respect to entropy is an intensive quantity which, multiplied by the increment of the entropy, gives the heat transferred to the (equilibrium) system. Later on we shall see that this derivative is the *temperature*, as it has all the properties we expect from temperature.

$$\left(\frac{\partial U}{\partial S} \right)_{V,\boldsymbol{n}} \equiv T. \tag{2.20}$$

One of its expected properties we already see that it is an intensive quantity.

Up to now, all we now about the partial derivative of the energy function $U(S, V, \boldsymbol{n})$ with respect to the amount of each chemical component is only that it is related to the chemical energy of the corresponding species. Let us call this quantity the *chemical potential of the i-th species*, denote it by μ_i and let us postpone to find its properties.

$$\left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_{j \neq i}} \equiv \mu_i. \tag{2.21}$$

Making use of the identification and notation of the partial derivatives in (2.19)–(2.21), the energy-based differential fundamental equation can be written in a formally simpler way:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1}^{K} \mu_i \mathrm{d}n_i. \tag{2.22}$$

Partial derivatives in (2.15) depend on the same variables as the function $U(S, V, \boldsymbol{n})$ itself. Consequently, all the intensive quantities in (2.22) are also functions of the variables S, V and $\boldsymbol{n}$:

$$T = T(S, V, \boldsymbol{n}), \tag{2.23}$$

$$P = P(S, V, \boldsymbol{n}), \tag{2.24}$$

$$\mu_i = \mu_i(S, V, \boldsymbol{n}). \tag{2.25}$$

T, P and all the μ_i-s are intensive quantities; therefore, the functions given by (2.23)–(2.25) are homogeneous zero order functions of their extensive variables. Equations (2.23)–(2.25) have a distinct name; they are called *equations of state*.

We can easily "rearrange" (2.22) to get the differential form of the entropy-based fundamental equation (2.6):

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum_{i=1}^{K} \frac{\mu_i}{T}dn_i. \tag{2.26}$$

It is worth noting that the intensive quantities emerging in this entropy-based differential fundamental equation represent functions that are different from those in (2.22); even their variables are different. These functions determining the entropy-based intensive quantities are called the *entropy-based equations of state*:

$$\frac{1}{T} = \frac{1}{T}(U, \ V, \ \boldsymbol{n}), \tag{2.27}$$

$$\frac{P}{T} = \frac{P}{T}(U, \ V, \ \boldsymbol{n}), \tag{2.28}$$

$$\frac{\mu_i}{T} = \frac{\mu_i}{T}(U, \ V, \ \boldsymbol{n}). \tag{2.29}$$

2.2.3   The Scale of Entropy and Temperature

From previous studies in mechanics and chemistry, the scales of internal energy, volume, amount of substance and pressure are already known. The scale of the chemical potential is easy to get from the defining equation (2.21); as energy related to the amount of chemical components, it is measured in J/mol units, and its zero point corresponds to the arbitrarily chosen zero of the energy.

The definition of entropy and temperature are closely related and so are their choice of scale and units as well. To measure temperature, several empirical scales have been used already prior to the development of thermodynamics, mostly based on the thermal expansion of liquids. Two of these scales survived and are still widely used in everyday life. The Celsius scale[2] is commonly used in Europe and most part

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[2]This scale has been suggested by the Swedish astronomer Anders Celsius (1701–1744).

of Asia. Its unit is the degree centigrade (or degree Celsius) denoted as °C. Its zero point is the freezing point and 100°C is the boiling point of pure water at atmospheric pressure. The Fahrenheit scale[3] is commonly used in North America and many other countries. Its unit is the degree Fahrenheit denoted as °F. Its zero point is the freezing point of saturated aqueous salt (NaCl) solution and 100°F is the temperature that can be measured in the rectum of a cow. (Though there exist different versions to explain the choice of the two fixed scale points.) To get the Celsius temperature, 32 should be subtracted from the Fahrenheit temperature and the result should be divided by 1.8. Thus, the freezing point of water is 32°F, its boiling point is 212°F. Common room temperature is around 70°F compared to approximately 21°C, and normal human body temperature is about 98°F compared to 36.7°C.

As we can see, none of these scales is in accordance with the postulates of thermodynamics. Postulate 3 requires a nonnegative temperature and Postulate 4 fixes its zero point. This latter means that we can only fix one single temperature to completely fix the scale. The SI unit of temperature has been fixed using the former Kelvin scale.[4] According to this, the triple point of water (where liquid water, water vapor and water ice are in equilibrium) is exactly 273.16 K; thus, the division of the scale is the same as that of the Celsius scale. The unit of the Kelvin scale is denoted simply by K – without the "degree" sign °. The temperature of the triple point of water on the Celsius scale is 0.01°C; therefore, we get the temperature in SI units by adding 273.15 to the value of temperature given in °C units:

$$T/K = t/°C + 273.15. \tag{2.30}$$

The unit of entropy should be determined taking into account the units of energy and temperature, for we know that their product TS should be energy. From statistical thermodynamics (Chap. 10) we know that entropy should be a dimensionless number. Consequently, energy and temperature should have the same dimension; they only could differ in their actual scale. The ratio of the units of these scales, i.e., that of joule and Kelvin, is $k_B = 1.380\,6504 \times 10^{-23}$ JK^{-1}, and it is called the *Boltzmann constant*. It follows from this result that entropy should also have the unit J/K. However, as temperature is intensive and entropy is extensive, we should multiply the Boltzmann constant by the number of particles to get the extensive unit of entropy. The number of particles is dimensionless, so it would not change the unit if we used the number of particles N to specify the extent of the system. In chemistry, it is more common to use the amount of substance n. The dimension of entropy is not changed by this, as the amount of substance differs only by a "numerosity factor" from the number of particles; this is expressed by the *Avogadro constant* $N_A = 6.022\,141\,79 \times 10^{23}$ mol^{-1}. Thus, expressing the proportionality of temperature units to the energy units related to one mole of particles results in $R = k_B\,N_A = 8.314\,472$ JK^{-1} mol^{-1}, which

[3]This scale has been suggested by the German physicist Daniel Gabriel Fahrenheit (1686–1736).
[4]William Thomson (1824–1907) – after his ennoblement by Queen Victoria, Baron Kelvin of Largs or Lord Kelvin – was a Scottish physicist. He had an important contribution to the establishment of the science of thermodynamics.

is the ratio of the temperature to the molar entropy. Following from this result, $k_B T$ is energy per particle and RT is energy per mole.

2.2.4   Euler Relation, Gibbs–Duhem Equation and Equations of State

It is worth examining the relation between the equations (2.23)–(2.25) and the differential fundamental equation (2.15). Each equation of state only specifies one of the derivatives in the fundamental equation. To construct the complete fundamental equation, we need $K + 2$ derivatives. These derivatives – or equations of state – are mostly determined by experimental measurements.

It is easy to show that the equations of state are not independent of each other, based on the properties of homogeneous first order functions. If $f(x_1, x_2, \ldots, x_n)$ is a homogeneous first order function of the variables $x_1, x_2, \ldots, x_n$, the following Euler[5] theorem holds:

$$f(x_1, x_2, ..., x_n) = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i} \right)_{x_{j \neq i}} x_i. \tag{2.31}$$

Let us apply this theorem to the function $U(S, V, n_1, n_2, \ldots, n_K)$ which is homogeneous first order with respect to all its variables:

$$U = \left(\frac{\partial U}{\partial S} \right)_{V, \boldsymbol{n}} S + \left(\frac{\partial U}{\partial V} \right)_{S, \boldsymbol{n}} V + \sum_{i=1}^{K} \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}} n_i. \tag{2.32}$$

Substituting the partial derivatives identified before we get:

$$U = TS - PV + \sum_{i=1}^{K} \mu_i n_i. \tag{2.33}$$

This equation is usually called the (energy-based) *Euler relation*.

Let us write the differential form of this equation by explicitly writing the differentials of the products in each term on the right side:

$$dU = T dS + S dT - P dV - V dP + \sum_{i=1}^{K} \mu_i dn_i + \sum_{i=1}^{K} n_i d\mu_i. \tag{2.34}$$

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[5]Leonhard Euler (1707–1783) was a Swiss mathematician and physicist working mainly in Saint Petersburg (Russia). He was the most prolific and important scientist of the eighteenth century. His results concerning homogeneous functions are among his "humble" achievements compared to his other theorems.

Subtract from the above equation the following equation – identical to (2.22):

$$dU = TdS - PdV + \sum_{i=1}^{K} \mu_i \, dn_i. \tag{2.35}$$

The result is zero on the left side, and three terms only on the right side containing products of extensive quantities multiplied by increments of intensive quantities. By switching sides, we obtain the usual form of the *Gibbs–Duhem equation*:[6]

$$SdT - VdP + \sum_{i=1}^{K} n_i \, d\mu_i = 0. \tag{2.36}$$

Thus, the intensive variables T, P and $\mu_1, \mu_2, \ldots, \mu_K$ are not independent of each other as the constraint prescribed by the Gibbs–Duhem equation holds. This is in accordance with the observation we made of the intensive characterization of thermodynamic systems; the number of degrees of freedom becomes $K + 1$ instead of $K + 2$. In addition, it is also a useful quantitative relation which enables to calculate the missing equation of state if we already know $K + 1$ of them.

We can also write the *entropy-based Euler relation* from (2.6):

$$S = \frac{1}{T} U + \frac{P}{T} V - \sum_{i=1}^{K} \frac{\mu_i}{T} n_i, \tag{2.37}$$

from which the *entropy-based Gibbs–Duhem equation* follows immediately:

$$U d \left(\frac{1}{T} \right) + V d \left(\frac{P}{T} \right) - \sum_{i=1}^{K} n_i \, d \left(\frac{\mu_i}{T} \right) = 0. \tag{2.38}$$

2.2.5   The Fundamental Equation of an Ideal Gas

Based on the previous sections, we can construct the fundamental equation from equations of state determined by experimental measurements. In this section, we will demonstrate this procedure on the example of an *ideal gas*, widely used as an approximation to the behaviour of gaseous systems. The ideal gas is an idealized system for which we suppose the strict validity of approximate empirical relations obtained by experimental studies of low pressure and high temperature gases. It has

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[6]Josiah Willard Gibbs (1839–1903) was an American physicist. He was one of the first scientists in the United States who had all of his university studies in the US. His important contributions to thermodynamics included the general theory of phase equilibria and surface equilibria. His formal foundations of statistical thermodynamics are still in use.

been demonstrated that the strict validity of the Boyle–Mariotte, Gay-Lussac, and Avogadro laws known since the seventeenth and eighteenth century require that molecules constituting the gas should behave *independently of each other*. In other words, there should not be any interaction between them, and their size should be small enough so that the summed volume of the particles themselves be negligible compared to the volume of the gas.

One of the relevant equations of state is usually given in the peculiar form what most of us had seen during our studies:

$$PV = nRT. \tag{2.39}$$

This is the so-called *mechanical equation of state* that can be used also to calculate volume work. Another equation of state may also be familiar from previous studies. This is called the *thermal equation of state*:

$$U = \frac{3}{2} nRT. \tag{2.40}$$

(This particular form is valid only for a *monatomic gas*. If the molecules of the ideal gas contain more than one atom, the constant factor is greater than 3/2.) First of all we should decide of the above equations of state, which fundamental equation they are related to. The variables of the energy function given by the energy-based fundamental equation (2.13) are S, V and $\boldsymbol{n}$. (As the equations of state above refer to a one-component ideal gas, we shall replace the composition vector $\boldsymbol{n}$ by the scalar n specifying the amount of substance of this single component.) Apart from the intensive variable T in (2.40) we can find the internal energy U, which is the variable of the entropy function. In (2.39), there are two intensive variables P and T. Consequently, these two equations of state should belong to the entropy-based fundamental equation, so it is worth of writing them in the form of the entropy-based intensive quantities:

$$\frac{P}{T} = R \frac{n}{V}, \tag{2.41}$$

$$\frac{1}{T} = \frac{3}{2} R \frac{n}{U}. \tag{2.42}$$

We can note that P/T depends only on V and n, not on U, and that $1/T$ depends only on U and n, not on V. In both equations, n appears in the numerator of a fraction. Realizing that the division by n results in molar values, we can replace these fractions having n in the numerator by the reciprocal of the corresponding molar values:

$$\frac{P}{T} = \frac{R}{v}, \tag{2.43}$$

$$\frac{1}{T} = \frac{3}{2} \frac{R}{u}. \tag{2.44}$$

With the help of these equations of state, we can start to construct the fundamental equation. If we need the extensive fundamental equation, we also need the third equation of state (for the pure – one-component – ideal gas) specifying μ/T. Obviously, this can be calculated using the Gibbs–Duhem equation (2.38). Dividing it by the amount of substance n and rearranging, we get

$$\mathrm{d}\left(\frac{\mu}{T}\right) = u\,\mathrm{d}\left(\frac{1}{T}\right) + v\,\mathrm{d}\left(\frac{P}{T}\right). \tag{2.45}$$

Applying the chain rule, we can substitute the derivatives $\mathrm{d}\left(\frac{1}{T}\right) = \frac{\mathrm{d}\left(\frac{1}{T}\right)}{\mathrm{d}u}\mathrm{d}u$ and $\mathrm{d}\left(\frac{P}{T}\right) = \frac{\mathrm{d}\left(\frac{P}{T}\right)}{\mathrm{d}v}\mathrm{d}v$ on the right side. The resulting derivatives can be calculated by differentiating the functions specified in (2.44) and (2.43):

$$\mathrm{d}\left(\frac{\mu}{T}\right) = u\left(-\frac{3}{2}\frac{R}{u^2}\right)\mathrm{d}u + v\left(-\frac{R}{v^2}\right)\mathrm{d}v = -\frac{3}{2}\frac{R}{u}\mathrm{d}u - \frac{R}{v}\mathrm{d}v. \tag{2.46}$$

Integrating this function we can get the missing equation of state determining the function μ/T. The first term is a function of only u, the second term is a function of only v, and thus we can integrate the first term only with respect to u and the second one only with respect to v:

$$\int_{u_0,v_0}^{u_1,v_1} \mathrm{d}\left(\frac{\mu}{T}\right) = -\frac{3}{2}R\int_{u_0,v_0}^{u_1,v_0}\frac{1}{u}\mathrm{d}u - R\int_{u_1,v_0}^{u_1,v_1}\frac{1}{v}\mathrm{d}v. \tag{2.47}$$

Upon integration we get the following equation of state:

$$\frac{\mu}{T} = \left(\frac{\mu}{T}\right)_0 - \frac{3}{2}R\ln\frac{u}{u_0} - R\ln\frac{v}{v_0}. \tag{2.48}$$

Here, the integration constant $\left(\frac{\mu}{T}\right)_0 = \left(\frac{\mu}{T}\right)(u_0, v_0)$ is the value of the function $\frac{\mu}{T}$ at the reference state of molar energy u_0 and molar volume v_0.

Having all the three equations of state, we can substitute the appropriate derivatives into the Euler relation (2.37) to get the fundamental equation:

$$S = \frac{3}{2}Rn + Rn - n\left(\frac{\mu}{T}\right)_0 + nR\left[\frac{3}{2}\ln\frac{u}{u_0} + \ln\frac{v}{v_0}\right]. \tag{2.49}$$

To write this equation in terms of extensive variables, let us make use of the identities $\frac{u}{u_0} = \frac{U}{U_0}\frac{n_0}{n}$ and $\frac{v}{v_0} = \frac{V}{V_0}\frac{n_0}{n}$, rearrange terms by factoring out nR and rewrite sums of logarithms as logarithm of products to have a compact form:

$$S = \frac{5}{2}Rn - n\left(\frac{\mu}{T}\right)_0 + nR \ln \left[\left(\frac{U}{U_0}\right)^{\frac{3}{2}} \left(\frac{V}{V_0}\right) \left(\frac{n}{n_0}\right)^{-\frac{5}{2}} \right]. \tag{2.50}$$

As this equation specifies the S function, it is more practical to include the value of S itself in the reference state, instead of the chemical potential μ. Let us express this reference value as

$$S_0 = S_0(U_0, V_0, n_0) = \frac{5}{2}Rn_0 - n_0\left(\frac{\mu}{T}\right)_0. \tag{2.51}$$

Introducing this constant into the above expression of S, we obtain the compact form of the fundamental equation of an ideal gas:

$$S = \frac{n}{n_0}S_0 + nR \ln \left[\left(\frac{U}{U_0}\right)^{\frac{3}{2}} \left(\frac{V}{V_0}\right) \left(\frac{n}{n_0}\right)^{-\frac{5}{2}} \right]. \tag{2.52}$$

Now we can use this function to calculate equilibria upon any change of state of an ideal gas.

The procedure to get the intensive fundamental equation is less complicated. Having the extensive equation, of course we could simply divide each extensive variable (U, V and n) by n, and the reference values by n_0. However, it is worth constructing it directly from the two known equations of state (2.44) and (2.43). The intensive fundamental equation only consists of two terms instead of three, for the molar entropy of the pure substance does not depend on its amount:

$$ds = \frac{1}{T}du + \frac{P}{T}dv. \tag{2.53}$$

Substituting the appropriate derivatives after applying the chain rule (as before), we can easily integrate the differential equation thus obtained and get the intensive fundamental equation of an ideal gas:

$$s = s_0 + \frac{3}{2}R \ln u + R \ln v, \tag{2.54}$$

where the constant is the molar entropy in the reference state (u_0, v_0):

$$s_0 = \frac{3}{2}R \ln \frac{1}{u_0} + R \ln \frac{1}{v_0}. \tag{2.55}$$

It is worth noting that neither the extensive entropy of (2.52), nor the above molar entropy function does not fulfill the requirement stated in Postulate 4 of thermodynamics; the value of the function at $T = 0$ is not zero. We should not be surprised as we know that the ideal gas is a good approximation at high temperatures and it cannot be applied at very law temperatures at all. We can

emphasize also at this point that the coefficient $3/2\,R$ is valid only for *monatomic gases*. If the molecule has a more complex structure, this coefficient is greater. Later in the text we shall see that it is identical to the heat capacity at constant volume which of course depends on the structure of the molecule. (Cf. Chap. 10.)

2.2.6   The Fundamental Equation of an Ideal van der Waals Fluid

The equation of state of the ideal gas is not only used for approximate calculations in the case of *real gases* within the range of applicability, but many other equations of state in use are based on modifications of the ideal gas equation. Historically, one of the first equations aiming a greater generality was introduced by van der Waals[7] in 1873. Though the *van der Waals equation of state* does not provide a satisfactory description of the behavior of real gases, its underlying principles of including the non-ideal behavior are simple and rather pictorial. They also explain the vapor-liquid transition in a simple way. This is the reason we can find this equation of state along with its rationale in many textbooks. As an example for an alternative of the ideal gas equation, we shall also discuss this equation of state and the resulting fundamental equation. The word *fluid* in the title of the section – a comprehensive designation of liquids and gases – reflects the fact that this description is also valid for liquids, though in a restricted sense.

Let us write the mechanical equation of state in a form suggested by van der Waals:

$$P = \frac{RT}{v - b} - \frac{a}{v^2}. \tag{2.56}$$

There are two differences from that of the ideal gas equation (2.39). In the denominator of the first term, b is subtracted from the molar volume v, and there is an extra term $-a/v^2$. J.D. van der Waals argued that the two corrections reflect the difference between the ideal gas model and real gases. The equation of state (2.39) of the ideal gas can be deduced from a model where molecules are considered as point masses with no finite size and there are no interactions (attractive or repulsive) between them, only elastic collisions. This idealized model is easy to correct in a way to reflect the properties of real gases.

Firstly, the size of molecules is finite, though tiny. This is reflected in the term b which represents the volume excluded by one mole of the nonzero-size molecules, thus not available as free volume. Secondly, molecules attract each other. This

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[7]Johannes Diderik van der Waals (1837–1923), the Dutch physicist conceived the first equation of state describing both gases and liquids, later named after him. He also interpreted molecular interactions playing a role in the underlying principles, later called van der Waals forces.

attraction is compensated for in the bulk of the gas (far from the walls of the container) as each molecule is attracted isotropically; they do not "feel" any directional force. However, in the surface layer near the walls, forces acting from the interior of the gas are no more compensated for from the direction of the wall, as there are no gas molecules there. This results in a net force towards the interior of the gas thus decreasing the pressure exercised by the molecules hitting the wall. The force acted on a surface molecule is proportional to the density of molecules in the bulk, which is proportional to the reciprocal molar volume. The force is also proportional to the number of molecules in a surface position which is also proportional to the density, i.e., the reciprocal volume. As a result, the decrease of the pressure is proportional to the square of the reciprocal volume which gives rise to the term $-a/v^2$. Arguing somewhat differently, the force acting on the surface molecules, decreasing the pressure, is proportional to the number of *pairs* of molecules, as the attractive force is acting between two molecules adjacent to the surface. The number of pairs is proportional to the square of density, i.e., the square of the reciprocal molar volume. Before proceeding, we can rewrite (2.56) to express the entropy-based derivative P/T:

$$\frac{P}{T} = \frac{R}{v-b} - \frac{a}{v^2}\frac{1}{T}. \tag{2.57}$$

To construct the fundamental equation – similarly as in Sect. 2.2.5 for the ideal gas – we also need the thermal equation of state. As a first idea, we could use the same equation (2.42) as for the ideal gas. However, it is not a valid choice as it would not satisfy the properties required by the relations of thermodynamics. We have to alter the expression (2.42) of the derivative $1/T$ as a function of the molar energy u and the molar volume v to impose the thermodynamic consistency condition between the two equations of state. We know that $s(u, v)$ is a state function, thus its mixed second partial derivatives should be equal, irrespective of the order of derivation (A1.8):

$$\frac{\partial}{\partial v}\left(\frac{\partial s}{\partial u}\right)_v = \frac{\partial}{\partial u}\left(\frac{\partial s}{\partial v}\right)_u. \tag{2.58}$$

Substituting the first derivatives we get:

$$\frac{\partial}{\partial v}\left(\frac{1}{T}\right) = \frac{\partial}{\partial u}\left(\frac{P}{T}\right). \tag{2.59}$$

Knowing the function P/T, we can calculate the right-hand side as

$$\frac{\partial}{\partial u}\left(\frac{P}{T}\right) = \frac{\partial}{\partial u}\left(\frac{R}{v-b} - \frac{a}{v^2}\frac{1}{T}\right) = -\frac{a}{v^2}\frac{\partial}{\partial u}\left(\frac{1}{T}\right), \tag{2.60}$$

and rewrite the condition in the form

$$\frac{\partial}{\partial v}\left(\frac{1}{T}\right) = -\frac{a}{v^2}\frac{\partial}{\partial u}\left(\frac{1}{T}\right). \tag{2.61}$$

Let us multiply the numerator and denominator on the right side by $1/a$ and put the constant $1/a$ into the variable of the derivation:

$$\frac{\partial(1/T)}{\partial v} = -\frac{1}{v^2}\frac{\partial(1/T)}{\partial(u/a)}. \tag{2.62}$$

Using the chain rule (A1.19), the derivative on the left side can be written as

$$\frac{\partial(1/T)}{\partial v} = \frac{\partial(1/T)}{\partial(1/v)}\frac{d(1/v)}{d(v)} = -\frac{1}{v^2}\frac{\partial(1/T)}{\partial(1/v)}. \tag{2.63}$$

Comparing the two equations, the relation imposed is

$$\frac{\partial(1/T)}{\partial(1/v)} = \frac{\partial(1/T)}{\partial(u/a)}, \tag{2.64}$$

meaning that the searched-for function $1/T$ should have the property that its derivative with respect to the two variables $1/v$ and u/a should be equal. This condition is satisfied if $1/T$ depends only on $(1/v + u/a)$. Let us change (2.42) accordingly, replacing also the factor $3/2$ – applicable only for monatomic gases – by a general factor c:

$$\frac{1}{T} = \frac{cR}{u + a/v}. \tag{2.65}$$

The above equation has been obtained by adapting the equation of state of an ideal gas, thus we can call the system for which this equation along with (2.56) holds, the *ideal van der Waals gas*. Before proceeding, it is worth while to express (2.56) as an explicit function of u and v by substitution of the above expression of $1/T$:

$$\frac{P}{T} = \frac{R}{v - b} - \frac{acR}{uv^2 + av}. \tag{2.66}$$

Having the above equations for the two derivatives of s we can write the total differential

$$ds = \frac{1}{T}du + \frac{P}{T}dv. \tag{2.67}$$

Upon integration we get the intensive fundamental equation:

$$s = s_0 + R\ln\frac{(v - b)(u + a/v)^c}{(v_0 - b)(u_0 + a/v_0)^c}. \tag{2.68}$$

Multiplying this equation by the amount of substance n we obtain the extensive fundamental equation

$$S = S_0 + nR \ln \frac{(v - b)(u + a/v)^c}{(v_0 - b)(u_0 + a/v_0)^c}, \tag{2.69}$$

where $S_0 = n s_0$.

Typical values of the constant a are between 0.003 and 1 Pam^6, that of b between 2.5×10^{-5} and 10×10^{-5} m^3, while that of c varies between the minimal 3/2 and about 4, around room temperature. If the equation is used for actual calculations, the constants are determined from experimental data so that the equations of state would best fit the measured set of data P, V and T.

Problems

1. The energy of a particular gaseous system was found to obey the following equation under certain conditions:

$$U = 5PV + 10 \text{ J}. \tag{2.70}$$

The system is conducted through a cycle ABCD (represented by the continuous straight lines in the figure), starting and ending at point A. Calculate

(a) The internal energies at points A, B, C, and D
(b) Heat and work for all four processes (A→B, B→C, C→D, and D→A) of the cycle
(c) Heat and work, when the system undergoes the process from C to B along the dashed hyperbola h that is described by the following equation:

$$P = \frac{0.4 \text{ kPa}}{(V/\text{dm}^3) - 4}; \tag{2.71}$$

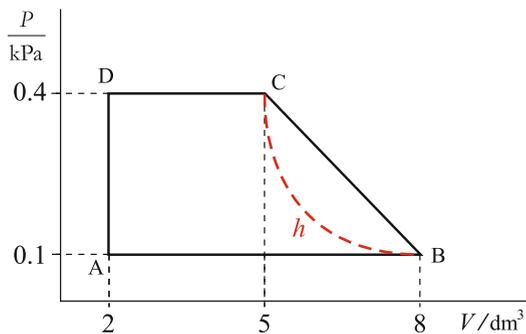(d) Find a parametric equation of an adiabatic process in the P–V plane.

Fig. 2.2 Processes of problem 1 shown in the P–V plane

Solution: (a) The energy in the four states can be calculated by using the formula of U provided in (2.70), reading the values of P and V from the figure: $U_A = 11$ J; $U_B = 14$ J; $U_C = 20$ J; $U_D = 14$ J.

Changes of internal energy for the individual process can be obtained by simple subtractions: $\Delta U_A^B = 3$ J; $\Delta U_B^C = 6$ J; $\Delta U_C^D = -6$ J; $\Delta U_D^A = -3$ J.

(b) In process D→A, the total change of internal energy occurs as heat, for – as it can be seen in the figure – dV is zero along the line DA, thus the work is zero as well. However, in processes A→B and C→D, the volume does change, and the work can be calculated by the definite integral

$$W = -\int_{\text{initial state}}^{\text{final state}} P dV.$$

Note that P is constant during both processes.

In process B→C, we have to find an equation of the pressure change in order to calculate the work done:

$$W_{BC} = \int_{8\text{dm}^3}^{5\text{dm}^3} \left(0.1 \frac{\text{kPa}}{\text{dm}^3} V - 0.9 \text{ kPa} \right) dV = 4.65 \text{ J}$$

(c) We can calculate the work in a similar way for the process from C to B along the hyperbola h, using the appropriate pressure change:

$$W_{CB,h} = \int_{5\text{dm}^3}^{8\text{dm}^3} -\frac{0.4\text{kPa}}{V/(1 \text{ dm}^3) - 4} dV = -3.42 \text{ J}$$

Heat exchange in the processes can be calculated using (2.5). The values of heat and work in the five processes are as follows:

Process	ΔU/J	W/J	Q/J
A→B	3	−0.6	3.6
B→C (straight)	6	0.75	5.25
C→D	−6	1.2	−7.2
D→A	−3	0	−3
C→B (hyperbolic)	−6	−0.5545	−5.44548

(d) To find an equation for adiabatic changes in the *P–V* plane, first we differentiate the U function given in (2.70):

$$dU = 5P dV + 5V dP.$$

In case of an adiabatic process, $T dS = 0$, thus $dU = -P dV$. [*Cf.* (2.22)]. Combining this latter with the above differential leads to the following differential equation:

$$6P dV + 5V dP = 0.$$

Separating the variables and solving the differential equation leads the following result:

$$PV^{\frac{6}{5}} = \text{constant}.$$

This is the general equation that applies for any adiabatic change. (The equation is also called as an "adiabat.")

2. *The Sackur–Tetrode* equation (*Cf*. Chap. 10) is a fundamental equation for a monatomic ideal gas:

$$S = nR \left[\frac{5}{2} + \ln \left(\frac{V}{n} \left[\frac{4\pi m\, U}{3\, h^2 n} \right]^{3/2} \right) \right]. \tag{2.72}$$

(R, m, π and h are constants.) Check whether the equation meets all the requirements concerning the entropy function that are imposed by the four postulates.

Solution: In order to prove that a particular entropy function meets the requirements imposed by the postulates, we have to prove that it is differentiable if its variables have physically reasonable values; that it is a homogenous first order function of its natural variables; and that it vanishes at $T = 0$.

The differentiability of the function S(U, V, n) can be demonstrated by formally differentiating the function and see if the derivatives obtained exist in the range of physically reasonable values of their variables. These derivatives are the following:

$$\left(\frac{\partial S}{\partial U} \right)_{V,\, n} = \frac{1}{T} = \frac{3nR}{2U},$$

$$\left(\frac{\partial S}{\partial V} \right)_{U,\, n} = \frac{P}{T} = \frac{3nR}{V},$$

$$\left(\frac{\partial S}{\partial n} \right)_{U,\, V} = \frac{\mu}{T} = -R \ln \left[\frac{V}{n} \left(\frac{4\pi m\, U}{3\, h^2 n} \right)^{3/2} \right].$$

We can see from the results that the derivatives do exist in the physically sound range of their variables.

Whether S is a homogenous first order function of its variables can be checked using the definition given in (2.7):

$$S(\lambda U, \lambda V, \lambda n) = \lambda nR \left[\frac{5}{2} + \ln \left(\frac{\lambda V}{\lambda n} \left[\frac{4\pi m\, \lambda U}{3\, h^2 \lambda n} \right]^{3/2} \right) \right] = \lambda S(U, V, n).$$

To check if the function S fulfils the requirements of Postulate 4, we express U as a function of T from the above derivative $(\partial S/\partial U)_{V,n}$:

$$U = \frac{3nR}{2T}.$$

Substituting this into (2.72), we get:

$$S = nR\left\{\frac{5}{2} + \ln\left[\frac{V}{n}\left(\frac{2\pi m\,RT}{h^2}\right)^{3/2}\right]\right\}.$$

It is easy to demonstrate from the above result that

$$\lim_{T\to 0} S = -\infty.$$

Summing up we can state that the entropy specified by the Sackur–Tetrode equation fulfils Postulates 1–3, but does not fulfil Postulate 4.

Further Reading

Callen HB (1985) Thermodynamics and an introduction to thermostatistics, 2nd edn. Wiley, New York

Mohr PJ, Taylor BN, Newell DB (2007) CODATA recommended values of the fundamental physical constants: 2006. National Institute of Standards and Technology, Gaithersburg, MD