Chapter 8
Side Effects of Transformations of Substances

Transformations of substances like chemical reactions, phase transitions, distribution in space, etc., are often accompanied by very striking side effects, such as glowing and flashing, fizzling and cracking, bubbling and rising of smoke. These side effects which make chemistry so fascinating are primarily based upon changes of volume that can cause violent explosions and implosions, exchange and generation of entropy, which is responsible for effects like glowing and heating up, and energy exchange that we use in muscles, motors, and batteries. The goal of this chapter is to understand and quantitatively describe these phenomena, and to sensibly make use of them. For this purpose, the so-called partial molar properties such as the (partial) molar volume or the (partial) molar entropy of a dissolved substance are introduced. For describing the changes of volume and entropy associated with transformations, we will use the quantities molar reaction volume and molar reaction entropy. The special role of entropy makes a further differentiation into latent, generated, and exchanged reaction entropy necessary. We will also learn how the chemical drive of a reaction, the corresponding exchange of energy, and eventually the generated entropy are interrelated. In closing, this relationship will be used for determining the chemical drive with the help of a calorimeter.

8.1 Introduction

In the following, we will be concerned with transformations of substances of the most varied kind. Among these will be

- Absorption or release of substances,
- Spreading or aggregation,
- Mixing and dissolving processes,
- Phase transitions and chemical reactions.

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All of these processes are accompanied by numerous side effects. Sometimes these are almost imperceptible, but more often they are very noticeable: something is glowing or flashing, fizzling or cracking, it is bubbling or smoke rises. These sorts of accompanying phenomena, which make chemistry so interesting, are based upon

- Changes of volume that can cause violent explosions and implosions,
- Exchange and generation of entropy, which is responsible for effects like glowing and heating up,
- Energy exchange that we use in muscles, motors, and batteries.

The goal of this chapter is to understand and quantitatively describe these phenomena, and to sensibly make use of them.

8.2 Volume Demand

Pure Substances We will begin with the simplest case, namely *change of volume* in transformations of substances. Every substance needs a certain amount of space. How much this is depends upon how much space is needed by its atoms and the gaps in between them. The volume taken up is greater, the more of the substance there is. In order to compare the volume needed by different substances (Experiment 8.1), one relates the volume to amount of substance. This so-called *molar volume* V_m then serves as the measure of the space needed by a pure substance:

$$V_{\mathrm{m}} = \frac{V}{n} \qquad \textit{molar volume of a pure substance.}$$

The names or formulas of a substance can take the place of the index $_m$, for example, $V_{H_2O} = 18.07\ \mathrm{cm^3\,mol^{-1}}$ or $V(H_2O) = 18.07\ \mathrm{cm^3\ mol^{-1}}$ for the molar volume of (liquid) water.

The volume demand of a substance is by no means constant, but also depends upon its milieu. Substances are compressible to some extent and can expand when

Experiment 8.1 *Volume demand of various pure substances*: How different the volume demand, i.e., the space taken up by various pure substances can be, is easy to show. Cylindrical blocks all representing an amount of substance of 1 mol are placed side by side.

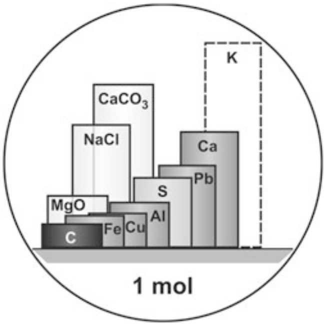
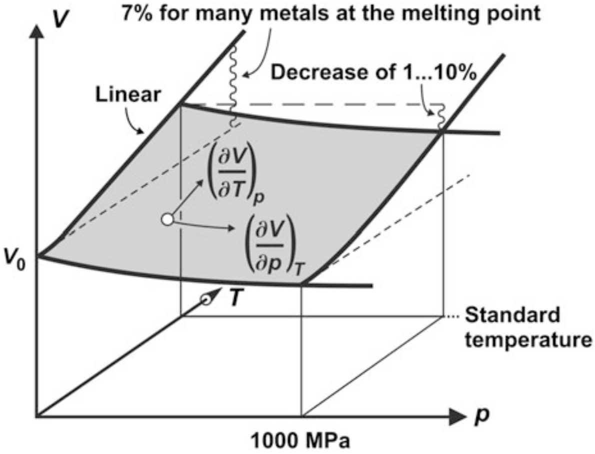


Fig. 8.1 Dependence of the volume of a solid substance upon pressure and temperature.



heated. Volume and molar volume depend upon pressure p as well as temperature T as demonstrated for a solid in Fig. 8.1.

When pressure increases, V generally decreases steeply at first and then more gradually. However, for solid substances, hundreds of MPa are necessary for attaining a noticeable change of volume. Gases, on the other hand, need much less pressure (some tens of kPa) for this. The $V(p, T)$ surface often rises in nearly a straight line in the T direction. For many metals, the increase of volume from 0 K up to the melting point is about 7 % (Grüneisen's rule). Toward lower temperatures, the tangent to the surface becomes horizontal.

Also in the case of molar volume the standard value is the value at "room conditions," meaning 298 K and 100 kPa. As before, we add the symbol $^\ominus$ as upper index to the symbol of the quantity, for example,

$$V_\mathrm{m}^\ominus(\mathrm{H_2O}) = 18.07\,\mathrm{cm^3\,mol^{-1}} \quad \text{at} \quad 298\,\mathrm{K} \quad \text{and} \quad 100\,\mathrm{kPa}.$$

The standard values for some pure substances are summarized in Table 8.1. Molar volume also depends upon the state of aggregation, as the example of water shows.

The lowest molar volume at standard conditions is found for diamond with 3.4 $\mathrm{cm^3\ mol^{-1}}$. The values for solids and liquids are usually of the order of 10 $\mathrm{cm^3\ mol^{-1}}$ (where 1 mol refers to 6×10^{23} atoms of any type). In contrast, gases display a considerably greater molar volume of just a little less than 25 L $\mathrm{mol^{-1}}$. Why this is will be discussed in Sect. 10.2.

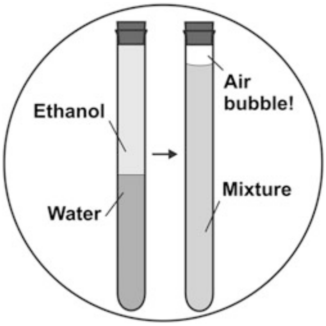
If the volume is known at a point p, T (e.g., for standard conditions), it is possible to approximately calculate the values in the vicinity of this point. For this we need the gradients of the surface in the direction of the p and T axes, $(\partial V/\partial p)_T$ and $(\partial V/\partial p)_p$ (see Fig. 8.1). The first coefficient measures the compressibility of the substance; the second measures its thermal expansion. The molar volume V_m for other p and T values can be calculated analogously to the method used for the

Table 8.1 Molar volumes of some pure substances under standard conditions (298 K, 100 kPa) as well as temperature and pressure coefficients (for corresponding reference values).

Substance	Formula	$V_m^\ominus$ $(\text{cm}^3\,\text{mol}^{-1})$	$(\partial V_m/\partial T)_p^\ominus$ $(\text{cm}^3\,\text{mol}^{-1}\,\text{K}^{-1})$	$(\partial V_m/\partial p)_T^\ominus$ $(\text{cm}^3\,\text{mol}^{-1}\,\text{kbar}^{-1})$
Graphite	C|graphite	5.5	0.00004	−0.017
Diamond	C|diamond	3.4	0.00001	−0.001
Iron	Fe|s	7.1	0.00025	−0.004
Lead	Pb|s	18.3	0.00161	−0.045
Water ice	H_2O|s	19.7	[0.0010]	[−0.6]
Water	H_2O|l	18.1	0.0046	−0.836
Water vapor	H_2O|g	24.8×10^3	83.1	-25×10^7

The value for water ice was extrapolated linearly from 273 to 298 K. The values in brackets are valid for 273 K

Experiment 8.2 *Reduction of volume by mixing water and ethanol*: A test tube is half-filled with water (colored with an appropriate dye). Subsequently, it is filled to the top with ethanol and closed with a rubber stopper. After inverting the tube repeatedly, the formation of a gas bubble meaning a decrease in volume of the mixture can be observed.



chemical potential by applying the appropriate pressure coefficient $(\partial V_m/\partial p)_T$ or temperature coefficient $(\partial V_m/\partial p)_p$, respectively.

Dissolved Substances It is noteworthy that the volume demand for a substance also depends upon what kind of a chemical environment it is in. Consider this example. 1 mol of pure water with a volume of about 18 cm^3 is stirred into 1 m^3 of concentrated sulfuric acid, and then the warmed mixture is cooled back down to the initial temperature. One finds that the entire volume has increased by only 8.5 cm^3 and not by 18 cm^3 as might have been expected. Obviously, water dissolved in sulfuric acid requires less space and the molar volume is smaller in this milieu:

$$V_m^\ominus(H_2O \text{ in conc. } H_2SO_4) = 8.5\ \text{cm}^3\,\text{mol}^{-1}.$$

If sulfuric acid of half this concentration is used, one finds 17.5 cm^3 mol^{-1}. A similar but much smaller reduction of volume of about 4 % can be observed by mixing equal parts of water and ethanol (Experiment 8.2).

The volume demand for some substances in certain solvents can even be *negative*. The volume shrinks when such a substance is dissolved. An example of this is the solution of sodium hydroxide in water:

$$V_{\mathrm{m}}^{\ominus}(\mathrm{NaOH\ \ in\ \ H_2O}) = -6.8\,\mathrm{cm^3\,mol^{-1}}.$$

When 1 mol of sodium hydroxide in form of pellets is dissolved in 1 m^3 of water, the volume of the solution shrinks by 6.8 cm^3, as long as the temperature and pressure are kept constant (Experiment 8.3). This contraction is caused by the H_2O molecules (which are rather loosely packed when in pure water) being concentrated more densely in the hydration shells of the Na^+ and OH^- ions.

As we have seen, the molar volume for a pure substance can be easily defined and calculated. How should we proceed, though, when we want to find the volume demand of a substance distributed inside another material environment?

Consider a body that absorbs a small amount of a substance. It will generally expand somewhat (Fig. 8.2). The volume grows because the substance now inside the body needs space, and by taking this space, the particles loosen the body's atomic structure. An example would be the volume demand of water penetrating a more or less moist block of wood causing the wood to expand more. The measure of

Experiment 8.3 *Negative volume demand of NaOH in water*: The flat-bottomed flask is filled with colored water up to the mark (with the cooling water running). Subsequently, as many pellets of sodium hydroxide as possible are put into the flask. After dissolution of the sodium hydroxide and cooling down of the resulting solution, the water level is considerably lower than before.

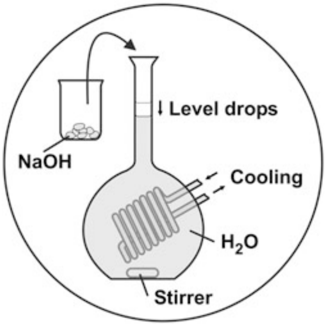
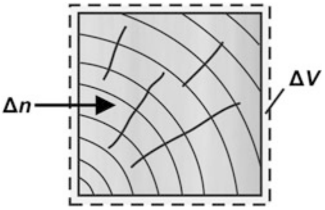


Fig. 8.2 Increase of volume ΔV of a block of wood when a small amount Δn of a substance (e.g., water) is added (strongly simplified description; in reality, the dimensional change with changing moisture content is anisotropic because of the inhomogeneity of wood).



volume demand of the substance added is the small observed change of volume ΔV, relative to the small amount of substance Δn added:

$$V_{\mathrm{m}} \approx \frac{\Delta V}{\Delta n} \quad \text{for a small amount } \Delta n. \tag{8.1}$$

In our example, this is of the order of 15 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$.

To be precise, the added amount Δn (added to an amount n_0 possibly already present) should be kept as small as possible to keep the body from changing too much. The volume demand by water in a dry block of wood is different from that in wood which is already moist. We can express the changeover to infinitesimally small amounts of substance by replacing the difference quotient by the differential quotient. Naturally, the pressure p, temperature T, and the amounts n', n'', . . . of all other substances inside the body must be kept constant during the entire process. This is necessary so that no changes occur during volume measurements due to mechanical compression, thermal expansion, and/or compositional changes while the substance is being added. In short, the milieu has to remain fixed. This can be expressed by adding the symbols of these quantities as indices to the differential quotient (see Sect. A.1.2 in the Appendix):

$$V_{\mathrm{m}} \equiv \left(\frac{\partial V}{\partial n}\right)_{p,T,n',n'',\ldots} \qquad (\textit{partial})\ \textit{molar volume of a dissolved substance}. \tag{8.2}$$

More graphically: The molar volume of a substance corresponds to the change of volume which occurs when 1 mol of a substance is put into a very large sample of a given composition. The great excess ensures that the composition of the sample, as requested, will remain practically unchanged when the substance is added. This method is not only useful for mixtures, but for single substances as well. We can therefore forego using the epithet "partial."

We use the value of V_{m} at infinite dilution ($c \to 0$) as the *basic value* $\overset{\circ}{V}_{\mathrm{m}}$ of the molar volume of a dissolved substance, meaning the volume demand of the substance in the practically pure solvent. The basic value at standard temperature and pressure is, again, called *standard value* $V_{\mathrm{m}}^{\ominus} = \overset{\circ}{V}_{\mathrm{m}}(T^{\ominus}, p^{\ominus})$. For example, the molar volume of water strongly diluted in ethanol is not 18.1 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$ but only about 14 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$. As a result of the different packing densities of the molecules, the basic value of a dissolved substance also depends upon what kind of solvent it is in. Thus, the molar volume of water in concentrated sulfuric acid decreases to only about 9 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$, as we have seen.

Depending upon the overall composition of a mixture, the molar volume of a substance can take very different values. The values can vary between the extremes of the pure state and the state of infinite dilution. Figure 8.3 shows how the molar volume of water depends upon the mole fraction of ethanol in an ethanol–water mixture at 298 K. The molar volume of ethanol is also dependent upon the

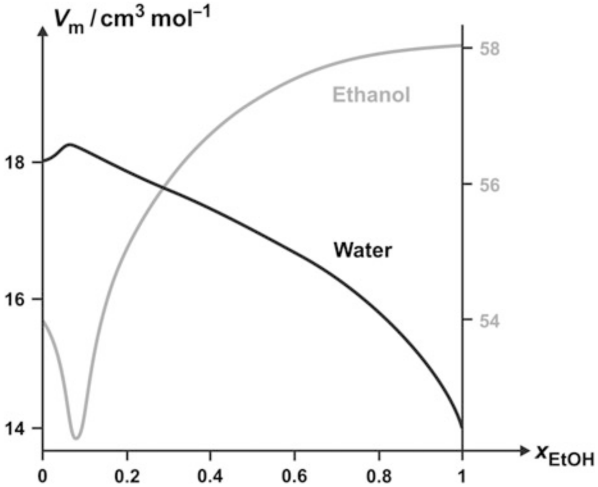


Fig. 8.3 Molar volume of water and ethanol in water–ethanol mixtures as a function of the ethanol content at 298 K. [Note the differing scales for water (*left*) and ethanol (*right*).]

composition. The minimum of the ethanol curve and the maximum of the water curve are found at the same mole fraction.

If the molar volumes V_A and V_B in a mixture of A and B are known for a certain composition, the volume of a portion of this mixture results from the amounts and volume demands of the components:

$$V = n_A \cdot V_A + n_B \cdot V_B. \tag{8.3}$$

(Here we have abbreviated $V_{m,A}$ or $V_{m,B}$ to V_A and V_B.) In order to derive this relation, we consider the increase of volume dV when we add small amounts dn_A and dn_B to a mixture of substances A and B while keeping pressure p and temperature T constant:

$$\mathrm{d}V = \underbrace{\left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} \mathrm{d}n_A}_{\mathrm{d}V_{\to n_A}} + \underbrace{\left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} \mathrm{d}n_B}_{\mathrm{d}V_{\to n_B}} = V_A \mathrm{d}n_A + V_B \mathrm{d}n_B.$$

We have chosen to use the arrow in the index to make clear that we have increases in the directions of different variables. However, as mentioned in Sect. 3.11, this way of writing is optional. The equation itself looks more complicated than it actually is. The quantities p and T do not change here, so they can be left out, making the expressions seem somewhat simpler. We can imagine the graph of the function $V(n_A, n_B)$ as a mountainside with different slopes in the n_A und n_B directions (see Sect. A.1.2 in the Appendix). The first differential quotient shows the gradient $m_{\to n_A}$ in the n_A direction (imagine it as going east) and the second the gradient $m_{\to n_B}$ in the n_B direction (going northward). The product $m_{\to n_A}\mathrm{d}n_A$ is then simply the increase $\mathrm{d}V_{\to n_A}$ of "altitude" V, when one proceeds a small distance dn_A

in the n_A direction. The same holds true for movement in the n_B direction. The total increase dV for a change in both directions is simply the sum of both of these. Hopefully, the above equation is now clear.

Let us now imagine adding substances A and B at constant proportions, and right from the beginning when n_A and n_B are still both zero. The composition of the growing regions will then remain unchanged over the entire process, as will the volume demands V_A and V_B of both substances. The contribution of each individual substance to the total volume V is then simply the product of $V_A \cdot n_A$ or $V_B \cdot n_B$ and V itself is the sum of these.

In closing, a reminder that molar volume is not a measure of the volume which the molecules themselves fill, but only a measure of the space they lay claim to. This space can be much greater. For instance, in its gaseous state at room conditions, a substance requires about a thousand times the volume that it would in its condensed state. However, it can be much smaller (even negative), for instance when it causes the molecules of the substance it is mixed with to move more closely together, as we have seen happen with NaOH in a dilute aqueous solution. Naturally, the salt in the solution must have a positive volume, but if the volume contraction due to hydration is greater than the proper volume of the added ions, the total volume decreases.

8.3 Changes of Volume Associated with Transformations

The changes of volume observed during a chemical reaction are essentially the result of the volume demands of reactants and products. We will consider the reaction of pure or dissolved substances in order to calculate the effect at an arbitrary extent ξ of the reaction,

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

The starting as well as the final substances may be present concurrently in large or small amounts and in pure or dissolved states. We assume the pressure and temperature to remain constant during the whole process in order to avoid unwanted effects caused by compressibility and thermal expansion. We also require that no other reaction runs in parallel, i.e., ξ', ξ'', ... are constant. A *small extra* conversion $\Delta\xi$ then results in the following change of volume (instead of $V_{m,B}$ for a substance B, we use, as mentioned, the abbreviated V_B, etc.):

$$\Delta V = V_D \cdot \Delta\xi + V_{D'} \cdot \Delta\xi + \ldots - V_B \cdot \Delta\xi - V_{B'} \cdot \Delta\xi - \ldots . \qquad (8.4)$$

This follows from $\Delta n_B = \Delta n_{B'} = \ldots = -\Delta\xi$ and $\Delta n_D = \Delta n_{D'} = \ldots = +\Delta\xi$, respectively.

Every product requires an additional volume $V_m \cdot \Delta\xi$, while every reactant releases a volume $V_m \cdot \Delta\xi$. V_m denotes the required space of a given substance at extent ξ of the reaction. In order for the volume demands to have definite values, concentrations may not change noticeably. This can be achieved by allowing only small conversions. However, when all participating substances are in pure states, this limitation is unnecessary.

Because the change of volume ΔV is proportional to the conversion $\Delta\xi$ (at least as long as $\Delta\xi$ remains small), it is more useful to relate information of this kind to the conversion. Instead of ΔV, we use the quantity

$$\Delta_{\mathrm{R}}V \equiv \frac{\Delta V}{\Delta\xi} = V_{\mathrm{D}} + V_{\mathrm{D'}} + \ldots - V_{\mathrm{B}} - V_{\mathrm{B'}} - \ldots \quad \text{for small } \Delta\xi;\, p, T, \xi', \xi'', \ldots \text{const.} \tag{8.5}$$

$\Delta_{\mathrm{R}}V(\xi)$ is the *molar reaction volume* which is the measure of how strongly the transformation of the substances taking place changes the volume at a particular extent ξ of reaction. The index $_{\mathrm{R}}$ refers to "reaction" and serves to differentiate the molar reaction volume (unit $\mathrm{m}^3\ \mathrm{mol}^{-1}$) from a change of volume ΔV (unit m^3).

The expression on the right can be made somewhat easier to understand with the help of the conversion numbers v_i. So far, for the sake of simplicity, we have chosen $v_{\mathrm{B}} = v_{\mathrm{B'}} = \ldots = -1$ and $v_{\mathrm{D}} = v_{\mathrm{D'}} = \ldots = +1$ in the conversion formula. Thus, only plus and minus signs have appeared in Eq. (8.5). In the more general case

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

we obtain

$$\Delta_{\mathrm{R}}V = \frac{\Delta V}{\Delta\xi} = v_{\mathrm{B}}V_{\mathrm{B}} + v_{\mathrm{B'}}V_{\mathrm{B'}} + \ldots + v_{\mathrm{D}}V_{\mathrm{D}} + v_{\mathrm{D'}}V_{\mathrm{D'}} + \ldots = \sum_i v_i V_i. \tag{8.6}$$

The conversion numbers for the reactants are negative and they are positive for the products. Therefore, the expression in the middle can be read as a difference, which explains the Δ in the symbol used for the quantity $\Delta_{\mathrm{R}}V$.

In the limit, we require the $\Delta\xi$ to be infinitesimally small in Eq. (8.5). 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:

$$\Delta_{\mathrm{R}}V \equiv \left(\frac{\partial V}{\partial\xi}\right)_{p,T,\xi',\xi'',\ldots} = \sum v_i V_i. \tag{8.7}$$

It should not be difficult to transfer this to other types of transformations such as phase transitions, dissolving processes, etc., that can be considered special cases of reactions. Depending upon the process (change of modification, melting, sublimation, dissolving, …), one may write $\Delta_{\alpha\beta}V, \Delta_{\mathrm{sl}}V, \Delta_{\mathrm{sg}}V, \Delta_{\mathrm{sd}}V, \ldots$ or in more detail

$\Delta_{\alpha\to\beta}V, \Delta_{s\to l}V, \Delta_{s\to g}V, \Delta_{s\to d}V, \ldots$. Conversely, $\Delta_{\to}V$ can be used when the type of transformation is unimportant.

A few numerical values are useful for orientation. Volume increases generally around 3 % during melting. Water ice, whose volume actually decreases during melting is a well-known but rare exception. Evaporation volume is determined almost solely by the volume demand of the vapor with 25 L mol^{-1} at room conditions. (Compared to that, the volume required by the same substance in its condensed state is so small that it can be ignored.)

8.4 Entropy Demand

Pure Substances A substance that contains no entropy is absolutely cold. In order to bring it up to room temperature at standard pressure, a certain amount of entropy is necessary. This can be generated internally or added from outside. The amount of entropy necessary varies from substance to substance. It is proportional to the amount of substance, so we relate the entropy required by a substance to the amount needed for 1 mol of substance. This quantity, which we were introduced to in Sect. 3.9, is called *molar entropy*:

$$S_m = \frac{S}{n} \quad molar\ entropy\ for\ pure\ substances.$$

Both entropy and molar entropy depend upon pressure and temperature. Therefore, if the temperature is kept constant, a solid body exposed to a pressure of 1,000 MPa loses about 1 % … 10 % of its entropy. In an ideal cooling process to 0 K, S decreases to $S_0 = 0$ Ct. Figure 8.4 illustrates the dependence of the entropy of a solid substance upon p and T. In the case of an ideal solid substance, the S surface originates at the p axis with a horizontal tangent and transforms into a rather

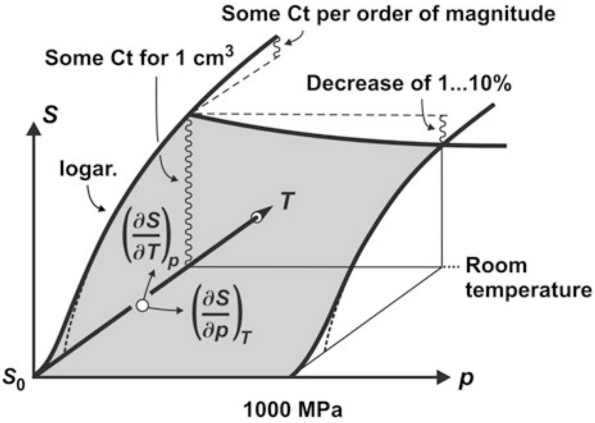


Fig. 8.4 Dependence of the entropy of a solid substance upon pressure and temperature.

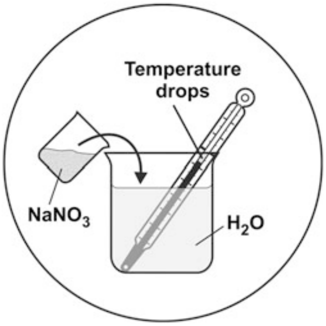
logarithmically increasing slope. In this range, S increases a few Ct for 1 cm^3 of matter, if the temperature increases by one order of magnitude. The decrease of entropy in the direction parallel to the p axis is similar to the decrease of volume with rising pressure. Gases do not behave much differently within their range of existence. However, the entropy density is about a thousand times smaller at room conditions than it is in liquid or solid substances. So as the pressure rises, the decrease of entropy is very slight. It is only about 1 Ct for an increase of pressure of one order of magnitude, if one assumes 1 dm^3 of gas at standard conditions. The rise in the T direction is logarithmic such as that for solids, but steeper, some Ct per order of magnitude.

The standard value is indicated, as usual,

$$S_m^{\ominus}(H_2O) = 69.9\,\text{Ct mol}^{-1} \quad \text{at} \quad 298 \ \text{K} \quad \text{and} \quad 100 \ \text{kPa}.$$

The values of the entropy at a point p, T (such as at standard conditions) can be converted to other p and T values if the gradients of the surfaces in the p and T directions are known at the former point, i.e., if $(\partial S/\partial p)_T$ and $(\partial S/\partial p)_p$ are known. The first coefficient describes the substance's loss of entropy by increase of pressure. The second one corresponds to its entropy capacity $\mathcal{C}$, which we were introduced to in Sect. 3.9.

Dissolved Substances The entropy required by a substance distributed within a body differs from what it requires in its pure state. It is mostly considerably greater because the atomic disorder increases when atoms or molecules are scattered over a larger volume. $NaNO_3$ in a 1 kmol m^{-3} aqueous solution at room conditions requires just about twice as much entropy as it does in its solid state. Therefore, when $NaNO_3$ is dissolved in water, the solution cools down so strongly due to the salt extracting entropy from the water so that the glass it is in fogs up (Experiment 8.4). In order to keep the temperature constant, entropy must be absorbed from the surroundings. As is the case in almost every process, entropy is generated here too, but it is not enough to cover the high additional entropy demand of the salt.



Experiment 8.4 *Cooling during dissolving of $NaNO_3$ in water*: Solid sodium nitrate is poured all at once into the water and subsequently, one stirs vigorously with a glass rod. A strong decrease in temperature can be observed.

Distributing a tiny amount Δn of a substance inside a body results in a small change of entropy ΔS. The entropy change relative to the small amount of substance is used for defining a measure of the entropy demand of the substance:

$$S_\mathrm{m} \approx \frac{\Delta S}{\Delta n} \quad \text{for small } \Delta n. \tag{8.8}$$

To be exact, one must again deal with the limit of infinitesimally small additional amounts Δn of the substance, keeping pressure, temperature, and the amounts of all other substances constant in the process:

$$S_\mathrm{m} \equiv \left(\frac{\partial S}{\partial n}\right)_{p,T,n',n'',\ldots} \quad \textit{(partial) molar entropy of a dissolved substance.} \tag{8.9}$$

The molar entropy corresponds to the change of entropy required by the addition of a small amount of the component in order to keep the temperature constant at a given pressure, *extrapolated linearly* to 1 mol. Statements of this type can make things difficult at first, but actually come up a lot in everyday life. An example: when a car traveling at 50 km/h crosses some zebra stripes, it might take 1 s to do so. If we linearly extrapolate the width of the stripes by a factor of 3,600, we obtain a distance of 50 km. That's the meaning of "traveling at 50 km/h."

Like molar volume, molar entropy of dissolved substances can be negative. This occurs mostly with polyvalent ions in aqueous solution, for example, with Ca^{2+}. When such ions are put into water, they *organize* water molecules, previously distributed in an *unorganized* way in the liquid, into their hydration shells. The effect can be so great that a state emerges that is more strongly organized overall, although the arbitrary distribution of the ions in the solvent actually increases disorder. The entropy can then decrease. The decrease of entropy just described does not contradict the second law! The process does not *destroy* entropy, the entropy is pressed out of the water going into the hydration shells into the surrounding liquid, warming it. If the temperature is to be kept constant, this surplus entropy must be removed. The entropy of the solution decreases only as a result of this removal. The entropy demand is now smaller.

The molar entropy grows along with increasing dilution. It always grows by the same magnitude ΔS_m, if the concentration is multiplied by a fixed factor (<1) *no matter what the substance is and what milieu it is in.* Conversely, the molar entropy decreases when the concentration increases. If, for example, the concentration increases by a factor of 10, the molar entropy (at 298 K) decreases by

$$S_\mathrm{d} \approx -19\,\mathrm{Ct\,mol^{-1}} \quad \text{for } c \to 10c, \text{ as long as } c \ll c^\ominus.$$

We have seen a similar kind of behavior with the chemical potentials (remember the decapotential $\mu_\mathrm{d} = 5.7$ kG in Sect. 6.3). Indeed, the two patterns of behavior are closely related to each other. We will show this later on in Sect. 9.3 (S–n coupling). We conclude that S_m must depend logarithmically upon c:

$$S_m = S_{m,0} - R\ln\frac{c}{c_0} \quad \text{for } c, c_0 \ll c^{\ominus}. \tag{8.10}$$

This resembles the mass action equation. If we use $c = 10c_0$, we recover the result for S_d mentioned above. We can use the value of 19 Ct mol^{-1} for rough estimates. This equation, which we accept for now on empirical grounds [and which we are going to derive later (Sect. 13.4)], holds strictly for low concentrations. Deviations occur at higher concentrations.

Unlike with molar volume, we cannot use the values for infinite dilution as the *basic values* $\overset{\circ}{S}_m$ for molar entropy S_m because they would be infinite. A value at finite concentration, the standard concentration $c^{\ominus} = 1\,\text{kmol}\,\text{m}^{-3}$, is used instead. The true values $S_m(c^{\ominus})$ are not used but one extrapolates from the measured or calculated values for small concentrations to $c^{\ominus}$, according to the relation given above. Just like the basic values of the chemical potentials, those of molar entropies are fictive values. Written in terms of the basic value, the equation above is

$$S_m = \overset{\circ}{S}_m - R\ln\frac{c}{c^{\ominus}} \quad \text{for } c \ll c^{\ominus}. \tag{8.11}$$

In general, the *standard values* (the basic values at standard temperature and standard pressure) are tabulated, $S_m^{\ominus} = \overset{\circ}{S}_m(T^{\ominus}, p^{\ominus})$.

The amount of entropy contained in a portion of a mixture is obtained analogously to its volume from the amounts and entropy demands of its components, for example, components A and B:

$$S = n_A \cdot S_A + n_B \cdot S_B. \tag{8.12}$$

The derivation which we forgo here can be accomplished according to the same pattern used for volume [Eq. (8.3)].

8.5 Changes of Entropy Associated with Transformations

In a chemical reaction, the substances involved produce new ones with changed entropy demands. Here, we are interested in the amount of entropy ΔS which is added or removed for compensation when a reaction takes place at constant pressure and constant temperature. Let us consider the reaction of 0.1 mol of iron and 0.1 mol of sulfur forming 0.1 mol of iron sulfide, at room conditions:

$$\begin{array}{lccl}
 & \text{Fe} \quad + \text{S} & \rightarrow\ \text{FeS} & \\
\cline{2-3}
S_\text{m}^\ominus\ (\text{Ct}\,\text{mol}^{-1}) & 27 \qquad 32 & 60 & \\
S\ (\text{Ct}) & \underbrace{2.7 \qquad 3.2}_{5.9} & 6.0 & \text{contained in each 0.1 mol.}
\end{array}$$

We see that exactly $\Delta S = 0.1$ Ct is lacking. This is what is needed to cover the entropy demands of the FeS produced by a conversion of $\Delta\xi = 0.1$ mol. This amount of entropy ΔS must be introduced from outside if the iron sulfide is to be as warm at the end of the reaction as the iron and sulfur were before the process began. Without this added entropy, it would be colder. If the conversion is multiplied, the required entropy multiplies correspondingly.

Our example results in the following for an arbitrary conversion $\Delta\xi$:

$$\Delta S = S_\text{FeS} \cdot \Delta\xi - S_\text{Fe} \cdot \Delta\xi - S_\text{S} \cdot \Delta\xi,$$

where S_FeS, S_Fe, and S_S each represent the molar entropies of the corresponding substances. The additional demand ΔS is proportional to the conversion if temperature and pressure are kept constant during the reaction and no side reactions take place. Because of this proportionality, it makes sense to relate the additional requirement to the conversion:

$$\Delta_\text{R} S = \frac{\Delta S}{\Delta\xi} = S_\text{FeS} - S_\text{Fe} - S_\text{S} \quad \text{for small } \Delta\xi;\ p, T, \xi', \xi'', \ldots \text{const.}$$

This conversion-related quantity is called the *molar reaction entropy* $\Delta_\text{R} S$. In our example, the caveat "for small $\Delta\xi$" is unnecessary because only pure substances are participating in the reaction. However, if dissolved substances appear in the conversion formula, we can then only allow small additional conversions $\Delta\xi$ for any arbitrary extent ξ of the reaction. This is to ensure that the composition of the solution and, therefore, the entropy demands of the substances in it do not change noticeably.

For an arbitrary reaction between pure and dissolved substances,

$$|\nu_\text{B}|\text{B} + |\nu_{\text{B}'}|\text{B}' + \ldots \rightarrow \nu_\text{D}\text{D} + \nu_{\text{D}'}\text{D}' + \ldots,$$

we can calculate the molar reaction entropy according to the pattern used for many other conversion-based "extensive" (often substance-like) quantities, which we were introduced to through the example of molar reaction volume:

$$\Delta_\text{R} S = \nu_\text{B} S_\text{B} + \nu_{\text{B}'} S_{\text{B}'} + \ldots + \nu_\text{D} S_\text{D} + \nu_{\text{D}'} S_{\text{D}'} + \ldots = \sum \nu_i S_i. \tag{8.13}$$

The molar reaction entropy is the change of entropy—based upon the conversion—at constant p and T. It equals the sum of the molar entropies of the reaction partners weighted by the conversion numbers. Using our iron-and-sulfur example, we have $\Delta_R S = S_{FeS} - S_{Fe} - S_S = 1\,\text{Ct}\,\text{mol}^{-1}$ because of $\nu_{Fe} = \nu_S = -1$ and $\nu_{FeS} = +1$.

The conditions added to the equation above can be expressed as for the case of molar reaction volume by replacing the Δ by ∂ in the difference quotient and adding the quantities which will be kept constant to the index:

$$\Delta_R S = \left(\frac{\partial S}{\partial \xi}\right)_{p,T,\xi',\xi'',\ldots} = \sum \nu_i S_i. \tag{8.14}$$

If the standard values for the molar entropies of all the reaction participants are applied, one obtains $\Delta_R S^\ominus$ as the standard value.

The following considerations can be helpful for estimating reaction entropy: In the case of liquids and especially in the case of gases, the values of molar entropies are generally far above those of solid substances. The algebraic sign and the absolute value of $\Delta_R S$ are therefore primarily determined by how much the number of liquid or gaseous molecules changes during a reaction. The more the number of liquid or gas molecules increases in a reaction, the more positive the molar reaction entropy will be. In a net consumption of gas or liquid molecules, the reaction entropy decreases so that in the reaction

$$2\,H_2|g + O_2|g \rightarrow 2\,H_2O|l$$

we have a strong decrease of entropy of $\Delta_R S^\ominus = -327\,\text{Ct}\,\text{mol}^{-1}$ which results from the formation of a liquid from two gases.

As in the case of volume (see end of Sect. 8.3), it should be easy to relate this to other kinds of transformations of substances such as phase transitions, dissolving processes, etc. We can write $\Delta_{\rightarrow} S$ instead of $\Delta_R S$ if we wish to emphasize that we mean any type of transformation and not only reactions. Egon Wiberg (Wiberg E (1972) Chemical Affinity, 2nd edn. de Gruyter, Berlin, New York, p. 103) suggested calling processes with positive transformation entropy, $\Delta_{\rightarrow} S > 0$, *endotropic*, and those with negative $\Delta_{\rightarrow} S < 0$, *exotropic*.

However, in contrast to the case of volume, the effects caused by the differing entropy demands of substances can be masked by others because energy is released in many processes which then generates entropy. In order to better understand the consequences of this circumstance, we will now deal with energy released or used by these processes.

Again, it would be good to note some reference values. For monoatomic substances, the increase of entropy in a melting process is about 10 Ct mol^{-1} (Richards's rule), while for all substances boiling at normal pressure, it is around 100 Ct mol^{-1} (Pictet–Trouton's rule).

8.6 Energy Conversion in Transformations of Substances

As we have seen in the introduction to the chemical potential (Sect. 4.8), in order to increase the amount n of a substance B, against its own "tendency to transform" μ, we need an amount of energy equal to

$$W_{\rightarrow n} = \mu \cdot \Delta n \quad \text{for small } \Delta n \qquad \text{or} \qquad \mathrm{d}W_{\rightarrow n} = \mu \mathrm{d}n \tag{8.15}$$

(Fig. 8.5). Whether the growth is caused from production inside or by addition from outside makes no difference. If the substance is produced inside it only means that at the same time a certain amount of one or more substances participating in the creation of B either disappear or are produced. This can be included separately by the corresponding expressions $\mathrm{d}W_{\rightarrow n'} = \mu' \mathrm{d}n'$, $\mathrm{d}W_{\rightarrow n''} = \mu'' \mathrm{d}n''$, … and can therefore be ignored here.

If we want to obtain the contribution $W_{\rightarrow n}$ from the change ΔW of the energy content W of the system, we have to make sure that no other substances, entropy, or similar quantities are added as well. Furthermore, the volume must be kept constant. This can be achieved by fixing the amounts of all other substances, the entropy, the volume, etc., of the body

$$W_{\rightarrow n} = (\Delta W)_{S,V,n',n'',\ldots} \text{ or } \mathrm{d}W_{\rightarrow n} = (\mathrm{d}W)_{S,V,n',n'',\ldots}.$$

This is not different from what we learned in the example of the bathtub (compare Sect. 1.6). The way water flows in and out of the bathtub over various paths is also valid here for energy. The energy content W of the area is a state variable, but the amounts of energy $W_{\rightarrow V}$, $W_{\rightarrow S}$, $W_{\rightarrow n}$, $W_{\rightarrow n'}$, … that are exchanged with the surroundings over different paths are not. They are so-called process quantities whose combined effect can best be imagined by considering a process taking place in time t. $P_V(t) = \mathrm{d}W_{\rightarrow V}/\mathrm{d}t, P_S(t) = \mathrm{d}W_{\rightarrow S}/\mathrm{d}t$, etc., represent the energy currents flowing over various paths, while $\dot{W} = \mathrm{d}W/\mathrm{d}t$ tells us how quickly the amount of energy increases as a result:

$$\dot{W} = P_V + P_S + P_n + P_{n'} + \ldots \quad \text{"Continuity equation."}$$

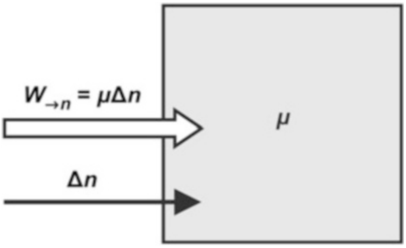


Fig. 8.5 The energy needed to increase the amount n of a substance inside a material system (where the potential equals μ) by adding or producing a small amount of Δn.

The energy current P_n flowing over path n can be formally described by $\dot{W}$ if we imagine all other pathways to be blocked, $P_n = \left(\dot{W}\right)_{S,V,n',n'',\ldots}$. When we use this method to calculate the energy $\mathrm{d}W_{\rightarrow n}$ flowing in during a short time span $\mathrm{d}t$, we obtain the equation we started with:

$$\mathrm{d}W_{\rightarrow n} = P_n \cdot \mathrm{d}t = \left(\dot{W} \cdot \mathrm{d}t\right)_{S,V,n',n'',\ldots} = (\mathrm{d}W)_{S,V,n',n'',\ldots}.$$

The following fact is remarkable and important. If entropy S_g is generated (possibly by friction) in an area at temperature T, this costs an additional amount of energy $W_\mathrm{b} = T \cdot S_\mathrm{g}$. The condition that S must be kept constant just means that S_g and therefore W_b cannot remain in the area but must be removed. Whether or not energy is “burnt” and entropy is generated in the procedure does not affect the result and can, therefore, be ignored.

We arrive at the chemical potential μ if we divide $\mathrm{d}W_{\rightarrow n}$ in the equation above by $\mathrm{d}n$, which leads us back to the following equation we know from Sect. 4.8:

$$\mu = \left(\frac{\partial W}{\partial n}\right)_{S,V,n',n'',\ldots}. \tag{8.16}$$

The energy W_t necessary for *transferring* a small amount n_t of a substance from a body 1 with the chemical potential μ_1 to another body 2 with the potential μ_2 (Fig. 8.6) results from the effort $\mu_2 \cdot n_\mathrm{t}$ for supplying the amount n_t to body 2, less the profit $\mu_1 \cdot n_\mathrm{t}$ resulting from the removal from body 1:

$$W_\mathrm{t} = (\mu_2 - \mu_1) \cdot n_\mathrm{t} = \Delta\mu \cdot n_\mathrm{t} \quad \text{for small } n_\mathrm{t}. \tag{8.17}$$

If $\mu_2 > \mu_1$, and therefore the substance is pumped “up the potential hill,” W_t is positive, and increasingly so, the greater the potential lift is.

Conversely, energy can be gained when a substance goes from higher μ to lower μ, and W_t becomes negative. Similar to thermal engines where the temperature fall

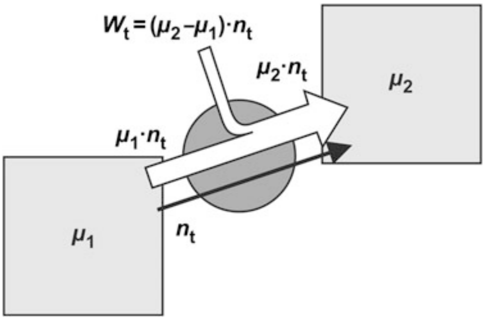


Fig. 8.6 Flow diagram for energy and amount of substance of an “ideal substance pump” (*gray circle*). In reality, entropy is constantly generated—possibly by friction—which costs extra energy.

of entropy is used, corresponding "*chemical engines*" can be constructed. Such chemical engines are to be found all over in nature in the form of muscles and the flagella of single-celled organisms. A simple apparatus of this type that makes use of the potential difference of liquid water in a glass and water vapor in the air of the room is the toy known as the "drinking duck" (Experiment 8.5).

Chemical reactions can be described using the same paradigm. It makes no difference whether or not the substances all appear in the same homogeneous area, or if they are distributed over various areas. For a reaction

$$\mathrm{B} + \mathrm{B}' + \ldots \rightarrow \mathrm{D} + \mathrm{D}' + \ldots$$

the total effort $W_{\rightarrow\xi}$ for an increase of the conversion by a small $\Delta\xi$ is simply the sum of the positive or negative contributions due to changes of amount $\Delta n_\mathrm{B} = -\Delta\xi$, $\Delta n_{\mathrm{B}'} = -\Delta\xi$, … of the reactants and $\Delta n_\mathrm{D} = \Delta\xi$, $\Delta n_{\mathrm{D}'} = \Delta\xi$, … of the products:

$$W_{\rightarrow\xi} = \mu_\mathrm{B}\Delta n_\mathrm{B} + \mu_{\mathrm{B}'}\Delta n_{\mathrm{B}'} + \ldots + \mu_\mathrm{D}\Delta n_\mathrm{D} + \mu_{\mathrm{D}'}\Delta n_{\mathrm{D}'} + \ldots .$$

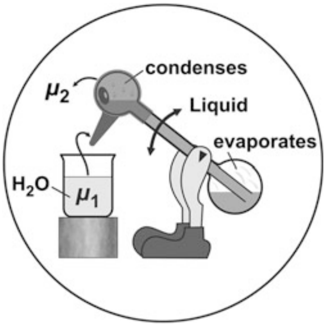
The sums of the chemical potentials can be combined to give the chemical drive of the reaction:

$$W_{\rightarrow\xi} = -(\mu_\mathrm{B} + \mu_{\mathrm{B}'} + \ldots - \mu_\mathrm{D} - \mu_{\mathrm{D}'} - \ldots) \cdot \Delta\xi = -\mathcal{A} \cdot \Delta\xi.$$

Generalizing this for the case where the conversion numbers are not only +1 or −1 is just a formality. The energy $W_{\rightarrow\xi}$ needed for the general reaction

$$0 \rightarrow v_\mathrm{A}\mathrm{A} + v_\mathrm{B}\mathrm{B} + v_\mathrm{C}\mathrm{C} + \ldots \qquad \text{or} \qquad 0 \rightarrow \sum_i v_i \mathcal{B}_i$$

(compare Sect. 1.7) with $\Delta n_\mathrm{A} = v_\mathrm{A}\Delta\xi$, $\Delta n_\mathrm{B} = v_\mathrm{B}\Delta\xi$, … or, alternatively, $\Delta n_i = v_i\Delta\xi$, equals



Experiment 8.5 *Drinking duck*: First, the felt of the duck's head is wetted. After a short while, the duck begins to "drink," i.e., it slowly swings back and forth, finally dips its beak into the water, and comes back up nodding. After a number of oscillations, the process starts anew.

$$W_{\to\xi} = \mu_A \Delta n_A + \mu_B \Delta n_B + \mu_C \Delta n_C + \ldots$$

and so

$$W_{\to\xi} = (\nu_A \mu_A + \nu_B \mu_B + \nu_C \mu_C + \ldots) \cdot \Delta\xi = \left(\sum_i \nu_i \mu_i\right) \cdot \Delta\xi = -\mathcal{A} \cdot \Delta\xi.$$

The final formula is very simple and remains the same for both cases. The more "negative" drive $\mathcal{A}$ (the greater $-\mathcal{A}$) and the greater the conversion $\Delta\xi$ are, the more the energy needed increases:

$$W_{\to\xi} = -\mathcal{A} \cdot \Delta\xi \quad \text{for small } \Delta\xi. \tag{8.18}$$

One might call $-\mathcal{A}$ a measure of "reverse force," meaning how strongly a reaction resists when it is forced to proceed against its own drive. This is not different from what we know from mechanics when a spring is stretched or a weight is lifted.

As a reaction progresses, the composition of the mixture changes and along with it, the chemical drive. In order for Eq. (8.18) to remain generally valid, the conversion $\Delta\xi$ (and consequently, the energy $W_{\to\xi}$) must stay small enough. This is usually expressed by using differentials:

$$\mathrm{d}W_{\to\xi} = -\mathcal{A} \cdot \mathrm{d}\xi. \tag{8.19}$$

In the case of spontaneous reactions, where the drive $\mathcal{A}$ is positive, we have $W_{\to\xi} < 0$, and energy is therefore released. This released energy is usually "burnt," thereby generating entropy. This generally leads to a heating up of the reaction mixture (Sect. 8.7). The energy may, however, be available for lots of other uses. For instance, muscles use the energy released by glucose oxidation. This does not happen perfectly, but with a higher efficiency as if the glucose were burnt in a thermal power plant:

$$\begin{array}{llllll} & \underline{C_6H_{12}O_6|w\ + \quad 6\ O_2|g \quad \to \quad 6\ CO_2|w \quad + 6\ H_2O|l} & & & & \\ \mu^\ominus(\text{kG}): & -915 \qquad\quad 6 \times 0 \qquad\quad 6 \times (-386) \quad 6 \times (-237) & \Rightarrow & \mathcal{A}^\ominus = +2821\ \text{kG}. \end{array}$$

For a conversion of $\Delta\xi = 1$ mol, the result is an energy requirement of $W_{\to\xi} = -\mathcal{A} \cdot \Delta\xi$, meaning a gain of $-W_{\to\xi} = \mathcal{A} \cdot \Delta\xi = 2{,}821\,\text{kG}$ in the ideal case. Flashlight batteries, for example, use the energy released by zinc oxidation through MnO_2.

8.7 Heat Effects

Preliminary Remarks In the introduction to entropy in Chap. 3, we mentioned that this quantity describes exactly what we consider "amount of heat" in everyday life. Phenomena are called *caloric* when the *amount* of heat is the primary characteristic and called *thermal* when temperature is most significant. It is easiest to understand the caloric effects that accompany all types of transformations of substances through entropy and not through energy. Entropy is the characteristic substance-like quantity for effects of this type. Energy also plays its role, not only here but in (almost) all other effects as well. It is important but nonspecific. If one is paying too much attention (or is only paying attention) to energy, the wrong parameter is being emphasized.

"Great things cast long shadows" is a saying we all know. One can find out a lot from shadows alone, such as the form, motion, and behavior of whatever is producing the shadow. However, some things get lost such as colors or the actual shape and form of the body in question. Everything that happens in nature leaves behind traces at the level of energy. In many cases, these shadow images suffice and are even very good for describing an important aspect: conservation of energy—but this is not the only important aspect. It is like the floor plan of a house that does not give a sufficiently clear picture of its habitability.

An energy "shadow" belongs to every change of entropy dS in a system no matter if it occurs as a result of exchange with the surroundings (dS_e) or through generation inside (dS_g), or both:

$$\begin{aligned} \mathrm{d}S &= \mathrm{d}S_\mathrm{e} + \mathrm{d}S_\mathrm{g} && \text{level of entropy,} \\ T\mathrm{d}S &= T\mathrm{d}S_\mathrm{e} + T\mathrm{d}S_\mathrm{g} && \text{level of energy.} \end{aligned} \tag{8.20}$$

In order to understand the basics, it suffices if, for now, we limit ourselves to systems that do not exchange substances with their surroundings. As long as changes are small or the temperature T remains constant, the shadow is a good image of what happens at the entropic level: $T\Delta S = T\Delta S_\mathrm{e} + T\Delta S_\mathrm{g}$. If this condition is breached in any way, a distorted image emerges. It may be distorted only slightly, but just as easily it can be deformed to the point of being unrecognizable. Only $T\mathrm{d}S_\mathrm{e}$ (or the sum of such contributions, $\int_{\text{initial}}^{\text{final}} T\,\mathrm{d}S_\mathrm{e}$), is usually called "heat" (compare Sect. 3.11). We will return to this at the end of this section.

Many of the characteristic quantities that describe caloric effects hold for isothermal conditions. In this case, T represents a fixed scale factor between the original entropic image and the secondary image at the energy level. Luckily, we are only dealing with isothermal effects in this section. Therefore, it hardly makes any difference whether we discuss things at the entropic level or rewrite them in terms of energy quantities. Although it is unusual, we will choose the first approach because it better clarifies the essentials.

Interaction of Two Effects Let us consider a simple system with uniform pressure p and temperature T which conform to the values p^* and T^* in the surroundings. Moreover, only one reaction may occur inside this system. Now there are three pathways over which the energy content W of the system can be changed:

$$\mathrm{d}W = -p\mathrm{d}V + T\mathrm{d}S - \mathcal{A}\mathrm{d}\xi. \tag{8.21}$$

In order to direct the energy to take a particular path, the system as well as the surroundings must be adjusted to this. We might need heat conducting walls and an entropy reservoir outside to absorb or deliver energy thermally. Cylinders, pistons, and transmission gears are used in order to make the energy mechanically useful. Finally, electrodes, diaphragms, ion conductors, and the like are employed to use the energy made available chemically. It is unimportant here how these devices are constructed.

Let us now imagine a system and its surroundings equipped for energy to be exchanged via all three paths. When the reaction progresses by a small $\mathrm{d}\xi$, the amounts of substances change and their volume and entropy demands change along with them:

$$\mathrm{d}V = \Delta_\mathrm{R}V \cdot \mathrm{d}\xi \quad \text{and} \quad \mathrm{d}S = \Delta_\mathrm{R}S \cdot \mathrm{d}\xi. \tag{8.22}$$

The increases $\mathrm{d}V$ and $\mathrm{d}S$ occur at the cost of the surroundings, i.e., $\mathrm{d}V = -\mathrm{d}V^*$ and $\mathrm{d}S = -\mathrm{d}S^*$. This is the case as long as no entropy is generated, which we will assume for the present. There is an exchange of energy connected with this. Because we have assumed pressure and temperature to be the same inside and outside, $p = p^*$ and $T = T^*$, no energy is released. The word *released* means that it is then available for other purposes. In this case, what is released on one side is used on the other side so that nothing is left over: $p\mathrm{d}V + p^*\mathrm{d}V^* = 0$ and $T\mathrm{d}S + T^*\mathrm{d}S^* = 0$; therefore, nothing is released. This type of energy exchange in which energy is passed on for an *intended purpose* cannot be tapped into and is therefore uninteresting.

The situation is different for the third path. The energy $-\mathrm{d}W_{\to\xi} = \mathcal{A}\mathrm{d}\xi$ released in a spontaneous reaction (with $\mathcal{A} > 0$) cannot, as a rule, be used completely. To express this, we introduce an efficiency $\eta < 1$. The *useful* energy which the surroundings (Index *) receives, is then $\mathrm{d}W^*_\mathrm{use} = \eta\mathcal{A}\mathrm{d}\xi$. The rest $\mathrm{d}W^*_\mathrm{b} = (1-\eta)\mathcal{A}\mathrm{d}\xi$ is "burnt," thereby generating entropy. With $\mathrm{d}S_\mathrm{g} = \mathrm{d}W^*_\mathrm{b}/T$, we have:

$$\mathrm{d}S_\mathrm{g} = \frac{\mathrm{d}W^*_\mathrm{b}}{T} = \frac{(1-\eta)\mathcal{A}\mathrm{d}\xi}{T}. \tag{8.23}$$

The "burnt" energy is transferred thermally together with the contribution $-T\mathrm{d}S$ (e.g., through rigid but thermally conducting walls) into the surroundings (Fig. 8.7):

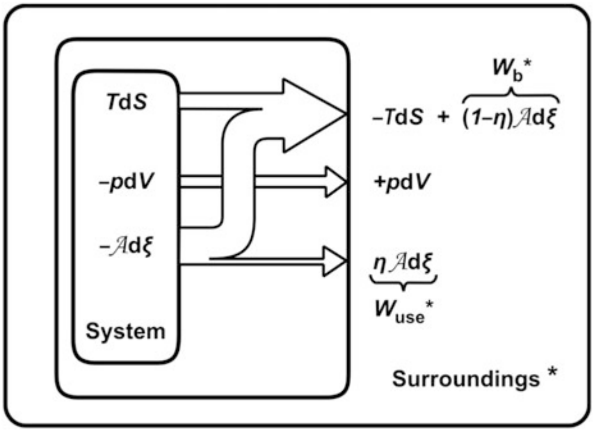


Fig. 8.7 Energy flow diagram for a material system when pressure and temperature are the same inside and outside. The energy released inside during a small conversion $\mathrm{d}\xi$ is used with an efficiency of η.

$$\begin{array}{rcccl}
\mathrm{d}W & = & -p\mathrm{d}V & +T\mathrm{d}S \qquad -\mathcal{A}\,\mathrm{d}\xi & & \text{system,}\\
 & & \downarrow & \downarrow \qquad\qquad\qquad \downarrow & \searrow & \\
\mathrm{d}W^* & = & \underbrace{+p\mathrm{d}V}_{-p\mathrm{d}V^*} & \underbrace{-T\mathrm{d}S \quad +(1-\eta)\mathcal{A}\,\mathrm{d}\xi}_{T\mathrm{d}S^*} & \underbrace{+\eta\,\mathcal{A}\,\mathrm{d}\xi}_{\mathrm{d}W_{\mathrm{use}}^*} & \text{surroundings *.}
\end{array}$$

One could say that the third path is “leaky,” meaning that a part of the useful energy transported along this path may get lost and finally dissipates in the surroundings. The other paths are not impervious to loss, either. It is just the lack of pressure and temperature gradients that hinder them being tapped.

When dealing with only one system and its surroundings, there are stipulations for the signs: Inflows to the system receive positive signs and outflows receive negative ones. Whatever happens in the surroundings is described accordingly. The entropy content S of a system can, as we know, change through exchange or generation (compare Sect. 3.6):

$$\mathrm{d}S = \mathrm{d}S_\mathrm{e} + \mathrm{d}S_\mathrm{g}$$

or rearranged:

$$\mathrm{d}S_\mathrm{e} = \mathrm{d}S - \mathrm{d}S_\mathrm{g}. \tag{8.24}$$

While $\mathrm{d}S$ describes the entropic effect inside, $\mathrm{d}S_\mathrm{e} = -\mathrm{d}S^*$ indicates the effect that can be noticed outside. If $\mathrm{d}S_\mathrm{e} < 0$, the process is called *exothermic* and if $\mathrm{d}S_\mathrm{e} > 0$, it is called *endothermic*. In contrast, the sign of $\mathrm{d}S$ is the deciding factor for the terms *exotropic* and *endotropic* introduced in Sect. 8.5:

$$\begin{array}{llll} \mathrm{d}S < 0 & \text{exotropic,} & \mathrm{d}S > 0 & \text{endotropic,} \\ \mathrm{d}S_\mathrm{e} < 0 & \text{exothermic,} & \mathrm{d}S_\mathrm{e} > 0 & \text{endothermic.} \end{array}$$

$\mathrm{d}S_\mathrm{e}$ is *not* a simple quantity. According to Eq. (8.24), it is made up of two dissimilar contributions. Along with the process itself, we will call these contributions exothermic or endothermic depending upon their signs. Both are proportional to the conversion $\mathrm{d}\xi$ but have different origins and depend upon very different parameters:

$$\mathrm{d}S = \Delta_\mathrm{R}S \cdot \mathrm{d}\xi \quad [\text{according to Eq.}(8.22)]$$

- Can be either positive or negative, providing consequently an endothermic or exothermic contribution.
- Has nothing directly to do with the chemical drive $\mathcal{A}$ of the process.
- Is independent of whether or not and how the released energy is used or wasted.

$$\mathrm{d}S_\mathrm{g} = (1 - \eta)\mathcal{A}\mathrm{d}\xi/T \quad [\text{according to Eq.}(8.23)]$$

- Is always positive and therefore always provides an exothermic contribution.
- Is directly proportional to the chemical drive $\mathcal{A}$ of the process.
- Varies between 0 and 100 % depending upon the type of energy usage.

Because of these differences it is a good idea to discuss the two contributions always separately and not to try to combine them as is usual in chemistry. $\mathrm{d}S$ and $\mathrm{d}S_\mathrm{g}$ are proportional to the conversion $\mathrm{d}\xi$ so it makes sense relating them to the conversion, especially when giving concrete values:

$$\left(\frac{\mathrm{d}S}{\mathrm{d}\xi}\right)_{p,T} = \Delta_\mathrm{R}S \text{ and } \frac{\mathrm{d}S_\mathrm{g}}{\mathrm{d}\xi} = \frac{(1-\eta)\mathcal{A}}{T}. \tag{8.25}$$

We have inserted into the first expression the condition that p and T are to be kept constant, which is unnecessary in the second expression because it is independent of this condition. Another difference emerges that makes it advisable to keep the two effects separate. When the entropy S is given as a function of p, T, and ξ, $S = f(p, T, \xi)$, then $\Delta_\mathrm{R}S$ can be calculated as the derivative of f with respect to ξ at constant p and T (according to the usual mathematical rules). Formally, this is expressed by replacing the straight d by the rounded ∂: $\Delta_\mathrm{R}S = (\partial S/\partial \xi)_{p,T}$.

Latent Entropy The consideration above is correspondingly valid for other types of transformations of substances. In phase transitions such as melting, boiling, etc., the drive disappears at the corresponding transition points, $\mathcal{A} = 0$. This is analogously valid for dissolving processes at saturation and generally for transformations at equilibrium. The second expression becomes zero in each case and the entropic effects (and the caloric ones along with them) in the system and its surroundings become equal, $\mathrm{d}S = \mathrm{d}S_\mathrm{e}$ (or $T\mathrm{d}S = T\mathrm{d}S_\mathrm{e}$). In this special case, it has long been customary to use the term "latent heat," namely for the infinitesimal quantity $T\mathrm{d}S$ and, respectively, its integral $T\Delta S$.

The term "latent heat" originated in the eighteenth century when people had only vague conceptions about the nature of heat and its characteristics. The most common belief was that heat was an entity contained in objects to greater or lesser degree that was movable and could be exchanged between them, comparable to a substance. When something felt warm or hot, it was because there was more of this entity contained within it, and when something felt cold, it meant there was less of it. This describes almost exactly the characteristics we have attributed to entropy, with the difference that it was assumed back then that the entity could be neither generated nor destroyed.

Already in the eighteenth century it was clear that heat had to be added to vaporize water, and heat had to be withdrawn if steam was to condense. Even though the produced steam takes much more heat than is needed to heat the cold water to the boiling point, the temperature of the steam is not higher than the boiling temperature. It is as if the heat is "hiding"; it has become *latent* according to the term used back then. When the steam condenses to its liquid, the latent (hidden) heat is released and becomes *sensible*.

We have taken over this name for lack of a better one in order to distinguish between the effects caused by differences of entropy demands and those caused by entropy generation. In Eq. (8.25), the expression on the left represents the *latent molar reaction entropy* and the one on the right, the *generated molar reaction entropy*.

Balance of Entropy Only the difference of these two effects is noticeable outside due to $\mathrm{d}S_\mathrm{e} = \mathrm{d}S - \mathrm{d}S_\mathrm{g}$:

$$\left(\frac{\mathrm{d}S_\mathrm{e}}{\mathrm{d}\xi}\right)_{p,T} = \left(\frac{\mathrm{d}S - \mathrm{d}S_\mathrm{g}}{\mathrm{d}\xi}\right)_{p,T} = \left(\frac{\mathrm{d}S}{\mathrm{d}\xi}\right)_{p,T} - \frac{\mathrm{d}S_\mathrm{g}}{\mathrm{d}\xi}$$

or

$$\underbrace{\left(\frac{\mathrm{d}S_\mathrm{e}}{\mathrm{d}\xi}\right)_{p,T}}_{\text{exchanged}} = \underbrace{\Delta_\mathrm{R}S}_{\text{latent}} - \underbrace{\frac{(1-\eta)\mathcal{A}}{T}}_{\text{generated}} \quad \text{molar reaction entropy.} \tag{8.26}$$

Naturally, formal symbols corresponding to the various reaction entropies can be introduced, which are more or less self-explanatory. This allows us to abbreviate the three molar entropies introduced above, and their integral counterparts, to:

$$\Delta_\mathrm{R}S_\mathrm{e} = \Delta_\mathrm{R}S_\ell - \Delta_\mathrm{R}S_\mathrm{g} \quad \text{and} \quad \Delta S_\mathrm{e} = \Delta S_\ell - \Delta S_\mathrm{g} \quad \text{(balance of entropy)} \tag{8.27}$$

The index $_\ell$ for "latent" is only inserted for the sake of clarity. We assume pressure and temperature to be constant, as stated at the beginning. Remember that merely $\Delta_\mathrm{R}S_\ell\ (\equiv \Delta_\mathrm{R}S)$ is determined only by the state parameters p, T, ξ used here. $\Delta_\mathrm{R}S_\mathrm{g}$ and

$\Delta_R S_e$ along with it depend upon the efficiency η and therefore upon other parameters such as "resistances" of various types inside or upon the devices that make exchange of energy between system and surroundings possible.

$\Delta_R S_e$ is mostly negative because the absolute value of latent entropy in chemical reactions is in general much smaller than the generated entropy, $|\Delta_R S| \ll \Delta_R S_g$. This results in most chemical reactions being exothermic, so that

- The entropy must flow off for the temperature and pressure to be retained or
- The temperature will rise if the outflow of entropy is hindered.

Let us return to the reaction of iron with sulfur with a conversion of $\Delta\xi = 0.1$ mol (compare Sect. 8.5). In order for the resulting iron sulfide not to emerge sub-cooled from the reaction, we noticed that 0.1 Ct of entropy was lacking, which needed to be absorbed from the surroundings. However, we know that iron sulfide actually forms as a brightly glowing product which must emit quite a lot of entropy in order to attain the original temperature of the starting substances (see Experiment 3.5). Where does all this excess entropy come from?

The energy $\mathcal{A} \cdot \Delta\xi$ is released during the reaction. It is easy to calculate $\mathcal{A}$ with the help of the chemical potentials. This energy can be used for anything we want, for example, if we manage to couple the reaction process in a galvanic cell with an electric current, which itself drives a motor, light bulb, electrolysis cell, etc. If, however, a mixture of iron and sulfur powder is ignited in the open, the released energy is used to generate entropy. This entropy is deposited in the end at temperature T which lies around 300 K. Therefore, according to $\mathcal{A} \cdot \Delta\xi = T \cdot \Delta S_g$, the amount of entropy *finally* generated, i.e., S_g, equals

$$\Delta S_g = \frac{\mathcal{A} \cdot \Delta\xi}{T} = \frac{(\mu(\text{Fe}) + \mu(\text{S}) - \mu(\text{FeS}))\Delta\xi}{T}$$
$$= \frac{\left(0 + 0 - \left(-102 \times 10^3\,\text{G}\right) \times 0.1\,\text{mol}\right)}{300\,\text{K}} = 34\,\text{Ct}.$$

The large value of the excess entropy mentioned above comes from the *generated entropy* S_g. What the temperatures in the interim are, or how the entropy actually comes to be generated, makes no difference to the final result.

The general rule is that all released energy remains unused, meaning it is used up to generate entropy. However, if the energy involved is not simply "burnt," but is used with an efficiency of η, say of 70 % (possibly by a galvanic cell driving a motor), then only $(1 - \eta)\mathcal{A}\Delta\xi$ is available for generating entropy:

$$S_g = \frac{(1 - \eta)\mathcal{A}\Delta\xi}{T} = \frac{(1 - 0.7) \times 102 \times 10^3\,\text{G} \times 0.1\,\text{mol}}{300\,\text{K}} = 10\,\text{Ct}.$$

In the ideal case of a complete use of energy ($\eta = 1$), the term S_g would disappear and the previous exothermic reaction would become endothermic. Galvanic cells, which allow such usage, were not actually developed for the reaction between iron and sulfur, but for the reaction of sulfur with sodium. We will discuss the design of such cells in electrochemistry, later on.

Accompanying Exchange of Energy We mentioned above that until the middle of the nineteenth century, certain characteristics were attributed to heat that correspond well to the properties attributed to entropy discussed in Chap. 3, with the exception that heat was considered a quantity that cannot be generated. Discoveries during the nineteenth century increasingly contradicted this assumption and finally led to a restructuring of the whole intellectual edifice. Since then, heat has been considered a special form of energy transfer. Formally, this rededication leads to the differential $T\mathrm{d}S_e$ or, more precisely, the integral $\int T\mathrm{d}S_e$being called heat Q (rather than S):

$$\mathrm{d}Q = T\mathrm{d}S_e \text{ or } Q = \int_{\text{initial}}^{\text{final}} T\mathrm{d}S_e.$$

While the step from the quantity S to Q is comparatively easy, reversing this is very difficult. One reason is that we cannot see anymore on which path the energy arrived once it is in the system, similar to how we cannot tell the way a person arrived at work, whether on foot, by bicycle, in a car, etc., once he or she is in the office. Formally, this means that Q (differently from S) is not a state variable; it is not determined by the state of the system.

Another reason is that the (*thermodynamic*) *temperature* T can be defined easily based on entropy, but only in a temporary form and awkwardly without this concept. Without entropy, this definition is commonly achieved via the thermal expansion of gases. However, one usually forgoes demonstrating that the temperature θ defined this way actually corresponds to the thermodynamic T. Let us overlook this difficulty! When the equation $\mathrm{d}Q = T\mathrm{d}S_e$ above is solved for $\mathrm{d}S_e$ and then integrated, the result is:

$$\mathrm{d}S_e = \frac{\mathrm{d}Q}{T} \text{ and } \Delta S_e = \int_{\text{initial}}^{\text{final}} \frac{\mathrm{d}Q}{T}.$$

We have not reached our goal yet. What we are looking for is $\Delta S = \Delta S_e + \Delta S_g$ and not ΔS_e. Therefore, we must also make sure that $\Delta S_g = 0$. In order to assure this, the whole process must be *reversible* and this is indicated by the index $_{\text{rev}}$ for Q:

$$\mathrm{d}S = \frac{\mathrm{d}Q_{\text{rev}}}{T} \text{ and } \Delta S = \int_{\text{initial}}^{\text{final}} \frac{\mathrm{d}Q_{\text{rev}}}{T}.$$

The effects we are dealing with at the moment occur at constant temperature so that the relation between exchanged entropy ΔS_e and the accompanying transfer of energy or heat $Q = T\Delta S_e$ is very simple. If one wishes to discuss the accompanying energy exchange, it is enough in this case to multiply the corresponding entropies by T. Taking it a step further, and multiplying the balance of entropy (8.27) by T, we obtain the following expression:

$$\underbrace{T\Delta S_e}_{Q_e} = \underbrace{T\Delta S_\ell}_{Q_\ell} - \underbrace{T\Delta S_g}_{Q_g}. \qquad \text{“exchanged” = “latent” – “generated heat.”}$$

If we were to abide by the usual rules of terminology, we would only call the first element heat and use the symbol Q for it (without the index $_e$), even though the other contributions cause the same effects. We will overlook this limitation, though, because it means nothing to us and only creates an unnecessary obstacle.

Gibbs–Helmholtz Equations One of these equations (of which there are different versions) will serve here as an example for applying the balance of entropy discussed above. The most common version of this equation describes the relation between drive $\mathcal{A}$ and the heating effect that is observed when a reaction runs *freely* at constant p and T, meaning that the released energy $\mathcal{A} \cdot \Delta\xi$ is “burnt” without any use ($\eta = 0$), so that $\mathcal{A} \cdot \Delta\xi = T \cdot \Delta S_g = Q_g$. Again, we assume $\Delta\xi$ to be small. The fame of these equations can be traced to an error, the idea common at that time, that the emitted heat $-Q_e$ or the “heat tone” as it was called was a measure of the drive $\mathcal{A}$ of a reaction (Berthelot’s principle, 1869). $Q_g = -Q_e + Q_\ell$ would have been correct, instead of $-Q_e$ alone. The error was not immediately seen because the latent heat Q_ℓ is generally considerably smaller than the observable heat effects. The attractiveness of this approach was that there existed simple calorimetric methods to measure Q_e. This gave people at that time a much simpler procedure for determining or at least estimating the drive $\mathcal{A}$ than had been possible until then. Before that, one had to be content with simply ranking the drives for certain reactions.

Therefore, there was good reason to measure these heats and to collect the data. The error was only gradually dealt with by the work of Josiah Willard Gibbs, Hermann von Helmholtz, and Jacobus Henricus van’t Hoff who all showed that the “heat tone” $-Q_e$ itself did not represent the correct measure for the drive, but that a positive or negative contribution corresponding to the latent heats Q_ℓ (such as was known from phase transitions) had to be added:

$$\mathcal{A} \cdot \Delta\xi = \underbrace{-Q_e + Q_\ell}_{Q_g} \qquad \text{(a version of the Gibbs–Helmholtz equation).}$$

8.8 Calorimetric Measurement of Chemical Drives

The concept is simple: In a reaction, the released energy $\mathcal{A} \cdot \Delta\xi$ is “burnt” during a certain conversion $\Delta\xi$ at given values of p and T and the generated entropy ΔS_g is then determined calorimetrically. Because $\mathcal{A} \cdot \Delta\xi = T \cdot \Delta S_g$, $\mathcal{A}$ is then easy to calculate from the measured data.

Unfortunately, the latent entropy becomes a problem because depending upon the type of substances, the entropy demands S_m and therefore the entropy content ΔS of the sample change in the reactor. A positive ΔS becomes noticeable as a negative contribution $-\Delta S$ in the calorimeter (Index *) so that not ΔS_g but $\Delta S^* = \Delta S_g - \Delta S = -\Delta S_e$ is measured there.

This value is only useful if it is possible to also determine ΔS in some way. This step is easy to imagine. One measures the entropy content S_1 of the sample before the reaction and then the value S_2 afterwards. The value being sought is the difference $\Delta S = S_2 - S_1$. In Sect. 3.9, we indicated how such a measurement might look. The fact that the sample must be cooled down to a temperature of just about absolute zero causes such entropy measurements to be technically complicated, comprising the greatest obstacle to this method. In fact, when possible, such entropy values are measured separately for the individual substances and then tabulated as molar entropies. The missing value for ΔS is then calculated from these tabular values.

How, then, is the first part of the measurement carried out, meaning how is $\Delta S^* = -\Delta S_e$ determined? We might make use of one of the "ice calorimeters" described in Sect. 3.7 and deduce the entropy from the amount of melted water. More often, though, a calorimeter is used that determines the exchanged entropy through the small temperature changes in a water bath (or in a metal block). It is essentially made up of a container in which the reaction takes place and the water bath (or metal block) mentioned above as well as a sensitive thermometer (Fig. 8.8). The entire device is completely thermally insulated from the surroundings. The calorimeter must be calibrated before (or perhaps after) the actual measurement. For this, the measuring assembly receives a well-determined amount of entropy and the changes of temperature associated with this are measured. The easiest way to put entropy at a certain place is to generate it in an electric heating coil directly

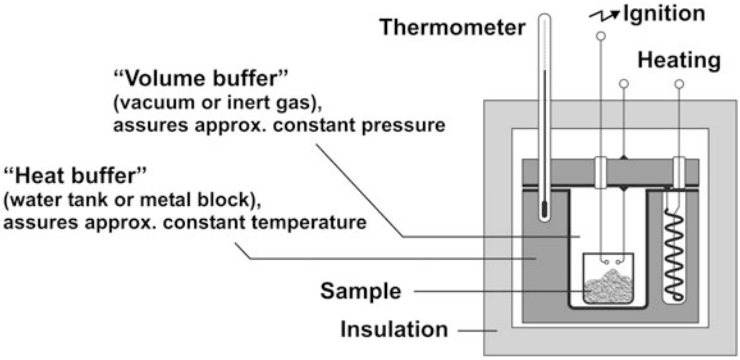
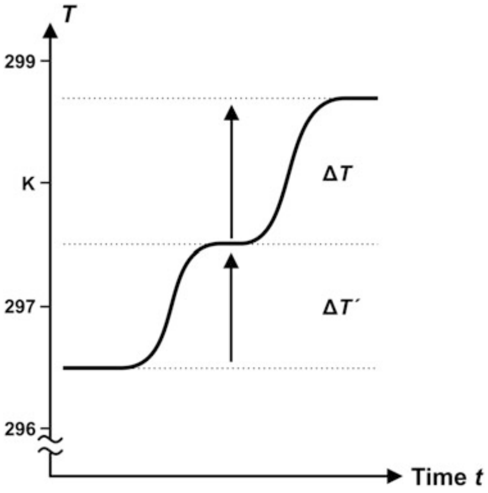


Fig. 8.8 Calorimeter.

Fig. 8.9 Increases of temperature $\Delta T'$ and ΔT in the calorimeter as a result of the electrically generated entropy for calibrating $\Delta S'_{\mathrm{g}}$ and the entropy $\Delta S_{\mathrm{e}} = \Delta S_{\mathrm{g}} - \Delta S$ emitted subsequently during the reaction.



where it is wanted. The expended electric energy W_{b} can be easily calculated from the current I, voltage U, and the power-on time Δt, according to

$$W_{\mathrm{b}} = I \cdot U \cdot \Delta t. \tag{8.28}$$

The “burnt” energy, divided by the measured temperature T, results in the increase of entropy $\Delta S'_{\mathrm{g}}$ that leads to the small temperature rise of $\Delta T'$ (Fig. 8.9). If we start a reaction in the container, it is possible to calculate the entropy $\Delta S^* = -\Delta S_{\mathrm{e}}$ released by the sample, from the observed changes of temperature ΔT.

To make this procedure somewhat clearer, let us return one last time to our example of the reaction of iron and sulfur into iron sulfide at room conditions. Again, 0.1 mol each of iron and sulfur are used:

$$\mathrm{Fe|s + S|s \rightarrow FeS|s} \quad \text{at } T = T^{\ominus} \text{ (influence of pressure is negligible).}$$

- *Determining the latent entropy* ΔS by measuring the entropy in the sample in its initial state (Fe + S) and final state (FeS):

  Method: Cooling the sample down to approximately 0 K and measuring the entropy S needed for heating up to T, both before and after the reaction (or instead, calculating from the tabulated data obtained via the same procedure).

  Result: $\Delta S = 6.0\ \mathrm{Ct} - 2.7\ \mathrm{Ct} - 3.2\ \mathrm{Ct} = 0.1\ \mathrm{Ct}$.
- *Measuring the entropy* $-\Delta S_{\mathrm{e}}$ *emitted by the sample during the reaction*:

  Calibration: Warming by $\Delta T' = 1.0$ K by electrically generated entropy $\Delta S'_{\mathrm{g}} = 28.0$ Ct. A heater with a power of $P = 60$ W needs to be operated for a time span of $\Delta t = 139$ s for this: $\Delta S'_{\mathrm{g}} = P \cdot \Delta t / T^{\ominus} = 60 \times 139/298\ \mathrm{Ct} = 28.0\ \mathrm{Ct}$.

Measurement: Warming by $\Delta T = 1.2$ K due to the entropy $-\Delta S_e$ emitted by the sample during the reaction.

Analysis: $\Delta T/\Delta T' = \Delta S^*/\Delta S^{*\prime} = -\Delta S_e/\Delta S'_g$ is valid for small changes; therefore,

$$\Delta S_e = -\frac{\Delta T}{\Delta T'}\Delta S'_g = -\frac{1.20\,\mathrm{K}}{1.00\,\mathrm{K}}28.0\,\mathrm{Ct} = -33.6\,\mathrm{Ct}.$$

- *Summing up of the calorimetric partial results*:

  The entropy generated during the reaction, calculated from the balance of entropy $\Delta S = \Delta S_e + \Delta S_g$:

  $$\Delta S_g = \Delta S - \Delta S_e = 0.1\,\mathrm{Ct} - (-33.6\ \mathrm{Ct}) = 33.7\ \mathrm{Ct}.$$

  Chemical drive, calculated from the relation $\mathcal{A}\cdot\Delta\xi = T\cdot\Delta S_g$:

  $$\mathcal{A} = \frac{T\cdot\Delta S_g}{\Delta\xi} = \frac{298\ \mathrm{K}\times 33.7\ \mathrm{Ct}}{0.1\,\mathrm{mol}} = 100\ \mathrm{kG}.$$

Historically, this purely calorimetric method represents the first accessible way to determine chemical drives. At the same time, our example shows just how small the contribution of latent entropy ($\Delta S_\ell \equiv$) $\Delta S = 0.1$ Ct is, compared to the generated entropy $\Delta S_g = 33.7$ Ct, so it is no surprise that this small amount was overlooked at the beginning.

However, the situation changes as soon as gases are consumed or produced. We will look a little closer at an example, the reaction of oxyhydrogen (a mixture of hydrogen and oxygen gases):

$$\begin{array}{lllll}
 & \underline{H_2|g\ +} & \underline{\tfrac{1}{2}O_2|g\ \rightarrow} & \underline{H_2O|l} & \text{at } T = T^\ominus,\ p = p^\ominus \\
\mu^\ominus(\mathrm{kG}): & 0 & \tfrac{1}{2}\times 0 & -237 & \Rightarrow \mathcal{A}^\ominus \quad = +237\,\mathrm{kG}. \\
S^\ominus(\mathrm{Ct\,mol^{-1}}): & 131 & \tfrac{1}{2}\times 205 & 70 & \Rightarrow \Delta_R S^\ominus = -164\,\mathrm{Ct\,mol^{-1}}.
\end{array}$$

The following values for generated, latent, and exchanged entropies are the result of a conversion of $\Delta\xi = 0.1$ mol at standard conditions:

$$\begin{aligned}
\Delta S_g &= \frac{\mathcal{A}\cdot\Delta\xi}{T} = \frac{237\times 10^3\,\mathrm{G}\times 0.1\,\mathrm{mol}}{298\,\mathrm{K}} && = +80\ \mathrm{Ct}, \\
\Delta S_\ell &= \Delta_R S\cdot\Delta\xi = -164\ \mathrm{Ct\,mol^{-1}}\times 0.1\ \mathrm{mol} && \underline{= -16\ \mathrm{Ct},} \\
\Delta S_e &= \Delta S_\ell - \Delta S_g && = -96\ \mathrm{Ct}.
\end{aligned}$$

In this case the latent entropy plays a significant role.