Chapter 1
Introduction and First Basic Concepts

In this first chapter, we will be introduced briefly to the field of *matter dynamics*. This field is concerned in the most general sense with the transformations of substances and the physical principles underlying the changes of matter. As a consequence, we have to review some important basic concepts necessary for describing such processes like substance, content formula and amount of substance, as well as homogeneous and heterogeneous mixture and the corresponding measures of composition. But in this context, the *physical state* of a sample is also of great importance. Therefore, we will learn how we can characterize it qualitatively by the different states of aggregation as well as quantitatively by state variables. In the last section, a classification of transformations of substances into chemical reactions, phase transitions, and redistribution processes as well as their description with the help of conversion formulas is given. The temporal course of such a transformation can be expressed by the extent of conversion ξ. Additionally, we will take a short look at the basic problem of measuring quantities and metricizing concepts in this chapter.

1.1 Matter Dynamics

The term *dynamics* is derived from the word "dynamis," the Greek word for "force." In physics, dynamics is the study of forces and the changes caused by them. The field of mechanics uses this word in particular when dealing with the motion of bodies and the reasons why they move. This term is then expanded to other areas and is reflected in such expressions as *hydrodynamics*, *thermodynamics,* or *electrodynamics*. When we discuss the field of *matter dynamics* we will generally be talking about transformations of substances and the "forces" driving them. States of equilibrium (treated in the field of statics, also called "chemical thermodynamics") will be covered in addition to the temporal course of transformations (kinetics) or the effects of electrical fields (electrochemistry).

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What makes this field so valuable to chemistry and physics as well as biology, geology, engineering, medicine, etc., are the numerous ways it can be applied. Matter dynamics allows us to predict in principle

- Whether or not it is possible for a given chemical reaction to take place spontaneously,
- Which yields can be expected from this,
- How temperature, pressure, and amounts of substances involved influence the course of a reaction,
- How strongly the reaction mixture heats up or cools down, as well as how much it expands or contracts,
- How much energy a chemical process needs to run or how much it releases, and much more.

This kind of knowledge is very important for developing and optimizing chemical processes, as well as preparing new materials and active ingredients by using energy carriers efficiently and avoiding pollution, etc. It plays an important role in many areas of chemistry, especially in chemical engineering, biotechnology, materials science, and environmental protection. Moreover, this knowledge can equally help us to understand how substances behave in our everyday lives at home, when we cook, wash, clean, etc.

Although we will mainly deal with chemical reactions, it does not mean that matter dynamics is limited to this. The concepts, quantities, and rules can, in principle, be applied to every process in which substances or different types of particles (ions, electrons, supramolecular assemblies, and lattice defects, to name a few) are exchanged, transported, or transformed. As long as the necessary data are also available, they help in dealing with and calculating various types of problems such as

- The amount of energy supplied by a water mill,
- Melting and boiling temperatures of a substance,
- Solubility of a substance in a solvent,
- The construction of phase diagrams,
- How often lattice defects occur in a crystal,
- The potential difference caused by the contact between different electric conductors

and much more. Matter dynamics can also be very useful in discussing diffusion and adsorption processes or questions about metabolism or transport of substances in living cells, as well as transformation of matter inside stars or in nuclear reactors. It is a very general and versatile theory whose conceptual structure reaches far beyond the field of chemistry.

Now we can ask for the causes and conditions that are necessary for the formation of certain substances and their transformations into one another. This can be done in different ways and on different levels:

1. *Phenomenologically*, by considering what happens macroscopically. This means directly observing processes taking place in a beaker, reaction flask, carius tube, or spectrometer when the substance in it is shaken, heated, other substances are added to it dropwise, poured off, filtered, or otherwise altered.
2. *According to molecular kinetics*, by considering the reacting substances to be more or less orderly assemblies of atoms where the atoms are small, mutually attracting particles moving randomly but always trying to regroup to attain a statistically more probable state.
3. *According to chemical bonding theory*, by emphasizing the rules and laws according to which different types of atoms come together to form assemblies of molecules, liquids, or crystals in more or less defined relationships of numbers, distances, and angles. The forces and energies that hold the atoms together in these associations can also be investigated.

All of these points of view are equally important in chemistry. They complement one another. In fact, each is inextricably interwoven with the others. To give an example, we operate at the third level when the structural formula of the substance to be produced is written down. On the second level, one might make use of plausible reaction mechanisms for planning a synthesis pathway. The first level is applied when, for instance, the substances to be transformed are put together in a laboratory. To work economically, it is important to be able to switch between these different points of view unhindered. Our goal is not so much a concise explication of the individual aspects mentioned above, as it is a unified representation in which the knowledge gained from these differing points of view merges into a harmonic overall picture. Conversely, the individual aspects can also be easily derived from this overall picture.

One might say that the phenomenological level forms the "outer shell" of the theory. It relates the mathematical structure to phenomena observed in nature. The first step toward expressing such relationships is to prepare the appropriate concepts, which helps the facts gained by experience to be formulated, put into order, and summarized. It follows that these expressions will appear in farther-reaching theories as well. The phenomenological level constitutes the natural first step into a chosen area of investigation.

In the next sections as well as in the next chapter, important fundamental terms and concepts will be discussed. Among these will be substance, amount of substance, measures of composition, and energy, all of which students are probably familiar with from high school. For this reason, it should be easy to start right in with Chap. 3 (Entropy) or even Chap. 4 (Chemical Potential). Chemical potential puts us right at the heart of matter dynamics. Using this as a starting point opens up a multitude of areas of application. Chapters 1 and 2 can then be considered reference work for fundamental terms and concepts.

1.2 Substances and Basic Substances

When we think about *substances*, we think about kinds of matter and their actual or imagined constituents. Simply stated, we think of substances being what the tangible things of our environment are made up of. They are that formless something that fills up space when we disregard the shape of things. There are a multitude of substances around us that we give names to such as iron, brass, clay, rubber, soap, milk, etc. We characterize these substances individually or as members of a category. We use the term *matter* when it is unimportant what kind of substance we are discussing.

Some things appear totally uniform materially, such as a glass or the water in it. If the macroscopic characteristics of a substance such as its density, index of refraction, etc., are the same overall, it is considered *homogeneous*. Wine, air, stainless steel, etc., are other examples of homogeneous substances. Aside from these, there are *heterogeneous* substances that are composed of dissimilar parts, i.e., they are made up of clearly different components. Examples are a wooden board or a concrete block. On the one hand, we tend to think of even these materials as substances on their own. On the other hand, we imagine them to be made up of several substances. We do this even when we consider the sweetened tea or diluted wine that look to be homogeneous. This ambivalence is a striking characteristic of our concept of substance that reflects a noteworthy aspect of the world of substances.

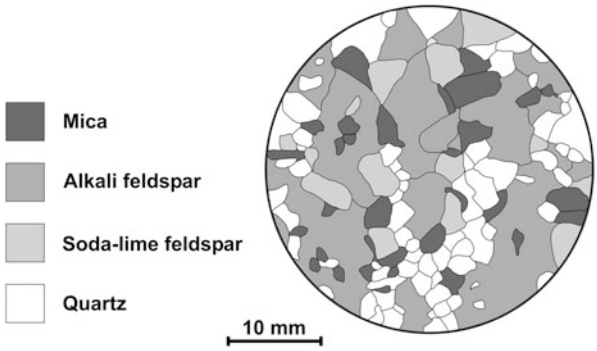
Imagine breaking down some matter into certain components. We find that these components can be broken down into their own components, as well. These subcomponents can also be called substances. The process can be repeated at different levels and in varying ways.

At the heart of the matter lies the following characteristic, one we will need later on: on every level, we can choose certain *basic substances* A, B, C, ... from which all the other substances on this level can be produced. Moreover, none of the basic substances can be made up of any other basic substance. In a way, the basic substances form the coordinate axes of a "material" reference system comparable to the more familiar spatial coordinate systems. In the same way a point in space can be described by three coordinate values in a spatial reference system, a substance can be characterized by its coordinates in a material reference system. The coordinate values of a substance are given by the amounts or the fractions of its individual components.

Therefore, on a given level, every substance can be assigned a *content formula*

$$\mathrm{A}_{\alpha}\mathrm{B}_{\beta}\mathrm{C}_{\gamma}\ldots$$

which gives its composition in terms of the basic substances. The content numbers $g_i = \alpha, \beta, \gamma \ldots$ express the ratios of amounts,



Experiment 1.1 *Polished cross section of granite*: Magnification shows clearly different minerals: the dark mica, the brownish-red alkali feldspar, the sallow beige soda–lime feldspar, and the translucent quartz (the colors of the minerals can vary strongly depending upon tiny amounts of impurities).

$$\alpha : \beta : \gamma : \ldots = n_A : n_B : n_C : \ldots ,$$

with which every basic substance participates in the chemical structure. They correspond to the coordinate values in the chosen material reference system. At the moment we will leave open the question of how to determine the amount n of a substance. In principle, the content numbers can also be negative although we attempt to choose the basic substances so that this does not occur.

Let us consider a concrete example. If a geologist were asked what a paving stone is made up of, he might say granite, basalt, or some other rock. The substances of his world are *rocks*, and his basic substances are *minerals*. From these minerals a multitude of rocks can be formed, depending upon the types, proportions, and grain formation of the individual minerals involved. Let's take a look at a polished cross section of some typical granite (Experiment 1.1).

The granite pictured above may serve as an example for a "petrographical content formula":

$$[\mathrm{Q}_{0.3}\mathrm{AlkF}_{0.15}\mathrm{Plag}_{0.4}\mathrm{Bi}_{0.15}].$$

Here, the numbers indicate the fraction by volume of the "basic geological substances": Q = Quartz, AlkF = *Alk*ali *F*eldspar, Plag = *Plag*ioklas (soda–lime feldspar), Bi = *Bi*otite (magnesium mica).

Mineralogists, on the other hand, see these individual rock components (the basic substances for geologists) as themselves being made up of other components. A mineralogist will see that the soda–lime feldspar, one of the main components of basalts and granites, is a mixed crystal with changing fractions of both soda feldspar and lime feldspar. On the next lower level, these crystals can be considered to be unions of various oxides ("earths"), silicium oxide (siliceous earth), aluminum oxide, calcium oxide, and sodium oxide (chemically SiO_2, Al_2O_3, CaO, Na_2O).

What we have found out about minerals can be used in discussions about a myriad of substances, such as resins, oils, wine, schnaps, etc. These substances are also made up of simpler components that they can decompose into and they can be formed from again by the process of *mixing*. Chemists call the basic substances of

such homogeneous mixtures "pure" substances or *chemical substances*. An example for a "content formula" of a mixture is that of schnaps: [$\mathrm{Ethanol}_{0.2}\mathrm{Water}_{0.8}$]. In this case, the relative amounts are not given as volume ratios, as is done in the liquor business, but as it is done in chemistry by stating the ratios of the physical quantity called *amount of substance*, which we will go into more deeply in Sect. 1.4.

On a higher level of complexity, we can produce heterogeneous mixtures—in analogy to rocks—from homogeneous mixtures (more about this in Sect. 1.5) by using these mixtures as basic substances, such as whitewash from chalk dust and sizing solution, or egg white foam from air and egg whites. In a similar fashion, we can, given the right means, decompose the chemical substances into lower level basic substances or we can form them from these basic substances. For chemists, the basic "building blocks" are made up of the roughly 100 chemical elements. Some of these are hydrogen H, helium He, . . ., carbon C, nitrogen N, oxygen O, etc. A special characteristic here is that the ratios of the amounts of elements in the content formulas of individual substances cannot vary continuously; rather, they are quantized in integer multiples. This is known as the "law of multiple proportions." If the measure of amount of substance is suitably chosen, the content numbers introduced above will themselves become integers. Examples are the formulas for water or lime,

$$\mathrm{H_2O} = \mathrm{H_2O_1} \quad \text{or} \quad \mathrm{CaCO_3} = \mathrm{Ca_1C_1O_3}.$$

At the time it was made, this discovery was one of the most important reasons why matter was not considered continuous, but quantized. Indeed, matter was thought of in a simplified mechanistic way to be made of small, mobile geometric entities called atoms. These atoms can assemble into small groups called molecules, which then can merge into extensive networks and lattices creating the matter we know.

On this level, the content formula corresponds in the most simple and frequent case to the so-called *empirical* or *stoichiometric formula*. However, for a more unambiguous identification of the substance in question, it can be suitable to consider the actual number of atoms of each type in a molecule meaning the content formula can be a (integer) multiple of the empirical formula. For example, the content formulas for formaldehyde, acetic acid, and glucose can be given as $\mathrm{CH_2O}$, $\mathrm{C_2H_4O_2}\left(=(\mathrm{CH_2O})_2\right)$, and $\mathrm{C_6H_{12}O_6}\left(=(\mathrm{CH_2O})_6\right)$.

Just giving the type and proportion of the constituents is often not sufficient to describe a substance completely. More characteristics are necessary. In addition, the spatial arrangement of the atoms of the basic substances is important. In chemical formulas this "structure" is often indicated by dashes, brackets, etc., or by a particular grouping of element symbols. The pair made of ammonium cyanate and urea (carbamide) (Fig. 1.1) is an example. Both of these substances have the same content formula, $\mathrm{CH_4ON_2}$, but their structural formulas differ. This is called *structural isomerism*.

In general, we expect a substance to be something that can be produced in "pure form" and, maybe, filled into a bottle. However, there are substances that cannot be

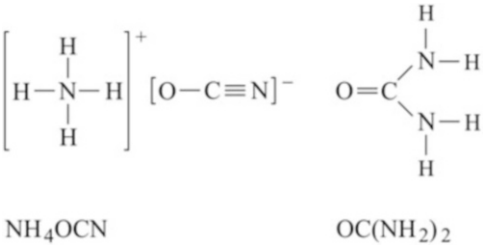


Fig. 1.1 Structural formulas of ammonium cyanate (*left*) and urea (*right*) as examples of two different substances with the same composition (*above*: detailed "valence dash formula," *below*: condensed formula).

understood this way even though they resemble what we normally call a substance in all other chemical and physical characteristics. This category contains the actual carbonic acid H_2CO_3 which forms in trace amounts in aqueous carbon dioxide solutions. The carbonic acid is stable enough to be detected within the thousandfold excess of CO_2, but it is too short-lived to be produced in its pure form.

We consider many substances to be produced from a type of lower level substances, the so-called *ions*. The symbols for table salt NaCl or limestone $CaCO_3$ can be formulated to emphasize their ionic structures

$$[Na]^+[Cl]^- \text{ and } [Ca]^{2+}[CO_3]^{2-}.$$

The brackets are usually left off when dealing with simple ions. For clarity we leave them in because substances of differing rank appear next to each other. We can also include metals such as silver and zinc in this scheme,

$$[Ag]^+[e]^- \text{ and } [Zn]^{2+}[e]_2^-,$$

where the electrons e form the negative partner. In homogeneous mixtures such as crystalline phases, solutions, or plasmas, the individual types of ions, including the electrons, basically behave like independent substances. It is therefore advisable to treat them as such even though they can concentrate into pure form only temporarily and in imponderably small amounts. Their electric charge inevitably drives them apart. The electromagnetic interaction forces electrical neutrality of all parts of matter and allows only a trace of excess of positive relative to negative ions or vice versa. Apart from that, they have all the freedom that uncharged substances have.

There is a substance appearing in the formulas for metals whose composition cannot be expressed by the chemical elements: the *electrons* e. One must therefore introduce a new basic substance. The most obvious candidate would be the electrons themselves. Consequently, negative ions like chloride ions or phosphate ions would obtain the content formulas

$$[\mathrm{Cl}]^- = \mathrm{Cl}_1\mathrm{e}_1 \text{ and } [\mathrm{PO}_4]^{3-} = \mathrm{PO}_4\mathrm{e}_3.$$

Positive ions such as sodium ions and uranyl ions, which lack electrons, correspondingly obtain the formulas

$$[\mathrm{Na}]^+ = \mathrm{Na}_1\mathrm{e}_{-1} \text{ and } [\mathrm{UO}_2]^{2+} = \mathrm{UO}_2\mathrm{e}_{-2}.$$

Here we have negative content numbers.

The concept of basic substances and material coordinate systems is used for making order of the great multitude of substances. It is only possible to make quantitative descriptions of transformation processes by use of content formulas.

1.3 Measurement and Metricization

Before we turn to the first important quantity, amount of substance, we will take a short look at the basic problem of measuring quantities and metricizing concepts.

Measurement To measure a quantity means to determine its value. Very different methods are used when measuring the length of a table, the height of a mountain, the diameter of the Earth's orbit, or the distance between atoms in a crystal lattice. Length, width, thickness, and circumference are different names for quantities that we consider to be the same *kind of quantity* that we call length. Already in everyday language, length is used in the sense of a metric concept, meaning it quantifies an observable characteristic. *Values* are given as wholes or fractions of a suitably chosen unit.

In 1908, Wilhelm Ostwald already stated that "[It is] extremely easy to measure extensity factors (lengths, volumes, surface areas, amounts of electricity, amounts of substance, weights ...). One arbitrarily chooses a piece of it to be the unit and connects so many units together until they equal the value to be measured. If the chosen unit is too rough a measure, correspondingly smaller ones can be created. The simplest way to do this would be 1/10, 1/100, 1/1000, etc. of the original unit." Ostwald's method is valid for *direct* measurement processes. But what does this mean? Let us return to the example of length. In the past, it was customary to *directly* measure the length of a path by counting how many steps were necessary to walk its distance (Fig. 1.2). The arbitrarily chosen unit in Ostwald's sense was one *step*. If one step corresponds with one meter, we get our results in SI units [SI stands for the international metric unit system (from the French **S**ystème **I**nternationale d' Unités)].

But quantities are often determined *indirectly* as well, meaning they are found by calculation from other measured quantities. In the field of geodesy, the science of measuring and mapping the Earth's surface, lengths and altitudes have mostly been determined through calculations based on measured angles (Fig. 1.3). When he

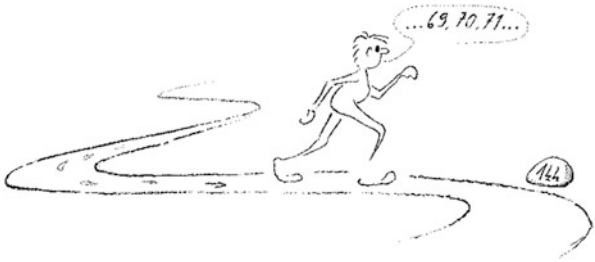


Fig. 1.2 Length of a path measured directly by number of steps.

Fig. 1.3 Indirectly determining distance and altitude in impassable terrain by measuring angles.

used this method to measure the acreage of his sovereign, the German mathematician Carl Friedrich Gauss developed error analysis and non-Euclidean geometry.

It is generally necessary when working in industrial arts, engineering, and the natural sciences to have agreement about how quantities will be applied, what units will be used, and how the numbers involved will be assigned. The process of associating a quantity with a concept (that usually carries the same name)—which is the basis of constructing this quantity—is called *metricization*. Determination of values of this quantity is called *measurement*. Measurement can take place only after a corresponding metricization has been established.

Most physical quantities are established through *indirect metricization*, which means they are explained as *derived concepts*. We specify how they are gained from known, previously defined quantities. This is how the density (more exactly, mass density) ρ of a homogeneous body can be defined as the quotient of mass m and volume V, $\rho = m/V$, and the velocity v of a body moving uniformly in a straight line as the quotient of the distance traversed s and the time needed for it t, $v = s/t$.

A totally different method for defining quantities is the *direct metricization* of a concept or characteristic. A concept, initially only understood qualitatively, is then quantified by specifying an appropriate instruction for measurement. This is the usual procedure for quantities considered basic concepts (length, duration, mass,

etc.), from which other quantities such as area, volume, velocity, etc., are derived. However, this procedure is not limited to just these quantities.

Direct Metricization of the Concept of Weight A simple example for the direct metricization of a concept would be the introduction of a measure for that what is called *weight* in everyday language. When we talk about a low or high (positive) weight G of an object, we are expressing how strongly the object tends to sink downward. (We use the letter G instead of the usual W in order to avoid confusion with other quantities such as energy W.) There are essentially three stipulations that must be met in order to determine a measure for weight:

(a) *Algebraic sign*. The weight of an object that, if let go, sinks downward is considered to be positive, $G > 0$. Consequently, a balloon flying upward will have a negative weight, $G < 0$. The same applies to a piece of wood floating upward toward the surface after being submerged in water. Something just floating has zero weight, $G = 0$.
(b) *Sum*. If we combine two objects with the weights G_1 and G_2 so that they can only rise or fall as a unit (for example, by putting them together onto the plate of a scale), then we assume that the weights add up: $G_{\text{total}} = G_1 + G_2$.
(c) *Unit*. In order to represent the unit of weight γ, we need something whose weight never changes (when appropriate precautionary measures are taken). For example, we might choose the International Prototype Kilogram in Paris. This is a block of a platinum–iridium alloy representing the unit of mass of 1 kilogram.

The weight G in the sense we are using it here is not an invariable characteristic of an object, but depends upon the milieu it is in. A striking example of this would be a block of wood (Wd), floating to the surface of water (W), $G(\text{Wd}|\text{W}) < 0$, while in air (A), it sinks downward, $G(\text{Wd}|\text{A}) > 0$. As a first step, we will consider the environment to be constant so that G is also constant. In the second step, we can investigate what changes when different influences are taken into account.

These few and roughly sketched specifications for

(a) Algebraic sign
(b) Sum
(c) Unit

are sufficient to *directly metricize* the concept of *weight* as we speak of it in everyday language. This means that we do not need to refer to other quantities in order to associate a measure with the concept. *Measuring* the weight G of an object means determining how many times heavier it is than the object representing the weight unit γ. *Direct measurement* means that the value is determined by direct comparison with that unit and not by calculations from other measured quantities. Figure 1.4 shows how this can be done even without using a scale. First, an object has to be chosen that represents the weight unit γ (Fig. 1.4a). Then, along with the object of unknown weight G, one looks for things that have a weight of $-G$, helium balloons for instance, that will hold the object just enough for it to float in the air

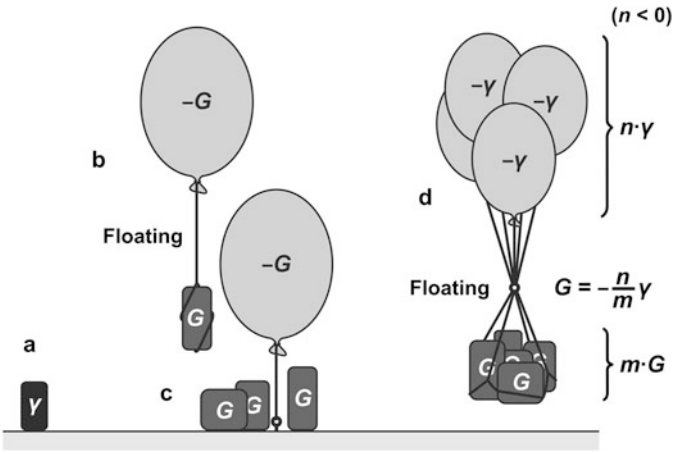


Fig. 1.4 Direct measurement of weights: (**a**) Object representing the weight unit γ, (**b**) "Bundle" consisting of an object with the unknown weight (+G) and a balloon (−G) which just floats in the air, (**c**) Searching further objects with weight +G by means of the balloon, (**d**) Combination of m objects having the same weight +G with n balloons representing the negative weight unit $-\gamma$ to a "bundle" just floating in the air.

(Fig. 1.4b). One of these balloons can be used to easily find further objects with a weight $+G$, meaning ones that the balloon can just lift (Fig. 1.4c). The weight units $+\gamma$ and $-\gamma$ can be multiplied correspondingly. Now in order to measure the weight of an object, for example, a sack, we need only as many things (balloons) representing the negative weight unit $-\gamma$, to bind to the sack until it floats. If n specimens are needed, then $G = n \cdot \gamma$. The number of objects with negative unit weight is expressed in terms of a negative n. If we now want to determine a weight G more accurately, say to the mth part of the unit, we only need to connect m objects having the same weight G with a corresponding number of (positive or negative) unit weights (Fig. 1.4d). If the entire "bundle" floats, it has a total weight equal to 0 according to the specification above:

$$G_{\text{total}} = m \cdot G + n \cdot \gamma = 0 \;\text{ or }\; G = (-m/n) \cdot \gamma.$$

Because any real number can be approximated arbitrarily closely by the quotients of two integers, this method can be used for measuring weights to any desired degree of precision without the use of any special equipment. The measurement process can be simplified if a suitably graded set of weights is available. Negative weights are unnecessary if an equal arm balance can be used because an object can be placed on one side of the balance so that the other side automatically becomes a negative weight. These are, however, all technicalities that are important for practical applications, but are unimportant to basic understanding.

Indirect Metricization of the Concept of Weight Metricization can also be accomplished indirectly. For example, the weight of an object can be determined

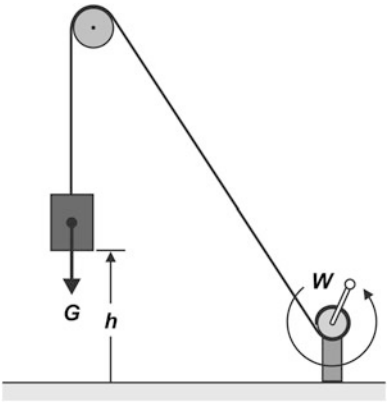


Fig. 1.5 Determining indirectly the weight G through the energy W and lifting height h.

via the energy W needed to lift the object a height h counter to its own weight (Fig. 1.5). (We will go more deeply into the concept of energy and its metricization in Chap. 2.) Both the amount of energy W expended at a winch to lift a block from the ground up to a height h and the height h itself are measurable quantities. The greater the weight, the more energy W is necessary to lift it, so it is possible to find the weight of the block by using W. Because W is proportional to h (as long as h remains small), it is not W itself that is suitable as a measure for the weight, but the quotient $G = W/h$. Using the unit Joule (J) for the energy and the unit meter (m) for the height, we obtain the unit of weight J m^{-1}. The object embodying the weight unit γ mentioned above can also be measured this way so that the old scale can be related to the new one.

When the lifting height h measured above ground level is too high, W and h are no longer proportional. At great heights, the tendency of the weight to fall decreases due to the lessening of the Earth's gravitational pull and the increase of centrifugal force caused by its spinning. If $G = \Delta W/\Delta h$ is used where ΔW means the additional energy needed to increase the lifting height by a small amount Δh, the definition of the quantity G can be expanded to include this case. Thereby, the symbol Δ indicates the difference of final value minus initial value of a quantity, for example, $\Delta W = W_2 - W_1$. In order to indicate that the differences ΔW and Δh are intended to be small, the symbol for difference, i.e., Δ, is replaced by the differential symbol d. One writes

$$G = \frac{\mathrm{d}W}{\mathrm{d}h} \quad \text{or more detailed,} \quad G(h) = \frac{\mathrm{d}W(h)}{\mathrm{d}h}.$$

For the sake of simplicity, although it is not completely mathematically sound, we will consider the differentials to be very small differences. This will suffice for all

or nearly all of the applications we will present in this book. Above and beyond this, it gives us an effective (heuristic) method of finding a mathematical approach to a physical problem. Dealing with differentials is described in more detail in Sect. A.1.2 in the Appendix.

Note that in the expression on the left in the equation above, W and G take the roles of the variables y and y'. In the expression on the right, they appear in the roles of the function symbols f and f'. It is actually a common but not fully correct terminology to use the same letters for both cases, but if one is careful, it should not cause serious mistakes.

In order to lift something, we must set it in motion and this takes energy too. The greater the velocity v attained, the more energy is needed. Therefore, W does not only depend upon h, but upon v as well. This is expressed by $W(h, v)$. In order to introduce a measure for weight also in this case, we must expand the definition above:

$$G = \frac{\partial W(h, v)}{\partial h}.$$

Replacing the straight differential sign d by the curved ∂ means that when calculating a derivative, only the quantity in the denominator (in this case h) is to be treated as variable, while the others appearing as argument (in this case only v) are kept constant (so-called *partial derivative*, more about this in Sect. A.1.2 in the Appendix). A constant v, and therefore, $\mathrm{d}v = 0$, means that the increase of energy $\mathrm{d}W$ has only to do with the shift in height $\mathrm{d}h$ and not with change of velocity.

There is another notation which is preferred in (physical) chemistry where the dependent variable (here it is W) is in the numerator while the independent variables (in this case h and v) appear in the denominator and the index, respectively. The variable to be kept constant is added to the expression of the derivative (placed inside parentheses) as index:

$$G = \left(\frac{\partial W}{\partial h}\right)_v.$$

We can go a step further and imagine the object in question to be like a cylindrical rubber plug with changeable length l and cross section A. These changes also consume energy and the total amount of energy needed now depends upon four variables h, v, l, A. In order to eliminate possible additional contributions due to changes to l and A, they (along with v) must be kept constant. This can be expressed as follows:

$$G = \left(\frac{\partial W}{\partial h}\right)_{v,l,A}.$$

We find that defining the weight G in terms of energy becomes increasingly more complicated, the more generally one attempts to comprehend the concept. This is

why we will introduce important quantities such as energy (Chap. 2), entropy (Chap. 3), and chemical potential (Chap. 4) through direct metricization.

1.4 Amount of Substance

There are various measures used for amount of substance, so we need to consider what properties we expect to see in the quantity we are looking for.

It seems reasonable to claim that a certain amount of a substance within a specified volume can only change if parts of it are emitted, are added from outside, or are consumed or produced by chemical reaction. Just displacing, heating, compressing, segmenting, removing accompanying substances, etc., should not change the amount of substance in question. If we wish to adhere to these properties, we automatically eliminate certain measures of amount such as volume which is the one most often used in everyday life. Examples of this are a solid cubic meter of wood, a liter of water, a cubic meter of gas, etc. According to Einstein's relation ($W = m \cdot c^2$; W: energy, c: speed of light), the mass m of a substance that grows also when only energy is added to it, must be—strictly speaking—excluded as well. Because such changes are much smaller than what can be measured with any precision, mass is nevertheless widely used in science and commerce. It is, however, not fully satisfactory if one considers that when 1 cm^3 of water is heated by 1°, its mass grows only by 5×10^{-14} g, but this change corresponds to about one billion water molecules.

It is plausible to assume that two amounts of the same substance are identical if they occupy the same space or have the same weight if conditions such as the form of the area, temperature, pressure, field strength, etc., are all identical. In order to measure a certain amount of substance, it is enough to fill the substance into equal sized containers or segment it into equal parts and then to count them (Fig. 1.6)—again under uniform conditions. This *direct* measurement of amounts of substance by dividing it into equal unit portions and then counting them has been used since ancient times and is still used today in the household, in trade, and in business. Unit portions have mostly been established by filling and emptying a defined "cavity" such as a bushel basket. Other types of measurements have also been created. Examples would be 1 pinch of salt, 2 teaspoons of sugar, 3 bunches of radishes,

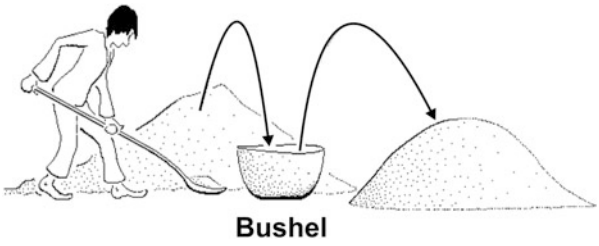


Fig. 1.6 Direct measurement of amounts of substance by dividing it into unit portions and counting them (for example, in the past determination of the amount of harvested grain by use of bushel baskets).

or 10 scoopfuls of sand. Alternatively, the unit portions can be established and counted automatically (such as in the water or gas meters in every household).

Due to the atomic structure of matter, there is a natural division into atoms, or rather, the constantly repeating groups of atoms described in the chemical formula. It is therefore obvious to have the unit be such an elementary entity, such a "particle." The amount of substance corresponds to a number of units (like 24 apples or 120 cars). However, in macroscopic systems, the numbers of particles are very high and this can be problematic. For instance, 10 g of water contains about 10^{23} particles. Therefore, a more suitable unit must be found that is comparable to the everyday dozen (12 units) or score (20 units). In chemistry, the measure of amount called *mole* (derived from the Latin word "moles" meaning "huge mass") has been determined as follows:

One mol is a portion of substance made up of 6.022×10^{23} particles (units).

or more exactly stated:

One mol is a portion of substance made up of as many elementary entities (particles) as there are atoms in exactly 12 g of the pure isotope carbon-12 (^{12}C).

$N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$ is also called the *Avogadro constant*. Because it is possible to directly or indirectly count the atoms or groups of atoms in a given sample, the so-defined *amount of substance n* is in principle a measurable quantity.

The fact above can be stated differently. Instead of saying that a substance is made up of countable particles, one might say that there is a smallest possible portion of substance, an *elementary amount* (*of substance*) τ. The following is valid for this elementary amount:

$$\tau = \frac{1}{N_A} = \frac{1}{6.022 \times 10^{23}\ \text{mol}^{-1}} = 1.6605 \times 10^{-24}\ \text{mol}. \tag{1.1}$$

The amount of substance therefore is given by

$$n = N \cdot \tau, \tag{1.2}$$

where N represents the number of particles in the given portion of substance. Quantities $\mathcal{G}$ with real but discrete and therefore countable definite values are called *quantized*. We introduce a *quantum number* g to number the values. If the values are not only discrete, but equidistant as well, the quantity is said to be integer quantized. In the simplest case, the values are integer multiples g of a universal quantum γ:

$$\mathcal{G} = g \cdot \gamma. \tag{1.3}$$

In the case of the variable $\mathcal{G}$, which represents various physical quantities, we use another font in order to avoid confusion (for example, with weight G). We do this as well for g (instead of g) and γ (instead of γ).

The amount of substance n is therefore integer quantized with N as the quantum number and τ as the corresponding quantum of amount of substance. This is comparable to the more familiar integer quantization of the charge Q of an ion,

$$Q = z \cdot e_0 \tag{1.4}$$

with the charge number z in the role of the quantum number and the elementary charge e_0 in that of the charge quantum ($e_0 = 1.6022 \times 10^{-19}$ C).

The relation between the amount of substance n and the mass m is determined by the *molar mass* M. This quantity corresponds to the quotient of the mass of a sample of the substance and the amount of substance in the sample:

$$M = \frac{m}{n} \left(\text{SI unit: kg mol}^{-1}\right). \tag{1.5}$$

With the help of the molar mass we can convert the more easily measured mass to amount of substance:

$$n = \frac{m}{M}. \tag{1.6}$$

1.5 Homogeneous and Heterogeneous Mixtures, and Measures of Composition

We will now look more closely at the term homogeneous mixture, mentioned in Sect. 1.2. We will also contrast it with the concept of heterogeneous mixture. There is, unfortunately, no unified way of wording this, so we will give a short explanation of how we will use the terminology. *Mixture* is used as superordinate term. A *homogeneous mixture* is homogeneous in the sense that it has a molecular dispersion with granularity of <1 nm, and all its constituents A, B, C, ... are considered equal. If there is an excess of one of the components in a homogeneous mixture, we will speak of a *solution*. The main component A is then called the *solvent* and the minor constituents B, C, ... the *dissolved substances* or *solutes*. Unlike a homogeneous mixture, a *heterogeneous mixture* is coarsely dispersed with granularity $>$ 100 nm. Microheterogeneous *colloids* are a special case (granularity 1 ... 100 nm). However, not every kind of material system made up by two and more different substances fits into this scheme.

A homogeneous region, meaning a region that is uniform in all of its parts, is called a *phase*. One can differentiate between pure phases made up of one substance and *mixed phases* made up of more than one. Homogeneous mixtures are always single phases. Examples of single-phase systems are air, wine, glass, or stainless steel. Heterogeneous mixtures are, by contrast, multi-phase, wherein the equal homogeneous parts form together a phase. Fog, construction steel, soldering tin (Pb-Sn), slush, etc., are all examples of two-phase heterogeneous mixtures. A very esthetic example of a two-phase system is a so-called lava lamp with its wax-water

Experiment 1.2 *Lava lamp*: When the lamp is turned on, blobs of heated wax ascend slowly from the bottom to the top where they cool and then descend to the bottom again, causing a constant movement of both phases.

filling (Experiment 1.2). The granite shown in Experiment 1.1, however, is essentially composed of four phases.

As a rule, one does not specify the amounts of substance of all the components in order to characterize homogeneous mixtures, but the *content* of selected components. The superordinate concept "content" meaning the material fraction of a substance in the mixture can be quantified by various measures of composition. Several of these measures will be introduced in the following.

The *mole* (or *amount*) *fraction x* of a component B corresponds to the quotient of the amount of substance n_B and the total amount n_{total} of all the substances present in the mixture:

$$x_B = \frac{n_B}{n_{total}} \left(\text{SI unit: 1 or } \text{mol}\,\text{mol}^{-1}\right). \tag{1.7}$$

The mole fraction is a relative quantity where $0 \leq x \leq 1$. The sum of all the mole fractions must always result in 1, so for a complete characterization of a binary mixture (a mixture of two components A and B), only *one* mole fraction is necessary. The second one will result according to $x_A = 1 - x_B$.

If the amount of substance is replaced by the mass, another measure of composition results, the *mass fraction w*:

$$w_B = \frac{m_B}{m_{total}} \left(\text{SI unit: 1 or } \text{kg}\,\text{kg}^{-1}\right). \tag{1.8}$$

The composition of solutions is often expressed by concentration. The *molar* (or *amount*) *concentration c* (formerly called molarity) of a dissolved substance B results from the quotient of the amount of solute n_B and the volume of solution V:

Table 1.1 Conversion of the most common measures of composition for binary mixtures.

$x_B =$	x_B	$\frac{M_A c_B}{\rho - c_B(M_B - M_A)}$	$\frac{M_A b_B}{1 + M_A b_B}$
$c_B =$	$\frac{\rho x_B}{M_A + x_B(M_B - M_A)}$	c_B	$\frac{\rho b_B}{1 + b_B M_B}$
$b_B =$	$\frac{x_B}{M_A(1 - x_B)}$	$\frac{c_B}{\rho - M_B c_B}$	b_B

$$c_B = \frac{n_B}{V} \left(\text{SI unit: } \text{mol m}^{-3}\right). \tag{1.9}$$

The unit mol L^{-1} ($=$ kmol m^{-3}) (abbreviation M) is often used in place of the SI unit. When referring to *the* concentration in chemistry one usually means the quantity c.

Sometimes the *mass concentration* β is used that can be calculated from the quotient of substance mass m_B and volume V of solution:

$$\beta_B = \frac{m_B}{V} \left(\text{SI unit: } \text{kg m}^{-3}\right). \tag{1.10}$$

The disadvantage of these two easily accessible concentrations is that they are both temperature and pressure dependent. This is due to corresponding changes of total volume and can be avoided if the mass of the solvent is used instead. The *molality* b corresponds to the quotient of amount of substance n_B of the solute B and the mass m_A of the solvent A:

$$b_B = \frac{n_B}{m_A} \left(\text{SI unit: } \text{mol kg}^{-1}\right). \tag{1.11}$$

In Table 1.1, the relations for converting the individual measures of composition have been compiled using molar mass M and density ρ.

1.6 Physical State

System and Surroundings We tend to consider (material) *systems* as strongly simplified, often idealized, parts of the natural world around us in which we have a special interest. For example, we can be interested in a rubber ball, a block of wood, a raindrop, the air in a room, a solution in a test tube, a soap bubble, a ray of light, or a protein molecule. We assume that systems can appear in various (physical) states, where the word *state* means a momentary specific condition of a sample of matter determined by macroscopic characteristics. States can differ qualitatively due to characteristics such as state of aggregation or crystal structure or quantitatively in the values of suitably chosen quantities such as pressure, temperature, and amount of substance.

Everything outside of the system in question we call the *surroundings*. If the system is completely *isolated* from its surroundings, we can ignore anything

happening there (in the surroundings). However, this requirement is hardly ever fulfilled, so we must deal to a certain extent with the conditions in the surroundings. When considering the pressure or temperature of a system as prescribed, one usually thinks of some equipment in the surroundings that establishes these values. In a lab, this is generally a cylinder with a moveable piston that will allow us to set up the pressure and a "heat reservoir" with a defined temperature that is connected to the system through heat conducting walls.

Types of States The classical *states of aggregation*, *solid*, *liquid*, and *gaseous*, serve as a first rough characteristic for distinction. Seen macroscopically, the following is valid for a substance enclosed in a container:

- A *solid* has a fixed volume and withstands shear. This means that it retains its volume and shape regardless of the shape of the container it occupies.
- A *liquid* has a fixed volume and is able to flow. It retains its volume, but its shape is unstable and adapts to the walls of the container.
- A *gas* is able to flow and fills the whole space it is in. It assumes the volume and shape of the container.

Information about the state of aggregation of a substance can be added to its formula by using a vertical stroke and the abbreviation s for solid, l for liquid, and g for gaseous. Ice is then characterized by $H_2O|s$, liquid water by $H_2O|l$, and water vapor by $H_2O|g$. We prefer this way of writing to the usual form with parentheses because it prevents the confusing overabundance of parentheses occurring when formulas of substances appear in the argument of a quantity [for example, the mass density $\rho(H_2O|l)$ instead of $\rho(H_2O(l))$].

A deeper look into the nature of states of aggregation can be gained if one leaves the phenomenological level and moves to the molecular-kinetic level (Fig. 1.7). A particle model lets us create a relation between the macroscopic properties of matter and the behavior of the particles—atoms, ions, or molecules of which it is composed.

- From the atomistic point of view, the particles in *solids* are packed closely and well-ordered due to their strong reciprocal attraction. They have only very limited space to move in, meaning that they essentially stay on one site, but oscillate somewhat around that position.
- The particles of *liquids* are still rather closely packed, but not in an orderly way. Motion of the particles is so strong that the reciprocal attraction is not intense enough to hold them in one position. Although they stay in contact, they are able to slide by each other freely.
- The particles in *gases* are packed very loosely and disorderly. Their constant movement is quick and chaotic and they tend to be far apart from each other except for occasional collisions. The typical distance between the particles of the air in a room is about ten times the diameter of the particles themselves.

There is a somewhat different but comparable point of view which uses *crystalline*, *amorphous*, and *gaseous* for classification.

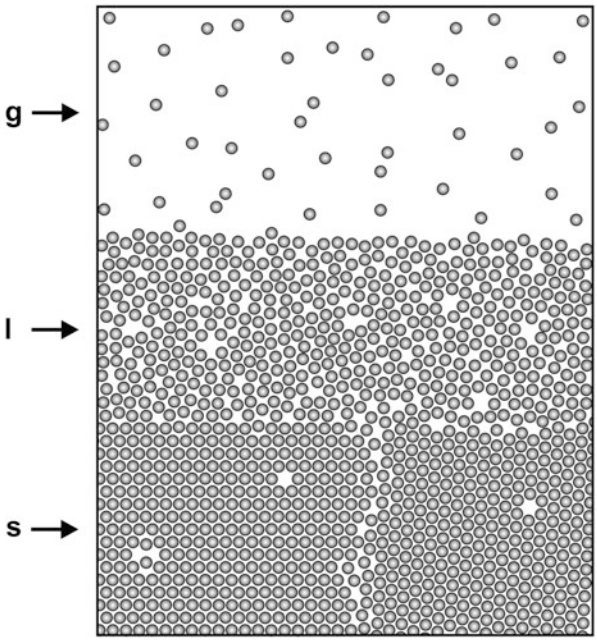


Fig. 1.7 Molecular-kinetic illustration of the three states of aggregation, solid (s), liquid (l), and gaseous (g). The strict order of a solid can be disturbed by defects or by a grain boundary (a fault zone where differently oriented regions that have otherwise identical crystal structure (grains) adjoin each other).

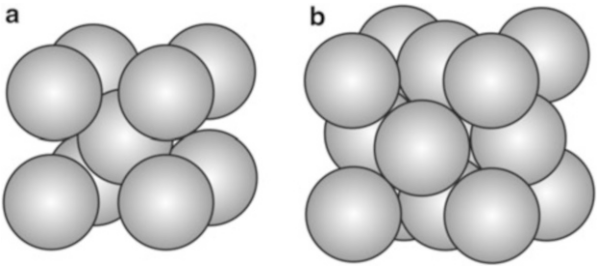


Fig. 1.8 (**a**) Body-centered cubic crystal lattice, (**b**) Face-centered cubic crystal lattice.

- A substance can be categorized as *crystalline* if it is inherently stable and if its components are packed in a regularly ordered, repeating pattern that continues in all three directions over long distances (long-range order). This crystalline state is generally characterized by |c. Different crystal structures appearing at the level of chemical bonding theory and which are created by different ways of packing their components are indicated by Greek letters or the appropriate mineral names. For example, iron can have a body-centered cubic structure (Fe|α) or a face-centered cubic structure (Fe|γ) (Fig. 1.8), and carbon can exist in the form of hexagonal graphite (C|Graphite) or in the cubic diamond structure (C|Diamond). These different forms of a substance are called *modifications*.
- The components in an *amorphous* substance only show some short-range order. Macroscopically, the substance can be either solid or liquid. The symbol used for

amorphous is |a. A typical amorphous solid would be glass, but also spun sugar (candyfloss, cotton candy) can be counted in this category.
- The *gaseous* state is defined in the usual sense.

If a substance appears in dissolved form in a homogeneous mixture, it is characterized by |d. Water is by far the most common solvent. We therefore give substances dissolved in water their own symbol |w.

State Quantities Besides the qualitative description of a system discussed above its quantitative properties can be characterized by physical quantities. A quantity that describes the state of a system or is defined by the instantaneous state of a system is a *state variable*. Depending upon the conditions involved, the same type of quantity might or might not be a state variable. The time-dependent amount of air $n(t)$ in a ventilated room is a state variable, but the amount of incoming air n_{in} supplied by ventilation, or the amount of outgoing air n_{out}, escaping around windows or doors, is not:

$$\Delta n = n_{\text{in}} - n_{\text{out}} \text{ or in more detail } \Delta n(t) = n_{\text{in}}(t) - n_{\text{out}}(t).$$

Analogously, the volume of water V in a bathtub is a state variable, but the volume of water flowing in through the water tap (V_{A}) or shower head (V_{B}) and spilling over (V_{O}) is not (Fig. 1.9):

$$V = V_{\text{A}} + V_{\text{B}} - V_{\text{O}}. \tag{1.12}$$

The water level h in the bathtub is a more complex example of a state variable. h not only depends upon the water volume V but upon the volume V_{d} displaced by the person standing, sitting, or lying in it, $h = h(V, V_{\text{d}})$. If the tub had straight walls, i.e., if the cross section A were constant, we could easily write:

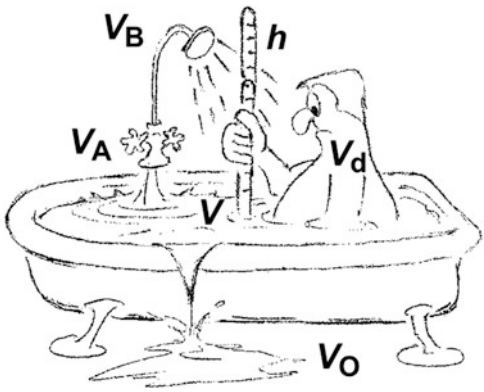


Fig. 1.9 Volume of water V and water level h in a bathtub as examples of state variables.

$$h = (V + V_d)/A \qquad \text{“Equation of state.”} \tag{1.13}$$

In contrast to Eq. (1.12), Eq. (1.13) relates only state variables (the quantities whose values are determined only by the momentary state of the system, independent of the path by which that state was reached). The advantage of applying such relations is that one can reach conclusions without having to know the details that led to this state. This type of equation is called an “*equation of state*” and functions such as $h = h(V, V_d)$ are called *state functions* (or *state variables*). Even though each of these quantities can have a value that changes with time, the equations of state relating these quantities are timeless. However, the division of V into the three values V_A, V_B, and V_O, as shown in Eq. (1.12), depends upon the *process* by which the bathtub was filled. Such quantities can be called “*process quantities*” to distinguish them from the state variables.

The considerations that hold for the volume of water in a tub also hold for the energy of a system if several possibilities exist for inflow and outflow. The excess energy in hot cooking water or in a charged car battery is a state variable, but the energy we are charged for every year by the electricity company or that our kitchen stove consumes when we are preparing food, is not. We will deal with this in more detail in later chapters.

Different Forms of Notation State variables are easier to handle mathematically. Therefore, if possible, all calculations are carried out with these quantities and unknowns, results, and parameters are expressed by them. This is especially valid when dealing with an abstract quantity that we cannot imagine or only imagine insufficiently. The characteristic of being a state variable is an important and helpful orientation device. We will now use an example to illustrate the approach that is also graphic and understandable.

A small increase of water volume $\mathrm{d}V_A$ flowing out of a water tap and into the tub can be expressed as the increase $\mathrm{d}V$ of the water volume in the tub if inflow through the showerhead and outflow over the edge of the bathtub are not allowed (either in reality or just in our model). We will express this increase by the symbol $(\mathrm{d}V)_{B,O}$. When we correspondingly deal with V_B and V_O, an equation results where the V in all the terms is the same quantity, the water volume in the bathtub:

$$\mathrm{d}V = (\mathrm{d}V)_{B,O} + (\mathrm{d}V)_{A,O} - (\mathrm{d}V)_{A,B}.$$

Sometimes instead of d, the symbol δ or đ is used in the case of “process quantities.” One then writes δV_A or $đV_A$, respectively. However, in the following we will avoid doing this.

The changes of volume per time on the right describe the strengths of the water currents J into and out of the bathtub. These are the water flowing out of the water tap J_A and the shower head J_B, and the water spilling over the edge of the tub J_O:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \left(\frac{\mathrm{d}V}{\mathrm{d}t}\right)_{\mathrm{B,O}} + \left(\frac{\mathrm{d}V}{\mathrm{d}t}\right)_{\mathrm{A,O}} - \left(\frac{\mathrm{d}V}{\mathrm{d}t}\right)_{\mathrm{A,B}}.$$

When $\mathrm{d}V/\mathrm{d}t$ is abbreviated to $\dot{V}$, the resulting equation is the same but has a more compact form. It can also be more easily understood:

$$\dot{V} = J_{\mathrm{A}} + J_{\mathrm{B}} - J_{\mathrm{O}} \qquad \text{“Continuity equation.”}$$

Expressed in words: “The rate of increase of the amount of water in the tub equals the sum of the water currents flowing into it (and out of it).” This is a very simple example of applying an equation that appears in a myriad of ways in various areas of physics.

However, another aspect is more important for us here. In Sect. 1.3, we were introduced to similar expressions where instead of the straight d, the somewhat differently written curved ∂ appeared. Although we could actually do without the curved ∂ and always use d, without making a formula wrong, this does not work both ways. In an expression like $(\partial y/\partial u)_{v,w}$, it is always assumed that the quantity in the numerator can be written as a function of the quantities in the denominator and the index, i.e., $y = f(u, v, w)$. Thereby, the index $_{v,w}$ means that only u occurs as an independent variable, while v and w are treated as constant parameters. We will illustrate this by crossing out these quantities in the argument of the function: $y = f(u, \cancel{v}, \cancel{w})$, but just this one time, and not in general. The derivative can now be calculated as usual by applying the rules of school math (compare to Sect. A.1.2 in the Appendix). If we indicate the derivative with the usual $'$, i.e., $y' = f'(u, \cancel{v}, \cancel{w})$, we obtain:

$$\left(\frac{\mathrm{d}y}{\mathrm{d}u}\right)_{v,w} = \left(\frac{\partial y}{\partial u}\right)_{v,w} = f'(u, \cancel{v}, \cancel{w}).$$

The derivative with respect to the other variables is calculated accordingly:

$$\left(\frac{\mathrm{d}y}{\mathrm{d}v}\right)_{u,w} = \left(\frac{\partial y}{\partial v}\right)_{u,w} = f'(\cancel{u}, v, \cancel{w}) \text{ and so on.}$$

Unlike u, v, w, the indices A, B, and O in the expressions above do not denote quantities. However, that is not important at this point. What is important is that both cases express that the increase of the numerator is caused by changes of the quantity in the denominator, while all other influences are eliminated.

Coupled Changes The bathtub can help us once again to understand another aspect that we will need to deal with later on. In the above, we discussed the special features resulting when the same entity (measured by the same quantity: water volume) of a system can be exchanged with its surroundings simultaneously via various paths. Let us now replace the person in the tub with an expandable rubber

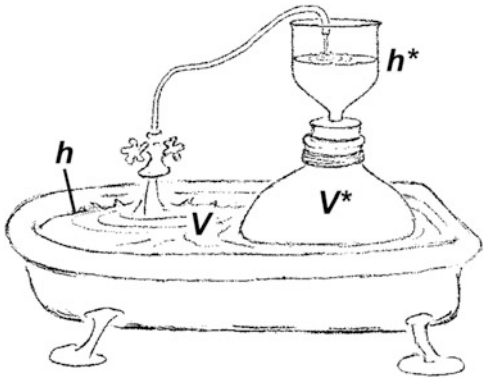


Fig. 1.10 Example for reciprocal coupling between different types of quantities.

sack (Fig. 1.10). The water volume V in the tub is separated from that in the sack V^*, so that the water levels in the bathtub and the sack, h and h^*, can be different. In this case, all four quantities V, h, V^*, h^* are state variables. They are all "geometric" and therefore it appears to us that they are comparably simple.

Despite their separation, the two parts of the system influence each other so that an increase of water level in one causes an increase of the water level in the other and vice versa. This reciprocal coupling between different types of quantities, mechanical, thermal, chemical, electrical, etc., is central to thermodynamics and matter dynamics. We will go into this more deeply in Chap. 9 when we have acquired the necessary background.

Extensive, Intensive, Substance-Like The concept of substance is primary to the discussion of systems of matter dynamics. The simplest case would be a *homogeneous* domain, meaning one where all the parts are uniform and where the form and size are unimportant. Such a formless domain represents what we call substance, whether it is pure or a mixture of various components. Some quantities describing the state of a domain, such as mass, volume, concentration, energy, entropy, etc., add up when two uniform domains are merged into one. Other quantities such as mass density, pressure, temperature, concentration, refractive index, etc., do not change. The first group is made up of the so-called *extensive* parameters and the second, of *intensive* parameters. One group describes *global* characteristics for the entire domain in question. The second group describes *local* characteristics, attributed to one place. These concepts can be applied analogously and with good accuracy to material systems that are not homogeneous in their entirety but are approximately uniform in small sections—at close range.

Classification is not always clear. Let us consider the surface A of a liquid droplet in fog. When we put two sections of the fog together, the surfaces add up so that A appears to be an extensive quantity. However, if we unite two round droplets into one, A is clearly not additive.

The extensive quantities $\mathcal{G}$ which we can imagine as a "something" distributed in space are called *substance-like*. Mass m, amount n_B of a substance B, and electric charge Q are some of these, and so are energy, momentum, and entropy, which are

often considered quite abstract concepts. We will get back to them later in more detail (Chaps. 2 and 3). Their distribution need not to be uniform and the density $\rho_{\mathcal{G}}$ of the "something" can change in space and time by being used up, produced, or redistributed. A quantity that distinctly exhibits this behavior is the amount n_{B} of a substance B that diffuses and reacts. If $\mathcal{G}$ is a so-called conserved quantity, like energy, for example, the "something" can be neither created nor can it decay. It can only migrate inside the system or be exchanged with its surroundings. When the "something" disappears in one location, it must reappear somewhere nearby. From there it can be transfered further and further. This process can be considered a kind of flow.

1.7 Transformation of Substances

In Sect. 1.2, we saw that the multitude of substances can be understood as combinations of relatively few basic substances, where the ratio is quantitatively expressed by the content formula. In chemistry, we have seen that chemical elements play the role of basic substances and when indicated, electrons e, if the totality of ions is considered a "charged" substance.

We use *transformation* here and in the following as the superordinate term for processes that are otherwise more differentiated, such as *reaction*, *transition* (change of state of aggregation, etc.), and the (spatial) *redistribution* of substances. This is done simply because these processes can all be described using the same paradigm. Whether a transformation of substances is chemical or physical, it can be expressed by a *conversion formula*, also called a *reaction equation* or *reaction formula*. Usually, the content formulas of the starting substances (also called reactants) are to the left of the reaction arrow, and the end products are to the right. The term "reaction equation" is not exactly apt because we do not have an equation in the usual sense here. The name comes from the fact that the amounts of the chemical elements—either free or bound—remain unchanged during the transformation from initial to final substances. The number of symbols for each element must, therefore, be the same on both the left and the right.

A simple example of a reaction is synthesizing ammonia from nitrogen and hydrogen. One usually finds different substances $\mathcal{B}_i$ ($i = 1, 2, 3 \ldots$) participating in such processes, each of which can be assigned a number. For example, nitrogen N_2 can be given the number 1, hydrogen H_2 the number 2, and ammonia NH_3 the number 3. This can be accomplished by simply setting the numbers above the substances in the conversion formula:

$$\overset{1}{\mathrm{N}_2} + 3\,\overset{2}{\mathrm{H}_2} \rightarrow 2\,\overset{3}{\mathrm{NH}_3}\,,$$

but also by the order they are put into in the formula, a table, or some other type of list, for instance:

$$\mathcal{B}_1 = \mathrm{N}_2, \mathcal{B}_2 = \mathrm{H}_2, \mathcal{B}_3 = \mathrm{NH}_3, \mathcal{B}_4 = \mathrm{CO}_2 \ldots .$$

Note that the index for $\mathcal{B}$ is arbitrary, while the content numbers in the content formulas are well defined. In the case of the variable $\mathcal{B}$, we use another font in order to avoid confusion but also because we use B as well as B for other purposes.

It is a good idea to write all of the initial and final substances on one side in order to avoid having to distinguish between different cases, for example as follows:

$$0 \rightarrow -1\,\mathrm{N}_2 - 3\,\mathrm{H}_2 + 2\,\mathrm{NH}_3$$

or, in general, for various substances A, B, C, ... of the set $\mathbb{S}$ of all possible substances

$$0 \rightarrow \nu_\mathrm{A}\mathrm{A} + \nu_\mathrm{B}\mathrm{B} + \nu_\mathrm{C}\mathrm{C} + \ldots \quad \{\mathrm{A}, \mathrm{B}, \mathrm{C} \ldots\} \subset \mathbb{S}.$$

A symbolic "0" appears on the left that does not actually represent the number 0, but a substance represented by a content formula in which all content numbers disappear. If we consider the substances to be numbered as discussed above, the expression can be written more compactly using the summation operator $\sum$:

$$0 \rightarrow \sum_{i=1}^{n} \nu_i \mathcal{B}_i.$$

The chemical elements participating in a transformation are always conserved. This means that their total amount does not change, whether they are free or bound. Therefore, the *conversion numbers* (*stoichiometric coefficients*) ν_i in front of the content formulas should be chosen so that the number of element symbols is the same on both sides. This also holds for electrons when they appear, so to speak, as an additional basic substance in the conversion formula where ions participate. They appear openly with the symbol e or more hidden with the superscript charge numbers. The more unusual way of writing that uses "0" on the left side has the advantage that the conversion numbers appear with the correct algebraic signs as factors in front of the content formulas. ν is negative for starting substances and positive for final products, for example, $\nu_{\mathrm{N}_2} = -1, \nu_{\mathrm{H}_2} = -3, \nu_{\mathrm{NH}_3} = +2, \nu_{\mathrm{CO}_2} = 0$, ... If the index itself contains subscripts it is better to refer back to the numbering scheme $\nu_1 = -1, \nu_2 = -3$, etc., or to use the form with arguments $\nu(\mathrm{N}_2) = -1$, $\nu(\mathrm{H}_2) = -3$, etc. As the lower formulas above imply, we have to sum over all the basic substances, meaning the chemical elements, the electrons, as well as their combinations. However, for the overwhelming number of substances $\nu_i = 0$ and the corresponding substances can be ignored so that, in the example above, $\nu_{\mathrm{CO}_2} = 0$, and the same would hold for ν_{Fe}, ν_{NaCl}, etc.

The amounts of the substances change in the course of a reaction and these changes can be used to measure the progression of the process. Substances are not all formed or consumed in the same ratio. A look at the conversion formula for

ammonia synthesis shows hydrogen converting at three times the rate of nitrogen. Changes of amounts are proportional to the conversion numbers ν. In order to attain a quantity that is independent upon the type of substance B, the observed changes Δn_B are divided by the corresponding conversion numbers ν_B:

$$\xi = \frac{\Delta n_B}{\nu_B} = \frac{n_B - n_{B,0}}{\nu_B} \qquad \text{“}\textit{basic stoichiometric equation}\text{.”} \tag{1.14}$$

n_B is the instantaneous amount of substance and $n_{B,0}$ stands for the initial amount. Note that both Δn_B and ν_B are negative for reactants, so the quotient is positive which is also true for the products. Of course, the reacting material system must be isolated from its surroundings, meaning that no exchange of substances or secondary reactions may be allowed to occur so that the amounts of substance converted during the process can be clearly identified.

The following is valid for different substances A, B, C, . . .:

$$\xi = \frac{\Delta n_A}{\nu_A} = \frac{\Delta n_B}{\nu_B} = \frac{\Delta n_C}{\nu_C} \quad \text{or} \quad |\xi| = \frac{|\Delta n_A|}{|\nu_A|} = \frac{|\Delta n_B|}{|\nu_B|} = \frac{|\Delta n_C|}{|\nu_C|} = \ldots . \tag{1.15}$$

Just one quantity, the time-dependent quantity ξ, is enough to describe the temporal course of the reaction. We will call it the *extent of reaction* or *extent of conversion*. In the case of ammonia synthesis, the value of ξ indicates what the momentary extent of the production of ammonia is after a given period. The same unit used for amount of substance, the mol, is normally used for this quantity. Take $\xi = 1$ mol. This means that since the process started, 1 mol of nitrogen and 3 mol of hydrogen have been consumed and 2 mol of ammonia have been produced. For the same value ξ (the same extent of reaction), the changes of amounts Δn can be very different (with regard to both the absolute value and the sign involved). It is important to remember that the ξ values only make sense in relation to a certain conversion formula. If the same reaction is described by another formula, such as

$$\tfrac{1}{2}\,N_2 + \tfrac{3}{2}H_2 \rightarrow NH_3,$$

the meaning of the ξ values changes. At any given moment, the extent of reaction ξ is only half as great for the same amounts of converted substances. The conversion formula must therefore always be specified.

The usual stoichiometric calculations can be carried out directly or indirectly using Eq. (1.15). Therefore, we call it and its source, Eq. (1.14), the *basic stoichiometric equations*. These equations allow us to calculate the change of amount of a substance C from the change of amount of a substance A. For example, knowing the consumption of an acid in titration Δn_A, we can calculate the original amount of a base Δn_B, or knowing the amount of a precipitate Δn_P, we can find the amount of the substance Δn_S which was precipitated out from the initial solution. Here, the conversion numbers are to be taken from the neutralizing or the precipitation reaction, respectively. Since in most cases only the absolute values of Δn matter,

and not their algebraic signs, the simpler variant where no algebraic sign need be dealt with [Eq. (1.15) right] is the one most often used.

Often, it is not directly the amount of substance n that is interesting or known to us but rather a volume ΔV of a reagent solution that is either given or consumed, the concentration c of a sample or standard solution, or the increase of mass Δm of a filtering crucible where a precipitate was collected, etc. The Δn values are then expressed by the given, measured, or the sought quantities. For example, $\Delta n_\mathrm{A} = c_\mathrm{A} \cdot \Delta V$ for the consumed acid or $\Delta n_\mathrm{P} = \Delta m / M_\mathrm{P}$ for the weighted precipitate, where M_P stands for the molar mass of P.

Here is a short example showing this. For the titration of 25 mL of sulfuric acid, 20.35 mL of sodium hydroxide solution (0.1 mol L^{-1}) is consumed. We are looking for the concentration of the acid. The conversion formula for this is

$$\mathrm{H_2SO_4} + 2\,\mathrm{NaOH} \rightarrow \mathrm{Na_2SO_4} + 2\,\mathrm{H_2O}$$

and the basic equation (1.15), where A stands for the sulfuric acid and B for the sodium hydroxide solution, is

$$\frac{|c_\mathrm{A} \cdot \Delta V_\mathrm{A}|}{|\nu_\mathrm{A}|} = \frac{|c_\mathrm{B} \cdot \Delta V_\mathrm{B}|}{|\nu_\mathrm{B}|} \quad \text{or} \quad c_\mathrm{A} = c_\mathrm{B} \cdot \left| \frac{\Delta V_\mathrm{B} \cdot \nu_\mathrm{A}}{\Delta V_\mathrm{A} \cdot \nu_\mathrm{B}} \right|.$$

Using numerical values, we obtain

$$c_\mathrm{A} = 0.1\,\mathrm{mol\,L^{-1}} \frac{20.35\,\mathrm{mL} \cdot 1}{25\,\mathrm{mL} \cdot 2} = 0.041\,\mathrm{mol\,L^{-1}}.$$

The basic stoichiometric equation can be transformed somewhat so that for any arbitrary substance i:

$$n_i = n_{i,0} + \nu_i \xi. \tag{1.16}$$

This equation can basically be used for any substance, even when it does not participate in the reaction taking place, because $\nu_i = 0$. In this respect, this equation is more general than our initial equation (1.14), for which $\nu_i \neq 0$ needs to be the case for the denominator.

We call a change in the extent of a reaction $\mathcal{R}$, $\Delta\xi$, the *conversion* of reaction $\mathcal{R}$ or the conversion *according to* reaction $\mathcal{R}$. Every conversion leads to changes in the amounts of the participating substances, which are proportional to their conversion numbers:

$$\Delta n_i = \nu_i \cdot \Delta\xi. \tag{1.17}$$

Conceptually, the *extent* and *conversion* of a reaction are related to each other in the same way that *location* and *displacement* of a mass point are.

Equation (1.17) can be expanded easily so that it remains useful when several reactions $\mathcal{R}$, $\mathcal{R}'$, $\mathcal{R}''$, ... run simultaneously where each one is described by its own quantity ξ, ξ', ξ'', etc.:

$$\Delta n_i \;=\; \nu_i \cdot \Delta\xi + \nu_i{}' \cdot \Delta\xi' + \nu_i'' \cdot \Delta\xi'' + \ldots \quad \text{for all substances } i. \tag{1.18}$$

Not only can chemical reactions be described in this way, but also a simple exchange of a substance B with the surroundings can as well,

$$\mathrm{B}|\mathrm{outside} \rightarrow \mathrm{B}|\mathrm{inside} \;\text{ or }\; 0 \rightarrow -1\ \mathrm{B}|\mathrm{outside} + 1\ \mathrm{B}|\mathrm{inside},$$

so that we can apply equations of the type (1.18) very generally for calculating changes in amounts of substance.