Chapter 9
Coupling

As we have seen in previous chapters, it is possible to act on a material system mechanically (by expansion and compression ...), thermally (by heating and cooling ...), and chemically (by addition or reaction of substances). All these actions are accompanied by changes of energy. These energy changes can be combined into a single equation, the so-called *main equation*.

The quantities appearing in this equation (such as p, V, S, T, $\mathcal{A}$, ξ), the *main quantities*, depend on each other in many ways. These dependencies can be described quantitatively by different coefficients such as $(\partial S/\partial T)_{p,\xi}$. Between the coefficients, there exist plenty of cross relations (couplings) which can be found in two ways: First, by using energy balances for appropriate cyclic processes and second as a direct result of a mathematical operation we call "flipping." Important couplings like the equivalence of the temperature coefficient of μ and the negative molar entropy are easily deduced by special "flip rules." We also discuss the relationship between coupling of main quantities and Le Chatelier–Braun's principle.

9.1 Main Equation

Introduction Homogeneous regions, in which pressure, temperature, and composition are the same throughout, form the basic building blocks of the systems that matter dynamics deals with. A region of this type is called a *phase* (Sect. 1.5). When two parts of such a phase are combined, the quantities such as volume V, entropy S, amount of substance n_i, etc., add up while pressure p, temperature T, the chemical potential μ_i, etc., remain the same. The first type of quantities are called extensive quantities and the second intensive quantities (Sect. 1.6). Not every quantity fits into one of these categories. For instance, V^2 and $\sqrt{S}$ are neither one nor the other and there are others like them.

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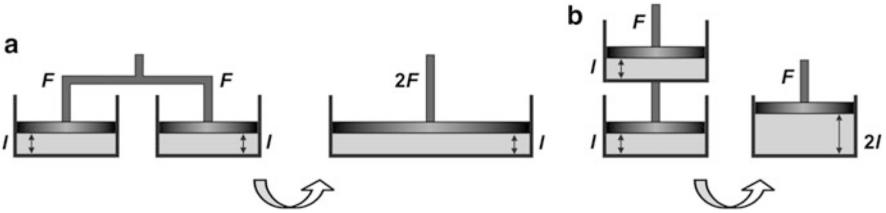


Fig. 9.1 Merging of two identical gas-filled regions (in *gray*), enclosed in cylinders with pistons: (**a**) Parallel connection: the force F is doubled, the length l remains constant, (**b**) Series connection: the force remains constant, the length is doubled.

Let us imagine a gas in a cylinder with a piston. The material system we observe is the gas and the concrete system we operate with is the gas-filled cylinder. Keeping the gas in the enclosure allows us to control the mechanical quantities p and V. We specify the force F upon the piston being pushed inside the cylinder, and a length l to quantify its position such as the distance between the piston and the bottom of the cylinder. We now imagine two identical gas-filled cylinders. How do the two quantities F and l behave when we merge the two systems into one? This is not initially clear and depends upon how this step is carried out (Fig. 9.1).

Similar problems appear in many other systems as well, such as in the galvanic cells which we will discuss in Chap. 23. In parallel and series connections, voltage U and transported charge Q behave like F and l in our example. The possibility of classifying quantities as either extensive or intensive is a distinctive feature of homogeneous systems and should not be thoughtlessly generalized.

Main Equation As we have seen in previous chapters, a material system can be affected mechanically (by expanding, compressing, . . .), thermally (by heating, cooling, . . .), chemically (by addition or reaction of substances. . .), etc. Each of these effects is related to changes of energy ΔW of the system involved. For example, energy is absorbed when a body is compressed and the more that it is absorbed, the greater the loss of volume $-\Delta V$ and the higher the pressure p (Sect. 2.5),

$$\Delta W = -p \cdot \Delta V.$$

Inflow of entropy also leads to an increase in the content of energy (Sect. 3.11) of

$$\Delta W = T \cdot \Delta \mathrm{S}.$$

The same holds for the addition of a substance that results in absorption of energy according to

$$\Delta W = \mu \cdot \Delta n$$

(Sects. 4.8 and 8.6). As mentioned in Sect. 4.8, all of these changes of energy can be combined into a single equation, the so-called *main equation*. In a homogeneous region, where pressure p, temperature T, and the chemical potentials $\mu_1, \mu_2, \mu_3, \ldots$ are the same throughout, the following is valid for small changes of volume V, entropy S, and amounts of substance $n_1, n_2, n_3, \ldots$:

$$\Delta W = -p \cdot \Delta V + T \cdot \Delta S + \mu_1 \cdot \Delta n_1 + \mu_2 \cdot \Delta n_2 + \mu_3 \cdot \Delta n_3 + \ldots \quad \text{(Gibbs 1876)}. \tag{9.1}$$

The summation of the terms associated with the amounts of substance can be abbreviated with the help of the symbol for a sum, $\sum$:

$$\Delta W = -p \cdot \Delta V + T \cdot \Delta S + \sum_{i=1}^{n} \mu_i \cdot \Delta n_i. \tag{9.2}$$

This "main or fundamental equation" is the key to many important statements for systematically constructing the field of matter dynamics.

We are considering only loss-free systems that are able to fully release the energy put into them when the process is reversed. This means that no entropy may be generated inside the system, i.e., $S_g = 0$, so that the amount of entropy contained there can only vary by exchange from outside, $\Delta S = \Delta S_e$.

The quantities p, T, and n_i are considered easily measurable, so they are mostly chosen as independent variables. If a material system, possibly a body, is brought into contact with an electrical or magnetic field, or if it was charged or accelerated, etc., further terms would be added to the sum above; this we will ignore for the moment.

When no substances are exchanged with the surroundings but are only transformed inside the system, it is more advantageous to indicate its state by using the momentary extent ξ of a reaction in progress. The main equation then simplifies to

$$\Delta W = -p \cdot \Delta V + T \cdot \Delta S - \mathcal{A} \cdot \Delta \xi \quad \text{(De Donder 1920)}. \tag{9.3}$$

The condition of sufficiently small changes can be emphasized by using differentials. We would then obtain the following in the case of Eq. (9.3):

$$\mathrm{d}W = -p \cdot \mathrm{d}V + T \cdot \mathrm{d}S - \mathcal{A} \cdot \mathrm{d}\xi. \tag{9.4}$$

We already encountered another relation of this type, Eq. (8.21) in Sect. 8.7. There was a short discussion about concrete experimental conditions necessary for exchange of energy with the surroundings along all three paths. Unlike in Chap. 8, we will assume that it is possible for an exchange to occur without loss via the third path. This means that it always runs reversibly with no generation of entropy, i.e., the efficiency is $\eta = 1$. This also means that we can set the drive $\mathcal{A}$ and/or the extent ξ of the reaction in question by making use of appropriate aids.

This is similar to setting the pressure p through the force upon the piston or prescribing the volume V through its position in the cylinder. We consider $\mathcal{A}$ and ξ as adjustable parameters, like p and V or T and S, with whose help we can bring about certain states of a system and make changes over certain paths.

Main Quantities Certain mechanical ($-p$, V), thermal (T, S), and chemical *main quantities* (μ, n or $-\mathcal{A}$, ξ) appear on the right side of the main equations and are always pairs made up of an intensive quantity (without Δ- or d-symbol in front, and with proper signs $-p$, T, μ, $-\mathcal{A}$) and a corresponding extensive, mostly substance-like quantity (with Δ- or d-symbols in front: V, S, n, ξ). One says that these two quantities are *conjugated* with respect to each other, or more precisely, they are energetically conjugated. The intensive quantity belonging to a substance-like quantity can also be considered the potential having an effect upon it. So understood, the chemical potential μ belongs to the amount of substance n, and the "thermal potential" T belongs to entropy S. We will encounter more such examples in the next chapters. We will see that calculations and descriptions are simple and clear when it is possible to formulate a problem using these main quantities. This is especially true in the case of heat effects. These are best calculated using entropies because it is the entropy accompanying an exchange of energy that actually qualifies it as "heat" (exchange of "disordered energy").

In order to simplify our terminology, we will allow volume V to be considered "substance-like." V represents an *improper* quantity of this kind with degenerate but simple characteristics: a conserved quantity with constant density equal to 1. Whatever volume a system loses, the surroundings gain. The negative pressure $-p$ would be the corresponding potential. The energy expended to increase a volume (volume "inflow") from the surroundings with a pressure of p_1 into the system with higher pressure p_2 is negative and amounts to $\Delta W = (-p_2 \cdot \Delta V) - (-p_1 \cdot \Delta V)$. The equation is completely analogous to those for transferring entropy or a substance:

$$\Delta W = [(-p_2) - (-p_1)] \cdot \Delta V, \quad \Delta W = [T_2 - T_1] \cdot \Delta S, \quad \Delta W = [\mu_2 - \mu_1] \cdot \Delta n.$$

We should not be too narrow in our choice of terminology if we want to discuss systems of more general type, i.e., those made up of more than just one phase, such as systems like the gas plus cylinder and piston, or a galvanic cell as a whole. If, for example, the term $-p \cdot \mathrm{d}V$ is replaced by $-F \cdot \mathrm{d}l$ or the term $-\mathcal{A} \cdot \mathrm{d}\xi$ by $-U \cdot \mathrm{d}Q$ (where U is the voltage and Q the charge), we obtain the following equation,

$$\mathrm{d}W = -F \cdot \mathrm{d}l + T \cdot \mathrm{d}S - U \cdot \mathrm{d}Q, \tag{9.5}$$

which is of the same nature as the one formulated before. It is the main equation for our new, expanded system. However, the terminology of extensive and intensive does not necessarily work with all the quantities in it now, at least not in the sense it is used today. We can refer to a term introduced by Hermann von Helmholtz for help (compare Sect. 2.7). He called the quantities on the right side of our main equation that represent differentials "(position) coordinates" and the factors in front "forces." Both were meant in a general sense. Referring back to this, we call the quantities l, S, Q in the main equation (9.5) "position-like," and F, T, and U, "force-like."

Main Effects When a main quantity is changed, this affects the conjugated quantities as well. The type of effect in which one observes the reciprocal dependency of two associated quantities is called *main effect*. The main effect of an increase

- Of volume V is a decrease of pressure, meaning an increase of $-p$ (note that it is not V and p that are conjugated, but V and $-p$ or $-V$ und p),
- Of entropy S is warming, meaning an increase of temperature T,
- Of an amount n of a (dissolved) substance is an increase of its chemical potential μ,
- Of the extent ξ of a reaction (in solutions) is a decrease of its drive, meaning there is an increase of $-\mathcal{A}$ (here, too, it is important to notice the sign).

Conversely, the effect of an increase of $-p$, T, μ, $-\mathcal{A}$ in the surroundings, is an increase of V, S, n, ξ in the system.

Coefficients quantitatively describe main effects. In the strict sense, such coefficients are differential quotients whose numerators and denominators contain conjugated main quantities. In order to refer to them more easily, we will call them and their offspring (which only differ by certain factors) *main coefficients*. If we allow only small changes, we can use difference quotients instead of differential quotients, which simplifies things. To give an example, the following coefficients, which we were introduced to in Sect. 3.9 as *entropy capacities*, can characterize the main effect of an increase of temperature on the De Donder system above:

$$\left(\frac{\partial S}{\partial T}\right)_{p,\xi}, \left(\frac{\partial S}{\partial T}\right)_{V,\xi}, \left(\frac{\partial S}{\partial T}\right)_{p,\mathcal{A}}, \ldots \quad \text{or} \quad \left(\frac{\Delta S}{\Delta T}\right)_{p,\xi}, \left(\frac{\Delta S}{\Delta T}\right)_{V,\xi}, \left(\frac{\Delta S}{\Delta T}\right)_{p,\mathcal{A}}, \ldots$$

The first coefficient describes the most common case, namely how much entropy ΔS flows in if the temperature outside and (also inside as a result of entropy flowing in) is raised by ΔT and the pressure p and extent ξ of the reaction are kept constant. In the case of the second coefficient, volume is maintained instead of pressure (this only works well if there is a gas in the system). In the case of $\mathcal{A} = 0$, the third coefficient characterizes the increase of entropy *during equilibrium*, for example when heating nitrogen dioxide (NO_2) (see also Experiment 9.3) or acetic acid vapor (CH_3COOH) (both are gases where a portion of the molecules are dimers). Multiplied by T, the coefficients represent *heat capacities* (the isobaric C_p at constant pressure, the isochoric C_V at constant volume, etc.). It is customary to relate the coefficients to the "size" of the system, possibly the mass or the amount of substance. The corresponding values are then presented in tables. In the case above, they would be tabulated as specific (mass related) or molar (related to amount of substance) heat capacities. The qualifier "isobaric" and the index $_p$ will only be used if necessary for clarity. As a rule, when these attributes are lacking, it is the isobaric coefficients that are being described:

$$C = T\left(\frac{\partial S}{\partial T}\right)_{p,\xi}, \qquad c = \frac{T}{m}\left(\frac{\partial S}{\partial T}\right)_{p,\xi}, \qquad C_{\mathrm{m}} = \frac{T}{n}\left(\frac{\partial S}{\partial T}\right)_{p,\xi}.$$

("global") specific molar [isobaric] heat capacity.

Side Effects When a pair of conjugated main quantities is changed, there are always *side effects* to a greater or lesser degree affecting other main quantities. Almost all bodies tend to expand when entropy S is added to them. Volume V increases as long as the pressure is kept constant. If expansion is hindered, the pressure p inside will rise. In this case, S and V are *coupled in the same direction* which is expressed by $S \uparrow\uparrow V$. The relationship is reciprocal. When the volume is increased, the body also seeks to increase S by absorbing entropy from the surroundings. If this entropy absorption is obstructed, the temperature T will drop. Here, the material behaves similarly to a sponge in water as mentioned previously (Sect. 3.6). It "swells up" as it absorbs entropy and, when pressed, releases it again. There are very few exceptions to this. Ice water—meaning water between 0 and 4 °C—is the best example of these exceptions. The coupling here is *in the opposite direction*, $S \uparrow\downarrow V$. When ice water is pressed, it becomes even colder so that entropy begins to flow into it from the surroundings. When the pressure is released, the water becomes warmer and the entropy flows back out again.

This type of reciprocal relation between V and S is called a *mechanical–thermal* or in short a *V–S coupling*. All pairs of main quantities influence each other similarly. Change at one position almost always causes side effects somewhere else. A *coupling* of two processes in which one facilitates the other is said to go *in the same direction*. However, if one process impedes the other, we speak of a *coupling in the opposite direction*. It is always the behavior of the "position-like" partners in two main quantity pairs which is being compared and not the "force-like" ones.

Coefficients also can quantitatively describe side effects. However, in this case, the main quantities appearing in the numerator and denominator are not conjugated. Therefore, there is a large number of possible coefficients. For example, the first side effect mentioned above, the one having to do with S upon V, can be described by the following differential quotients in the upper line and the inverse one, V upon S, by the ones in the line below:

$$\left(\frac{\partial V}{\partial S}\right)_{p,n} \text{ or } \left(\frac{\partial p}{\partial S}\right)_{V,n}, \quad \text{but also} \quad \left(\frac{\partial V}{\partial T}\right)_{p,n} \text{ or } \left(\frac{\partial p}{\partial T}\right)_{V,n},$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} \text{ or } \left(\frac{\partial T}{\partial V}\right)_{S,n}, \quad \text{but also} \quad \left(\frac{\partial S}{\partial p}\right)_{T,n} \text{ or } \left(\frac{\partial T}{\partial p}\right)_{S,n}.$$

There are numerous cross relations between these types of coefficients, which we will call *side coefficients*. We will deal with these relations in the following.

The law of conservation of energy requires the reciprocal influence to be symmetrical and certain coefficients describing these effects to be identical (*mechanical–thermal cross relation*). The same holds for all the side effects.

9.2 Mechanical–Thermal Coupling

Introductory Example We will investigate the interactions between mechanical and thermal changes in a body. For the time being, we will ignore chemical changes (n or ξ, respectively, remain constant).

There are many cross relations. Here is one of the most important:

$$\left(\frac{\partial S}{\partial(-p)}\right)_{T,\xi} = \left(\frac{\partial V}{\partial T}\right)_{p,\xi} \quad \text{or} \quad \left(\frac{\partial S}{\partial p}\right)_{T,\xi} = -\left(\frac{\partial V}{\partial T}\right)_{p,\xi}. \tag{9.7}$$

This is one of the so-called *Maxwell relations*. The expression on the left lets us recognize its origin more easily. The one on the right shows the most common form. The coefficient on the far left of the upper line of equations describes entropy absorption during decompression (lowering of pressure); multiplied by T, this corresponds to the heat absorption. The one next to it on the right, divided by V, is the *cubic expansion coefficient* γ,

$$\gamma = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,\xi} \quad \text{“expansion coefficient,”} \tag{9.8}$$

which has been tabulated in many cases for pure substances. γ not only describes the relative volume increase of a body during heating, but also the amount of entropy emitted per unit of volume during compression as well.

Maxwell's Method There are various methods for derivation of cross relations. We will look at the one that nineteenth-century Scottish mathematical physicist James Clerk Maxwell used. Although it is rather complicated, it best allows us to see the relation to the law of conservation of energy. To accomplish this, we will determine the balance of energy for the following cyclic process, by keeping all the changes small (the curves appearing as short straight lines) and inhibiting reaction (ξ constant):

1. Expansion of the body as a consequence of change of pressure by $\Delta(-p)$ at constant temperature, as required by the first coefficient, where the entropy $\Delta S = (\Delta S/\Delta(-p))_{T,\xi} \cdot \Delta(-p)$ is absorbed.
2. Heating of the body by ΔT at constant pressure $(p - \Delta p)$, as required by the second coefficient. The volume then increases by $\Delta V = (\Delta V/\Delta T)_{p,\xi} \cdot \Delta T$.
3. “Reversal” of step 1: Compression of the body by Δp, while the temperature is kept constant at $T + \Delta T$ and entropy ΔS is emitted.

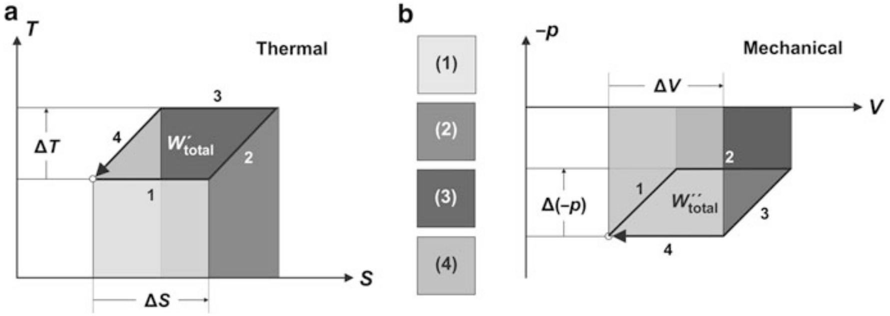


Fig. 9.2 (**a**) Cyclic process in a (T, S) or (**b**) in a ($-p$, V) diagram. The individual steps are indicated by *various shades of gray*.

4. "Reversal" of step 2: Cooling of the body by ΔT at constant pressure, whereby V takes the original value again and the initial state is attained once more; the cycle is complete.

The process can now be schematically represented in a so-called (T, S) diagram where the temperature T and the entropy S are shown (Fig. 9.2a), as well as in a ($-p$, V) diagram where negative pressure ($-p$) and volume V appear (Fig. 9.2b).

The energy W' thermally added to the body at each step (left), as well as the energy W'' added mechanically (right), corresponds to the absolute value of the area below each piece of the curve through which the process runs. The amounts of energy are considered positive in motion in the direction of the x-axis, i.e., when S or V increases, and negative for movement in the opposite direction. The sign must be changed for areas below the x-axis. Let us use the diagram on the left to look more closely at this. The total amount of energy expended is made up of four contributions:

$$W'_{\text{total}} = W'_1 + W'_2 + W'_3 + W'_4.$$

W'_2 and W'_4 have the same absolute value, but different signs, so they cancel. Because of $W'_1 = T \cdot \Delta S$ and $W'_2 = -(T + \Delta T) \cdot \Delta S$, we have:

$$W'_{\text{total}} = T \cdot \Delta S - (T + \Delta T) \cdot \Delta S = -\Delta T \cdot \Delta S.$$

W'_{total} then corresponds to the area enclosed by the cycle in the (T, S) diagram, appearing as a parallelogram, which is to be considered negative here. Analogously, we can calculate the energy added mechanically, except that now W'_1 and W''_3 cancel each other out. We are left with the contribution in the second step that results in $(-p + \Delta(-p)) \cdot \Delta V$, as well as the one in the fourth step which equals $-(-p) \cdot \Delta V$:

$$W'_{\text{total}} = (-p + \Delta(-p)) \cdot \Delta V - (-p) \cdot \Delta V = \Delta(-p) \cdot \Delta V.$$

The thermally expended energy corresponds to $-\Delta T \cdot \Delta S < 0$, and the mechanically expended energy corresponds to $\Delta(-p) \cdot \Delta V > 0$. Because energy can neither be created nor destroyed, the sum of both contributions disappears, meaning that

$$-\Delta T \cdot \Delta S + \Delta(-p) \cdot \Delta V = 0 \text{ or written differently } \Delta S / \Delta(-p) = \Delta V / \Delta T.$$

We can still add the indices—the pressure should be changed at constant temperature and the temperature should be changed at constant pressure, while ξ is kept constant—and replace the symbol Δ by either "d" or "∂," because we are only considering small changes. We finally obtain the sought-after Eq. (9.7):

$$\left(\frac{\Delta S}{\Delta(-p)}\right)_{T,\xi} = \left(\frac{\Delta V}{\Delta T}\right)_{p,\xi} \text{ and finally } \left(\frac{\partial S}{\partial p}\right)_{T,\xi} = -\left(\frac{\partial V}{\partial T}\right)_{p,\xi}.$$

Flip Rule Cross relations can be found in two ways. First, by using energy balances for appropriate cyclic processes and second as a direct result of a mathematical operation we call "*flipping*." Naturally, the *flip rule* can be derived mathematically (see end of the Chapter), but we will give instructions here in the form of a kind of "recipe": Take the differential quotient in question (or difference quotient) you wish to transform and

1. Exchange numerator and denominator, simultaneously replacing the main quantities there with the corresponding partner in each case,
2. If the quantities in the numerator and denominator are of the same type, change the sign,
3. And insert as indices all the main quantities that appeared unpaired in the original expression (and the pairs of main quantities that were totally missing there).

The most important pairs of main quantities that change their partners in the first step are $-p \leftrightarrow V, T \leftrightarrow S, \mu_i \leftrightarrow n_i, -\mathcal{A} \leftrightarrow \xi, \ldots$,, where the algebraic sign should not be forgotten. It makes no difference here which partner it is assigned to. When we are talking about "main quantities of the same type" we mean that both are either "position-like" or that both are "force-like." "Unpaired" means that the corresponding partner is missing. The addition in parentheses in step 3 usually affects only rather exotic coefficients, so it can generally be ignored.

When applied to a side coefficient, the end result of this operation is a new differential quotient and therefore one of the cross relations of interest to us. Let us look at the approach using our concrete example. Again, we will start with the differential quotient $(\partial S/\partial(-p))_{T,\xi}$.

1. T is assigned to S and V is assigned to $(-p)$. Therefore, in the flipped differential quotient, T is in the denominator and V in the numerator.
2. The algebraic sign remains positive because T is a "force-like" quantity and V is a "position-like" quantity.
3. In the original expression, p and ξ were unpaired (because the corresponding partners V and $(-\mathcal{A})$ were missing) and therefore have to be inserted into the new index. Additional pairs should not be added because each pair of main quantities is represented by at least one quantity in the given coefficient.

$$\left(\frac{\partial S}{\partial(-p)}\right)_{T,\xi} \overset{1)}{\times} \left(\frac{\partial V}{\partial T}\right) \xrightarrow{2)} \left(\frac{\partial V}{\partial T}\right) \xrightarrow{3)} \left(\frac{\partial V}{\partial T}\right)_{p,\xi} .$$

The cross relation in question, which is one of Maxwell's relations, is here obtained directly through flipping. If a main coefficient is flipped, it is generally reproduced; there is no new information as we can easily see:

$$\left(\frac{\partial S}{\partial T}\right)_{p,\xi} \overset{1)}{\times} \left(\frac{\partial S}{\partial T}\right) \xrightarrow{2)} \left(\frac{\partial S}{\partial T}\right) \xrightarrow{3)} \left(\frac{\partial S}{\partial T}\right)_{p,\xi} .$$

9.3 Coupling of Chemical Quantities

The fact that pressure and temperature influence the chemical potential of substances and therefore the drive for transformations can be considered a result of coupling of mechanical, thermal, and chemical quantities. With rare exceptions, volume V or entropy S and the amounts of substance n_i are coupled in the same direction: $V \uparrow\uparrow n_i$ and $S \uparrow\uparrow n_i$. However, the couplings between V and ξ as well as between S and ξ exhibit no directional preference because starting and final substances can exchange their roles according to which conversion formula is chosen.

The most commonly used state variables in chemistry are T, p, n, or ξ. Therefore, the coefficients in which these quantities are used to characterize changes of state are the most important ones. We will discuss only these in the following. Cross relations will be written in two ways: In the first, they will be expressed with main quantities; in the second we will apply the previously used symbols.

S–n Coupling Let us first turn to the temperature coefficient α of the chemical potential. We want to formulate it as a differential quotient: $(\partial\mu/\partial T)_{p,n}$. For practice, we will again show the process of "flipping" in detail:

1. n is assigned to μ and S is assigned to T. This means that in the flipped differential quotient, n is in the denominator and S is in the numerator.
2. The sign must change because both n and S are "position-like" quantities.
3. In the original expression, T and p are unpaired and therefore to be put into the new index:

$$\left(\frac{\partial\mu}{\partial T}\right)_{p,n} \xrightarrow{1)} \left(\frac{\partial S}{\partial n}\right) \xrightarrow{2)} -\left(\frac{\partial S}{\partial n}\right) \xrightarrow{3)} -\left(\frac{\partial S}{\partial n}\right)_{T,p}.$$

This finally leads to:

$$\left(\frac{\partial\mu}{\partial T}\right)_{p,n} = -\left(\frac{\partial S}{\partial n}\right)_{T,p}. \tag{9.9}$$

The same procedure applied to a component (1) of a mixture of two substances (1 and 2, main equation $\mathrm{d}W = -p\mathrm{d}V + T\mathrm{d}S + \mu_1\mathrm{d}n_1 + \mu_2\mathrm{d}n_2$) results in:

$$\left(\frac{\partial\mu}{\partial T}\right)_{p,n_1,n_2} \xrightarrow{1)} \left(\frac{\partial S}{\partial n_1}\right) \xrightarrow{2)} -\left(\frac{\partial S}{\partial n_1}\right) \xrightarrow{3)} -\left(\frac{\partial S}{\partial n_1}\right)_{T,p,n_2},$$

thus

$$\left(\frac{\partial\mu}{\partial T}\right)_{p,n_1,n_2} = -\left(\frac{\partial S}{\partial n_1}\right)_{T,p,n_2}. \tag{9.10}$$

These are further important cross relations analogous to those derived by James Clerk Maxwell. The expressions on the right are the molar entropies of the substance in a pure state S_m or in a mixture $S_{\mathrm{m},1}$. Positive S_m means that entropy tries to flow into a body along with any substance penetrating it, or that the temperature falls when the inflow of entropy is prevented. Since there are no walls that let a substance pass but not entropy, the effect cannot be observed directly. It becomes noticeable, though, when a substance is formed inside the body. This can only occur when another substance disappears, so there are always two or more effects which are superimposed additively or subtractively. Raising temperature not only increases S, but promotes absorption of substances, i.e., lowers the potential, as long as we do not allow matter to flow in. The conclusions of cross relations are simple, but possibly surprising. Along with the entropy demand of a substance, the molar entropy also describes the negative temperature coefficient α of its chemical potential:

$$\alpha = -S_\mathrm{m} \quad \text{or more generally} \quad \alpha_i = -S_{\mathrm{m},i}. \tag{9.11}$$

This relation easily results in the fact that α is always negative for pure substances and almost always negative for dissolved substances. This is because the molar entropy is just about always positive. Moreover, the molar entropy of a liquid is greater than for a solid and the molar entropy of a gas is much greater than that of a liquid, which leads to the ordering

$$\alpha(\mathrm{B}|\mathrm{g}) \ll \alpha(\mathrm{B}|\mathrm{l}) < \alpha(\mathrm{B}|\mathrm{s}) < 0$$

presented in Sect. 5.2. The form of the $\mu(T)$ curve in Fig. 5.1 can now be better justified by theoretical means. It begins with a horizontal tangent as long as the entropy content for $T = 0$ disappears like it should according to the third law of thermodynamics, and then falls more and more steeply. This drop is steeper for gases and substances in a dilute solution than for pure condensed substances (solids and liquids) because of the greater amount of entropy contained in them.

By means of the relation (9.10) we can also derive Eq. (8.10). The chemical potential of a dissolved substance is described by the mass action equation 1 [Eq. (6.4)] (or one of its variants):

$$\mu = \mu_0 + RT\ \ln\frac{c}{c_0}.$$

Its derivative with respect to T,

$$\left(\frac{\mathrm{d}\mu}{\mathrm{d}T}\right)_{p,n} = \left(\frac{\mathrm{d}\mu_0}{\mathrm{d}T}\right)_{p,n} + R\ \ln\frac{c}{c_0},$$

represents the negative molar entropy of the substance in question as long as the pressure and the amount of substance are held constant. Consequently, we obtain

$$-S_{\mathrm{m}} = -S_{\mathrm{m},0} + R\ \ln\frac{c}{c_0} \quad \text{or} \quad S_{\mathrm{m}} = S_{\mathrm{m},0} - R\ \ln\frac{c}{c_0}.$$

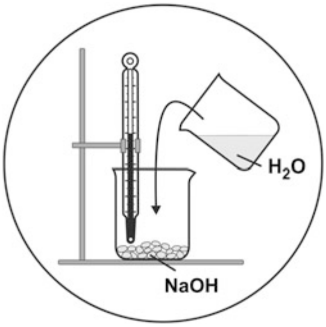
which corresponds to Eq. (8.10).

***S*–*ξ* Coupling** Starting from the main equation (9.4), $\mathrm{d}W = -p\mathrm{d}V + T\mathrm{d}S - \mathcal{A}\mathrm{d}\xi$, we can use the flip rule to convert the temperature coefficient α of the drive of a reaction or any other type of transformation of substances:

$$\left(\frac{\partial(-\mathcal{A})}{\partial T}\right)_{p,\xi} = -\left(\frac{\partial S}{\partial \xi}\right)_{T,p} \text{ or } \left(\frac{\partial \mathcal{A}}{\partial T}\right)_{p,\xi} = \left(\frac{\partial S}{\partial \xi}\right)_{T,p}. \tag{9.12}$$

The temperature coefficient α corresponds to the molar reaction entropy $\Delta_{\mathrm{R}}S$ introduced in Sect. 8.5, or more generally, to the corresponding entropy $\Delta_{\rightarrow}S$ of a transformation:

Experiment 9.1 *Changing the position of equilibrium*: If we mix equal weights of solid NaOH and water, the resulting solution reaches about 100 °C. The process is strongly exothermic. On the other hand, in a saturated solution at 100 °C, the proportion of $n(\text{NaOH})$ to $n(\text{H}_2\text{O})$ is about three times that at 25 °C. The solubility of NaOH strongly increases with rising temperature. While the formation of a diluted or concentrated solution of water and solid NaOH runs exothermically, dissolving NaOH in an (almost) saturated sodium hydroxide solution is an endothermic (endotropic) process. Only this effect is responsible for changing the position of equilibrium.



$$\alpha = \Delta_R S \quad \text{or} \quad \alpha = \Delta_{\rightarrow} S. \tag{9.13}$$

This shows us that the drive of an endotropic reaction ($\Delta_R S > 0$) increases with rise of temperature, $\alpha > 0$. If the reaction is in equilibrium, $\mathcal{A} = 0$, then a rise in temperature leads to the drive $\mathcal{A}$ becoming positive and pushing the process further forward in favor of the products. This is especially true for common phase transitions such as melting, boiling and sublimation, all of which are endotropic. The opposite holds for exotropic reactions. If the initial drive is zero (equilibrium), it will become negative as T increases and the equilibrium moves in the direction of the starting substances.

The drive disappears when equilibrium is reached, so the terms endotropic and endothermic as well as exotropic and exothermic all overlap (compare Sect. 8.7) and become interchangeable. However, this only holds for the equilibrium state and can lead to mistakes when applied elsewhere. Equilibrium constants for example are calculated from data valid for (often idealized) states that are mostly nowhere near equilibrium. It is rather amazing to find that the heat effects observed or theoretically calculated under these circumstances actually result in useful, if limited, conclusions about change of equilibrium conditions.

An explanatory example might be useful here (Experiment 9.1).

We could have used the concept of coupling without performing any calculations to correctly predict the *qualitative* behavior, i.e., to say whether heating causes the drive to increase or decrease or the equilibrium to shift forward or backward. Let us imagine an endotropic reaction. S and ξ would then be coupled in the same direction ($S \uparrow\uparrow \xi$). If ξ increases, S does as well and when S increases, so does ξ. If an equilibrium exists it will shift forward when heating takes place (increase of S).

The coupling is not rigid, though, and a change to the second quantity as a result of change to the first can be overridden by other effects. A reaction can be blocked, forcing ξ to remain constant. In this case, the addition of entropy (heating) will lead to an increase of $\mathcal{A}$ so that, although ξ itself does not increase, the drive for this change becomes stronger. We conclude that heating intensifies the drive of an endotropic reaction.

Something similar holds for the reverse effect. Inflow of entropy can be blocked so that S cannot change. An increase of ξ would then become noticeable in a lowering of temperature because the missing entropy cannot be replaced.

***V–n* Coupling** The pressure coefficient β of the chemical potential can be derived analogously to the temperature coefficient α. Using the main equation for a pure phase $\mathrm{d}W = -p\mathrm{d}V + T\mathrm{d}S + \mu\mathrm{d}n$, and by flipping, we obtain

$$\left(\frac{\partial\mu}{\partial(-p)}\right)_{T,n} = -\left(\frac{\partial V}{\partial n}\right)_{T,\,p} \tag{9.14}$$

or, based on the main equation for a mixture of two substances (1 and 2), $\mathrm{d}W = -p\mathrm{d}V + T\mathrm{d}S + \mu_1\mathrm{d}n_1 + \mu_2\mathrm{d}n_2$, we have

$$\left(\frac{\partial\mu}{\partial(-p)}\right)_{T,n_1,n_2} = -\left(\frac{\partial V}{\partial n_1}\right)_{T,\,p,n_2}. \tag{9.15}$$

These are two forms of a further cross relation. If the volume of a body grows when a substance is added to it, the molar volume V_m $(= \partial V/\partial n)_{p,T}$ is positive. Raising the pressure will therefore impede the absorption of the substance, i.e., more energy will be needed for this. Correspondingly, the potential rises. V_m does not only indicate the volume demand of a substance but also the pressure coefficient of its potential:

$$\beta = V_\mathrm{m} \text{ or more generally } \beta_i = V_{\mathrm{m},i}. \tag{9.16}$$

The molar volumes of pure substances are fundamentally positive, and those of dissolved substances almost always are. Therefore, the pressure coefficient of the chemical potential is almost always positive. The molar volume of gases is, as we have discussed (Sect. 8.2), about a factor of 1,000 times greater than that of condensed phases (liquids and solids). The molar volume for the liquid phases of most substances is greater than that of the solid phase. This all results in the ordering discussed in Sect. 5.3:

$$0 < \beta(\mathrm{B|s}) < \beta(\mathrm{B|l}) <<<< \beta(\mathrm{B|g}).$$

In regions of solid and liquid matter, where molar volume depends very little upon pressure ($V_\mathrm{m} \approx$ const.), μ increases almost linearly with p. This is different from gases where the $\mu(p)$ curve runs almost logarithmically and much more steeply (Fig. 5.7).

***V–ξ* Coupling** The pressure coefficient β of the drive $\mathcal{A}$ results from the same pattern as the temperature coefficient α. We start with the same main equation for both: $\mathrm{d}W = -p\mathrm{d}V + T\mathrm{d}S - \mathcal{A}\mathrm{d}\xi$. By flipping we obtain:

$$\left(\frac{\partial(-\mathcal{A})}{\partial(-p)}\right)_{T,\xi} = -\left(\frac{\partial V}{\partial \xi}\right)_{T,p} \quad \text{or} \quad \left(\frac{\partial \mathcal{A}}{\partial p}\right)_{T,\xi} = -\left(\frac{\partial V}{\partial \xi}\right)_{T,p}; \tag{9.17}$$

this means that the pressure coefficient β equals the negative molar reaction volume $\Delta_R V$,

$$\beta = -\Delta_R V. \tag{9.18}$$

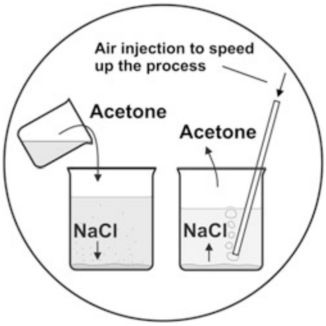
Assume that the volume increases during a reaction ($\Delta_R V > 0$). Then its drive $\mathcal{A}$ weakens if we impede expansion by raising the pressure. If equilibrium has been established in a reaction of this type and therefore $\mathcal{A} = 0$, an increase of pressure causes $\mathcal{A}$ to become negative. The process then begins to run backward.

We can obtain the same result qualitatively and without calculations if we consider V and ξ to be coupled. If the coupling is in the same direction, i.e., $V\uparrow\uparrow\xi$, a rise in pressure will decrease the volume and ξ along with it, as long as the process is not blocked.

***n–n* Coupling** Basically, a coupling in the same or in opposite directions can exist between any two "position-like" quantities. Experiment 9.2 shows an effect based upon coupling of two amounts of substances n_1 and n_2, more precisely upon their coupling in the opposite direction ($n_1 \uparrow\downarrow n_2$).

An example of coupling in the same direction ($n_1 \uparrow\uparrow n_2$) would be a small amount of undissolved $PbCl_2$ in a beaker with water that dissolves when KNO_3 is added ("salting-in effect"). The first substance's rise in potential can be used to measure the strength of reciprocal action caused by the second substance. This is the so-called *displacement coefficient* $(\partial\mu_1/\partial n_2)_{T,p,n_1}$. The opposite effect, the displacement of the second substance by the first, which we describe by $(\partial\mu_1/\partial n_2)_{T,p,n_1}$ is just as great, as we can see by applying the flip rule:

Experiment 9.2
Precipitation of table salt resulting from the addition of acetone: When drops of acetone are added to an almost saturated aqueous solution of table salt, the salt begins to precipitate but as the acetone evaporates it begins dissolving again.



$$\left(\frac{\partial \mu_1}{\partial n_2}\right)_{T,\,p,n_1} = \left(\frac{\partial \mu_2}{\partial n_1}\right)_{T,\,p,n_2}. \tag{9.19}$$

The reverse effect can easily be shown using our first example: When table salt is added to a 1:1 mixture of acetone and water, the acetone separates into a second layer on top of the solution ("salting-out effect," compare Experiment 13.5).

We conclude that we can directly obtain all kinds of cross relations by flipping. The flip rule can be considered a memory aid for all such relations. Using it in this way is advantageous:

- Coefficients that are difficult to measure can be calculated from more easily accessible ones.
- Many coefficients do not need their own symbols; in the literature, we often find α, β, α, β replaced by $-S_m$, V_m, $\Delta_R S$, $-\Delta_R V$ in the final results.

Le Chatelier–Braun's Principle or "Principle of Mobile Equilibrium" This "principle" was presented already at the end of the nineteenth century and is often mentioned in connection with our current discussion. Chemists use it to predict whether the extent ξ of a reaction in equilibrium will be shifted forward or backward when certain parameters are changed, especially pressure, temperature, amounts of reactants and products, etc. We have found our answers in what we have already discussed, so we can avoid using this "principle." For completeness sake, and because of the problems it causes even today, we will deal with it briefly. We will choose one of the various ways it can be formulated which is close to its original version, but we will avoid misunderstandings by using explanatory additions [in square parentheses]:

When a system at equilibrium is disturbed by changing one of the ["force-like"] equilibrium parameters [possibly by compressing, i.e., by an increase in pressure due to decreasing volume], the system responds with a change of state [$\Delta\xi$], in which the parameter changes in the opposite direction [this means that as long as the volume is kept constant during this step, the pressure goes down] and a new equilibrium is established.

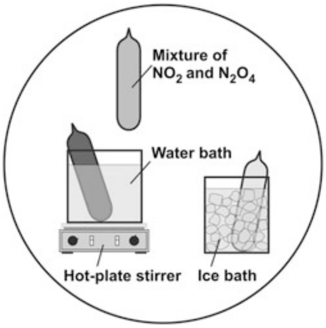
This formulation of Le Chatelier–Braun's principle discusses how the pair of main quantities $(-\mathcal{A}, \xi)$ interacts with another such pair, here $(-p, V)$ in the special case of $\mathcal{A} = \text{const.}$ (or even $\mathcal{A} = 0$, which is unnecessarily special).

Let us consider the reaction between nitrogen gas and hydrogen gas to synthesize ammonia:

$$\mathrm{N_2|g + 3\,H_2|g \rightleftarrows 2\,NH_3|g}.$$

There are more gas molecules on the left-hand side of the conversion formula (4 in total) than on the right-hand side (2). Thus, compressing the system causes the equilibrium position to shift in the direction that leads to a reduction in the number of particles in the gas phase, as this tends to reduce the pressure and therefore to minimize the effect of compression. Consequently, a higher yield of ammonia is

Experiment 9.3 *Equilibrium between nitrogen dioxide and dinitrogen tetroxide*: A sealed tube containing a slightly brown mixture of NO_2 and N_2O_4 is submerged in a hot water bath. The color of the gas mixture becomes darker. However, if the tube is placed in an ice bath, the gas mixture becomes lighter in color.



obtained. This effect was actually the solution to Fritz Haber's dilemma: Only when he carried out the synthesis at high pressure, he succeeded finally in 1909 in producing ammonia with sufficiently high yields.

If we imagine replacing the pair $(-p, V)$ by (T, S) or (μ, n), we could reformulate the corresponding parts of the text above:

> When a system at equilibrium is disturbed by adding entropy to it so that the temperature rises, the system responds with a change of state $\Delta\xi$ where the temperature decreases (as long as no more entropy is allowed to be added).
>
> When a system at equilibrium is disturbed by raising the chemical potential of one of the substances participating in the reaction by adding it from outside, the system responds with a change of state $\Delta\xi$ in which the potential decreases (as long as we impede that more substance comes in).

For the first case above, this means that raising the temperature shifts the equilibrium of an endotropic reaction in the direction of increased ξ. In the case of an exotropic reaction, this happens in the opposite direction. We have seen this before. But let us have again a look at an example, an equilibrium mixture between brown nitrogen dioxide and colorless dinitrogen tetroxide (Experiment 9.3) (see also Sect. 9.1):

$$2\,NO_2|g \rightleftarrows N_2O_4|g$$

The reaction is exotropic $\left(\Delta_R S^\ominus = -176\,\mathrm{Ct\,mol^{-1}} < 0\right)$. If the temperature is raised, the equilibrium shifts in the direction of reduced ξ meaning in the direction of the reactant; a decrease in temperature, however, favors the formation of the final product.

The second case above [pair (μ, n)] does not show us anything we do not already know, either. As long as a reactant in a system is in a dissolved state, adding to it increases its chemical potential, driving the reaction forward. Adding more of a product to the system drives the reaction backward.

Recapulating, we can formulate in short: When a constraint is applied to a system in equilibrium, the equilibrium will shift so as to counteract the effect of the constraint. Constraint means here the change of a "force-like" (not a "position-like") parameter.

We are making only qualitative statements here, so it is naturally possible to replace one quantity with another one proportional to it or one that changes in the same direction. Pressure can be replaced by density, the chemical potential by concentration, the added entropy by the added heat or by a corresponding increase of internal energy or another appropriate state quantity. Trying to include all these possibilities makes formulating this principle difficult and the formulations become opaque. It has also led to phenomena being included that appear similar but do not belong here and to examples where the “principle” appears to fail.

Coupling of Several Pairs of Quantities Predicting behavior becomes more difficult when dealing with a coupling not just between two pairs of quantities, but maybe between three such pairs. When a dissolved substance is added, the solvent is also added at the same time so that the potentials of all other dissolved substances change. We saw such behavior in Sect. 6.6 with the formation of the red iron thiocyanate complex (Experiment 6.1):

$$\left[\mathrm{Fe(H_2O)_6}\right]^{3+}|\mathrm{w} + 3\,\mathrm{SCN^-}|\mathrm{w} \rightleftarrows \left[\mathrm{Fe(H_2O)_3(SCN)_3}\right]|\mathrm{w} + 3\,\mathrm{H_2O}|\mathrm{l}.$$

Adding the starting substances $\left[\mathrm{Fe(H_2O)_6}\right]^{3+}|\mathrm{w}$ and $\mathrm{SCN^-}|\mathrm{w}$ drives the reaction forward. Adding water drives it backward because the decrease of potential caused by dilution with water is four times as strong on the left than on the right. If a too strongly diluted solution of $\mathrm{Fe^{3+}}$ is added, the second effect can override the first so that the solution becomes paler red instead of deeper red, as would be expected.

The effect is similar in gas reactions when they are carried out at constant pressure. Addition of any kind of gas increases the volume, causing a diluting effect upon all the other gases. This diluting effect can override the increase of potential caused by addition of a reactant and the expected increase of the drive $\mathcal{A}$ along with it, driving the process backward and not forward. For example, in the case of ammonia synthesis,

$$\mathrm{N_2}|\mathrm{g} + 3\,\mathrm{H_2}|\mathrm{g} \rightleftarrows 2\,\mathrm{NH_3}|\mathrm{g},$$

addition of $\mathrm{N_2}$ leads to a higher yield of $\mathrm{NH_3}$, if the molar fraction of nitrogen in the reaction volume $x(\mathrm{N_2})$ is smaller than $\frac{1}{2}$, and leads to a decrease if $x(\mathrm{N_2})$ is greater than $\frac{1}{2}$.

9.4 Further Mechanical–Thermal Applications

In closing, we will apply what we have learned in this chapter to mechanical–thermal phenomena. We will consider only the simplest case, a body at rest at isotropic pressure p having a uniform temperature T, consisting of just one substance, such as a drop of water. The main equation for this is:

$$\mathrm{d}W = -p \cdot \mathrm{d}V + S \cdot \mathrm{d}T. \tag{9.20}$$

Previously, we have discussed two coefficients from this field, two varieties of entropy capacity $\mathcal{C}$ (Sect. 3.9),

$$\underset{\text{("global")}}{\mathcal{C} = \left(\frac{\partial S}{\partial T}\right)_p}, \qquad \underset{\text{molar entropy capacity}}{\mathcal{C}_\mathrm{m} = \frac{1}{n}\left(\frac{\partial S}{\partial T}\right)_p},$$

and the "cubic expansion coefficient" γ (Sect. 9.2),

$$\gamma = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p. \tag{9.21}$$

We will not need the energetic version of entropy capacity, heat capacity $C = T \cdot \mathcal{C}$, which itself comes in different variants [Eq. (9.7)].

$\mathcal{C}$ is an extensive quantity that affects an entire body. $\mathcal{C}_\mathrm{m}$ and γ are intensive quantities, properties of the substance making up the body. Another important property is *compressibility* χ,

$$\chi = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T. \tag{9.22}$$

It describes how easy it is to compress a material. It is especially high for gases, which are easily compressed. Although it is, of course, possible to form other differential quotients, as well, the three coefficients $\mathcal{C}_\mathrm{m}$, γ, and χ suffice for calculating all the first derivatives of the main quantities or coefficients made up of them.

Conversion of Differential Quotients We will need some more computational rules for differential quotients. There are essentially four of which some will remind us of the usual rules of arithmetic with fractions and are therefore easy to remember. We will present them here briefly and without deriving them and show some examples of how they can be used.

(a) *Inverting* a differential quotient:

$$\left(\frac{\partial p}{\partial q}\right)_{r\ldots} = 1 \Big/ \left(\frac{\partial q}{\partial p}\right)_{r\ldots}.$$

Numerator and denominator are exchanged, like with fractions, and the index remains unchanged.

(b) *Expanding* a differential quotient with a new quantity (here it is s):

$$\left(\frac{\partial p}{\partial q}\right)_{r\ldots} = \left(\frac{\partial p}{\partial s}\right)_{r\ldots} \cdot \left(\frac{\partial s}{\partial q}\right)_{r\ldots} .$$

The differential quotient is expanded like a fraction with ∂s; the indices are the same in all expressions.

(c) *Insertion* of a quantity (here it is r) from the index of a differential quotient:

$$\left(\frac{\partial p}{\partial q}\right)_{r\ldots} = -\left(\frac{\partial p}{\partial r}\right)_{q\ldots} \cdot \left(\frac{\partial r}{\partial q}\right)_{p\ldots} .$$

The differential quotient is expanded with ∂r, and the sign is changed; in the index the quantity missing from the complete set p, q, r, ... is inserted.

(d) *Replacement* of a quantity in the index of a differential quotient with a new one:

$$\underbrace{\left(\frac{\partial p}{\partial q}\right)_{r\ldots}} = \underbrace{\left(\frac{\partial p}{\partial q}\right)_{s\ldots}} + \underbrace{\left(\frac{\partial p}{\partial s}\right)_{q\ldots}} \cdot \underbrace{\left(\frac{\partial s}{\partial q}\right)_{r\ldots}} .$$

In order to replace r with s in the index, the differential quotient is written with the changed index. The original expression that was expanded with ∂s is added as a "correction." The new quantities s, q, ... appear as independent variables in the first term and the old q, r, ... in the second term.

For these computational rules to be valid, all the differential quotients appearing on the left and right sides must make sense. This means that the quantities in the numerator must really be differentiable functions of the variables appearing in the denominator and index.

Of the four main quantities $-p$, V, T, S mentioned above, $-p$ and T are most easily controlled ($-p$ or p because one often works in the laboratory with containers which are open to the atmosphere) so they are the preferred independent variables. These "preferred" quantities appear in the denominator or index of the differential quotients that, possibly multiplied by certain factors, can be found in Tables. The three coefficients $\mathcal{C}_\mathrm{m}$, γ, χ mentioned above, are of this type. Consequently, we will attempt to convert a given coefficient so that only "preferred" quantities (in this case, p and T) appear in the denominator or index of the differential quotient, but never in the numerator. If we abbreviate all the other quantities with a, a', ... and the "preferred" ones with b, b', ... (here we have only two of these, but the method remains the same even when there are more), the given differential quotients are to be replaced by some of the type $(\partial a/\partial b)_{b',\ldots}$.

First, attention should be paid to the quotient itself. This defines the first step:

$$\begin{array}{cccc} \left(\dfrac{\partial a}{\partial b}\right)_{\ldots}, & \left(\dfrac{\partial b}{\partial a}\right)_{\ldots}, & \left(\dfrac{\partial a}{\partial a'}\right)_{\ldots}, & \left(\dfrac{\partial b}{\partial b'}\right)_{\ldots}. \\ \text{remains,} & \text{inverting,} & \text{expanding,} & \text{inserting.} \end{array}$$

We "expand" with a quantity b which does not appear in the index, and "insert" a quantity a from the index. Two new differential quotients are created by this. The second of these is inverted, resulting in all the quotients now having the desired form $(\partial a/\partial b)\ldots$. If an undesired quantity a is still in the index of one of the new expressions, it can be replaced by one of the "preferred" b, b', ... This process is then repeated until all the expressions have the form $(\partial a/\partial b)_{b',\ldots}$.

Let us look at this approach using a concrete example, the relative pressure coefficient β_r, which is a measure of how steeply pressure rises when a body is heated at constant volume:

$$\beta_\mathrm{r} = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V. \tag{9.23}$$

It can be expressed by the cubic expansion coefficient γ and the compressibility χ,

$$\beta_\mathrm{r} = \frac{\gamma}{p\chi}, \tag{9.24}$$

where the following conversions led to this result:

$$\beta_\mathrm{r} = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V = -\frac{1}{p}\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{p}\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial V}{\partial p}\right)_T^{-1} = -\frac{1}{p}\cdot\frac{V\gamma}{-V\chi}$$
$$= \frac{\gamma}{p\chi}.$$

A few words of explanation: The initial quotient has the form $(\partial b/\partial b')_a$. The undesired quantity a in the index is inserted into the quotient leading to a negative sign. The first of the two new quotients of the type $(\partial b/\partial a)\ldots$ is inverted. All of the differential quotients then have the desired form. What now remains to be done is to replace the expressions with the usual coefficients [Eqs. (9.21) and (9.22)].

We will calculate the difference of the two entropy capacities $\mathcal{C}_p - \mathcal{C}_V$ as our second example. These are the usual isobaric $\mathcal{C} \equiv \mathcal{C}_p$ (at constant pressure) and the more rarely used isochoric capacity $\mathcal{C}_V$ (at constant volume). The latter must be smaller than $\mathcal{C} \equiv \mathcal{C}_p$ (as implied in Sect. 3.9), because the absorption of entropy is made more difficult if the change of volume (positive or negative) related to it is impeded. It makes no difference whether V and S are coupled in the same or in the opposite direction, i.e., $V \uparrow\uparrow S$ or $V \uparrow\downarrow S$, $\mathcal{C}_p \geq \mathcal{C}_V$ is always valid. To calculate the difference

$$\mathcal{C}_p - \mathcal{C}_V = \left(\frac{\partial S}{\partial T}\right)_p - \left(\frac{\partial S}{\partial T}\right)_V,$$

we have to replace the index $_V$ by $_p$ in the second differential quotient and to delete the terms that cancel:

$$\mathcal{C}_p - \mathcal{C}_V = \left(\frac{\partial S}{\partial T}\right)_p - \left[\left(\frac{\partial S}{\partial T}\right)_p + \left(\frac{\partial S}{\partial p}\right)_T \cdot \left(\frac{\partial p}{\partial T}\right)_V\right] = -\left(\frac{\partial S}{\partial p}\right)_T \cdot \left(\frac{\partial p}{\partial T}\right)_V.$$

We could stop the calculations at this point because both differential quotients are now known to us: According to Eqs. (9.7) and (9.8), $(\partial S/\partial p)_T$ corresponds to $-V \cdot \gamma$; on the other hand, according to Eqs. (9.23) and (9.24), $(\partial p/\partial T)_V$ corresponds to γ/χ. We obtain for the difference of the entropy capacities:

$$\mathcal{C}_p - \mathcal{C}_V = V\frac{\gamma^2}{\chi}. \tag{9.25}$$

We also could have just continued to obtain the following result in which all the differential quotients take the desired form $(\partial a/\partial b)_{b',\ldots}$:

$$\mathcal{C}_p - \mathcal{C}_V = -\left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial V}{\partial p}\right)_T^{-1} \left(\frac{\partial V}{\partial T}\right)_p.$$

We know that some differential quotients can be converted into more easily measured forms by flipping them. We need only to check those that represent side coefficients quantifying some effects of coupling. Here, this would mean the first and the last quotients. Let us take a look at the results of this operation

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

It is only worth flipping the differential quotient on the left but not the one on the right because this operation is just the inverse of the first one. The second-to-last step of this systematic operation for calculating a given differential quotient is to check whether or not the result can be improved by flipping. The very last step is then to replace the remaining differential quotients with the pertinent coefficients.

By the way, the flip rule itself can be derived by the four computational rules mentioned at the beginning. There are better ways of doing this, but it is not worth going into that here. Readers interested in the mathematics of this can take a look at Job G (1972) Neudarstellung der Wärmelehre. Akademische Verlagsgesellschaft, Frankfurt am Main, pp. 52–56, as well as Job G (1970) Zur Vereinfachung thermodynamischer Rechnungen. Das “Stürzen” einer partiellen Ableitung. Z. Naturforsch. 25a:1502–1508.