Appendix

A1 Useful Relations of Multivariate Calculus

From a mathematical point of view, thermodynamics is a subject mostly based on relations of differentials and partial derivatives of multivariate functions. Many of these relations are of paramount importance in thermodynamics. This part of the appendix contains a collection of the most important relations, usually without any proof, only as "rules" that can be applied. Thermodynamic chapters of the book do not always make explicit reference to the rules described in the Appendix, but the rules are always mentioned under the same name as described here.

A1.1 Differentiation of Multivariate Functions

Let us consider the bivariate function f depending on the variables x_1 and x_2. Rules that apply for this function are readily generalized for more than two variables, but it is easier to describe the rules in case of only two of them.

The *partial derivative* of the function f is the function we get in a similar manner as an ordinary derivative with the differentiation of a univariate function, considering one of the variables of the bivariate function $f(x_1, x_2)$ as a constant during the differentiation. A bivariate function has two partial derivatives:

$$\left(\frac{\partial f}{\partial x_1}\right)_{x_2} \quad \text{and} \quad \left(\frac{\partial f}{\partial x_2}\right)_{x_1}. \tag{A1.1}$$

To discern partial differentiation from ordinary one (i.e., of a univariate function) we use the symbol ∂. (When reading formulae, ∂ is also pronounced as "dee"; "dee ef over dee ex one", or, if we want to stress that it is a partial derivative, we can say "dee ef partial over dee ex one".) It is common practice in thermodynamics (and it is also adopted in this book) to denote a function and its value with the same

E. Keszei, *Chemical Thermodynamics*,
DOI 10.1007/978-3-642-19864-9,

symbol; thus, it is not always clear what the actual function is whose derivative is considered. This is the reason why partial derivatives are written within brackets, and variables not involved in the derivation are shown as lower right subscripts of the closing bracket, thus identifying the proper function. We read such notation as "the partial derivative of f with respect to x_1 when x_2 is constant". Note, however, that x_2 is only constant from the point of view of derivation; it is clear that the partial derivative is in general a function of *both* variables.

The *total differential* of a function can be written with the help of the partial derivatives as follows:

$$df = \left(\frac{\partial f}{\partial x_1}\right)_{x_2} \mathrm{d}x_1 + \left(\frac{\partial f}{\partial x_2}\right)_{x_1} \mathrm{d}x_2. \tag{A1.2}$$

The symbol df means the (infinitesimal) *change* of the function as a consequence of the (infinitesimal) *increments* dx_1 and dx_2 of the variables x_1 and x_2. By summing products of partial derivatives and increments, we can specify arbitrary increments, not only that of a function of the variables. Thus, the expression (A1.2) is a total differential (or exact differential) only if the function whose change is on the left-hand side is a unique function of the variables of derivation on the right-hand side. From a thermodynamic point of view, it means that f is a state function uniquely determined by the thermodynamic variables x_1 and x_2.

The *second partial derivatives* (also called as second-*order* partial derivatives) of the function f – again, similarly to the second derivative of a univariate function – are the partial derivatives of the (first-order) partial derivatives. There are more second partial derivatives than first ones, as we can differentiate each (first-order) partial derivative with respect of all the variables. Let us denote the first-order partial derivatives in the following way:

$$\left(\frac{\partial f}{\partial x_1}\right)_{x_2} = g_1 \quad \text{and} \quad \left(\frac{\partial f}{\partial x_2}\right)_{x_1} = g_2. \tag{A1.3}$$

Accordingly, the "pure" second partial derivatives can be written as

$$\left(\frac{\partial^2 f}{\partial x_1^2}\right)_{x_2} = \left(\frac{\partial g_1}{\partial x_1}\right)_{x_2}, \quad \left(\frac{\partial^2 f}{\partial x_2^2}\right)_{x_1} = \left(\frac{\partial g_2}{\partial x_2}\right)_{x_1}, \tag{A1.4}$$

and the "mixed" second partial derivatives as

$$\frac{\partial}{\partial x_2}\left(\frac{\partial f}{\partial x_1}\right)_{x_2} = \left(\frac{\partial^2 f}{\partial x_2 \partial x_1}\right) = \left(\frac{\partial g_1}{\partial x_2}\right)_{x_1}; \quad \frac{\partial}{\partial x_1}\left(\frac{\partial f}{\partial x_2}\right)_{x_1} = \left(\frac{\partial^2 f}{\partial x_1 \partial x_2}\right) = \left(\frac{\partial g_2}{\partial x_1}\right)_{x_2}. \tag{A1.5}$$

The symbol $\partial/\partial x_2$ denotes the action of taking the partial derivative with respect to x_2; thus, it is called a *differential operator*. It has the effect of partial differentiation on the function written after the operator. (It can also be called a *partial* differential operator.) Thus, the expression $(\partial^2 f/\partial x_1^2)_{x_2}$ does *not* contain the square of the symbol ∂ or the square of x_1, but two subsequent applications of the differential operator. Accordingly, it is read as "dee two ef over dee ex two".

For the second-order derivatives of multivariate functions, *Young's theorem* holds; second partial derivatives are equal, irrespective of the order of differentiation. We can write it formally for the above function as[1]:

$$\left(\frac{\partial^2 f}{\partial x_2 \partial x_1}\right) = \left(\frac{\partial^2 f}{\partial x_1 \partial x_2}\right). \tag{A1.6}$$

The *second-order differential* of the function $f(x_1, x_2)$ can be written with the help of its second partial derivatives as follows:

$$\mathrm{d}^2 f = \left(\frac{\partial^2 f}{\partial x_1^2}\right)_{x_2} (\mathrm{d}x_1)^2 + \left(\frac{\partial^2 f}{\partial x_2^2}\right)_{x_1} (\mathrm{d}x_2)^2 + 2\left(\frac{\partial^2 f}{\partial x_1 \partial x_2}\right) \mathrm{d}x_1 \mathrm{d}x_2. \tag{A1.7}$$

Note that the equality of the mixed second partial derivatives is included in the above definition. Let us rewrite (A1.6) using the notation introduced in (A1.3):

$$\left(\frac{\partial g_1}{\partial x_2}\right)_{x_1} = \left(\frac{\partial g_2}{\partial x_1}\right)_{x_2}. \tag{A1.8}$$

In thermodynamics, the theorem stating the equality of mixed second partial derivatives is not referred to as Young's theorem but – written in the above form – as a *Maxwell relation*. To facilitate the generalization for more than two variables, Maxwell relations and the second-order differential is given below for a trivariate function $h(x_1, x_2, x_3)$. These Maxwell relations contain the following variables:

$$\left(\frac{\partial h}{\partial x_1}\right)_{x_2, x_3} = g_1; \quad \left(\frac{\partial h}{\partial x_2}\right)_{x_1, x_3} = g_2; \quad \text{and} \quad \left(\frac{\partial h}{\partial x_3}\right)_{x_1, x_2} = g_3. \tag{A1.9}$$

Equalities of the second derivatives can be written as follows:

$$\left(\frac{\partial^2 h}{\partial x_2 \partial x_1}\right)_{x_3} = \left(\frac{\partial^2 h}{\partial x_1 \partial x_2}\right)_{x_3}, \quad \left(\frac{\partial^2 h}{\partial x_3 \partial x_1}\right)_{x_2} = \left(\frac{\partial^2 h}{\partial x_1 \partial x_3}\right)_{x_2}$$
$$\left(\frac{\partial^2 h}{\partial x_2 \partial x_3}\right)_{x_1} = \left(\frac{\partial^2 h}{\partial x_3 \partial x_2}\right)_{x_1}. \tag{A1.10}$$

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[1] Second-order partial derivatives can be arranged in a matrix called the *Hessian matrix*, named after the German mathematician Ludwig Otto Hesse (1811–1874). According to Young's theoreme, the Hessian matrix is symmetrical.

They can be rewritten by substitution of the first partial derivatives as defined above:

$$\left(\frac{\partial g_1}{\partial x_2}\right)_{x_1,x_3} = \left(\frac{\partial g_2}{\partial x_1}\right)_{x_2,x_3}, \quad \left(\frac{\partial g_1}{\partial x_3}\right)_{x_1,x_2} = \left(\frac{\partial g_3}{\partial x_1}\right)_{x_2,x_3}, \quad \left(\frac{\partial g_3}{\partial x_2}\right)_{x_1,x_3} = \left(\frac{\partial g_2}{\partial x_3}\right)_{x_1,x_2}. \quad \text{(A1.11)}$$

These forms are properly called as Maxwell relations.

The second-order differential of the function $h(x_1, x_2, x_3)$ can be written as follows:

$$\mathrm{d}^2h = \left(\frac{\partial^2 h}{\partial x_1^2}\right)_{x_2,x_3}(\mathrm{d}x_1)^2 + \left(\frac{\partial^2 h}{\partial x_2^2}\right)_{x_1,x_3}(\mathrm{d}x_2)^2 + \left(\frac{\partial^2 h}{\partial x_3^2}\right)_{x_1,x_2}(\mathrm{d}x_3)^2 + 2\left(\frac{\partial^2 h}{\partial x_1 \partial x_2}\right)_{x_3}\mathrm{d}x_1\mathrm{d}x_2 + 2\left(\frac{\partial^2 h}{\partial x_1 \partial x_3}\right)_{x_2}\mathrm{d}x_1\mathrm{d}x_3 + 2\left(\frac{\partial^2 h}{\partial x_2 \partial x_3}\right)_{x_1}\mathrm{d}x_2\mathrm{d}x_3. \quad \text{(A1.12)}$$

A1.2 Differentiation of Composite Functions

Let us consider the case when the variables of the function $f(x_1, x_2)$, x_1 and x_2, are not independent, but both are functions of a third variable u. In this case, the increments $\mathrm{d}x_1$ and $\mathrm{d}x_2$ in (A1.2) can be written as

$$\mathrm{d}x_1 = \frac{\mathrm{d}x_1}{\mathrm{d}u}\mathrm{d}u \quad \text{and} \quad \mathrm{d}x_2 = \frac{\mathrm{d}x_2}{\mathrm{d}u}\mathrm{d}u. \quad \text{(A1.13)}$$

By resubstituting this in the total differential (A1.2), we get:

$$\mathrm{d}f = \left[\left(\frac{\partial f}{\partial x_1}\right)_{x_2}\frac{\mathrm{d}x_1}{\mathrm{d}u} + \left(\frac{\partial f}{\partial x_2}\right)_{x_1}\frac{\mathrm{d}x_2}{\mathrm{d}u}\right]\mathrm{d}u. \quad \text{(A1.14)}$$

This can also be written as

$$\frac{\mathrm{d}f}{\mathrm{d}u} = \left(\frac{\partial f}{\partial x_1}\right)_{x_2}\frac{\mathrm{d}x_1}{\mathrm{d}u} + \left(\frac{\partial f}{\partial x_2}\right)_{x_1}\frac{\mathrm{d}x_2}{\mathrm{d}u}, \quad \text{(A1.15)}$$

which is the equivalent of the *chain rule* for multivariate differentials.

Rules of differentiation concerning sums (differences), products and ratios of functions are also related to composite functions. Simplified relations (omitting variables) in case of two functions f and h are shown below:

$$\mathrm{d}(f+h) = \mathrm{d}f + \mathrm{d}h, \tag{A1.16}$$

$$\mathrm{d}(fh) = f\mathrm{d}h + h\mathrm{d}f, \tag{A1.17}$$

$$\mathrm{d}\left(\frac{f}{h}\right) = \frac{h\mathrm{d}f - f\mathrm{d}h}{h^2}. \tag{A1.18}$$

A1.3 Differentiation of Implicit Functions

Let us consider the implicit function specified by the equation $F(x, y, z) = 0$, and the variable w which can be given as a function of any two of the variables x, y, z. (In thermodynamics, this means that x, y, z and w are state variables, and x, y, z and w can be expressed as explicit functions from the implicit function F and that the system whose state is described by the functions mentioned has two degrees of freedom.)

The extension of the chain rule for partial derivatives can be written as follows:

$$\left(\frac{\partial x}{\partial w}\right)_z = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial w}\right)_z. \tag{A1.19}$$

Using this rule, we can express the partial derivative of a function knowing the partial derivatives of two other functions if their variables are in accordance with the above formula.

To *differentiate an inverse function*, the following relation can be used:

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}. \tag{A1.20}$$

To *change a variable*, we can use the following identity, where the variable w is changed for z:

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z. \tag{A1.21}$$

The following *cyclic rule* (or *triple product rule*) can also be applied in thermodynamics:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \tag{A1.22}$$

Here, in both the numerator and the denominator, as well as in the subscripts outside the brackets, variables follow each other always in the same order; in other words, they are cyclic permutations of the set x–y–z. This rule can be applied, for example, if we want to get a derivative from the one whose variable is the "constant" (i.e., outside the bracket) so that this variable should be inside the bracket, and another one appears outside. As an example, the partial derivative where the variable z is outside the bracket and expressed with derivatives where z is within the bracket can be obtained with the following rearrangement:

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial x}{\partial z}\right)_y \quad \text{or} \quad \left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y}. \tag{A1.23}$$

However, it is easier to memorize the rule in the form of the triple product equal to -1.

A1.4 Integration of Multivariate Functions

Let us write the total differential of the function $f(x, y)$ in the following form:

$$\mathrm{d}f = \left(\frac{\mathrm{d}f}{\mathrm{d}x}\right)_y \mathrm{d}x + \left(\frac{\mathrm{d}f}{\mathrm{d}y}\right)_x \mathrm{d}y = g_1\mathrm{d}x + g_2\mathrm{d}y. \tag{A1.24}$$

This can be integrated in several ways. In thermodynamics, it is convenient to use simple constraints to calculate changes of state functions. (Changes of state functions do not depend on the path of the change but the starting point and the endpoint.) Accordingly, we can perform an integration first while keeping y constant; i.e., applying the condition $\mathrm{d}y = 0$, which only concerns the first term. Having done this, we can continue integrating the second term while keeping x constant; i.e., applying the condition $\mathrm{d}x = 0$. The formal statement of this procedure can be written in the following way:

$$\Delta_0^1 f = f_1(x_1, y_1) - f_0(x_0, y_0) = \int_{x_0, y_0}^{x_1, y_1} \mathrm{d}f = \int_{x_0, y_0}^{x_1, y_0} g_1\mathrm{d}x + \int_{x_1, y_0}^{x_1, y_1} g_2\mathrm{d}y. \tag{A1.25}$$

For the integration of a state function $f(x, y)$, the following relation can also be applied:

$$\oint \mathrm{d}f = \oint (g_1\mathrm{d}x + g_2\mathrm{d}y) \equiv 0. \tag{A1.26}$$

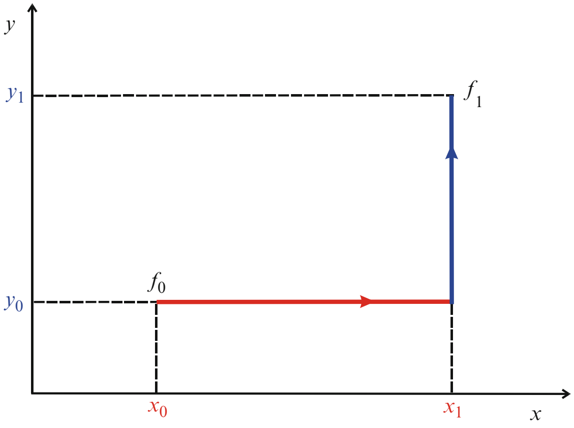

Fig. A1.1 Integrating a bivariate function; first with respect to one and then with respect to the other variable

The symbol $\oint$ (*cyclic integral* or closed contour integral) means integration along a closed curve; i.e., a path that returns to its starting point. In case of a state function, it is equivalent to a cyclic process where the state of the system returns to the initial state; thus, there is no change of state by the end of the process. The rationale behind this relation and (A1.25) is the same; the change of a state function is independent of the path of the change.

A1.5 The Euler Equation for Homogeneous First-Order Functions

Functions that are transformed as a consequence of a λ-fold multiplication of their variables according to the relation

$$f(\lambda x_1, \lambda x_2, ..., \lambda x_r) = \lambda^n f(x_1, x_2, ..., x_r) \tag{A1.27}$$

are called *homeogeneous functions of order n*.

Let us differentiate both sides of the above equation with respect to λ. On the right-hand side, the function $f(x_1, x_2, \dots, x_r)$ does not depend on λ; thus, the derivations yield $n\lambda^{n-1} f$. On the left-hand side, the derivation can be performed using the chain rule and summing for all variables x_i the following terms:

$$\frac{\partial f(\lambda x_1, \lambda x_2, ..., \lambda x_r)}{\partial(\lambda x_i)} \frac{\partial(\lambda x_i)}{\partial \lambda} = \left(\frac{\partial f}{\partial(\lambda x_i)}\right)_{x_{j \neq i}} x_i. \tag{A1.28}$$

This result is valid for any value of λ. By substituting $\lambda = 1$, we get the following result:

$$nf(x_1, x_2, ..., x_r) = \sum_{i=1}^{r} \left(\frac{\partial f}{\partial x_i} \right)_{x_{j \neq i}} x_i. \tag{A1.29}$$

This is called the *Euler equation*. If the function f (x_1, x_2, … , x_r) is a *homogeneous first-order function* of its variables x_1, x_2, … , x_r, it can be written in the following form:

$$f(x_1, x_2, ..., x_r) = \sum_{i=1}^{r} \left(\frac{\partial f}{\partial x_i} \right)_{x_{j \neq i}} x_i. \tag{A1.30}$$

The above equation – the *Euler equation for a homogeneous first-order function* has frequent application in thermodynamics.

Note that we can obtain this equation by substituting the increment of f as a function of the variables incremented by a ratio of (1 + dv):1 – i.e., x_i dv – into the total differential

$$\mathrm{d}f(x_1, x_2, ..., x_r) = \sum_{i=1}^{r} \left(\frac{\partial f}{\partial x_i} \right)_{x_{j \neq i}} \mathrm{d}x_i, \tag{A1.31}$$

according to the homogeneous first-order property:

$$\mathrm{d}f(x_1, x_2,\ ..., x_r) = \sum_{i=1}^{r} \left(\frac{\partial f}{\partial x_i} \right)_{x_{j \neq i}} x_i \mathrm{d}v, \tag{A1.32}$$

and integrating the expression from $v = 0$ to 1. From this derivation of the Euler equation it is also clear that, if there were some variables for which the function f is homogeneous zero-order, they would contribute by zero to the increment df; thus, they should simply be omitted from the sum.

A2 Changing Extensive Variables to Intensive Ones: Legendre Transformation

Summarizing energy-like potential functions in Sect. 4.4, we have mentioned that they can be obtained from the function $U(S,V,\boldsymbol{n})$ using *partial Legendre transformations*. This transformation changes one or two independent variables out of S, V, n_1, n_2, … , n_K for the derivative of the respective variable. In this Appendix, we shall first describe the Legendre transformation from a mathematical point of view, and then we shall derive important entropy-like potential functions obtained by Legendre transformation from the entropy function $S(U, V, \boldsymbol{n})$.

A2.1 Legendre Transformations

For the sake of simplicity, let us consider the univariate function $y = f(x)$, and denote its derivative with respect to x by m:

$$\frac{\mathrm{d}y}{\mathrm{d}x} = f'(x) = m. \tag{A2.1}$$

We would like to get a function $g(m)$ equivalent to the original function $f(x)$, so that the original function $f(x)$ can be calculated from $g(m)$. It is obvious that the function $y = h(m)$ does not have the required property as the equation specifying this function is a *differential equation*, whose solution yields the function $y = f(x)$ only to within an arbitrary additive constant of integration. To get a unique transformation, we can make use of the geometrical observation that the derivatives can be considered as tangent lines of the graph of the function. (The graph of the univariate function is a two-dimensional curve.) Each tangent line determines one point of the function (the point of tangency); thus, all the tangent lines determine the entire function, as it is illustrated in Fig. A2.1.

Accordingly, the proper transformation is expected to be derived from the tangent lines; specifying the loci (x, y) on the graph of the function $y = f(x)$ using the slope m and the intercept a which determine the tangent lines. By applying this technique, we determine the graph using the function $a = g(m)$, instead of the function $y = f(x)$ itself. By doing so, we arrive to our original goal of changing the variable x for m, as the function $g(m)$ completely determines the original function. We call Legendre transform the one that yields the function $a = g(m)$ from the original function $y = f(x)$.

The analytical formulation of the transformation is based on the equation of the tangent line. The tangent passes at the point (x, y), its slope is m and its intercept is a. From the equation of a line going through a point, having a slope m;

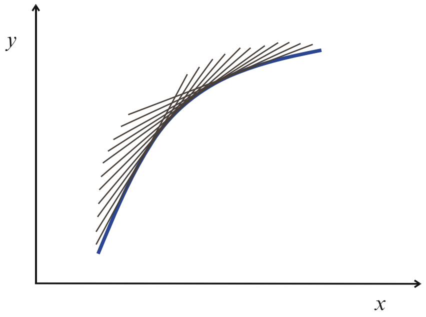

Fig. A2.1 The envelope of the tangent lines of the function $y = f(x)$ traces the function itself

$$m = \frac{y - a}{x - 0}, \tag{A2.2}$$

the searched-for relation is easily explained:

$$a = y - mx. \tag{A2.3}$$

From the original function

$$y = f(x) \tag{A2.4}$$

and its derivative with respect to x,

$$m = f'(x), \tag{A2.5}$$

we can express the explicit formula of the transformed function as follows:

$$a = g(m). \tag{A2.6}$$

The function g is called the *Legendre transform* of the function f.

The derivative $g' = \mathrm{d}a/\mathrm{d}x$ can also be determined from the above equations. Based on (A2.3), let us write the differential of the product and the difference in it; then let us substitute the relation $\mathrm{d}y = m\mathrm{d}x$:

$$\mathrm{d}a = \mathrm{d}y - m\mathrm{d}x - x\mathrm{d}m = -x\mathrm{d}m. \tag{A2.7}$$

From the result obtained, it is clear that the searched-for derivative is

$$\frac{\mathrm{d}a}{\mathrm{d}m} = -x. \tag{A2.8}$$

By summing up the above results, we can state the following. It is possible to construct a function whose independent variable is the derivative m of the original function, such that the original function $y(x)$ can be uniquely determined from this new function. The new function – the Legendre transform of $y(x)$ – is $a = y - mx$; it is a function of m and its derivative with respect to m is $-x$. The original function can be reconstructed by inverse Legendre transformation as $y = a + mx$. (These rules have been formulated in Sect. 4.4.)

The rules can be applied similarly for a multivariate function if we perform the transformation with respect to one variable only, as the transformation does not have any effect on the other variables. A Legendre transformation with respect to two variables can be formulated based on considerations in a three-dimensional subspace, instead of a two-dimensional section. The three-dimensional "section" is a continuous surface; the partial derivatives of the function determine tangent planes of this surface. By writing the equations of these planes, we can determine the Legendre transform and its derivatives, similarly to the one-dimensional case. The procedure can be extended to all the independent variables as well. If the transformation is not performed for all the variables but only some of them, it is called a *partial Legendre transformation*. Partial transformation has been applied to derive the function $F(T, V, \boldsymbol{n})$, using a transformation of the function $U(S, V, \boldsymbol{n})$ with respect to S; to derive $H(S, P, \boldsymbol{n})$ with the help of a transformation with respect to V; and to get the function $G(T, P, \boldsymbol{n})$ by transforming $U(S, V, \boldsymbol{n})$ with respect to both S and V.

A2.2 Legendre Transformation of the Entropy Function

Energy-like potential functions as results of partial Legendre transformations of the function $U(S,V,\boldsymbol{n})$ were introduced in thermodynamics by Gibbs in 1875. Six years before, Massieu[2] proposed entropy-like potential functions as a result of partial Legendre transformations of the function $S(U, V, \boldsymbol{n})$ to solve some thermodynamic problems in a simple way. This is the reason to call the Legendre transform with respect to two variables as Gibbs potential (or Gibbs function), and the entropy transform with respect to the variable U as *Massieu function*. The Legendre transform of the entropy function with respect to U and V was frequently used by Planck in his papers on statistical thermodynamics; thus, it is usually called as *Planck function*. (However, both of them are called sometimes as Massieu functions.)

The transformation of the function $S(U,V,\boldsymbol{n})$ can be performed using its derivatives with respect to U and V (i.e., $1/T$ and P/T) according to the following considerations. The transformation with respect to V is the function

$$X = S - \frac{P}{T}V. \tag{A2.9}$$

The equation $X = X(U, P/T, \boldsymbol{n})$ defining this function is a fundamental equation. The total differential of this function can be written as follows:

$$\mathrm{d}X = \frac{1}{T}\mathrm{d}U - V\mathrm{d}\left(\frac{P}{T}\right) - \sum_{i=1}^{K}\frac{\mu_i}{T}\mathrm{d}n_i. \tag{A2.10}$$

This function cannot be expressed in a simple way from the energy-like potential functions and is not used in thermodynamic practice; it does not even have a name. (It does not suit to any practical problem as it would need a reservoir which keeps P/T constant, while $1/T$ should change, which is not easily feasible.)

The transformation of S with respect to V is the *Massieu function*

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[2] François Jacques Dominique Massieu (1832–1896) was a French mathematician and physicist.

$$J = S - \frac{1}{T}U. \tag{A2.11}$$

The specification of this function in the form $J = J(1/T, V, \boldsymbol{n})$ is a fundamental equation. The total differential of the function can be written as follows:

$$\mathrm{d}J = -U\mathrm{d}\left(\frac{1}{T}\right) + \frac{P}{T}\mathrm{d}V - \sum_{i=1}^{K} \frac{\mu_i}{T}\mathrm{d}n_i. \tag{A2.12}$$

The function J can be easily expressed with the free energy F as follows:

$$J = S - \frac{U}{T} = -\frac{F}{T}. \tag{A2.13}$$

This is the reason to use also the function $J = J(T, V, \boldsymbol{n})$ in thermodynamical praxis. The total differential of this latter function can be written as follows:

$$\mathrm{d}J = \mathrm{d}S - \frac{T\mathrm{d}U - U\mathrm{d}T}{T^2}. \tag{A2.14}$$

Substitution of the total differential (2.26) of the entropy function $S(U, V, \boldsymbol{n})$ yields:

$$\mathrm{d}J = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V - \sum_{i=1}^{K} \frac{\mu_i}{T}\mathrm{d}n_i - \frac{1}{T}\mathrm{d}U + \frac{U}{T^2}\mathrm{d}T. \tag{A2.15}$$

By omitting terms whose sum results in zero and rearranging, we get the usual form of the total differential of the function $J = J(T, V, \boldsymbol{n})$:

$$\mathrm{d}J = \frac{U}{T^2}\mathrm{d}T + \frac{P}{T}\mathrm{d}V - \sum_{i=1}^{K} \frac{\mu_i}{T}\mathrm{d}n_i. \tag{A2.16}$$

From this result, it is easily seen that the partial derivative of the function J with respect to T is U/T^2, which is usually written in the following form:

$$\left(\frac{\partial(F/T)}{\partial T}\right)_{V,\boldsymbol{n}} = -\frac{U}{T^2}. \tag{A2.17}$$

The transformation of S with respect to U and V is the *Planck function*:

$$Y = S - \frac{1}{T}U - \frac{P}{T}V. \tag{A2.18}$$

By specifying this function in the form $Y = Y(1/T, P/T, \boldsymbol{n})$, we get a fundamental equation. The total differential of the Planck function can be written as follows:

$$\mathrm{d}Y = -U\mathrm{d}\left(\frac{1}{T}\right) - V\mathrm{d}\left(\frac{P}{T}\right) - \sum_{i=1}^{K} \frac{\mu_i}{T}\mathrm{d}n_i. \tag{A2.19}$$

The function Y can be expressed from the function G as follows:

$$Y = S - \frac{U}{T} - \frac{PV}{T} = -\frac{G}{T}. \tag{A2.20}$$

Accordingly, we can easily express Y as a function of T, P and $\boldsymbol{n}$. The total differential of this function $Y = Y(T, P, \boldsymbol{n})$ can be written based on the above equation:

$$\mathrm{d}Y = \mathrm{d}S - \frac{T\mathrm{d}U - U\mathrm{d}T}{T^2} - \frac{T(P\mathrm{d}V + V\mathrm{d}P) - PV\mathrm{d}T}{T^2}. \tag{A2.21}$$

Upon substitution of the total differential (2.26) of the entropy function, the elimination of terms that sum to zero, and the substitution of H in place of $U - PV$ we get:

$$\mathrm{d}Y = \frac{H}{T^2}\mathrm{d}T - \frac{V}{T}\mathrm{d}P - \sum_{i=1}^{K} \frac{\mu_i}{T}\mathrm{d}n_i. \tag{A2.22}$$

It is easily seen that the partial derivative of the Planck function $Y(T, P, \boldsymbol{n})$ with respect to temperature is H/T^2, which can also be written in the following form:

$$\left(\frac{\partial(G/T)}{\partial T}\right)_{P,\boldsymbol{n}} = -\frac{H}{T^2}. \tag{A2.23}$$

This relation has a distinct name; it is called the *Gibbs–Helmholtz equation*. [(A2.17) is also called Gibbs–Helmholtz equation, but it is less frequently used in the chemical praxis.]

A3 Classical Thermodynamics: The Laws

The expression "classical" in the title of this section means that the theory to be described here was the first one formulating the exact science of thermodynamics. As it is mentioned in the Introduction, this theory had been elaborated as a result of an attempt in the middle of nineteenth century to improve the efficiency of transformation of heat into mechanical work. Steam engines were already in use in the eighteen century. (Their highly developed versions, steam turbines are largely used even nowadays in thermal power plants as well as in nuclear power plants.) These engines were first constructed by mechanicians based on their empirical experience, without any theoretical background. The first key step to optimize their performance was made by James Watt. He called attention to the importance of the (missing) theoretical background already in the 1760s.

The first study that had a great impact on the theory of heat engines was written by Sadi Carnot. Though it was published in 1824 (see Sect. 5.2), it remained unknown to the scientific community for more than 20 years. Development of the theory had a great impact as a consequence of experimental studies made by James Joule (see Sect. 5.4.3), who performed a series of carefully planned measurements to confirm that the quantity of heat transferred is "equivalent" to the quantity of work transferred to a system. Following the publication of these studies, many scientists contributed to the development of the theory of heat. The comprehensive treatment of what we call today thermodynamics has been written by Rudolf Clausius in 1867, and in a more general approach by Henry Poincaré[3] in 1892. At the beginning of the twentieth century, several scientists have reformulated the theoretical basis. One of the consequences of these activities is that the second law of thermodynamics has more than ten equivalent wording.

Classical thermodynamics has retained the character of its historical development. Physical quantities and relations are formulated in a "language" of experimental evidence concerning heat engines. Another feature is that "heat" is thought of within the framework of the theory as a distinct substance, as statistical physics based on microscopical considerations was only moderately successful in explaining thermal phenomena at that time. Thus, the laws of thermodynamics are describing heat as an "imponderable fluid," which can flow from one body into another. (Telltale examples are expressions still used nowadays such as heat flow and heat capacity.) In the rest of this part of the appendix, we give a concise description of classical thermodynamics which is based on an exact mathematical background but also reflects the physical meaning of the laws. We will not treat all the details; instead we often make reference to what is described in the chapters on the postulates of thermodynamics.

A3.1 Zeroth Law and Temperature

Basic statements of classical thermodynamics are termed as *laws* in English, which is related to the original German name *Hauptsatz*[4] used for them. The order of the

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[3] Jules Henri Poincaré (1852–1912) was a French mathematician and theoretical physicist. His activity was most important in the field of relativity theory, but he also dealt with thermodynamics and quantum mechanics.

[4] The German word can be translated as "main proposition" or "independent clause".

laws which is manifested in their numbering does not reflect either the historical order of their formulation, or their inclusion into the set of the laws. The first one that has been formulated (Carnot 1824) is the second law. Next came the first law (Joule 1847) and then the third one (Nernst[5] 1907 and Planck[6] 1911). Finally, it has been realized that, to have a complete set of postulates, a fourth law is also needed. However, due to its basic importance, it has been named as the *zeroth law*, as this latter clarifies the notion of equilibrium.

As thermodynamics was developing, it has become only slowly clarified that the theory is only valid for *equilibrium systems*; thus, the definition of a (thermodynamic) system seemed not to be necessary for a while. There was a distinction of isolated, adiabatic, closed and open systems, without mentioning the importance of this distinction. However, the theory was primarily based on considerations concerning isolated and closed adiabatic systems. It is due to this missing definition of the subject of thermodynamics that several textbooks still describe the (thermodynamic) system as "that part of the physical universe that is under consideration", or "the part of the world in which we have a special interest". The "rest of the world" is then called *surroundings*. Equilibrium is typically mentioned in context of relations containing the signs $\leq$ or $\geq$, where equality refers to equilibrium (or *quasistatic* changes), and inequality to nonequilibrium changes.

Prior to the development of thermodynamics, mechanical quantities (energy, work, pressure, compressibility, etc.), geometrical quantities (volume, surface) and quantities related to electric, magnetic and gravitational interactions were already known. It was also known that the state of a simple closed system can be described in terms of only two variables: pressure and volume. (We use the term simple system in the same sense as in Sect. 2.1, when describing Postulate 1; i.e., the system can exchange only heat and volume work with its surroundings. Closeness also means that the chemical composition is not allowed to change.) The main task was to determine relevant quantities related to heat, based on these experimental evidences.

This goal is reflected in the **zeroth law,** which announces the *existence of thermal equilibrium* and specifies the intensive quantity characterizing this equilibrium. According to this law, thermodynamic (equilibrium) systems can be *arranged in a unique series* on the basis of their thermal states. If the order of two systems cannot be distinguished (they have the same ranking), their *temperature* is identical and they are in *thermal equilibrium* which relation is *transitive*. Transitivity is the consequence of ordering; if systems A and B are in equilibrium and systems A and C are also in equilibrium, then all of them should have the same ranking; thus, B and C should also be in equilibrium. It is the consequence of the zeroth law that

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[5] Walter Hermann Nernst (1864–1941) was a German physicist and chemist. Besides the relation defining the potential of an electrode reaction, the third law of thermodynamics also bears his name. This latter made it possible to calculate chemical equilibrium constants from thermodynamic data. He received his Nobel-prize for this result in 1920.

[6] Max Planck (1858–1947) was a German physicist who wrote his Ph.D. thesis on the second law of thermodynamics. He initiated quantum theory by properly describing black-body radiation. He interpreted the zero value of entropy at 0 K temperature based on quantum mechanical reasoning.

temperature defined this way (let us denote it by the Greek letter θ) is necessarily a state function; thus, it can be specified as $\theta = f(P, V)$, a function of temperature and pressure. Due to the unicity of this function, it can be inverted with respect to any of its variables. Thus, both state functions $V = f_1(P, \theta)$ and $P = f_2(V, \theta)$ can be expressed from θ. As we shall see, these consequences have an important role in formulating the first law.

A3.2 First Law and Energy

As we have already mentioned, the notion of work has been known from mechanics, electric and magnetic theory already before the development of thermodynamics. Known expressions of the infinitesimal work were, e.g., $-P\mathrm{d}V$, $\gamma\mathrm{d}A$, $\sigma\mathrm{d}l$, and $-E\mathrm{d}q$; where A denotes surface, γ is the surface tension, l is the length, σ is the modulus of elasticity, q is the electric charge, and E is the electric potential.

Adiabatic systems (those which cannot exchange heat with the surroundings) had a great role in setting fundamental rules of thermodynamics. Joule made a series of experiments between 1843 and 1848 by filling a thermally isolated container with water, examining the change of the state of the water due to the introduction of work in different manners. He introduced work the following ways.

- By means of a paddle wheel operated by a falling weight; the turbulent motion of water resulted in heating the water.
- By means of a diathermal cylinder immersed into the water; the compression of the gas resulted in heating the cylinder and thus the water.
- By means of two iron blocks in close contact inside the water bath; rubbing the plates against each other resulted in heating the water.
- By means of a metal coil immersed into the water; an external electric generator turned by a falling weight produced electric current in the coil, thus heating the water.

The work done on the paddle wheel, the piston in the cylinder, rods rubbing the iron blocks and the electric generator was always the same as it has been produced by the same falling weight over the same height. He has measured that – within the experimental error – to raise the temperature of 1 pound of water by 1 F, always the same amount of work was needed. He could get the same temperature rise by making diathermal contact between 1 font of water in an external container and the test container, while the temperature of the external water bath decreased by 1 F. He concluded that – *independently of the way of delivery* of either heat or work, *the change in the state of the water is the same*. Similar behavior was already known from the theory of gravitational, electric or magnetic fields. It was a natural consequence of these experiments to suggest the existence of a *potential* whose value depends only on the *state* (e.g., the height in the gravitational field of Earth), but does not depend on the way of change (or on the *path*).

The above results can be formulated by stating that *there exists an internal energy U*, whose change in adiabatic systems can be written as follows:

$$U_2 - U_1 = W. \tag{A3.1}$$

In a similar way, for changes when there is no work done on the system, and its energy can only change by means of heat delivery across a diathermal wall and then the same change of state can be characterized by the following relation:

$$U_2 - U_1 = Q. \tag{A3.2}$$

As the state of a closed simple system can be changed merely via work or heat exchanged with its surroundings; in case of both interactions, the following equality should hold for the same change of state:

$$U_2 - U_1 = Q + W. \tag{A3.3}$$

From a theoretical point of view, the most important consequence of these experiments is the *existence* of a *state function* $U = f(V, \theta)$. This function is unique, i.e., any changes $\Delta U = U_2 - U_1$ of this function due to interactions with the surroundings are independent of the way of interactions, or the "path" in the P, V, θ space. (This is, of course, true in either of the planes P, V or P, θ or θ, V.) This property of the potential U can also be formulated by stating that the change of U along any closed curve (where the initial state and the final state are identical) is zero:

$$\oint \mathrm{d}U = 0. \tag{A3.4}$$

Another consequence is that the expression

$$\mathrm{d}U = \frac{\partial U}{\partial V}\mathrm{d}V + \frac{\partial U}{\partial \theta}\mathrm{d}\theta \tag{A3.5}$$

is a total differential.

Despite these formally advantageous consequences, the **first law** of thermodynamics does not state any of the above relations. Instead, it usually is formulated as the differential form of the *conservation of energy* including heat effects:

$$\mathrm{d}U = \text{đ}Q + \text{đ}W. \tag{A3.6}$$

This relation stresses the fact that the conservation of energy is also valid if we include changes of energy via heat transfer. The symbol đ makes it obvious that, while the value of the function U is uniquely determined by the state of the system [i.e., its differential can be given by (A3.5)], this is not true for either heat or work. Consequently, both Q and W are also dependent on the path of the change during the delivery of heat or work, not only on the initial and final state. Thus, we can also say that the *fundamental notions* of classical thermodynamics – work and heat – do not uniquely determine the state of the system itself. That is why there was a need to derive strictly state-dependent functions from these two quantities. One of these derived functions is the *internal energy* contained in the first law.

A3.3 Second Law and Entropy

According to the first law, the extended principle of the conservation of energy is also valid in thermodynamics. However, there is a problem which does not occur either in mechanics, or in electrodynamics, or in magnetodynamics; spontaneous changes have a well-determined direction and will never occur spontaneously in the other direction. (In mechanics, if a point mass moves from A to B in a frictionless way and has a given momentum there, the exact opposite momentum would make it return to A, and its energy would change exactly with the same amount as when it moved from A to B.) If there is a heat effect accompanying changes, the original state cannot be restored with exactly the same amount of energy, except for some special cases. The consequence of this – among others – is also that heat engines cannot turn thermal energy (heat) completely to mechanical work. This latter problem was thoroughly treated by the book of Carnot published in 1824. In page 38 of the book, the following is written (in slightly modernized English translation of the French text[7]): “The motive power of heat is independent of the agents employed to realize it; its quantity is fixed solely by the temperatures of the bodies between which is effected, finally, the transfer of the heat.”

As it is written in Sect. 5.2, the efficiency of heat engines can be derived from the principle of conservation of energy as stated by the first law. Accordingly, the energy balance of the Carnot cycle shown in Fig. A3.1a can be written in the following way:

$$0 = \Delta U = Q + W = |Q_{\text{in}}| - |Q_{\text{out}}| + |W_{\text{in}}| - |W_{\text{out}}|. \tag{A3.7}$$

From this, we can express the net work gained:

$$W_{\text{net}} = |W_{\text{out}}| - |W_{\text{in}}| = |Q_{\text{in}}| - |Q_{\text{out}}|. \tag{A3.8}$$

The efficiency can be calculated as the ratio of the net work gained and the heat input:

$$\eta = \frac{|Q_{\text{in}}| - |Q_{\text{out}}|}{|Q_{\text{in}}|} = 1 - \frac{|Q_{\text{out}}|}{|Q_{\text{in}}|}. \tag{A3.9}$$

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[7] The original French text is the following: “La puissance motrice du feu est indépendante des agens mis en œuvre pour la réaliser; sa quantité est fixée uniquement par les températures des corps entre lesquels se fait en dernier résultat le transport du calorique.”

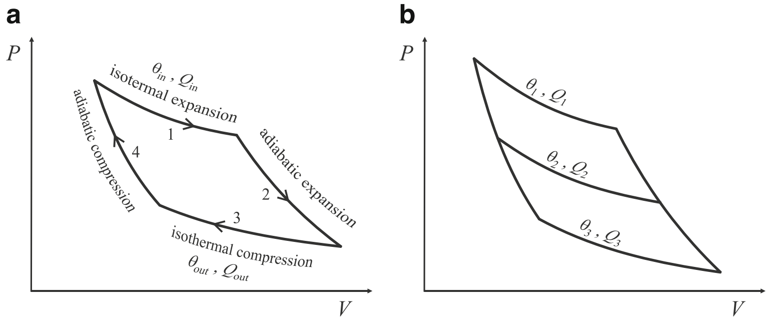

Fig. A3.1 Carnot cycle in a $P - V$ diagram. (**a**) Steps of the cycle are or also shown, along with the temperatures of the heat reservoirs and the transferred heat from (Q_{in}) and to (Q_{out}) them. (**b**) Three Carnot cycles are shown; working between reservoirs of temperatures of θ_1 and θ_2, θ_2 and θ_3, and θ_1 and θ_3, respectively

We can conclude that the efficiency depends only on the *ratio* of the heat exchangend in the two isothermal steps; Q_{in} and Q_{out}. The above statement cited from Carnot tells that the efficiency only depends on the temperature of the two heat reservoirs; thus, we can write the relation

$$\frac{|Q_{\text{in}}|}{|Q_{\text{out}}|} = f(\theta_{\text{h}}, \theta_{\text{c}}), \tag{A3.10}$$

where θ_{h} is the temperature of the hotter, and θ_{c} is that of the colder reservoir.

Let us examine the three possible Carnot cycles shown in panel (b) of the figure and apply the equality (A3.10) for all the three:

$$\frac{|Q_1|}{|Q_2|} = f(\theta_1, \theta_2); \quad \frac{|Q_2|}{|Q_3|} = f(\theta_2, \theta_3); \quad \frac{|Q_1|}{|Q_3|} = f(\theta_1, \theta_3). \tag{A3.11}$$

Let us extend the ratio in the third equality in the following way:

$$\frac{|Q_1|}{|Q_3|} = \frac{|Q_1|\,|Q_2|}{|Q_3|\,|Q_2|} = \frac{|Q_1|}{|Q_2|}\,\frac{|Q_2|}{|Q_3|}. \tag{A3.12}$$

Let us substitute into this identity the right-hand sides of the former three equalities:

$$f(\theta_1, \theta_3) = f(\theta_1, \theta_2)\, f(\theta_2, \theta_3). \tag{A3.13}$$

The left-hand side of this equation does not depend on θ_2; thus, the right-hand side cannot depend on it either. This condition is fulfilled if $f(\theta_1, \theta_3)$ can be explained in the form

$$f(\theta_1, \theta_3) = \frac{T(\theta_1)}{T(\theta_3)}, \tag{A3.14}$$

where T is only the function of the respective θ_i. It is easy to see that, in this case, the condition is really fulfilled:

$$f(\theta_1, \theta_3) = \frac{T(\theta_1)}{T(\theta_3)} = \frac{T(\theta_1)}{T(\theta_2)} \frac{T(\theta_2)}{T(\theta_3)} = f(\theta_1, \theta_2) f(\theta_2, \theta_3). \tag{A3.15}$$

Consequently, the function T defines a temperature scale such that the ratio of the heat transfer from the hot reservoir to that to the cold reservoir is identical to the ratio of the temperatures of the respective reservoirs:

$$\frac{|Q_\mathrm{h}|}{|Q_\mathrm{c}|} = \frac{T_\mathrm{h}}{T_\mathrm{c}}. \tag{A3.16}$$

It is obvious that the temperature scale defined this way is independent of the medium of either the material of the heat reservoirs or the working fluid of the Carnot engine. The possibility to define temperature this way was first discovered by William Thomson – called Lord Kelvin after his ennoblement. The unit of the corresponding temperature scale is named after him as kelvin. It is also called *absolute temperature* as there is no need to make use of the state function of an ideal gas used to the previous definition of temperature; thus, it is independent of the material whose temperature is measured.

The above result has a much more important consequence compared to the definition of an absolute temperature. To explore this, let us consider that the absorbed heat Q_h (h for “hot”) and the rejected heat Q_c (c for “cold”) have opposite signs; thus, their ratio is also negative if we do not take absolute values. Accordingly, we can write the two equivalent relations for the efficiency of the Carnot engine in the following forms:

$$\eta = 1 + \frac{Q_\mathrm{c}}{Q_\mathrm{h}} \quad \text{and} \quad \eta = 1 - \frac{T_\mathrm{c}}{T_\mathrm{h}}. \tag{A3.17}$$

As a consequence, we can also write the following three relations:

$$\frac{Q_\mathrm{c}}{Q_\mathrm{h}} = -\frac{T_\mathrm{c}}{T_\mathrm{h}}; \quad \frac{T_\mathrm{c}}{T_\mathrm{h}} + \frac{Q_\mathrm{c}}{Q_\mathrm{h}} = 0; \quad \frac{Q_\mathrm{h}}{T_\mathrm{h}} + \frac{Q_\mathrm{c}}{T_\mathrm{c}} = 0. \tag{A3.18}$$

The third relation has its validity for the entire Carnot cycle; i.e., there exists a temperature scale such that isothermal quasistatic heat divided by this temperature results in a *state function* – as seen from the fact that this ratio summed for the entire cyclic process is zero. Clausius was the first to realize this property and proposed to call it entropy, which became later denoted by the generally accepted letter S. The quotient can also be written for infinitesimal changes in the form:

$$\frac{đQ_{\mathrm{quasistatic}}}{T} = \mathrm{d}S. \tag{A3.19}$$

The function S thus defined has all properties of a state function; its change is not dependent on the path of the change, only on the initial and final state, and its cyclic integral is zero. We can conclude that, while the quasistatic heat is not a state function, the denominator T ensures upon integration that the value of the quotient depends only on the initial and final state.

Let us turn our attention back to the direction of changes. Experimental evidence shows that there are losses during the operation of a heat engine if the cyclic process is not quasistatic. These losses diminish the useful work; thus, $\eta \leq \eta_{\mathrm{qs}}$ for real processes. (Quasistatic processes are denoted by the subscript $_{\mathrm{qs}}$ here and further.) The efficiency of the Carnot engines can be written in terms of the heat absorbed from and rejected to the heat reservoirs:

$$1 + \frac{Q_{\mathrm{c}}}{Q_{\mathrm{h}}} \leq 1 + \frac{Q_{\mathrm{c,qs}}}{Q_{\mathrm{h,qs}}}. \tag{A3.20}$$

Subtracting one and multiplying the rest by -1 on both sides yields:

$$-\frac{Q_{\mathrm{c}}}{Q_{\mathrm{h}}} \geq -\frac{Q_{\mathrm{c,qs}}}{Q_{\mathrm{h,qs}}}. \tag{A3.21}$$

We can replace the right-hand side – based on the relations in (A3.18) – by the quotient of the respective temperatures:

$$-\frac{Q_{\mathrm{c}}}{Q_{\mathrm{h}}} \geq \frac{T_{\mathrm{c}}}{T_{\mathrm{h}}} \quad \text{from which} \quad 0 \geq \frac{Q_{\mathrm{h}}}{T_{\mathrm{h}}} + \frac{Q_{\mathrm{c}}}{T_{\mathrm{c}}}. \tag{A3.22}$$

From the result, we can conclude that the change of the function Q/T in isothermal changes during a cyclic process is *less* than zero, except when the process is quasistatic; in this case, it is exactly zero. We can formulate the same conclusion by writing the cyclic integral of this function:

$$\oint \frac{đQ}{T} \leq 0. \tag{A3.23}$$

Let us apply this for a process in which a particular system is brought from state A to state B with losses (as it is called in classical thermodynamics, in an *irreversible process*), and then it is brought back to state A in a quasistatic process, as shown below:

$$\mathrm{A} \xrightarrow{\text{irreversible}} \mathrm{B} \xrightarrow{\text{quasistatic}} \mathrm{A}. \tag{A3.24}$$

The total change during the entire process can be written as follows:

$$\int_{\mathrm{A}}^{\mathrm{B}} \frac{đQ}{T} + \int_{\mathrm{B}}^{\mathrm{A}} \frac{đQ_{\mathrm{qs}}}{T} < 0. \tag{A3.25}$$

The second integration contains quasistatic heat; thus, the quotient $đQ_{\mathrm{qs}}/T$ can be replaced by $\mathrm{d}S$:

$$\int_{\mathrm{A}}^{\mathrm{B}} \frac{đQ}{T} + \int_{\mathrm{B}}^{\mathrm{A}} \mathrm{d}S < 0. \tag{A3.26}$$

The inequality holds for infinitesimal changes as well (i.e., when A and B approach each other infinitely close):

$$\frac{đQ}{T} < \mathrm{d}S. \tag{A3.27}$$

This relation is valid for the case if there is an irreversible process involved. Thus, if we allow also for completely quasistatic processes, we should allow the equality as well:

$$\mathrm{d}S \geq \frac{đQ}{T}. \tag{A3.28}$$

The above inequality is the usual formal statement of the **second law** of thermodynamics. The connection between entropy and the direction of natural processes can be formulated most simply in an *isolated system*, which cannot exchange heat with its surroundings. In this case, the above equation simplifies to the following relation:

$$\mathrm{d}S \geq 0. \tag{A3.29}$$

This relation tells us that the entropy of isolated systems is increased in spontaneous (natural) processes, but it does not change in equilibrium. Consequently, the natural direction of thermodynamic processes in isolated systems is the one that increases entropy; they cannot proceed in the opposite direction.

It is worth noting that this is an important result, but it offers only the possibility of quantitative calculations for *equilibrium systems*. Therefore, we can say that the most important content of the second law from a thermodynamic point of view is the definition of entropy as a state function.

A3.4 Third Law and the Uniqueness of the Entropy Scale

As we have seen in Sect. 8.3, the uniqueness of the equilibrium constant of a chemical reaction is the consequence of the uniqueness of the entropy function [see (8.67)]. The third law announces this uniqueness. Historically, the first proposition was made by Nernst, in a "weak" form; namely, the entropy of change of phase transition of solid substances becomes smaller and smaller with decreasing temperature, and it goes to zero as temperature goes to 0 K. Planck gave a stronger form to this proposition a few years later. He concluded from quantum mechanical considerations that the degeneration in crystals should cease at 0 K as they only can have one equilibrium state; thus, the equilibrium entropy of all substances should be zero at 0 K.

Note that we know very little about the degeneracy of nuclei, but it does not change during thermodynamic processes at usual temperatures, including chemical reactions. Thus, it can be ignored in the calculation of entropy. It is also important to note that the nondegenerate state of crystals cannot always be achieved upon their cooling, as there is sometimes not enough energy available at the (rather low) temperature to the rearrangement of the crystal lattice. In these cases, there is a *residual entropy* which does not disappear even upon further cooling. However, the majority of substances do have zero entropy at zero temperature. This is the usual form of the **third law** of thermodynamics. It is worth noting that this is the only one of the four laws that is identical to one of the postulates (Postulate 4).

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