Chapter 24
Thermodynamic Functions

In addition to the terms discussed so far a number of other quantities and functions are used in thermodynamics without which textbooks that follow the conventional concept cannot manage. Because knowing these additional terms is essential for understanding traditional textbooks and the corresponding data collections, we will deal with the most important of them in this chapter and establish the relations to the concept chosen in this book. The major subsidiary terms are the four energetic quantities inner energy U, enthalpy H, Helmholtz energy A, and Gibbs energy G. The same quantity can serve different purposes depending on the variables chosen. The function $U(S, V, \ldots)$ characterizes the system under consideration. It is almost never explicitly stated (the abstractness of the variable S can be considered the underlying cause for this), but its differential plays a central role for all derivations. The functions $U(T, V, \ldots)$ and $H(T, p, \ldots)$ serve to describe the heat exchanged between system and surroundings under different experimental conditions (the first at constant volume, the second at constant pressure). The functions $A(T, V, \ldots)$ and $G(T, p, \ldots)$ play a similar role. Both are used to calculate the energy released during the considered process. This enables us to predict whether or not the process may run spontaneously. In the last section, we will discuss quantities such as activity, fugacity, etc. These quantities are used for describing deviations from what is considered ideal behavior of dissolved substances and gases.

24.1 Introduction

The subject of thermodynamics is a prime example of an axiomatic science whose basic assumptions are gained from everyday experiences. These basic assumptions first lead to *fundamental laws* from which a large number of other laws and relations are derived. The modest number of assumptions on the one hand and the abundance of derived results on the other is a widely admired characteristic of this science. Thermal effects are a part of almost every process dealt with in everyday life,

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including technological ones. These effects are often unnoticeable or undesirable, so that we are prone to overlook them. However, they do often rule the processes, making it necessary to deal with them. The ubiquity of thermal effects indicates the special role of heat in nature. It is therefore of great importance to know what this role is.

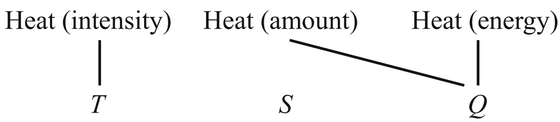
Thermodynamics, as it has developed in the last 150 years, is criticized for its lack of tangibility. Not only beginners complain of this, but sometimes even professionals do as well. This lack of tangibility makes it difficult to evaluate results qualitatively for their relevancy, algebraic signs, or orders of magnitude. Although many relations can be formally derived, one does not “understand” them as one would understand them in the field of mechanics, for example. Intuition is hindering and even misleading. Results must simply be accepted and the arguments that are allowed must simply be memorized. With growing routine, one will gradually forget one’s concerns.

The attempt has been made to compensate for this lack of tangibility by using an expanded formalism. The most noticeable differences between this expanded formalism and the presentation in this book are additionally introduced quantities such as enthalpy and free energy (in various forms), without which textbooks that follow the conventional concept cannot manage. Because knowing these new quantities is essential for understanding traditional textbooks and the corresponding data collections, we will deal with the most important of them in the following.

24.2 Heat Functions

Preliminary Remarks Thermodynamics is considered conceptually very difficult—even if this is not true for the mathematics involved. For example, Arnold Münster wrote 1969 in his textbook about chemical thermodynamics: “In contrast [to the mathematical formalism], the conceptualization in thermodynamics is especially abstract and this abstract conceptualization is the core of the difficulty of this scientific area.” This is due to the awkwardness of attribution of the heat quantities. Intuition and language from everyday experience give us preconceived structures. Because of their fuzziness, we are free to some degree in attributing everyday and physical concepts. However, ill-judged arbitrariness leads to difficulties.

The everyday expression “heat” has many meanings. In the field of thermodynamics, there are at least three quantities to which that name suits:



The name “heat (energy)” (or “thermal energy”) for Q is admittedly too general but for the moment it should suffice to grasp the underlying idea. The correlation of the terms shown vertically on top of each other should have been easy and natural. However, in 1850, a different decision was made indicated by the lines. The results of this decision can be summed up as follows:

- The quantity S cannot be interpreted macroscopically. Therefore one tends to avoid this quantity and to replace it with energetic terms.
- The quantity Q is automatically connected to characteristics that Q doesn't actually possess, leading to misconceptions. We will come back to this below. Q is mathematically inconvenient as a process quantity (see Sect. 1.6) so it also seems advantageous to avoid Q and to rewrite it using other quantities.
- In order to mitigate the conceptual difficulties and to bridge gaps in understanding, a number of new quantities have been introduced.

The question of how, in history, it could come to such a decision and why subsequent changes are difficult, if not impossible, would be a chapter in itself. Although this is an interesting and important question, we must exclude it here.

Let us now take a look at the most important of the additionally introduced quantities. In the conventional terminology of thermodynamics, *heat* (symbol Q) stands for the energy exchanged thermally between system and surroundings and *work* (symbol W) for the one exchanged mechanically. These terms will now and then appear in the following whereas we avoided them so far. In these and similar cases we spoke neutrally about expended (or released) energy. Therefore, a few words of explanation:

Work *W* and Heat *Q* As yet, we mentioned work W only shortly in Sect. 2.1. In more detail, we presented *mechanical work* by means of the relation "work = force times distance" as access route to an indirect introduction of the term energy. In mechanics, work generally describes a quantity which is defined as product of a displacement Δx (e.g., along the x-axis) with a force F_x, causing the displacement:

$$W_{\to x} = F_x \cdot \Delta x.$$

The same applies to displacements in arbitrary directions. Already in mechanics, the term is generalized. One considers an increase of volume ΔV, an increase of surface ΔA, etc., also as "displacement" and the pressure p in hydraulics (Sect. 2.5), the surface tension σ (Sect. 15.2), etc., as corresponding "force" causing the change:

$$W_{\to V} = p \cdot \Delta V,$$
$$W_{\to A} = \sigma \cdot \Delta A, \text{etc.}$$

The volume V, the surface A, ... are regarded as "generalized coordinates" and correspondingly p, σ, ... as "generalized forces."

In thermodynamics, one encounters the term "pressure–volume work" which relates to the compressibility of an elastic body (e.g., also of a gas). The more an object is pressed from all sides, meaning the more work has to be done, the more strongly volume V decreases. Therefore, a minus sign appears in the expression:

$$W_{\rightarrow V} = -p \cdot \Delta V. \tag{24.1}$$

As yet, also *heat Q* was only marginally mentioned such as in Sects. 3.1, 3.11, and 8.7. According to the traditional view, it characterizes the energy transferred thermally between a system and its surroundings because of differences in temperature. As a consequence of this type of energy exchange, the entropy of the system changes.

Process Quantities The phrase "work has to be done" in the case of something being displaced against a counteracting force or inhibition already expresses that work describes a certain aspect of a process. It causes therefore no difficulties to accept that work represents a so-called *process quantity* or corresponds to a process.

This is completely different in the case of the term heat. In everyday language but also in many fields of science and technology, one tends to the suggestion that the heat that is added to the body or generated in it is contained in the body (and therefore represents a state function). As long as energy exchange on other paths than the thermal one is negligibly small this simple suggestion ("The heat that goes in can only come out again as heat") actually suffices to explain qualitatively and quantitatively a lot of effects in context with heat in everyday life or in other fields such as in building industry. The suggestion fails, however, if the bodies in consideration can exchange energy on others than thermal paths. In this case, it makes no sense to speak of "heat content." In most of the textbooks on thermodynamics, the term "*heat*" as quantity Q indicates, as mentioned above, something different, namely a *mode of energy transfer*. It depends on the conditions under which the transfer process acting on energy takes place. According to this view, heat is like work a process quantity.

In order to avoid misunderstandings, we will use the symbol "δ" instead of the simple "d" for the cases of small changes of the process quantities *exchanged* heat Q_e and *expended* work W_e (see Sect. 1.6).

Internal Energy *U* Kinetic and potential energies W_{kin} and W_{pot} contribute to the total energy W_{total} of a body. It possesses these energies when it moves or when it is raised or lowered as a whole. These energies are mostly insignificant in chemistry. They are additive terms that depend upon the (linear) velocity v (such as W_{kin}) or elevation h (such as W_{pot}) and can be easily split off so that, as a rule, instead of W_{total}, only the residual, the so-called *internal energy U*, is considered. The internal energy of a body that can only exchange energy as heat Q_e (see Sect. 8.7) and work W_e (in this case "pressure–volume work" by increasing or decreasing its volume V [see Eq. (24.1)] with the surroundings, can change as follows:

$$\mathrm{d}U = \delta Q_e + \delta W_e = T\mathrm{d}S - p\mathrm{d}V \quad \left(\text{where } \mathrm{d}S_g = 0\right). \tag{24.2}$$

The energy absorbed by a body in different ways (mechanically, thermally, chemically, electrically, etc.) is *not* stored in these different forms. Rather, it forms a common energy supply (Fig. 24.1).

Fig. 24.1 Pond as model. The idea that a body would contain the added heat Q as such is unsupportable in the same way that it is impossible to see in a pond how much of the water came from rain, dew, or groundwater.

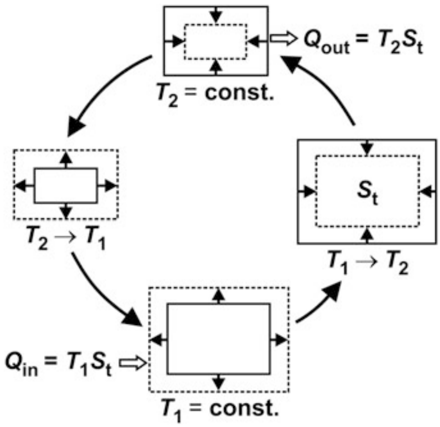


Fig. 24.2 Transfer of entropy S_t in a reversible cycle from a cold to a warm reservoir. Changes of volume are indicated by *arrows* (initial state: *contour line solid*, final state: *contour line dashed*). More heat Q flows off with the entropy S_t than in $Q_{out} > Q_{in}$, even though the body completely reverts to its initial state after every cycle and does not cool down at all. This means that energy is emitted as heat, which was not present in that form before but is generated. The question remains: what phase of the process does this happen in and how?

In the case of a body that can be expanded and heated, there is no quantity describing what might be called the amount of heat contained in it or simply its "*heat content*" (Fig. 24.2). One says that heat is a *process variable* and not a *state variable*. If we wish to describe the state of a body by using its temperature T and its volume V or its pressure p, for instance, in mathematical terms this means that the functions $Q(T, V)$ or $Q(T, p)$ or derivatives thereof do not exist. The consequences of this are aggravating, as we will soon see.

When there is only a single path available for an exchange of energy with the surroundings, such as in the case of "heat reservoirs" often used in thought experiments, energy can only be exchanged over this path. The heat Q that goes in can only come out again as heat. The situation is similar for a body having a pressure p that is either constant or is only dependent upon its volume V, $p = f(V)$ (Fig. 24.3). Whether or not it expands in the process is unimportant. However, if it does expand, a part of the energy which flowed in as heat is diverted to the outside over the mechanical path, but it flows back unchanged when energy is retrieved over the thermal path.

Such examples erroneously lead us to think of heat as being an entity contained in bodies (see above). Expressions such as "heat capacity" or "conduction of heat" support these images. They are holdovers of the time before heat was deemed a special mode of energy transfer.

Including Irreversible Processes Equation (24.1) changes when friction plays a role as it does in Fig. 24.4. Keep in mind that the *exchanged* entropy S_e, the *generated* entropy S_g, and the external pressure p_e are not state variables of the gas, but entropy S and internal pressure p are:

$$\underbrace{\mathrm{d}U}_{T\mathrm{d}S - p\mathrm{d}V} = \delta Q_e + \delta W_e = T\delta S_e - p_e\mathrm{d}V\ . \tag{24.3}$$

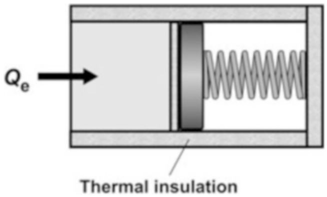


Fig. 24.3 Cylinder that uses a spring-loaded piston to press upon a gas contained in it.

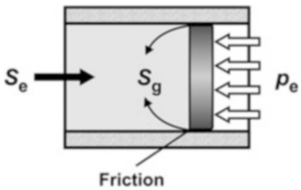


Fig. 24.4 Gas in a cylinder whose piston cannot move without friction. The work $\mathrm{d}W_e = -p_e\mathrm{d}V$ performed upon the piston by the external pressure p_e (>internal pressure p) when the volume changes, $\mathrm{d}V < 0$, is greater due to friction, while the amount of heat $\delta Q_e = T\delta S_e$ needed for same change of state is correspondingly smaller.

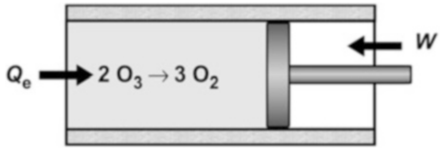


Fig. 24.5 Cylinder (with frictionless piston). A chemical reaction takes place inside the cylinder. Extent and drive of the reaction are described by ξ and $\mathcal{A}$, respectively.

Consider now not friction but a chemical reaction continuously running against inhibitions causing generation of entropy (Fig. 24.5). This is common in chemistry. The following is valid for the change of the internal energy:

$$\underbrace{\mathrm{d}U}_{T\mathrm{d}S - p\mathrm{d}V - \mathcal{A}\mathrm{d}\xi} = \delta Q_\mathrm{e} + \delta W_\mathrm{e} = T\delta S_\mathrm{e} - p\,\mathrm{d}V\ . \tag{24.4}$$

The last two formulas, Eqs. (24.2) and (24.3), specify an increase of energy dU which is caused by a small change of state. The expression under the curly brackets shows which state parameters are responsible and to what extent, while the expression on the right side describes how this increased demand is met. If we insert dS $= \delta S_\mathrm{e} + \delta S_\mathrm{g}$ (see Sect. 8.7), meaning $\delta S_\mathrm{e} = \mathrm{d}S - \delta S_\mathrm{g}$, and there and then solve for $T\delta S_\mathrm{g}$, we obtain formal expressions that we can easily visualize:

$$\underbrace{T\delta S_\mathrm{g}}_{\delta Q_\mathrm{g}} = \underbrace{-(p_\mathrm{e} - p)\cdot \mathrm{d}V}_{\delta W_\mathrm{b}}, \quad \text{and} \quad \underbrace{T\delta S_\mathrm{g}}_{\delta Q_\mathrm{g}} = \underbrace{\mathcal{A}\mathrm{d}\xi}_{\delta W_\mathrm{b}}\ . \tag{24.5}$$

Just as frictional work $-(p_\mathrm{e} - p)\cdot \mathrm{d}V$ is used to generate entropy, the equivalent is true for the work against reaction inhibitions.

Generated Heat Heat is generated by friction. Around the middle of the nineteenth century, this important insight led to upheaval in the field of thermodynamics. The effects of the energy contribution $T\delta S_\mathrm{g}$ upon the bodies involved are the same as the effects of heat added to them. It seems logical, therefore, to call this kind of contribution *heat* or, more exactly, *generated heat* δQ_g. Hence, it appears justified to call the expression $T\delta S_\mathrm{g}$ on the left of Eq. (24.5)—as is customary—the (generated) *frictional heat*, and, correspondingly, to call the one on the right the *generated reaction heat*.

The contribution δQ_g, which is always positive and only disappears in the limiting case, stands in opposition to the quantity dQ as the *exchanged heat*. For clarity, the latter is symbolized by δQ_e already used in this chapter. δQ_e can be either positive or negative, because during heat exchange heat can be added but also removed. The sum $\delta Q_\mathrm{e} + \delta Q_\mathrm{g} = \delta Q_\mathrm{total}$ would represent the *total amount* of heat collected. There appears to be no problem with adding up infinitesimally small contributions going over some path from a state I to a state II or to calculate the corresponding entropies after dividing the contributions by T:

$$S_e = \int_I^{II} \frac{\delta Q_e}{T}, \quad S_g = \int_I^{II} \frac{\delta Q_g}{T}, \quad \Delta S = \int_I^{II} \frac{\delta Q_{total}}{T}. \tag{24.6}$$

A conflict arises when we consider entropy generation in conduction of heat. When we have heat Q_t coming out of a hot reservoir (2) into a cold one (1) with a temperature of $T_2 > T_1$, the entropy generated by this is a result of the sums of the entropy changes $\Delta S_1 = Q_t/T_1$ and $\Delta S_2 = -Q_t/T_2$ of the two reservoirs: $S_g = Q_t/T_1 - Q_t/T_2$. S_g appears in the cold reservoir, so $Q_g = T_1 S_g$ should be the generated heat. This result seems ridiculous because heat conductance is considered a process where heat is conserved and remains constant.

However, this conclusion is not as absurd as it may appear at first glance. It can be justified if Q_g is considered compensation for the reduction of "free energy." If this energy is used in a "heat engine," it does so at the cost of the transferred heat Q, causing less of it to arrive at the cold reservoir. If this energy remains unused, it is "burnt" (dissipated) and the generated heat Q_g compensates for the expected decrease so that the same amount of heat arrives at the cold reservoir as is emitted from the hotter reservoir.

Two Prototypical Examples In chemistry, we are primarily interested in systems in which at least one chemical transformation takes place. The case in Fig. 24.5 gives us a concrete example where, instead of the slow decay of ozone, we can imagine some other kind of gas reaction. We will choose two special cases. The first one is the reaction of formation of water where the process can be controlled by turning a catalyst on or off. The second case is the dimerization of nitrogen dioxide (see Experiment 9.3) in which the participating gases, the brown nitrogen dioxide and its colorless dimer, are permanently in a strongly temperature dependent equilibrium:

$$\begin{array}{ll} 2\,H_2|g + O_2|g \rightarrow 2\,H_2O|g, & \text{inhibited,} \\ 2\,NO_2|g \rightleftarrows N_2O_4|g, & \text{uninhibited.} \end{array}$$

At first, our second example appears to be a rarely seen exception and hardly worth mentioning. It is, surprisingly, extremely common. An ensemble of molecules in a certain state of excitation, association, or conformation, can be considered an independent substance. Experiment 9.3 offers an example of such a case. Conversely, a mixture of chemicals where equilibrium between the individual components is established very quickly can be treated as one substance and calculations can be performed accordingly.

In order to characterize the state of the system in our simple prototypical examples, we need three parameters. Along with entropy S and volume V, we can use the extent of reaction ξ. The main equation for systems of this type (see Sect. 9.1), formulated with the help of the internal energy U, is:

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V - \mathcal{A}\mathrm{d}\xi. \tag{24.7}$$

In order to understand the conventional approach, we must first think of this equation as being unknown to us. It serves only as a background that allows us to consider the following development from another viewpoint.

Applying the First and Second Laws (of Thermodynamics) The equation $\mathrm{d}U = \delta Q_\mathrm{e} + \delta W_\mathrm{e}$ generally serves as a first step toward the calculus of thermodynamics to be created. It is considered an application of the First Law where the new state variable U can be constructed with the help of the two measurable process quantities Q_e and W_e. At first, we will limit ourselves to simple, *closed* systems, meaning systems without any exchange of substance with the surroundings and in which temperature and pressure are the same everywhere. Except as heat, energy can only be transferred in or out, without friction, by changes to the volume: $\delta W_\mathrm{e} = -p\mathrm{d}V$ and therefore

$$\mathrm{d}U = \delta Q_\mathrm{e} - p\mathrm{d}V. \tag{24.8}$$

In the second step, the process quantity δQ_e is replaced by $T\mathrm{d}S$ as an application of the Second Law. S is considered abstract but, like U, is actually a quantity that is measurable or obtainable from measured data. Because only processes for which $\delta Q_\mathrm{e} \leq T\mathrm{d}S$ can take place, Eq. (24.8) converts to:

$$\mathrm{d}U \leq T\mathrm{d}S - p\mathrm{d}V \quad \text{for spontaneous processes.} \tag{24.9}$$

This relation concisely summarizes the two Laws. Note that it only contains state variables. This is an important and helpful characteristic to keep in mind. Starting from this equation, a specific formalism with its own new quantities and terms is developed. These new quantities and terms are not necessary for understanding physical chemistry, but are crucial for understanding the pertinent literature.

Let us first consider changes of state that do not generate entropy. In this case, instead of the inequality above, the following equation is valid:

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \quad \text{for reversible processes.} \tag{24.10}$$

We know that the state of our model systems is determined by three parameters such as S, V, and ξ. Therefore, the formula above appears incomplete. It can be easily completed as follows:

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + ?\mathrm{d}\xi. \tag{24.11}$$

At this stage of the thermodynamic calculus formulated according to the traditional concept, the variable represented by the question mark is still unknown. It is important to close this gap. This is mathematically simple because except for the quantity we are seeking, all the others can be measured. The missing quantity equals the derivative of internal energy with respect to the extent of reaction at constant S and V:

$$? = \left(\frac{\partial U}{\partial \xi}\right)_{S,V}.$$

Nonetheless, one commonly sees a problem whose solution requires a specially created formalism. Why is this?

The abstractness of the variable S can be considered the underlying cause for this. When it appears as a function of quantities like the more or less familiar $T, p, V, \xi, \ldots$, it is already almost incomprehensible. The situation becomes even more difficult when S appears as a parameter upon which other variables depend in as yet unknown ways. The manipulation necessary to overcome this obstacle will be described in Sect. 24.3.

Equation (24.10) is a special case of Eq. (24.11) in which the expression $?\mathrm{d}\xi$ is left out. Under which conditions is this allowed? In anticipation of the subsequent derivation we equate $?\mathrm{d}\xi$ with $-\mathcal{A}\mathrm{d}\xi$. The answer to this will be different in each of our examples. The summand $-\mathcal{A}\mathrm{d}\xi$ disappears, because in the first example, ξ is constant so that $\mathrm{d}\xi = 0$. In the second example, equilibrium remains unaltered through all changes, so $\mathcal{A} = 0$ is always the case.

"Heat Content" It has already been mentioned at the beginning that there is no quantity of this type. There are replacements for this quantity in the traditional concept, though. For instance, internal energy U at constant volume (*isochoric* processes) can play this role. This results from the equation $\mathrm{d}U = \delta Q_\mathrm{e} - p\mathrm{d}V$ if we set $\mathrm{d}V = 0$. This is succinctly expressed in the formulas:

$$(\mathrm{d}U)_V = (\delta Q_\mathrm{e})_V \quad \text{or} \quad (\Delta U)_V = \Delta_V U = Q_{\mathrm{e},V}. \tag{24.12}$$

This relation can be used to define various other *isochoric* heat quantities such as integral and differential, molar and specific heats of reaction and the corresponding heat capacities. The most well known of these quantities is the "(global or integral) heat capacity at constant volume" or *isochoric heat capacity*, which we got to know briefly in Sect. 9.1:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{or more precisely,} \quad C_V = \left(\frac{\partial U}{\partial T}\right)_{V,\mathrm{rev}}. \tag{24.13}$$

The expression on the right specifically expresses what the one on the left implies. This is the fact that entropy may not be generated because this would reduce the amount of heat being supplied, falsifying the result. In the case of water formation, reversibility requires $\xi = \text{const.}$, and in the case of NO_2 dimerization, $\mathcal{A} = 0$:

$$\text{Case 1: } C_V = \left(\frac{\partial U}{\partial T}\right)_{V,\xi}, \quad \text{Case 2: } C_V = \left(\frac{\partial U}{\partial T}\right)_{V,\mathcal{A}=0}.$$

From another common point of view "heat capacity" is only a name for the expression on the left in line (24.13), regardless of whether or not it describes in reality a temperature-related quantity. We will return to the subject in a somewhat different context in the subsection "*Heat capacities*" below.

Enthalpy The quantity U can only appear in the role of "heat content" when volume V is constant. The most important case in practice, however, is the transfer of heat Q when pressure p is kept constant, instead of V (*isobaric* processes). In everyday life, but also in science and technology, many processes take place under conditions where the atmosphere ensures an approximately constant pressure (e.g., reactions in open flasks in the laboratory). A state quantity conceived for exactly this purpose is *enthalpy* H. Translated from the Greek it means "in-heat" or, more extensively, "heat content." It is defined as being derived from internal energy:

$$H := U + pV \qquad \text{with the differential} \qquad \mathrm{d}H = \underbrace{\delta Q_\mathrm{e} + V\mathrm{d}p}_{T\mathrm{d}S + V\mathrm{d}p - \mathcal{A}\mathrm{d}\xi}. \tag{24.14}$$

This formula is equivalent to Eq. (24.4)

The expression above, on the right, is the formal result of the defining equation when we first use the sum rule for the formation of differentials from two (and more) functions (see Sect. A.1.2 in the Appendix),

$$\mathrm{d}H = \mathrm{d}(U + pV) = \mathrm{d}U + \mathrm{d}(pV),$$

subsequently the corresponding product rule,

$$\mathrm{d}H = \mathrm{d}U + V\mathrm{d}p + p\mathrm{d}V,$$

and then insert $\mathrm{d}U = \delta Q_\mathrm{e} - p\mathrm{d}V$,

$$\mathrm{d}H = \delta Q_\mathrm{e} - \cancel{p\mathrm{d}V} + V\mathrm{d}p + \cancel{p\mathrm{d}V} = \delta Q_\mathrm{e} + V\mathrm{d}p.$$

The expression below the parentheses results when the main equation $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V - \mathcal{A}\mathrm{d}\xi$ [Eq. (24.7)] is used instead:

$$\mathrm{d}H = T\mathrm{d}S - \cancel{p\mathrm{d}V} - \mathcal{A}d\xi + V\mathrm{d}p + \cancel{p\mathrm{d}V} = T\mathrm{d}S + V\mathrm{d}p - \mathcal{A}d\xi.$$

The expression above the parentheses in Eq. (24.14) describes what one notices of the action in the system in the surroundings. The expression below describes what is actually happening in the system itself. As before, we have everything we need mathematically to calculate the missing quantity (represented again by the question mark and later identified as $\mathcal{A}$) from the measured data:

$$? = \left(\frac{\partial H}{\partial \xi}\right)_{S,\,p}.$$

Here the problem is the same as with internal energy: a quantity we do not understand (entropy) as an independent variable. For this reason, the purpose of the variable H is perceived differently, namely in its suitability for calculating *isobaric* heat effects. Equation (24.14) simplifies at constant pressure ($\mathrm{d}p = 0$):

$$(\mathrm{d}H)_p = (\delta Q_\mathrm{e})_p \quad \text{or} \quad (\Delta H)_p = \Delta_p H = Q_{\mathrm{e},\,p}. \tag{24.15}$$

As we have seen in the case above of internal energy [Eq. (24.12)], this relation can be useful for defining various *isobaric* heat quantities such as integral and differential, molar and specific heats of reaction, transition, solution, mixing, etc. These are all produced similarly at constant p and T and, depending upon the process in question, each one can have various symbols and names. We will be content with only two examples, one integral quantity and one differential quantity:

$$\begin{aligned} &(\Delta H)_{T,\,p} \equiv \Delta_{T,\,p} H \quad &&\text{general isothermal-isobaric change of enthalpy,}\\ &\left(\frac{\partial H}{\partial \xi}\right)_{T,\,p} \equiv \Delta_\mathrm{R} H \quad &&\text{(differential molar) enthalpy of reaction.} \end{aligned} \tag{24.16}$$

The word "heat" in names of quantities is almost always left out. One reason for this is that reaction enthalpies $\Delta_\mathrm{R}H$ can be defined for both spontaneous as well as forced processes; however, they appear as heat only in spontaneous processes. In the process $2\,H_2 + O_2 \rightarrow 2\,H_2O$, it would make sense to speak of the "heat of formation of water," while in the opposite case of $2\,H_2O \rightarrow 2\,H_2 + O_2$, it would make rarely sense to speak of "heat of decomposition of water."

We will take a closer look at the molar enthalpy of reaction of a spontaneously running process based upon Eq. (24.14). We will keep an eye on the effects on the surroundings (upper line) as well as what is happening inside the system (lower line). In both cases, we will make use of the possibility of writing a derivative as a differential quotient and to convert it using the rules of fractions:

$$\begin{aligned} \Delta_\mathrm{R} H &= \left(\frac{\partial H}{\partial \xi}\right)_{T,p} = \left(\frac{\mathrm{d}H}{\mathrm{d}\xi}\right)_{T,p} = \left(\frac{\delta Q_\mathrm{e} - \cancel{V\mathrm{d}p}}{\mathrm{d}\xi}\right)_{T,p} = \left(\frac{\delta Q_\mathrm{e}}{\mathrm{d}\xi}\right)_{T,p} \\ &= \left(\frac{T\mathrm{d}S - \cancel{V\mathrm{d}p} - \mathcal{A}\mathrm{d}\xi}{\mathrm{d}\xi}\right)_{T,p} = T\left(\frac{\mathrm{d}S}{\mathrm{d}\xi}\right)_{T,p} - \mathcal{A}\left(\frac{\cancel{\mathrm{d}\xi}}{\cancel{\mathrm{d}\xi}}\right)_{T,p} = T\cdot\Delta_\mathrm{R}S - \mathcal{A}\,. \end{aligned}$$

($V\mathrm{d}p$ disappears because $p = \text{const.}$, therefore $\mathrm{d}p = 0$, and the $\mathrm{d}\xi$ cancels out). The result in the upper line tells us that $\Delta_\mathrm{R}H$ describes an effect noticeable in the surroundings as exchanged heat. The lower line states that the effect in the system is made up of two contributions, "latent heat" and released energy; the latter can be arbitrarily made use of. In particular, it can be dissipated. There is more about this in Sects. 8.6 and 8.7. We will omit it here because in the traditional structure of thermodynamics, it can only be discussed later on (see Sect. 24.4).

Heat Capacities We will call the amount of entropy necessary for heating a body by 1 K the entropy capacity $\mathcal{C}$, while heat capacity C will describe the necessary heat (Q_e) for the same process. We also assume that no entropy (S_g) and therefore no heat (Q_g) is generated in the interior. The amount of entropy or heat the body can absorb depends upon whether it can expand or not—whether or not pressure p or volume V is constant. There may be additional conditions which need to be met. To be more mathematically correct, we might write:

$$\mathcal{C}_V = \left(\frac{dS}{dT}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V, \quad C_V = \left(\frac{\delta Q_e}{dT}\right)_V = \cancel{\left(\frac{\partial Q_e}{\partial T}\right)_V}.$$

The second to last expression in parentheses can be understood as a quotient of the *differential form* $\delta Q_e = TdS$ and the differential dT subject to the side condition $V = \text{const.}$ or $dV = 0$. The last expression, however, requires that the function whose derivative is to be taken, i.e., $Q(T, V)$, actually exists, which is not the case, as we have seen above. However, if we insert $\delta Q_e = TdS$ into the second to last differential quotient, we obtain:

$$C_V = \underbrace{\left(\frac{\delta Q_e}{dT}\right)_V = \left(\frac{TdS}{dT}\right)_V = T\left(\frac{dS}{dT}\right)_V}_{\text{not mandatory}} = T\mathcal{C}_V.$$

Equation $C_V = T\mathcal{C}_V$ appears so self-evident as to make the intermediate steps above superfluous. We also see that heat and entropy capacities only differ from each other by the factor T not only at constant volume but at constant pressure p as well, or if another quantity X is kept constant:

$$C_p = T\mathcal{C}_p, \quad C_X = T\mathcal{C}_X, \text{etc.}$$

Entropy is usually considered to be an abstract and especially difficult quantity. The attempt has therefore been made to perform calculations and derivations using other quantities, especially energetic quantities and to express the chemical data using those quantities. This works very well in the case of C_V because internal energy U at constant volume can play the role of "heat content" [cf. Eq. (24.12)]. If we write all the intermediate steps as above, we have:

$$C_V = \underbrace{\left(\frac{\delta Q_e}{dT}\right)_V = \frac{(\delta Q_e)_V}{dT} = \frac{(dU)_V}{dT} = \left(\frac{dU}{dT}\right)_V}_{\text{not mandatory}} = \left(\frac{\partial U}{\partial T}\right)_V,$$

in short,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{"(integral) heat capacity at constant volume."}$$

When pressure remains constant, enthalpy H plays the role of "heat content" [cf. Eq. (24.15)], and we can forgo writing the intermediate steps:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \text{"(integral) heat capacity at constant pressure."}$$

In fact, heat capacities are commonly not defined in terms of exchanged heat (Q_e), but are directly used as derivatives of internal energy U and enthalpy H. The disadvantage here is that, for every side condition (constant volume, constant pressure, constant X, etc.), a different quantity is necessary for the role of "heat content."

The fact that we have not addressed all the different types of heat capacities became evident at the end of the subsection on "*Heat content*" where a certain difficulty became apparent in our two prototypical example systems. Along with the integral quantities dealt with above, we need various specific (related to the mass) and molar (related to the amount of substance) quantities derived from them. We can omit them here because their definitions and applications follow known patterns.

24.3 Free Energy

Basic Idea Already in the nineteenth century it was assumed that the energy W_f released in a chemical transformation as well as the heat Q_g generated by it were a measure of the "driving force" of such a process. Energy was considered to be *free* when, for given conditions, it could be used for some other purpose, especially generation of entropy. W_f increases proportionally to the conversion $\Delta\xi$, so W_f itself is not the correct measure, but W_f, relative to the conversion, is: $W_f/\Delta\xi$ or, more exactly, $\delta W_f/d\xi$.

If the available energy W_f can be calculated for the process, then the "driving forces" can be derived from it and we can predict whether or not the process may run spontaneously. However, W_f cannot be determined only from a change to the total energy. The amount of it that can be released depends upon the particular circumstances. Depending upon the general conditions, different types of positive and negative contributions must be considered (see Fig. 24.6 and Experiment 24.1).

In Experiment 24.1 the free energy W_f of a raised body, which is lowered in water (case 1) and in air (case 2), is used to lift a second object. In the second case the lifting height is considerably greater. This energy W_f can be put to any number of other uses, especially for generation of entropy.

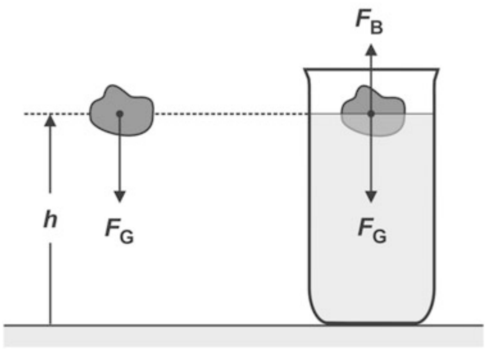
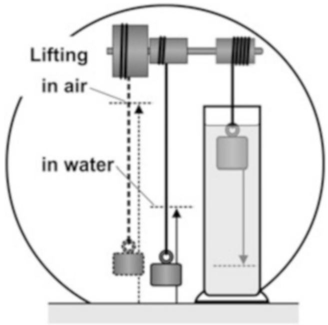


Fig. 24.6 A body sinking in air (*left*) and in water (*right*). The free and available energy W_f on the left is the total energy $W_f = F_G \cdot h$ originally expended to raise it in the air. Only a part of this, $W_f = (F_G - F_B) \cdot h$, is available on the right because energy is needed for pushing the body downward against the effect of buoyancy (F_G force of gravity, F_B buoyancy, h height).



Experiment 24.1 Using the free energy W_f of a raised body (on the *right*) to lift a second object (*middle*) using ropes and hoisting drums. The *dashed line* shows the change of position of the same object if the first object is lowered in air. W_f is greater here so that the attainable lifting height increases correspondingly.

***U* as Free Energy** Let us again consider the concrete system of water formation in our prototypical example system, where the process is controlled by a catalyst. Volume V and entropy S should be kept constant. In the case of volume, this can be accomplished by blocking the piston. It is more difficult to do for entropy because although the entropy leaves the system, all other exchanges of entropy should also be prevented. This can be done by not dissipating the released energy W_f in the system, but to first remove it electrically and to only produce the heat $Q_g = W_f$ outside of the system (Fig. 24.7).

In systems of this type, the internal energy U at constant S and V appears as stored free energy, which we can simply express in one or the other of the following ways:

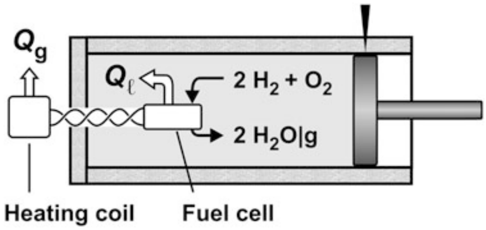


Fig. 24.7 A cylinder thermally insulated on all sides with built-in fuel cell. The fuel cell serves to remove the energy released by the reaction of H_2 and O_2 to $H_2O|g$ out of the cylinder, while the latent heat Q_ℓ that develops in the process of water formation cannot leave the cylinder. The piston remains stationary and therefore the volume constant.

$$W_f = (\Delta U)_{S,V} = \Delta_{S,V}U \quad \text{or} \quad \delta W_f = (\mathrm{d}U)_{S,V}.$$

Above, we have attempted to demonstrate such an implementation of an isentropic-isochoric process. This is not the point, though. All the necessary quantities are measurable so that the missing measure of the drive could be calculated:

$$\left(\frac{\delta W_f}{\mathrm{d}\xi}\right)_{S,V} = \left(\frac{\mathrm{d}U}{\mathrm{d}\xi}\right)_{S,V} = \left(\frac{\cancel{T\mathrm{d}S} - \cancel{p\mathrm{d}V} - \mathcal{A}\mathrm{d}\xi}{\mathrm{d}\xi}\right)_{S,V} = \left(\frac{-\mathcal{A}\cancel{\mathrm{d}\xi}}{\cancel{\mathrm{d}\xi}}\right)_{S,V} = -\mathcal{A}. \quad (24.17)$$

(Because S and V are constant, $T\mathrm{d}S$ and $p\mathrm{d}V$ disappear, so that $\mathrm{d}\xi$ cancels.) In order to get a feel for the traditional way of thinking about this, we must ignore the expression on the right. The goal is to develop a "deeper understanding" from the expression on the left (and ones similar to it, which we will go into later) of the actual causes of chemical transformations and what parameters can be used to influence them.

In this context, it is remarkable that Josiah Willard Gibbs chose this method of using energy at constant entropy to derive numerous results for the behavior of homogeneous and heterogeneous chemical systems. Except for the path for outflow of entropy, all other energy paths should be blocked. The actual trick of Gibbs' method is to *remove* entropy generation (S_g) from the system and the energy W_b that is used and dissipated along with it. Neither S_g nor W_b feed back upon the system; it is as if they did not exist. Under these conditions, if there is an entropy generating process, the internal energy U decreases. Equilibrium is reached if U has a minimum. The quantity U plays a role analogous to potential energy in mechanics. This applies to stability or lability of equilibria as well.

There is another notable point. The temperature in the system need not be temporally nor spatially constant. The transfer of a quantity of entropy S_t from a hot to a cold subarea by use of an auxiliary body that repeatedly undergoes a reversible cyclic process (see Fig. 24.2) delivers useful work to be stored in the system because all the possible paths for energy outflow have been blocked. Energy U remains constant in the process. Transferring the same amount of entropy S_t by

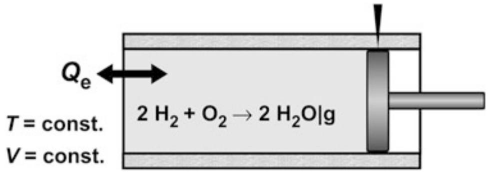


Fig. 24.8 Cylinder exchanging heat with a reservoir at constant temperature T. The piston is fixed so that V remains constant.

heat conduction, however, causes a decrease of U, while the same amount of entropy S_t as before is transferred from the hotter subarea to the colder subarea. U decreases, because under the conditions chosen by Gibbs also energy "flows out" together with the removal of entropy S_g from the location where it was generated.

Helmholtz Energy Let us again imagine a system at constant volume, but now at fixed temperature T, instead of fixed entropy S (Fig. 24.8). This may again be our example of the formation of water in a cylinder with a blocked piston, but in this case, heat exchange takes place with an exterior reservoir. In contrast to our previous case, the outflow of released and dissipated energy $W_f = Q_g$ during a given conversion $\Delta\xi$ requires no special measures because it runs by itself. The generated entropy $S_g = W_f/T$ does not enter into the entropy balance ΔS of our system because whatever is generated inside flows out. Not only $-W_f$ appears in the energy balance ΔU, but the (negative) term $T\Delta S$ does as well, which is caused by the change of chemical composition of our system:

$$\Delta U = T\Delta S - W_f \quad \text{or} \quad \text{more detailed,} \quad U_2 - U_1 = TS_2 - TS_1 - W_f.$$

The equation, solved for W_f, results first in

$$W_f = -(U_2 - TS_2) + (U_1 - TS_1) \quad \text{and finally in} \quad W_f = -\Delta\underbrace{(U - TS)}_{A}.$$

Here, T plays the role of a constant parameter.

The additional quantity $A := U - TS$ introduced in the traditional concept of thermodynamics actually appears as a reservoir of free energy W_f under the given conditions (constant temperature and volume, no exchange of substances with the surroundings). When the supply of A decreases, energy $W_f = -\Delta A$ becomes available for any purpose—depending upon the equipment being used. In general, without proper equipment, W_f will be dissipated. This is no different than when energy is used from other sources (sun, wind, water, coal). However, the contribution $T\Delta S$ cannot just be used freely. It is "*earmarked*" for a specific purpose—in this case, for shifting entropy between the system and the surroundings.

In the past, the quantity A was called "*free energy*." The fact that, under different conditions, there are other quantities that play the same role (for instance, U in closed systems at constant S and V) makes the name too general. It is therefore recommended calling the quantity A the *Helmholtz free energy* or just *Helmholtz energy*.

The fact that A can appear as "free energy" and under which circumstances this happens can be formally expressed similarly to how we did this in the case of the quantity U:

$$W_f = (\Delta A)_{T,V} = \Delta_{T,V}A \quad \text{or} \quad \delta W_f = (\mathrm{d}A)_{T,V}.$$

The definition of the quantity $A := U - TS$ and the main equation $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V - \mathcal{A}\mathrm{d}\xi$ of our example system lead to the following expression for the differential $\mathrm{d}A$ [by using the product rule for the term $\mathrm{d}(TS)$]:

$$\mathrm{d}A = \mathrm{d}(U - TS) = \mathrm{d}U - \mathrm{d}(TS) = (\cancel{T\mathrm{d}S} - p\mathrm{d}V - \mathcal{A}\mathrm{d}\xi) - (S\mathrm{d}T + \cancel{T\mathrm{d}S})$$

or

$$\mathrm{d}A = -S\,\mathrm{d}T - p\mathrm{d}V \underbrace{-\mathcal{A}\,\mathrm{d}\xi}_{(\mathrm{d}A)_{T,V} = \delta W_f} . \tag{24.18}$$

The idea behind dealing with "free energy" W_f was the possibility of gleaning a measure for the "driving force" of chemical transformation; actually, not W_f itself, but δW_f relative to the conversion $\mathrm{d}\xi$ was the sought-after measure:

$$\left(\frac{\delta W_f}{\mathrm{d}\xi}\right)_{T,V} = \left(\frac{\mathrm{d}A}{\mathrm{d}\xi}\right)_{T,V} = \left(\frac{-\cancel{S\mathrm{d}T} - \cancel{p\mathrm{d}V} - \mathcal{A}\mathrm{d}\xi}{\mathrm{d}\xi}\right)_{T,V} = \left(\frac{-\mathcal{A}\cancel{\mathrm{d}\xi}}{\cancel{\mathrm{d}\xi}}\right)_{T,V} = -\mathcal{A}. \tag{24.19}$$

(The terms $-S\mathrm{d}T$ and $-p\mathrm{d}V$ vanish because according to the chosen conditions, temperature T as well as volume V should be constant, meaning $\mathrm{d}T = 0$ and $\mathrm{d}V = 0$. Subsequently, $\mathrm{d}\xi$ cancels.)

We see that the quantity intended to be the "driving force"—in this case of the reaction of formation of water—can be written as a derivative of the state function $A(T, V, \xi)$. We already arrived at an equivalent result in Eq. (24.17). The essential difference here in contrast to before is that entropy S does *not* appear as an independent variable.

Gibbs Energy In practical cases, it happens much more often that not volume V but pressure p is kept constant along with temperature T. It is easy to include such cases (Fig. 24.9). Another pathway over which energy can be exchanged is the mechanical one through a moving piston. This does not change anything about the balance of entropy, but it does affect the balance of energy which now looks like this:

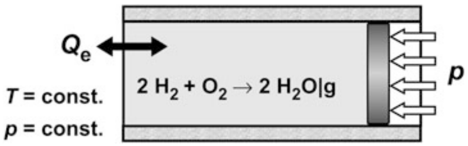


Fig. 24.9 Cylinder exchanging heat with a reservoir at constant temperature T. The piston is freely moveable at constant external pressure p.

$$\Delta U = T\Delta S - p\Delta V - W_\mathrm{f} \quad \text{or} \quad U_2 - U_1 = TS_2 - TS_1 - pV_2 + pV_1 - W_\mathrm{f}.$$

The equation, solved for W_f, results first in

$$W_\mathrm{f} = -(U_2 - TS_2 + pV_2) + (U_1 - TS_1 + pV_1)$$

$$\text{and finally in } W_\mathrm{f} = -\Delta(\underbrace{\overbrace{U + pV}^{H} - TS}_{G}).$$

Here, T as well as p appear in the role of a constant parameter.

As before the quantity A, the quantity $G := U + pV - TS = H - TS$, a further quantity introduced in the conventional concept of thermodynamics, acts as a reservoir of free energy W_f, but here under the changed conditions p, $T = \text{const.}$ (instead of V, $T = \text{const.}$). If G decreases under these conditions, energy $W_\mathrm{f} = -\Delta G$ becomes available for many uses, especially for dissipation.

In the past, the quantity $G = H - TS$ was called "*free enthalpy*," analogous to $A = U - TS$, which was called "free energy." Today *Gibbs free energy* or just *Gibbs energy* is the recommended expression (IUPAC). How and when G can appear in the role of "free energy" can be formally expressed very similarly to the cases of U and A:

$$W_\mathrm{f} = (\Delta G)_{T,V} = \Delta_{T,V} G \quad \text{or} \quad \delta W_\mathrm{f} = (\mathrm{d}G)_{T,V}.$$

We obtain the following expression for the differential $\mathrm{d}G$ from the definition $G := U + pV - T\,S$ and the main equation $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V - \mathcal{A}\mathrm{d}\xi$:

$$\begin{aligned}\mathrm{d}G &= \mathrm{d}(U + pV - TS) = \mathrm{d}U + \mathrm{d}(pV) - \mathrm{d}(TS)\\ &= (\cancel{T\mathrm{d}S} - \cancel{p\mathrm{d}V} - \mathcal{A}\mathrm{d}\xi) + (V\mathrm{d}p + \cancel{p\mathrm{d}V}) - (S\mathrm{d}T + \cancel{T\mathrm{d}S})\end{aligned}$$

and therefore

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p \underbrace{-\mathcal{A}\mathrm{d}\xi}_{(\mathrm{d}G)_{T,p} = \delta W_\mathrm{f}.}, \tag{24.20}$$

from which we can conclude that the quantity we are seeking as the "driving force" of a reaction can be expressed in numerous ways as the derivative of a state function, in the present case, as the derivative of the function $G(T, p, \xi)$ (same procedure as in the case of the derivative of the state function $A(T, V, \xi)$):

$$\left(\frac{\delta W_\mathrm{f}}{\mathrm{d}\xi}\right)_{T,\,p} = \left(\frac{\mathrm{d}G}{\mathrm{d}\xi}\right)_{T,\,p} = \left(\frac{-\cancel{S\mathrm{d}T}+\cancel{V\mathrm{d}p}-\mathcal{A}\mathrm{d}\xi}{\mathrm{d}\xi}\right)_{T,\,p} = \left(\frac{-\mathcal{A}\cancel{\mathrm{d}\xi}}{\cancel{\mathrm{d}\xi}}\right)$$
$$= -\mathcal{A}. \qquad (24.21)$$

As we have also seen with enthalpy H, there are numerous other quantities that can be derived using G as the basis. Here are just two examples, an integral and a differential quantity:

$$(\Delta G)_{T,p} \equiv \Delta_{T,p}G \quad \text{general isothermal-isobaric change of Gibbs energy,}$$
$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} \equiv \Delta_\mathrm{R}G \quad \text{(differential molar) Gibbs energy of reaction.}$$
$$(24.22)$$

Spontaneous Process The most commonly observed transformations in chemistry are, as already mentioned, those at constant temperature and constant pressure, which is why the mathematical tools are generally oriented toward these conditions. The heat function that we deal with the most is enthalpy $H(T, p, \xi, \ldots)$ and the quantity most often playing the role of free energy is the Gibbs energy $G(T, p, \xi, \ldots)$. Until now, we have only allowed a single parameter ξ, but it is also possible to observe two or more transformations or other types of change at the same time. Spontaneous changes in closed systems at constant T and p are only possible in the direction in which the free energy decreases, in this case, the Gibbs energy:

$$\begin{array}{lll} \mathrm{d}G < 0 & \text{spontaneously possible in closed} & \left\{\begin{array}{l}\text{isothermal-isobaric,}\\ \text{isothermal-isochoric,}\\ \text{isentropic-isochoric}\end{array}\right\} \text{systems.} \\ \mathrm{d}A < 0 & & \\ \mathrm{d}U < 0 & & \end{array}$$

We have included two further possibilities. These are different state functions depending upon the side conditions that must be met. For chemical transformations of all types, meaning the processes chemists are most interested in, all these conditions for spontaneous processes can be simply summed up as one, we already know very well and used very often (see e.g. Sect. 4.6): $\mathcal{A} > 0$ [cf. Eqs. (24.17), (24.19), and (24.21)].

If we have $(\mathrm{d}G)_{T,p} = 0$ for small changes of state, there will be no preferred direction and the system will be in equilibrium. Correspondingly, under other side conditions, $(\mathrm{d}A)_{T,V} = 0$, $(\mathrm{d}U)_{S,V} = 0$, etc., are valid. For chemical transformations this means simply $\mathcal{A} = 0$.

Coupling The thermodynamic functions $G(T, p, \xi)$, $A(T, V, \xi)$, $U(S, V, \xi)$, ..., allow for another type of application if we keep in mind that the mixed second derivatives are independent of the order in which the derivatives are taken

(Schwarz' theorem). Here, it is taken for granted that these derivations exist and are continuous.

In the case of a state function $Z = f(x, y)$ Schwarz' theorem states that

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial Z}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial Z}{\partial y}\right)_x\right)_y \quad \text{or alternatively formulated}$$

$$\left(\frac{\partial^2 Z}{\partial x \partial y}\right) = \left(\frac{\partial^2 Z}{\partial y \partial x}\right).$$

This can be used to derive several important relations between different coefficients. At first, Eq. (24.20) yields:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,\xi}, \quad V = +\left(\frac{\partial G}{\partial p}\right)_{T,\xi}, \quad \mathcal{A} = -\left(\frac{\partial G}{\partial \xi}\right)_{T,p}. \tag{24.23}$$

If one takes derivates of the quantities S, V, $\mathcal{A}$, represented themselves as derivatives, one can use Schwarz' theorem:

$$\left(\frac{\partial S}{\partial p}\right)_{T,\xi} = -\left(\frac{\partial^2 G}{\partial p \partial T}\right)_{\xi} = -\left(\frac{\partial^2 G}{\partial T \partial p}\right)_{\xi} = -\left(\frac{\partial V}{\partial T}\right)_{p,\xi},$$
$$\left(\frac{\partial S}{\partial \xi}\right)_{T,p} = -\left(\frac{\partial^2 G}{\partial \xi \partial T}\right)_{p} = -\left(\frac{\partial^2 G}{\partial T \partial \xi}\right)_{p} = +\left(\frac{\partial \mathcal{A}}{\partial T}\right)_{p,\xi},$$
$$\left(\frac{\partial V}{\partial \xi}\right)_{T,p} = +\left(\frac{\partial^2 G}{\partial \xi \partial p}\right)_{T} = +\left(\frac{\partial^2 G}{\partial p \partial \xi}\right)_{T} = -\left(\frac{\partial \mathcal{A}}{\partial p}\right)_{T,\xi}.$$

For better understanding, let us take a look at the first line. The parameter ξ should be always constant meaning it is enough if we focus on the function $G = f(T, p)$ and their differential $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$. To begin with, the derivative of this function is firstly taken with respect to T at constant p and secondly with respect to p at constant T:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial p}\right)_T = V.$$

Subsequently, the derivative of the expression on the left is taken with respect to p at constant T and that on the right with respect to T at constant p:

$$\left(\frac{\partial^2 G}{\partial T \partial p}\right) = \left(\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right)_p\right)_T = -\left(\frac{\partial S}{\partial p}\right)_T, \quad \left(\frac{\partial^2 G}{\partial p \partial T}\right) = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_T\right)_p = \left(\frac{\partial V}{\partial T}\right)_p.$$

Because the expressions on the left in both equations are equal according to Schwarz' theorem, this also holds true for the expressions on the right.

This same pattern can be used for finding numerous other relations. However, we do not need this method because the flip rule leads directly to the same result without taking the detour over a second derivative of an appropriately chosen thermodynamic function. The relation in the first line, for example, is already well known from Sect. 9.2 [Eq. (9.7)].

24.4 Partial Molar Quantities

Molar Enthalpy When dealing with enthalpy, it is common to use the same procedure as the one applied for quantifying a substance's volume demand and associating the volume demand of a mixture to the individual components (see Sect. 8.2). Enthalpy at fixed T and p for pure substances increases proportionally to the amount of substance n, so the characteristic molar quantity is the enthalpy relative to n:

$$H_\mathrm{m} = \frac{H}{n} \quad \textit{molar enthalpy}. \tag{24.24}$$

For a substance in a mixture of other substances, this is defined correspondingly [cf. Eq. (8.2)]:

$$H_\mathrm{m} = \left(\frac{\partial H}{\partial n}\right)_{T,\,p,n',n'',\ldots} \quad (\textit{partial})\ \textit{molar enthalpy of a substance}. \tag{24.25}$$

The enthalpy of the total mixture equals the sum of the contributions by the individual components A, B, C, ... We were introduced to this for volume and entropy before [cf. Eqs. (8.3) and (8.12)]:

$$H = n_\mathrm{A}H_\mathrm{A} + n_\mathrm{B}H_\mathrm{B} + n_\mathrm{C}H_\mathrm{C} + \ldots \ . \tag{24.26}$$

If we are interested in the (differential) molar enthalpy of reaction $\Delta_\mathrm{R}H(\xi)$ of a transformation which takes place in the system under consideration, we again start from the general conversion formula for an arbitrary reaction between pure or dissolved substances (like in Chap. 8):

$$|\nu_\mathrm{B}|\mathrm{B} + |\nu_{\mathrm{B}'}|\mathrm{B}' + \ldots \rightarrow \nu_\mathrm{D}\mathrm{D} + \nu_{\mathrm{D}'}\mathrm{D}' + \ldots \ .$$

For better understanding of the following approach it is recommendable to read the short Sect. 8.3 again. Analogously to the molar volume of reaction $\Delta_\mathrm{R}V(\xi)$ and the molar entropy of reaction $\Delta_\mathrm{R}S(\xi)$ discussed in the mentioned Section, we obtain for the molar enthalpy of reaction $\Delta_\mathrm{R}H(\xi)$ in the case of small conversions $\Delta\xi$ (when p, T, ξ', ξ'', . . . are kept constant):

$$\Delta_R H = \frac{\Delta H}{\Delta \xi} = \nu_B H_B + \nu_{B'} H_{B'} + \ldots + \nu_D H_D + \nu_{D'} H_{D'} + \ldots = \sum_i \nu_i H_i. \quad (24.27)$$

Applied to our prototypical example reaction $2\ H_2|g + O_2|g \rightarrow 2\ H_2O|g$, the equation becomes:

$$\Delta_R H = -2H(H_2|g) - H(O_2|g) + 2H(H_2O|g).$$

Because the conversion numbers of the reactants are negative and those of the products positive, the expression can be read as a difference:

$$\Delta_R H = \underbrace{2H(H_2O|g)}_{\text{products}} - \underbrace{(2H(H_2|g) + H(O_2|g))}_{\text{reactants}}.$$

This means we follow the familiar schema when calculating $\Delta_R H$: "The sum of the molar characteristic quantities of the products minus the sum of the molar characteristic quantities of the reactants."

In the limit, we require the $\Delta\xi$ to be infinitesimally small in Eq. (24.27). This is again expressed formally by using the symbol ∂ instead of the difference Δ. If we now introduce all the quantities that are to be kept constant as indices of the differential quotient, the equation takes the following form:

$$\Delta_R H = \left(\frac{\partial H}{\partial \xi}\right)_{p,T,\xi',\xi'',\ldots} = \sum_i \nu_i H_i. \quad (24.28)$$

This is the (differential) molar enthalpy of reaction $\Delta_R H$ mentioned above [see Eq. (24.16)].

Molar Gibbs Energy Other extensive thermodynamic quantities are dealt with in the same way. In the case of pure substances, they are considered a function of T, p, n, and for a substance in a mixture with other substances, as a function of T, p, n, n', n'', ... The Gibbs energy G is especially interesting in this context because in the conventional thermodynamic calculations, it is very closely connected with the chemical potential. In the case of a pure substance at fixed T and p, G is proportional to the amount of substance n. Therefore, G itself does not serve as the substance-specific characteristic, but the quotient G/n:

$$G_m = \frac{G}{n} \quad \textit{molar Gibbs energy}. \quad (24.29)$$

We proceed accordingly for a substance in a mixture with other substances:

$$G_{\mathrm{m}} = \left(\frac{\partial G}{\partial n}\right)_{T,\,p,n',n'',\ldots} \quad \textit{(partial) molar Gibbs energy of a substance.} \tag{24.30}$$

The values for the mixture as a whole are added up from the contributions by the individual components A, B, C, ... just as they are for volume, entropy, enthalpy:

$$G = n_{\mathrm{A}}G_{\mathrm{A}} + n_{\mathrm{B}}G_{\mathrm{B}} + n_{\mathrm{C}}G_{\mathrm{C}} + \ldots\ . \tag{24.31}$$

The (differential molar) *Gibbs energy of reaction* $\Delta_{\mathrm{R}}G$ of a transformation can be expressed analogously to how we dealt with the enthalpy of reaction $\Delta_{\mathrm{R}}H$. In the case of small conversions $\Delta\xi$, when p, T, ξ', ξ'', ... are again kept constant, we obtain:

$$\Delta_{\mathrm{R}}G = \frac{\Delta G}{\Delta\xi} = v_{\mathrm{B}}G_{\mathrm{B}} + v_{\mathrm{B'}}G_{\mathrm{B'}} + \ldots + v_{\mathrm{D}}G_{\mathrm{D}} + v_{\mathrm{D'}}G_{\mathrm{D'}} + \ldots = \sum_i v_i G_i \tag{24.32}$$

or more precisely for vanishingly small conversions $\mathrm{d}\xi$:

$$\Delta_{\mathrm{R}}G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T,\xi',\xi'',\ldots} = \sum_i v_i G_i. \tag{24.33}$$

This is the (differential molar) Gibbs energy of reaction already mentioned [cf. Eq. (24.22)].

Chemical Potential We obtain the differential $\mathrm{d}G$ from the definition for Gibbs energy $G := U + pV - TS$ and the main equation for a mixture $\mathrm{d}W = \mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} + \ldots$ [see Eq. (9.2)]:

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} + \ldots\ . \tag{24.34}$$

Because we consider the material system in question to be at rest and weightless, we can equate the total energy W to the internal energy U.

Let us have a closer look at the derivation of Eq. (24.34). For the differential $\mathrm{d}G$ we obtain from the definition of G:

$$\mathrm{d}G = \mathrm{d}U + \mathrm{d}(pV) - \mathrm{d}(TS) = \mathrm{d}U + V\mathrm{d}p + p\mathrm{d}V - S\mathrm{d}T - T\mathrm{d}S.$$

Substitution of the differential $\mathrm{d}U$ according to the main equation results in

$$\mathrm{d}G = \left(\cancel{T\mathrm{d}S} - \cancel{p\mathrm{d}V} + \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} + \ldots\right) + \left(V\mathrm{d}p + \cancel{p\mathrm{d}V} - S\mathrm{d}T - \cancel{T\mathrm{d}S}\right)$$

and therefore

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu_\mathrm{A}\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\mathrm{d}n_\mathrm{B} + \ldots .$$

For a substance B as a component of a mixture of other substances A, C, …, Eq. (24.34) formally results in the following:

$$G_\mathrm{B} = \left(\frac{\partial G}{\partial n_\mathrm{B}}\right)_{T,\,p,n_\mathrm{A},\ldots} = \left(\frac{\mathrm{d}G}{\mathrm{d}n_\mathrm{B}}\right)_{T,\,p,n_\mathrm{A},\ldots}$$
$$= \left(\frac{-\cancel{S\mathrm{d}T} + \cancel{V\mathrm{d}p} + \cancel{\mu_\mathrm{A}\mathrm{d}n_\mathrm{A}} + \mu_\mathrm{B}\cancel{\mathrm{d}n_\mathrm{B}} + \ldots}{\cancel{\mathrm{d}n_\mathrm{B}}}\right)_{T,\,p,n_\mathrm{A},\ldots} = \mu_\mathrm{B}.$$

"Chemical potential" and "partial molar Gibbs energy" of a substance are identical! This makes it possible to construct simple translation rules between conventional formalisms and the one used by us:

$$G_\mathrm{B} = \mu_\mathrm{B}, \qquad H_\mathrm{B} = \mu_\mathrm{B} + TS_\mathrm{B},$$
$$\Delta_\mathrm{R}G = -\mathcal{A}, \qquad \Delta_\mathrm{R}H = -\mathcal{A} + T\Delta_\mathrm{R}S.$$

If we insert $G_\mathrm{B} = \mu_\mathrm{B}$ into Eq. (24.33), we obtain:

$$\Delta_\mathrm{R}G = \nu_\mathrm{B}\mu_\mathrm{B} + \nu_{\mathrm{B}'}\mu_{\mathrm{B}'} + \ldots + \nu_\mathrm{D}\mu_\mathrm{D} + \nu_{\mathrm{D}'}\mu_{\mathrm{D}'} + \ldots = \sum_i \nu_i\mu_i.$$

This is nothing else than $-\mathcal{A}$ (see Sect. 8.6). The expression for H_B is obtained by using the definition for $G := H - TS$,

$$H_\mathrm{B} = G_\mathrm{B} + TS_\mathrm{B} = \mu_\mathrm{B} + TS_\mathrm{B},$$

and that for $\Delta_\mathrm{R}H$ by inserting the equation above into Eq. (24.28):

$$\Delta_\mathrm{R}H = \nu_\mathrm{B}(\mu_\mathrm{B} + TS_\mathrm{B}) + \nu_{\mathrm{B}'}(\mu_{\mathrm{B}'} + TS_{\mathrm{B}'}) + \ldots + \nu_\mathrm{D}(\mu_\mathrm{D} + TS_\mathrm{D}) + \nu_{\mathrm{D}'}(\mu_{\mathrm{D}'} + TS_{\mathrm{D}'}) + \ldots$$

and therefore

$$\Delta_\mathrm{R}H = (\nu_\mathrm{B}\mu_\mathrm{B} + \nu_{\mathrm{B}'}\mu_{\mathrm{B}'} + \ldots + \nu_\mathrm{D}\mu_\mathrm{D} + \nu_{\mathrm{D}'}\mu_{\mathrm{D}'})$$
$$+ T(\nu_\mathrm{B}S_\mathrm{B} + \nu_{\mathrm{B}'}S_{\mathrm{B}'} + \ldots + \nu_\mathrm{D}S_\mathrm{D} + \nu_{\mathrm{D}'}S_{\mathrm{D}'} + \ldots)$$

The expression in the first set of parentheses corresponds again to $-\mathcal{A}$ and that in the second set of parentheses to $\Delta_\mathrm{R}S$ [according to Eq. (8.13)].

In books of tables, usually the standard values of molar Gibbs free energies of formation $\Delta_\mathrm{f}G$ of substances are listed. $\Delta_\mathrm{f}G$ is the change of Gibbs free energy that accompanies the formation of 1 mol of the substance in question, pure or dissolved, from its elements under standard conditions. Because $\Delta_\mathrm{f}G$ is nothing else than a special case of $\Delta_\mathrm{R}G$, it corresponds to the negative "drive of formation" ($-\mathcal{A}$) or the positive "drive of decomposition" $\mathcal{A}$, respectively. In Sect. 4.6, however,

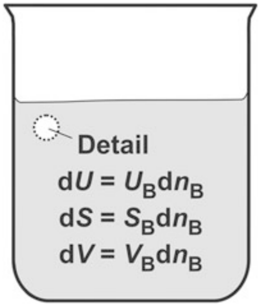


Fig. 24.10 Chemical potential μ_B visualized as the energy released when a small amount of dn_B disappears, shown here as a section of a larger area of a pure substance B. As B disappears in the section, the energy dU in it is released. The volume dV of the part shrinks down to a point while the entropy dS in it is moved to the surrounding matter. The shrinking down to a point causes a contribution to the released energy of $+p \cdot dV$ and the displacement of entropy causes one of $-T \cdot dS$.

we have learned that the chemical drive to decompose corresponds to the chemical potential of the substance. Therefore, the tabulated $\Delta_f G$ values are nothing else than the standard values of the chemical potential we have used in this book!

The "chemical potential μ" and "drive (affinity) $\mathcal{A}$" are not considered independent concepts in the conventional thermodynamic formalism. Therefore, one does not directly define the temperature and pressure coefficients α and β, as well as α and β; rather, they are always expressed in terms of different quantities:

$$\alpha_B = -S_B, \quad \beta_B = V_B \quad \text{[see Eqs.(9.11) and (9.16)]},$$
$$\alpha = \Delta_R S, \quad \beta = -\Delta_R V \quad \text{[see Eqs.(9.13) and (9.18)]}.$$

If one is interested, for example, in the temperature coefficient of the chemical potential of a substance, it is only necessary to find the value of the corresponding molar entropy in an appropriate table book and to change the sign.

If the equation $H_B = \mu_B + TS_B$ is solved for μ_B, and $H_B = U_B + pV_B$ is taken into consideration, we obtain a relation that can be interpreted descriptively (Fig. 24.10):

$$\mu_B = H_B - TS_B = U_B + pV_B - TS_B.$$

24.5 Activities

Basic Idea The quantities used for describing deviations from what is considered ideal behavior of gases and dissolved substances are another characteristic feature of the traditional formalism. We prefer to take the discrepancies into account by additional terms in the chemical potential because these quantities can be seamlessly inserted into the thermodynamic apparatus. By contrast, in the traditional approach, it is customary to introduce the necessary corrections as correcting factors to the measures of composition (concentration, etc.) and to use these modified quantities instead of the actual ones.

The basic idea is the same one as for mass action. The higher the concentration c_B of a dissolved substance B, the stronger its influence upon the formation of some product will be. The simplest case is a dissolved substance D. When compared to its content, the effect is simply proportional to the concentration c_B. We imagine this is valid as long as c_B remains small and the B atoms are therefore far enough apart from each other. At higher concentrations, the atoms begin to influence each other. This can either strengthen or weaken their influence upon the formation of product, just as if the concentration of B had increased or decreased. This apparent increase or decrease is described by a factor γ_B, the so-called *activity coefficient*, which multiplies c_B. $\gamma_B c_B$ is basically the "chemically effective" or "chemically active" concentration of B that can be greater or smaller than the actual c_B. The concentration c_B itself does not appear as the argument of a logarithmic function in the mass action equation, but rather the relative concentration $c_{r,B} = c_B/c$ or the *active relative concentration* $\gamma_B c_B/c$, which is usually but inaccurately called the *activity* of B:

$$\mu_B = \overset{\circ}{\mu}_B + RT\ln \underbrace{\frac{\gamma_B c_B}{c^{\pi}}}_{a_B} \quad \text{with } a_B \text{ as activity of B (on the } c \text{ scale).} \qquad (24.35)$$

Activities and activity coefficients are commonly used in order to rewrite some frequently used equations into more pleasing form. In this manner, some relations can be written in especially short form. There is a certain difficulty, though, in the fact that these quantities are introduced and applied in many variations. To introduce the subject, we will choose the most general form that is less often used but can be most easily understood.

Chemical Activity This quantity (symbol λ_B), which is assigned to a substance B, is formed by a simple scale transformation from the chemical potential μ_B:

$$\mu_B = RT\ln\lambda_B \quad \text{or} \quad \lambda_B = \exp\left(\frac{\mu_B}{RT}\right).$$

We call the quantity λ_B the *chemical activity*. This is based upon the name "chemical potential" for the quantity μ_B, from which it stems. The recommended name "absolute activity" is unfitting because, depending upon the choice of zero point for the scale of μ, other "relative" λ_B values can result that differ by fixed factors.

λ_B results from μ_B by transforming into an exponential scale. Conversely, the potential can be regained when the activities are transferred into a corresponding logarithmic scale. It becomes easy to understand why (except for some special cases) every statement that can be formulated with chemical potential can also be expressed by chemical activities and vice versa. Qualitatively seen, activities are measures of a substance's tendency to transform, just as potentials are.

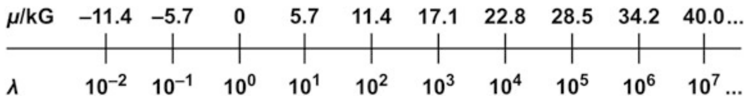


Fig. 24.11 Relationship between μ and λ scales at 298 K.

Such coexistence of various scales is not uncommon in science and technology. If a quantity changes by many orders of magnitude, it is common to start using logarithmic scales in order to represent the entire range of values more easily. For example, the concentration c_{H^+} of hydrogen ions changes by 14 orders of magnitude from that in a strongly acidic solution to that in a strongly basic one; and the acoustic power of an acoustic source changes by 13 orders of magnitude from the auditory threshold to the pain threshold. In the first case, instead of the c_{H^+} value, the preferred one is the pH value, which was originally introduced as a logarithmic measure for hydrogen ion concentration $\mathrm{pH} = -\lg(c_{H^+}/c)$ (see Sect. 7.3). In the second case, instead of the *acoustic power P*, it is the *acoustic power level* (or *sound power level*) $\lg(P/P_0)$ with the reference value $P_0 = 10^{-12}$ W that is used. Figure 24.11 illustrates how the μ and λ scales relate to each other.

Residual Activities In Chap. 13, we were introduced to the first steps of a kind of series expansion for the content dependence of chemical potential. The description can be refined by repeated splitting into a *basic value* describing a main effect and a *residual value* summing up the side effects:

$$\text{value} = \text{basic value} + \underbrace{\text{residual value}} \qquad \text{(step 1)}$$
$$\text{value*} = \text{basic value*} + \underbrace{\text{residual value*}} \qquad \text{(step 2)}$$
$$\text{value**} = \text{basic value**} + \underbrace{\text{residual value**}} \qquad \text{(step 3)}$$
$$\text{value***} = \ldots \qquad (\;\text{"}\;)$$

As a result, the quantity μ is split into a sum $\mu = \mu^\circ + \mu^* + \mu^{**} + \mu^{***} + \ldots$ which, depending upon how accurate it must be, can have more or fewer terms. The sum transforms into a product if the potentials are transformed into activities:

$$\lambda = \lambda^\circ \cdot \lambda^* \cdot \lambda^{**} \cdot \lambda^{***} \cdot \ldots .$$

At that point (Chap. 13), we only used a two-step approach [see Eq. (13.2)], so that $\mu(x)$ appeared to split into three terms: basic value $\overset{\bullet}{\mu}$ + basic value* $\overset{\times}{\mu}$ + residual value* $\overset{+}{\mu}$. Three factors then correspondingly appear in the activity scale:

$$\mu(x) = \overbrace{\overset{\bullet}{\mu}}^{\text{basic term}} + \overbrace{\overset{*}{\mu}(x)}^{\text{residual term}} \qquad \lambda(x) = \overbrace{\overset{\bullet}{\lambda}}^{\text{"basic activity"}} \times \overbrace{\overset{*}{\lambda}(x)}^{\text{"(residual) activity"}}$$
$$\overset{*}{\mu}(x) = \underbrace{\overset{\times}{\mu}(x)}_{\text{mass action term}} + \underbrace{\overset{+}{\mu}(x)}_{\text{extra term}} \qquad \overset{*}{\lambda}(x) = \underbrace{x}_{\text{measure of composition}} \times \underbrace{\overset{+}{\lambda}(x)}_{\text{activity coeff.}}$$

For clarity's sake, we will only use "basic term" and "residual term" for expressions

Fig. 24.12 Potential μ and activity λ for cane sugar in a glass of Turkish tea ($\vartheta = 50$ °C, $c = 1{,}000$ mol m^{-3}), divided into basic values $\overset{\circ}{\mu}$ and $\overset{\circ}{\lambda}$, mass action contributions $\overset{\times}{\mu}$ and $\overset{\times}{\lambda}$, as well as extra values $\overset{+}{\mu}$ and $\overset{+}{\lambda}$:

$$\mu = \overset{\circ}{\mu}_c + \overset{\times}{\mu}_c + \overset{+}{\mu}_c = (-1{,}575.59 + 0.00 + 0.65)\text{kG},$$

$$\lambda = \overset{\circ}{\lambda}_c \cdot \overset{\times}{\lambda}_c \cdot \overset{+}{\lambda}_c = 2.03 \times 10^{-245} \times 1.00 \times 1.27.$$

At the taste threshold at approximately 5 mol m^{-3}, the values are:

$$\mu = \overset{\circ}{\mu}_c + \overset{\times}{\mu}_c + \overset{+}{\mu}_c = (-1{,}575.59 - 14.23 + 0.003)\text{ kG},$$

$$\lambda = \overset{\circ}{\lambda}_c \cdot \overset{\times}{\lambda}_c \cdot \overset{+}{\lambda}_c = 2.03 \times 10^{-245} \times 5 \times 10^{-3} \times 1.001.$$

of the first step. Otherwise we will use appropriate alternative names such as "mass action term" for the basic term of step 2 and "extra term" for the corresponding residual term. The mass action term $\overset{\times}{\mu}(x)$ is given by the relation $\overset{\times}{\mu} = RT\ln x$. Correspondingly, the $\overset{\times}{\lambda}(x)$ value results in $\overset{\times}{\lambda} = \exp[(RT\ln x)/RT] = \exp[\ln x] = x$.

Going from potentials to exponentially growing activities leads to unwieldy values (see Fig. 24.12) which are not suitable for numerical calculations and tabulating of chemical data. This is why the basic values of λ are rarely used but usually only the residual values $\overset{*}{\lambda}$. The latter are commonly called "*activity*" and an independent symbol is introduced a ($\equiv \overset{*}{\lambda} = \overset{\times}{\lambda}(x) \cdot \overset{+}{\lambda}(x) = \overset{+}{\lambda}(x) \cdot x$ with $\overset{+}{\lambda}(x)$ in the role of an activity coefficient).

When dealing with mixtures and solutions, there are different approaches to separating basic and residual values (see Sect. 1.5). We tend to assume that the participating substances in a mixture can be dealt with uniformly; in particular, a substance can appear in a pure state in the same liquid or solid α-, β-, γ- . . . phase. In a solution, however, we contrast the *solvent* as the main component and the *solutes* B, C, . . . as the others. The sweetened tea in Fig. 24.12 is an example of such a solution. Considered as a mixture, this would mean that the sugar should be treated as a liquid component in the entire range of 0 to 100 %. For a solvent and all components of mixtures, we always use $\overset{\circ}{\mu}_\bullet \left(\equiv \overset{\bullet}{\mu}\right)$ or $\overset{\circ}{\lambda}_\bullet$ in the pure state as the basic value for potential μ or activity λ. For dissolved substances, in contrast, we choose $\overset{\circ}{\mu}$ or $\overset{\circ}{\lambda}$ which is extrapolated to the standard value $c, x(=1), b, \ldots$ starting from very low concentrations along an imagined ideal curve. In Sects. 6.2 and 13.2, we took a closer look at the method where the concentration c or the molar fraction x served as a measure of composition. We deal similarly with other measures of composition, at least with those that change proportionally to each other for small values. The basic values of the chemical potential for a substance B dissolved in a solvent A, $\overset{\circ}{\mu}_{\bullet\mathrm{B}}, \overset{\circ}{\mu}_{c,\mathrm{B|A}}, \overset{\circ}{\mu}_{x,\mathrm{B|A}}, \overset{\circ}{\mu}_{b,\mathrm{B|A}}, \ldots$ and the corresponding λ values $\overset{\circ}{\lambda}_{\bullet\mathrm{B}}, \overset{\circ}{\lambda}_{c,\mathrm{B|A}}, \overset{\circ}{\lambda}_{x,\mathrm{B|A}}, \overset{\circ}{\lambda}_{b,\mathrm{B|A}}, \ldots$ are all different. We will not discuss here how to convert one into another.

Activity Coefficients The (residual) activities a_B are themselves decomposed into a product of the particular concentration (or mole fraction) and its activity coefficient, as follows:

$$a_{\bullet\mathrm{B}} = x_\mathrm{B}\gamma_{\bullet\mathrm{B}}, \quad a_{c,\mathrm{B}} = c_{\mathrm{r,B}}\gamma_{c,\mathrm{B}}, \quad a_{x,\mathrm{B}} = x_\mathrm{B}\,\gamma_{x,\mathrm{B}}, \quad a_{b,\mathrm{B}} = b_{\mathrm{r,B}}\,\gamma_{b,\mathrm{B}}, \; \ldots \; .$$

Again, $c_{\mathrm{r,B}}$ describes the relative concentration c_B/c, while $b_{\mathrm{r,B}}$ is the relative molality b_B/b. Depending upon the chosen basic value, the resulting activities will vary and can be distinguished by indices. If it is clear which alternative is meant, extra identifiers can be omitted.

We use the abbreviation "Suc" for cane sugar (sucrose) in our example in Fig. 24.12. The following holds for the activity coefficient at the standard concentration of 1,000 mol m^{-3}: $\gamma_c(\mathrm{Suc}) \equiv \overset{+}{\lambda}_c(\mathrm{Suc}) = 1.27$. This value indicates graphically that the sugar in the tea glass behaves as if its concentration were 27 % higher than it actually is. Correspondingly, $\gamma_c(\mathrm{Suc}) = 1.001$ at the taste threshold, in other words at a concentration of only 5 mol m^{-3}, means that the deviations from ideal behavior are immeasurably small for such dilutions. This is true for neutral substances, while charged (ionic) ones still display noticeable deviations at concentrations below 10 mol m^{-3}.

In the limit of "infinite" dilution, when the content of B in A (but also the content of all other substances C, D, ... in A, if they exist) tends to 0, $\gamma_{c,\emptyset} = \gamma_{x,\emptyset} = \gamma_{b,\emptyset} = \ldots = 1$ is valid for the activity coefficients. $\gamma_{\bullet\emptyset} = 1$ is correspondingly valid for the solvent. We have chosen the "slashed zero" $_\emptyset$ as the index, as we did in Sect. 13.3 in order to characterize this state.

Viewing the (residual) activities a as modified measures of composition is quite graphic: the corresponding activity coefficient can be simply understood as a fitting correction factor. This approach can be applied independently of which of the usual measures of composition are being used, whether it is concentration c or c_r, mole fraction x, molality b or b_r, etc. It is also simpler than using the extra potential $\overset{+}{\mu}$, especially when we try to understand the basic quantities themselves as "partial molar Gibbs energies." However, understanding becomes more difficult when trying to capture and calculate the influence of parameters like pressure, temperature, contents of components in mixtures, etc.

Drives Activities are usually introduced to describe deviations of the functions $\mu(x)$ or $\mu(c)$, etc., from values considered ideal at the same temperature and pressure, $\mu = \overset{\circ}{\mu}_{\bullet} + RT\ln x$ or $\mu = \overset{\circ}{\mu}_{c} + RT\ln c_{\mathrm{r}}$ as well as $\mu = \overset{\circ}{\mu}_{x} + RT\ln x$. As mentioned right at the start, to correct for this, the actual measure of composition is replaced by the "active" one $a_{\bullet}, a_c, a_x, a_b, \ldots$ which results from the mutual interaction of the substances. A mixed approach is employed here in which we apply the basic values in the scale of the potential and the residual values in the activity scale. This is a compromise that lets us avoid the clumsy and extremely large or extremely small basic values of λ, while allowing for the graphic appeal of the λ residuals.

Let us now consider the familiar example of cane sugar decomposing into glucose and fructose: $\mathrm{Suc|w} + \mathrm{H_2O|l} \rightarrow \mathrm{Glc|w} + \mathrm{Fru|w}$ (see Sect. 6.3). The process runs slowly in our tea glass if the tea is slightly acidified (maybe with some lemon juice). We can write the drive $\mathcal{A}$ for this process using the approach discussed in Sect. 6.3: the relative concentrations c_{r} of the dissolved substances are replaced by the activities a_c. This time, though, we must remember that the potential of solvent A (in this case, water) can be markedly different due to possible higher concentrations of dissolved B, C, ... We can achieve this formally by including the residual value $RT \ln a_{\bullet\mathrm{A}}$ for the solvent as well:

$$\mathcal{A} = \underbrace{\overset{\circ}{\mathcal{A}}}_{\overset{\circ}{\mu}(\mathrm{Suc|w}) + \overset{\circ}{\mu}(\mathrm{H2O|l}) - \overset{\circ}{\mu}(\mathrm{Glc|w}) - \overset{\circ}{\mu}(\mathrm{Fru|w})} + \underbrace{\overset{*}{\mathcal{A}}}_{RT\ln\frac{a_c(\mathrm{Suc|w})\cdot a_{\bullet}(\mathrm{H_2O|l})}{a_c(\mathrm{Glc|w})\cdot a_c(\mathrm{Fru|w})}} .$$

Notice that we write the activity $a_{\bullet}$ and not a_c for the solvent. This is important because the indexes $_{\bullet}$ and $_c$, etc., are almost always omitted since it is generally clear from the context which one of these is meant. As before, the contributions of $\overset{*}{\mu}_{\bullet}$ or $a_{\bullet}$ are omitted for substances being converted in their pure states. Although they can be written for pure substances, $\overset{*}{\mu}_{\bullet} = 0$ and $a_{\bullet} = 1$, $\overset{*}{\mu}_{\bullet}$ as a summand or $a_{\bullet}$ as a factor does not affect the result. A simple example of this is dissolving cane sugar in water: $\mathrm{Suc|s} \rightarrow \mathrm{Suc|w}$:

$$\mathcal{A} = \underbrace{\overset{\circ}{\mathcal{A}}}_{\overset{\circ}{\mu}_{\bullet}(\mathrm{Suc|s}) - \overset{\circ}{\mu}_{c}(\mathrm{Suc|w})} + \underbrace{\overset{*}{\mathcal{A}}}_{RT\ln\frac{a_{\bullet}(\mathrm{Suc|s})}{a_c(\mathrm{Sac|w})} = RT\ln\frac{1}{a_c(\mathrm{Suc|w})}} .$$

The activity of the pure solid substance sucrose is, as mentioned, $a_{\bullet}(\mathrm{Suc|s}) = 1$.

The above can easily be transferred to other chemical transformations. For example:

$$\mathrm{B} + \mathrm{B'} + \ldots \rightarrow \mathrm{D} + \mathrm{D'} + \ldots \quad \text{or} \quad 0 \rightarrow \nu_{\mathrm{B}}\mathrm{B} + \nu_{\mathrm{B'}}\mathrm{B'} + \ldots + \nu_{\mathrm{D}}\mathrm{D} + \nu_{\mathrm{D}}\mathrm{D} + \nu_{\mathrm{D'}}\mathrm{D'} + \ldots .$$

The conversion numbers $\nu_{\mathrm{B}}, \nu_{\mathrm{B'}}, \ldots, \nu_{\mathrm{D}}, \nu_{\mathrm{D'}}, \ldots$ are always negative for reactants and positive for products. In our example on the left they are only −1 or +1, while on the right, they can be random or even fractions. In our example and especially further below, we should note that the more general way of writing on the right, despite its very different appearance, leads to the simpler one on the left if the conversion number +1 for the reactants and −1 for the products are used and the quantities suitably transposed.

The negative drive $-\mathcal{A}$ can be written as a sum of the potentials μ of the participating substances, weighted with the conversion numbers [cf. Eq. (4.3)]:

$$-\mathcal{A} = -\mu_B - \mu_{B'} - \ldots + \mu_D + \mu_{D'} + \ldots$$

or in general

$$-\mathcal{A} = \nu_B\mu_B + \nu_{B'}\mu_{B'} + \ldots + \nu_D\mu_D + \nu_{D'}\mu_{D'} + \ldots \ .$$

If we decompose the potentials into basic and residual terms, $\mu = \overset{\circ}{\mu} + RT\ln a$, we obtain:

$$\begin{aligned} -\mathcal{A} &= -\overset{\circ}{\mathcal{A}} - \overset{*}{\mathcal{A}} \\ &= (-\overset{\circ}{\mu}_B - \overset{\circ}{\mu}_{B'} - \ldots + \overset{\circ}{\mu}_D + \overset{\circ}{\mu}_{D'} + \ldots) + RT\ln\frac{a_D a_{D'}\ldots}{a_B a_{B'}\ldots}. \end{aligned} \quad (24.36)$$

or in general

$$\begin{aligned} -\mathcal{A} &= -\overset{\circ}{\mathcal{A}} - \overset{*}{\mathcal{A}} \\ &= (\nu_B\overset{\circ}{\mu}_B + \ldots + \nu_D\overset{\circ}{\mu}_D + \ldots) + RT\ln(a_B{}^{\nu_B} \cdot \ldots \cdot a_D{}^{\nu_D} \cdot \ldots). \end{aligned} \quad (24.37)$$

"Reactivities" Just as we can convert the chemical potentials μ into chemical activities λ, we can transform sums of potentials $\mu_B + \mu_C + \mu_D + \ldots$ into products of activities $\lambda_B \cdot \lambda_C \cdot \lambda_D \cdot \ldots$:

$$\exp\frac{\mu_B + \mu_C + \mu_D + \ldots}{RT} = \exp\frac{\mu_B}{RT} \cdot \exp\frac{\mu_C}{RT} \cdot \exp\frac{\mu_D}{RT} \ldots = \lambda_B \cdot \lambda_C \cdot \lambda_D \cdot \ldots \ .$$

Multiples of potentials $\nu\,\mu$ can be similarly converted into powers of activities λ^ν:

$$\exp\frac{\nu\mu}{RT} = \left(\exp\frac{\mu}{RT}\right)^\nu = \lambda^\nu.$$

Drives $\mathcal{A}$ can also be similarly converted into activities, either in their entireties or decomposed into basic and residual values, $\mathcal{A} = \overset{\circ}{\mathcal{A}} + \overset{*}{\mathcal{A}}$, or into basic, mass action, and extra terms $\mathcal{A} = \overset{\circ}{\mathcal{A}} + \overset{\times}{\mathcal{A}} + \overset{+}{\mathcal{A}}$,

$$\underbrace{\exp\frac{\mathcal{A}}{RT}}_{\mathcal{K}} = \underbrace{\exp\frac{\overset{\circ}{\mathcal{A}}}{RT}}_{\overset{\circ}{\mathcal{K}}} \cdot \underbrace{\exp\frac{\overset{*}{\mathcal{A}}}{RT}}_{\overset{*}{\mathcal{K}}} = \underbrace{\exp\frac{\overset{\circ}{\mathcal{A}}}{RT}}_{\overset{\circ}{\mathcal{K}}} \cdot \underbrace{\exp\frac{\overset{\times}{\mathcal{A}}}{RT}}_{\overset{\times}{\mathcal{K}}} \cdot \underbrace{\exp\frac{\overset{+}{\mathcal{A}}}{RT}}_{\overset{+}{\mathcal{K}}} . \quad (24.38)$$

Basically, the quantity $\mathcal{K}$ is a measure of the "drive" or "strength" of a reaction as much as the quantity $\mathcal{A}$, from which it stems. The only difference is that the scales are different and certain conditions are formulated differently. While $\mathcal{A} > 0$ means that the process runs forward, $\mathcal{A} < 0$ denotes a backward tendency, and $\mathcal{A} = 0$ indicates equilibrium, the corresponding conditions in the new, exponential scale are $\mathcal{K} > 1$, $\mathcal{K} < 1$, and $\mathcal{K} = 1$, respectively. In order to emphasize its relation to activity, $\mathcal{K}$ can be called "reactivity," but the name is actually unnecessary.

Mass Action Law The quantity $\mathcal{K}$ is itself extremely unusual, but the factors $\overset{\circ}{\mathcal{K}} \cdot \overset{*}{\mathcal{K}}$ or $\overset{\circ}{\mathcal{K}} \cdot \overset{\times}{\mathcal{K}} \cdot \overset{+}{\mathcal{K}}$, into which it can be decomposed, are not. When discussing the mass action law in Sect. 6.4, we encountered the quantity $\overset{\circ}{\mathcal{K}}$ as a "(numerical) equilibrium constant" or "equilibrium number" [Eq. (6.18)]. We are also familiar with $\overset{\times}{\mathcal{K}}$, not as itself but as the reciprocal value $\overset{\times}{\mathcal{K}}{}^{-1}$ (but we did not use this symbol as yet). Generally, $\overset{\times}{\mathcal{K}}{}^{-1}$ appears in the mass action law as a quotient where the numerator corresponds to the products and the denominator corresponds to the reactants.

This can be shown as follows. When the drive disappears, $\mathcal{A} = 0$, equilibrium is established, so that $\mathcal{K} = \overset{*}{\mathcal{K}} \cdot \overset{\circ}{\mathcal{K}} = 1$ or $\overset{\circ}{\mathcal{K}} = \overset{*}{\mathcal{K}}{}^{-1}$ (or $\overset{\circ}{\mathcal{K}} = \overset{\times}{\mathcal{K}}{}^{-1} \overset{+}{\mathcal{K}}{}^{-1}$) is valid. If we insert $\overset{*}{\mathcal{A}}$ from Eq. (24.36) or Eq. (24.37) into the expression for $\overset{*}{\mathcal{K}}$ in Eq. (24.38), we obtain the conditions for equilibrium in the following form:

$$\overset{\circ}{\mathcal{K}} = \left(\frac{a_{\mathrm{D}} \cdot a_{\mathrm{D'}} \cdot \ldots}{a_{\mathrm{B}} \cdot a_{\mathrm{B'}} \cdot \ldots}\right)_{\mathrm{eq.}} \quad \text{or} \quad \overset{\circ}{\mathcal{K}} = \left(a_{\mathrm{B}}{}^{\nu_{\mathrm{B}}} \cdot \ldots \cdot a_{\mathrm{D}}{}^{\nu_{\mathrm{D}}} \cdot \ldots\right)_{\mathrm{eq.}} .$$

If all the substances B, B′, ..., D, D′, ... are dissolved components in a dilute solution, the activities $a = \gamma_c\, c_{\mathrm{r}}$ can be replaced by the relative concentrations c_{r}, because we have in the case of strong dilution $\gamma_c = 1$. The conditions above then give way to the equations familiar to us from Sect. 6.4:

$$\overset{\circ}{\mathcal{K}} = \left(\frac{c_{\mathrm{r}}(\mathrm{D}) \cdot c_{\mathrm{r}}(\mathrm{D'}) \cdot \ldots}{c_{\mathrm{r}}(\mathrm{B}) \cdot c_{\mathrm{r}}(\mathrm{B'}) \cdot \ldots}\right)_{\mathrm{eq.}} \quad \text{or} \quad \overset{\circ}{\mathcal{K}} = \left(c_{\mathrm{r}}(\mathrm{B})^{\nu_{\mathrm{B}}} \cdot \ldots \cdot c_{\mathrm{r}}(\mathrm{D})^{\nu_{\mathrm{D}}} \cdot \ldots\right)_{\mathrm{eq.}} .$$

The expression in parentheses on the right side of the equation is just $\overset{\times}{\mathcal{K}}{}^{-1}$. In this case, $\overset{+}{\mathcal{K}} = 1$ is valid for the extra factor $\overset{+}{\mathcal{K}}$ in which the activity coefficients are summed up, because all activity coefficients, as mentioned, should be equal to 1. In the general case, however, we have:

$$\overset{+}{\mathcal{K}}^{-1} = \frac{\gamma_c(\mathrm{D}) \cdot \gamma_c(\mathrm{D}') \cdot \ldots}{\gamma_c(\mathrm{B}) \cdot \gamma_c(\mathrm{B}') \cdot \ldots} \quad \text{or} \quad \overset{+}{\mathcal{K}}^{-1} = \gamma_{c,\mathrm{B}}{}^{\nu_\mathrm{B}} \cdot \ldots \cdot \gamma_{c,\mathrm{D}}{}^{\nu_\mathrm{D}} \cdot \ldots \;.$$

The Special Case of Gases For a gas B in a mixture of gases, the partial pressure $p_\mathrm{B} = x_\mathrm{B} \cdot p$ or the relative partial pressure $p_{\mathrm{r,B}} = x_\mathrm{B} \cdot p/p$ are preferred measures of composition. Neither p_B nor $p_{\mathrm{r,B}}$ are themselves "chemically active" but a changed value $a_{p,\mathrm{B}} = \gamma_{p,\mathrm{B}} \cdot p_{\mathrm{r,B}}$ (according to general belief, this is the result of the interaction of the particles). Similar to the activities discussed above, $a_{c,\mathrm{B|A}}$, $a_{x,\mathrm{B|A}}, a_{b,\mathrm{B|A}}, \ldots$ and $\gamma_{c,\mathrm{B|A}}, \gamma_{x,\mathrm{B|A}}, \gamma_{b,\mathrm{B|A}}, \ldots$, the same scale transformation also produces $a_{p,\mathrm{B}}$ and $\gamma_{p,\mathrm{B}}$ from the corresponding potentials: $a_{p,\mathrm{B}} = \exp(\overset{*}{\mu}_{p,\mathrm{B}}/RT)$ and $\gamma_{p,\mathrm{B}} = \exp(\overset{+}{\mu}_{p,\mathrm{B}}/RT)$.

Still, there is an important difference here. A vacuum plays the role of solvent A as a medium in which the substances are dispersed. While A continues to exist even at finite pressures when no other substances are distributed within it, this is not true for a vacuum. Starting from a state of very low total pressure p_0, we extrapolate from $p_\mathrm{B} = x_\mathrm{B}\, p_0$ to $p_\mathrm{B} = x_\mathrm{B}\, p$ at constant temperature T and obtain a value which is used as basic value $\overset{\circ}{\mu}_{p,\mathrm{B}}$ of the chemical potential μ_B. Extrapolation is done along the ideal logarithmic curve $\mu = \mu_0 + RT\ln(p/p_0)$. Differently from the basic values $\overset{\circ}{\mu}_{c,\mathrm{B|A}}, \overset{\circ}{\mu}_{x,\mathrm{B|A}}, \overset{\circ}{\mu}_{b,\mathrm{B|A}}, \ldots$ of the potential μ_B of a substance B in a solid or liquid mixed phase, $\overset{\circ}{\mu}_{p,\mathrm{B}}$ is not dependent upon pressure. It is also not dependent upon a solvent, because there is none.

In 1901, Gilbert Lewis suggested the name "*fugacity*"—meaning volatility—for the modified pressure $\gamma_{p,\mathrm{B}} \cdot p_\mathrm{B}$ (not $\gamma_{p,\mathrm{B}} \cdot p_{\mathrm{r,B}}$!) and gave it its own symbol f_B. Correspondingly, the quantity $\gamma_{p,\mathrm{B}}$ is also known as the *fugacity coefficient* (symbol ϕ_B). Lewis described this quantity as a "tendency to transition" or "tendency to escape." He was describing the tendency of a substance in one phase to go into another one, and especially as a gas to volatilize. The concept of *activity* also came from Lewis, who introduced it in 1908 as modified concentration. This made it possible to treat substances that are not noticeably volatile but are easily dissolved in water (urea, glycerin, cane sugar, etc.) according to the same paradigm used for fugacious substances.