# Chapter 4
# Chemical Potential

The chemical potential $\mu$ is used as a measure of the general tendency of a substance to transform. Only a few properties are necessary for a complete phenomenological description of this new quantity. They are easy to grasp and can be illustrated by everyday examples. It is possible to derive quantitative scales of $\mu$ values (initially at standard conditions) by using these properties, and after choosing a convenient reference level. A first application in chemistry is predicting whether or not reactions are possible by comparing the sum of potentials of the initial and the final states. This is illustrated by numerous experimental examples. The quantitative description can be simplified by defining a "chemical drive" $\mathcal{A}$ as the difference of these sums. In this context, a positive value of $\mathcal{A}$ means that the reaction proceeds spontaneously in the forward direction. As a last point, a direct and an indirect measuring procedure for the chemical potential are proposed.

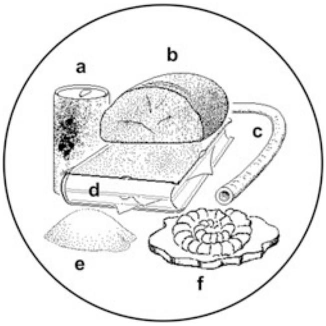
## 4.1 Introduction

The Greek philosopher Heraclitus concluded from observations of his environment already in the fifth century before Christ that "Everything flows—Nothing stands still (πάντα ρεῖ)." Creation and decay are well known in the living world but also in inanimate nature the things around us change more or less rapidly. A lot of such processes are familiar to us from everyday life (Experiment 4.1):

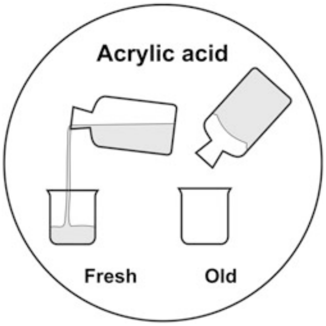
- Objects made of iron rust when they come into contact with air and water.
- Bread dries out if one leaves it at air for a longer time.
- Rubber bands or hoses become brittle.
- Paper turns yellow.
- Butter or fat becomes rancid.
- Copper roofs turn green (so-called patina).
- Even the seemingly stable rocks ("solid as a rock") weather.
- Conversely, mud or also wood petrifies.

G. Job, R. Rüffler, *Physical Chemistry from a Different Angle*,
DOI 10.1007/978-3-319-15666-8_4

**Experiment 4.1** *Changes in the world of substances*: (**a**) Rusted tin can, (**b**) Dried-out bread, (**c**) Embrittled rubber hose, (**d**) Yellowed and brittle pages of a book, (**e**) Quartz sand from eroded granite, (**f**) Petrified mud.



**Experiment 4.2** *Aging of acrylic acid*: Acrylic acid as pure substance is a water-clear liquid strongly smelling of vinegar. If left to stand alone in a completely sealed container, it will change by itself after some time into a colorless and odorless rigid glass.

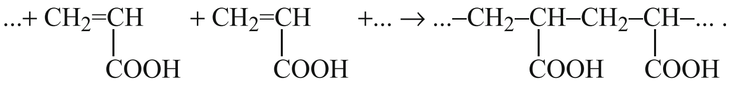


This list could be continued as long as one likes.

It would be possible to consider extraneous effects as the cause. For example, iron would not rust if oxygen were kept from it. However, this is not the point, because substances that are separated from the environment also change. For example, these objects “age” by themselves:

- Bread in a plastic bag,
- Tinned food in an unopened can,
- Chemicals in a sealed bottle such as acrylic acid (propenoic acid) (Experiment 4.2).

The hardening is caused by polymerization, meaning the small acrylic acid molecules combine to form long chains:



$$\ldots + \mathrm{CH_2{=}}\underset{\substack{|\\ \mathrm{COOH}}}{\mathrm{CH}} + \mathrm{CH_2{=}}\underset{\substack{|\\ \mathrm{COOH}}}{\mathrm{CH}} + \ldots \rightarrow \ldots\mathrm{-CH_2-}\underset{\substack{|\\ \mathrm{COOH}}}{\mathrm{CH}}\mathrm{-CH_2-}\underset{\substack{|\\ \mathrm{COOH}}}{\mathrm{CH}}\mathrm{-}\ldots .$$

The transformation of pure substances such as the weathering of natron ($Na_2CO_3 \cdot 10\ H_2O$) and Glauber’s salt ($Na_2SO_4 \cdot 10\ H_2O$) in ambient air where the large colorless crystals become covered with a white powdery crust as they lose water,

$$Na_2CO_3 \cdot 10\,H_2O \rightarrow Na_2CO_3 \cdot 7\,H_2O + 3\,H_2O,$$
$$Na_2SO_4 \cdot 10\,H_2O \rightarrow Na_2SO_4 + 10\,H_2O,$$

the slow transition of the almost colorless monoclinic β-sulfur into the yellow rhombic α-sulfur, or that of the low-molecular white phosphorus into the high-molecular red phosphorus,

$$S|\beta \rightarrow S|\alpha,$$
$$P|\text{white} \rightarrow P|\text{red},$$

all show that it is not an interaction between reaction partners that is the motor for the change of substances, but that the substances tend to transform by themselves. This means that each and every individual substance has a "*tendency to transform.*" This inherent tendency to transform is certainly not the same for all substances, and it has no particular "goal." One might say that all substances are "driven to transform" to one extent or another. They use every opportunity that comes up to follow this "drive," or tendency. A somewhat casual but catchy way to express this would be that they somehow want to "sneak off." Most substances known to us only survive over a longer period of time because many of the transformation processes are inhibited, and not because the drive for them does not exist.

From the transition of the white into the red phosphorus mentioned above, it can be concluded that the white type has the stronger tendency to transform and forces the formation of the red type against its own tendency to transform. Similarly, we can imagine that iron sulfide is formed because the starting substances iron and sulfur together have a stronger tendency to transform than the product FeS. When various metal powders (such as magnesium, zinc, iron, copper, and gold) react with sulfur, the differences are very pronounced. For example, magnesium, when mixed with sulfur and ignited, explodes violently. In contrast, the last metal powder, gold, does not react with sulfur at all:

$$\begin{array}{ccccccccc} Mg & \text{———} & Zn & \text{———} & Fe & \text{———} & Cu & \text{———} & Au\,! \\ \text{explosive} & & \text{glaring} & & \text{glowing} & & \text{glimmering} & & \text{nothing.} \end{array}$$

Here, it becomes immediately obvious that the suggested tendency to transform of the various metal sulfides (compared to the elements from which they are formed) is totally differently strong. On the basis of the violence of reaction, we arrive at the following sequence:

$$MgS < ZnS < FeS < CuS < \text{“AuS.”}$$

Obviously, magnesium sulfide is the easiest to produce, meaning it has the weakest tendency to transform. Gold sulfide, on the other hand, seems to have a relatively strong tendency to transform. It is possible, however, to obtain various compounds of gold and sulfur by indirect means, but they all tend to decompose into the elements involved. We can, therefore, confidently assume that AuS is not produced because its tendency to transform exceeds that of Au + S combined.

We will now go more deeply into the meaning of tendency to transform and its quantitative description with the help of the so-called chemical potential.

## 4.2 Basic Characteristics of the Chemical Potential

Before we attempt to quantify this new concept we will create an overview of what it means, what it is good for, and how it can be dealt with. In order to do this, we compile the most important characteristics of the chemical potential into a short outline, a kind of "wanted poster," which we will subsequently go into more deeply.

- The tendency of a substance
  - To decompose or to *react* with other substances,
  - To undergo a *transition* from one type of state to another,
  - To *redistribute* in space

  can be expressed by one and the same quantity—its chemical potential $\mu$.
- The strength of this tendency, meaning the numerical value of $\mu$, is not unchangeable but
  - Is determined by the *nature* of the substance,
  - By its *milieu*,

  but *neither* by the nature of reaction partners *nor* the resulting products.
- A *reaction, transition, redistribution*, etc., can only proceed spontaneously if the tendency for the process is more pronounced in the initial state than in the final state.

We can assume that any substance, let us call it B, has a more or less pronounced tendency to *transform*. This means a tendency to *decompose* into its elementary (or other) components, to *rearrange* itself into some isomer, $B \rightarrow B^*$, or to *react* with other substances $B'$, $B''$, . . .,

$$B + B' + \ldots \rightarrow \ldots .$$

Even less drastic *transformations* of substance B, such as changing the state of aggregation, the crystalline structure, the degree of association, etc., which can be symbolized for example as follows:

$$B|\alpha \rightarrow B|\beta$$

are driven by the same tendency to transform. This also holds for the tendency of a substance to redistribute in space. This means its tendency to migrate to another location or to move into a neighboring region:

$$\mathrm{B}|\text{location 1} \rightarrow \mathrm{B}|\text{location 2}.$$

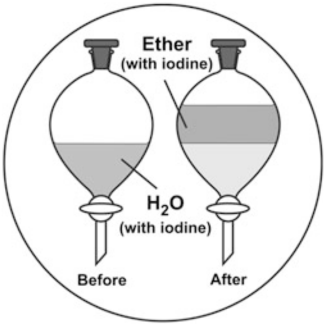
The *chemical potential* $\mu$ is a measure of the strength of this tendency. We write $\mu_\mathrm{B}$ or $\mu(\mathrm{B})$ to signify the potential of substance B. The greater the $\mu$, the more active or "bustling" the substance. The smaller the $\mu$, the more passive or "phlegmatic" it is.

As was mentioned earlier, the strength of the inherent tendency to transform, and with it the numerical value of $\mu_\mathrm{B}$, fundamentally depends upon the nature of the substance. In this context, we see the nature of a substance being determined by its chemical composition, characterized by its content formula, but also by its state of aggregation, its crystalline structure, etc. Hence, liquid water and water vapor as well as diamond and graphite will exhibit different chemical potentials under otherwise identical conditions and therefore need to be treated as different substances. In addition, the strength of the tendency to transform also depends upon the *milieu* in which the substance is located. By milieu we mean the totality of parameters such as temperature $T$, pressure $p$, concentration $c$, the type of solvent S, type and proportions of constituents of a mixture, etc., which are necessary to clearly characterize the environment of B. In order to express these relations, we may write

$$\mu_\mathrm{B}(T, p, c, \ldots, \mathrm{S}, \ldots) \qquad \text{or} \qquad \mu(\mathrm{B}, T, p, c, \ldots, \mathrm{S}, \ldots).$$

Experiment 4.3 illustrates how a substance reacts to a changed milieu. In this case, it is the change of solvent S. Obviously, iodine prefers ether as milieu compared to water. The tendency to transform and thereby the chemical potential of iodine is higher in the water than in the ether—under otherwise identical conditions. We will discuss the influence of the milieu in more detail in the following chapters.

An important characteristic of a substance's tendency to transform is that it is *not* dependent upon the partner it reacts with or what products result. $\mu$ is a characteristic of a single substance and not of a combination of substances. This reduces



**Experiment 4.3** *Iodine in different milieu*: Iodine dissolved in water (*left side*) separates out when it is shaken with ether (*right side*). The ether floats on top of the specifically heavier, now colorless layer of water. The brown color of the dissolved iodine allows us to easily see where it is.

dramatically the amount of data necessary because the number of possible combinations is much, much larger than the number of individual substances itself.

## 4.3 Competition Between Substances

When a substance disappears, one or even several substances are produced from it, or the substance reappears in another location. The produced substances, however, also show a tendency to transform just like the reactants, so the direction in which a certain process will run depends upon which side has the stronger tendency. Therefore, chemical processes resemble a competition between the substances on either side of the conversion formula.

An image commonly used for this competition is the relationship between things on the right and left pans of an equal-arm balance scale (or seesaw) (Fig. 4.1). The direction in which the scale tips depends solely upon the sum of the weights $G$ on each side of it. Even negative weights are allowed if the objects floating upward (maybe balloons) are attached to the scale.

This behavior can also be expressed mathematically: The left side wins, i.e., the objects B, B′, … on the left side of the balance scale or seasaw are successful against the objects D, D′, … on the right side in their attempt to sink downward if

$$G(\mathrm{B}) + G(\mathrm{B}') + \ldots > G(\mathrm{D}) + G(\mathrm{D}') + \ldots .$$

Equilibrium is established when the sums of the weights on the left and right side of the scale are just equal,

$$G(\mathrm{B}) + G(\mathrm{B}') + \ldots = G(\mathrm{D}) + G(\mathrm{D}') + \ldots .$$

The statements made here for weights correspond completely to the role of chemical potentials in transformations of substances. It makes no difference whether it is a reaction between several substances or a transition of a substance from one state to

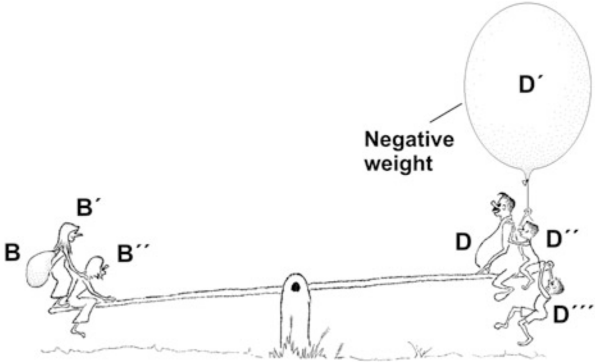


**Fig. 4.1** Seasaw as model for the interaction between starting substances on the one side and final products on the other side during a transformation, whereby the weights of the objects correspond to the chemical potentials of the substances.

another, or just a change of location. The direction in which such a process progresses, for example, the reaction

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

depends solely upon the sums of the chemical potentials $\mu$ of all the substances on either side. The substances on the left side prevail in their attempt to react if

$$\mu(\mathrm{B}) + \mu(\mathrm{B}') + \ldots > \mu(\mathrm{D}) + \mu(\mathrm{D}') + \ldots\,,$$

(see e.g. Fig. 4.2). Equilibrium is established when the sum of the chemical potentials on both sides is the same and therefore no particular direction preferred:

$$\mu(\mathrm{B}) + \mu(\mathrm{B}') + \ldots = \mu(\mathrm{D}) + \mu(\mathrm{D}') + \ldots\,.$$

For example, a candle burns because the starting substances combined [in this case, atmospheric oxygen and paraffin wax, formula $\approx(\mathrm{CH_2})$] have a higher chemical potential than the final products (in this case, carbon dioxide and water vapor):

$$3\,\mu(\mathrm{O_2}) + 2\,\mu((\mathrm{CH_2})) > 2\,\mu(\mathrm{CO_2}) + 2\,\mu(\mathrm{H_2O}).$$

Therefore, every feasible reaction may be viewed as representing a kind of balance scale that enables us to compare potential values or their sums, respectively. However, the measurement often fails because of inhibitions in the reactions; in other words, the scale is “stuck.” In the case of a drop in the chemical potential from the left to the right side, this means that in principle the process *can* proceed in this direction; however, it does not mean that the process will actually run. Therefore, this drop is a necessary but not sufficient condition for the reaction considered. This is not really surprising. An apple tends to fall downward, but it will not fall as long as it hangs from its stem. The coffee in a cup does not flow out over the table although the tendency to do so is there. The porcelain walls of the cup inhibit it from

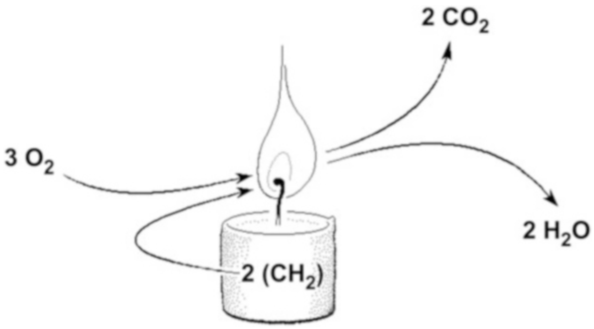


**Fig. 4.2** Burning candle as example of a reaction that proceeds spontaneously.

doing so. We do not even have to bore a hole in the cup for the barrier to be overcome. A bent straw that acts as siphon is already enough. When candle wax and air are put together, no fire occurs. The candle wick and flame work as a kind of “siphon” which helps to overcome the inhibitions. Inhibitions are an important part of our world. Without them, we would end up as carbon dioxide, water, nitrogen, and ashes in the sea of oxygen in which we live.

If a transformation tends to run in one direction, this does not mean that the opposite direction is impossible, it just does not happen *spontaneously*. By itself, sand always trickles downward. A mole can shovel it upward, though, just as a harsh desert wind can pile it up into high dunes, but these processes do not occur spontaneously. Hydrogen and oxygen exhibit a strong tendency to react to form water. The reverse process never runs by itself at room conditions, but can be forced to do so in an electrolytic cell. Predicting substance transformations based upon chemical potentials always presupposes that there are no inhibitions to the process and that no “outside forces” are in play. We will gradually go into what this exactly means and what we need to look out for.

The adjoining cartoon concludes this section. Despite its anthropomorphic viewpoint, it is useful as an image of the general behavior of substances:

More active, more “bustling” substances are transformed into more passive, more “phlegmatic” substances. They migrate from “busier” places (with a lot of “activity”) to “quieter” places (with weak “activity”). In short, matter aspires to a state of maximum “laziness.”

## 4.4 Reference State and Values of Chemical Potentials

**Reference Level** Up to now, what we have been missing in order to make concrete predictions are the $\mu$ values of the substances we have been dealing with. The chemical potential can be assigned an absolute zero value, just as temperature can. In principle, the absolute values could be used, but they are enormous. It would mean that in order to work with the tiny differences in potentials common in chemical and biological reactions, at least 11 digits would be necessary (the ratio between the potential differences and the absolute values is around one to one billion!). This alone would lead to numbers that are much too unwieldy, not to mention that the absolute values are not known accurately enough for this to be feasible.

**Fig. 4.3** Determining geographical elevations as an example for the selection of an appropriate reference level.

But there is a simple way out of this dilemma. The heights of mountains are not referred to the geocenter but to the sea level (Fig. 4.3). Everyday temperatures are not referred to absolute zero, but are given as Celsius temperatures based upon the freezing point of water. (The zero point of Daniel Gabriel Fahrenheit's original scale was determined by placing the thermometer in brine, here a mixture of ice, water, and ammonium chloride.)

It is similarly practical to choose a convenient level of reference for the values of the chemical potential because differences of $\mu$ can be determined much more precisely than absolute values. Moreover, because we only need to compare potential values or their sums, it does not matter what the unit is at first. The $\mu$ values could be expressed in various scales similarly to how temperature can be expressed (Celsius, Fahrenheit, Kelvin, Reaumur, etc.). We will use the SI coherent unit "*Gibbs*," abbreviated to G. This name has been proposed by the German chemist Egon Wiberg (Wiberg E (1972) Die chemische Affinität. De Gruyter, Berlin, p 164) to honor Josiah Willard Gibbs (1839–1903) who first introduced the concept of chemical potential. For use in chemistry, the unit kilo-Gibbs (kG), which corresponds to 1,000 Gibbs, is even handier.

**Elements Used for "Zero Levels"** Next, we will turn to the question of what reference states are suitable for measuring potential differences. It is useful to refer to the conventional basic substances in chemistry, the elements, as long as we limit the transformations of substances to chemical reactions in the broadest sense and exclude nuclear reactions. The values of the chemical potentials of substances are related to the chemical potentials of the elements they are composed of and can be determined experimentally by means of chemical reactions. Because it is not possible to transform one element into another by chemical means, the values of the various elements themselves are not related to each other. This means that in principle one could arbitrarily determine the reference level for each basic substance, i.e., for every element. Because in the case of chemical reactions the elements are preserved, i.e., an equal number of chemical symbols appears on both sides of a conversion formula, this has no effect upon the potential differences that are being observed and measured. Let us take a closer look at the synthesis of ammonia from nitrogen and hydrogen as an example:

$$\begin{array}{lllll}
 & N_2 + & 3\,H_2 & \rightarrow 2\,NH_3 & \\
\cline{2-4}
\mu(\mathrm{kG}): & 0 & 3\times 0 & 2\times(-16) & \Rightarrow \mu(N_2) + 3\,\mu(H_2) - 2\,\mu(NH_3) = +32\ \mathrm{kG} \\
 & 0 & 3\times 2{,}000 & 2\times 2{,}984 & \Rightarrow \mu(N_2) + 3\,\mu(H_2) - 2\,\mu(NH_3) = +32\ \mathrm{kG}
\end{array}$$

N appears two times on the left as well as on the right side of the conversion formula; H, however, appears six times. Therefore, if the chemical potential of a substance is increased by a fixed, although arbitrary summand (say 1,000 kG, as shown above in the third line) for every H appearing in its content formula, this added value cancels when we compute the potential difference and we end up with the same result as in the second line above. The same holds for nitrogen. This means that the reference level for any element could in principle be chosen arbitrarily as mentioned earlier. For the sake of simplicity, the value 0 is assigned to the chemical potential of all elements.

Additionally, one has to consider the following for the specification of a reference state: The state of an element depends upon its temperature and pressure. It also depends upon whether, for instance, hydrogen appears in atomic or molecular form, carbon in the form of graphite or diamond, or oxygen as O, $O_2$, or $O_3$, etc. As an easily reproducible reference state, we will choose the state of the most stable modification of a particular element in its "pure form" and in its natural isotope composition at *standard conditions* (meaning 298 K and 100 kPa, as discussed in Chap. 3). For example, in the case of carbon graphite is used as reference state. An exception to this is phosphorus where the more accessible white (in some tables it is also the red) modification is preferred to the more stable, but very difficult to produce, black modification. In general, we will use the symbol $\mu^{\ominus}$ to designate $\mu$ values at standard conditions. Thus, it follows that (if E represents any arbitrary element in its most stable modification):

$$\mu^{\ominus}(\mathrm{E}) = 0. \qquad (4.1)$$

For elements E such as H, N, O, Cl, etc., which, at standard conditions, usually appear as diatomic gases, 1 mol E simply means $\frac{1}{2}$ mol $E_2$ and $\mu(\mathrm{E})$ correspondingly $\frac{1}{2}\cdot\mu^{\ominus}(E_2)$.

Just as the average sea level serves as the zero level for geographical altitude readings, the state of matter where the substances are decomposed into their elements at standard conditions represents the "zero level" of the potential scale. Analogously, Celsius temperature readings usually used in everyday life can replace those of absolute temperature if melting ice is chosen as reference state.

**Substances of All Kinds** The chemical potential $\mu$ of an arbitrary pure substance itself depends upon temperature and pressure (and possibly other parameters), $\mu(T, p, \ldots)$. Therefore, it is usual in chemistry to tabulate the potentials of substances (referred to the elements that form them) in the form of *standard values* $\mu^{\ominus}$, i.e., for 298 K and 100 kPa. In Table 4.1 we find such standard values for some common substances.

Note that the potential value 0 for iron does not mean that iron has no "tendency to transform," but only that we have used its potential as the zero level to base the values of the potential of other iron-containing substances upon.

The selection of substances in the table shows that not only well-defined chemicals are referred to when speaking about chemical potential, but everyday substances as well. In the case of marble, certain impurities are responsible for its colors, but these substances have almost no effect upon the chemical potential of its main component, $CaCO_3$. However, in order to specify the potential $\mu$ of a substance, an appropriate content formula has to be assigned to it which shows how it is composed of the elements, and which would then be binding for all calculations. This is why this formula must be present in such a table. But the chemical potential of a pure substance also depends on its state of aggregation, its crystal structure, etc. For example, liquid water and water vapor exhibit different chemical potentials at the same temperature and pressure; the same is valid for example for diamond and graphite. In order to arrive at unambiguous specifications, we once again call attention to the relevant additions |s (for solid), |l (for liquid), and |g (for gaseous) to the symbol of a substance (cp. Sect. 1.6); modifications can be characterized by Greek letters |α, |β, . . . or the full name such as |graphite, |diamond, . . . etc.

**Table 4.1** Chemical potentials of several selected substances at standard conditions (298 K, 100 kPa, dissolved substances at 1 kmol m$^{-3}$).

| Substance | Formula | $\mu^{\ominus}$(kG) |
|---|---|---|
| *Pure substances* | | |
| Iron | Fe\|s | 0 |
| Graphite | C\|graphite | 0 |
| Diamond | C\|diamond | +3 |
| Water | $H_2O$\|l | −237 |
| Water vapor | $H_2O$\|g | −229 |
| Table salt | NaCl\|s | −384 |
| Quartz | $SiO_2$\|s | −856 |
| Marble | $CaCO_3$\|s | −1,129 |
| Cane sugar | $C_{12}H_{22}O_{11}$\|s | −1,558 |
| Paraffin wax | ≈$(CH_2)$\|s | +4 |
| Benzene | $C_6H_6$\|l | +125 |
| Acetylene (Ethyne) | $C_2H_2$\|g | +210 |
| *In water* | | |
| Cane sugar | $C_{12}H_{22}O_{11}$\|w | −1,565 |
| Ammonia | $NH_3$\|w | −27 |
| Hydrogen(I) | $H^+$\|w | 0 |
| Calcium(II) | $Ca^{2+}$\|w | −554 |

Because our immediate goal here is a first basic knowledge of the chemical potential, we will for the time being consider the $\mu$ values of substances as given, just as we would consult a table when we are interested in mass density or electric conductivity of a substance. Some measuring methods will be discussed in the concluding Sects. 4.7 and 4.8.

**Dissolved Substances** The potential of a substance B changes if it is brought into another milieu for example by dissolving it. Depending on the type of solvent S in question we obtain different values for the chemical potential. This type of state can be characterized in general by the addition |d (for dissolved) or more precisely by |S—if one would like to specify also the type of solvent. In the by far most common case, substances dissolved in water, we use the symbol |w. But, what matters in this context is not only the type of the solvent but also the concentration of B. Therefore, the concentration $c$ of a dissolved substance, for which the tabulated value will be valid, must be specified in addition to $p$ and $T$. The usual reference value is 1 kmol $\mathrm{m}^{-3}$ (= 1 mol $\mathrm{L}^{-1}$). There exist some peculiarities concerning the determination of these standard values (such as in the case of gases), but we will discuss them in Sect. 6.2.

We can summarize:

$$\begin{array}{lll} \mu^{\ominus} = \mu(T^{\ominus}, p^{\ominus}) & \text{for pure substances} & T^{\ominus} = 298\,\mathrm{K} \\ \mu^{\ominus} \approx \mu(T^{\ominus}, p^{\ominus}, c^{\ominus}) & \text{for dissolved substances} & p^{\ominus} = 100\,\mathrm{kPa} \\ & & c^{\ominus} = 1\,\mathrm{kmol\,m^{-3}} \end{array}$$

$T^{\ominus}, p^{\ominus}, c^{\ominus}$ indicate *standard temperature, standard pressure*, and *standard concentration.*

**Zero-Order Approximation** As long as the temperature does not vary by more than ±10 K, and pressure and concentration do not vary more than a power of ten, the changes of potential of substances of low-molecular mass remain about ±6 kG in general. Therefore, we can consider the $\mu$ values to be constant, at least very roughly. This precision is often sufficient for us so that we can use the $\mu^{\ominus}$ values found in tables. It is unnecessary to worry about temperature, pressure, and concentration dependencies of the potentials at the moment. We will only start dealing in more detail with these influences in the following chapters. The approximation used here is a kind of zero-order approximation.

**Charged Substances** Just like a substance, an assembly of ions can be assigned a chemical potential. When ions of a certain type are decomposed into their elements, there is a positive or negative amount $n_e$ of electrons left over along with the neutral elements, for example,

$$\mathrm{CO_3^{2-}} \rightarrow \mathrm{C} + {}^{3}\!/\!_{2}\,\mathrm{O_2} + 2\,\mathrm{e}^- .$$

The electrons appear here as a kind of additional element (cf. Sect. 1.6) that, like all elements, can be assigned the value $\mu^{\ominus} = 0$ in a certain reference state. However, electrons in a free state play no role in chemistry. Therefore, a value for $\mu^\ominus(e^-)$ has been arbitrarily chosen so that the most commonly appearing type of ion $H^+$ (in an aqueous solution and at standard conditions) receives the $\mu^\ominus$ value of zero:

$$\mu^\ominus(H^+|w) = 0. \tag{4.2}$$

At first, this seems surprising because we know that the chemical potential of an element at standard conditions is zero, i.e., $\mu^\ominus = 0$. This is of course also valid for hydrogen, $\mu^\ominus(H_2|g) = 0$. That is why we expect that other states of hydrogen would show divergent $\mu^\ominus$ values. But let us have a look at the system hydrogen gas/hydrogen ion, which is capable of providing electrons without major inhibitions under suitable conditions (the symbol := should be read as "equal by definition"):

$$H_2|g \rightleftarrows 2\,H^+|w + 2\,e^-$$

with

$$\underbrace{\mu^\ominus(H_2|g)}_{:=0} = 2\underbrace{\mu^\ominus(H^+|w)}_{0} + 2\underbrace{\mu^\ominus(e^-)}_{:=0}.$$

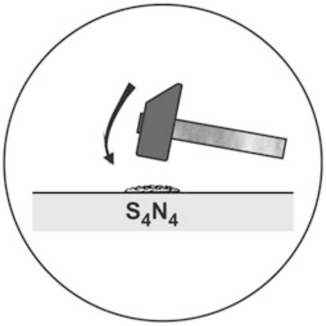
When $H_2$ and $H^+$ are present at standard conditions and *equilibrium* has been established, the chemical potential of the electrons, $\mu^\ominus(e^-)$, is supposed to be zero. (The electron potential $\mu(e^-)$, abbreviated $\mu_e$, will be discussed in more detail in Chap. 22.) Because $\mu^\ominus(H_2|g)$ disappears by definition, it follows necessarily that in a state of equilibrium, $\mu^\ominus(H^+|w)$ has to be zero as well.

## 4.5 Sign of the Chemical Potential

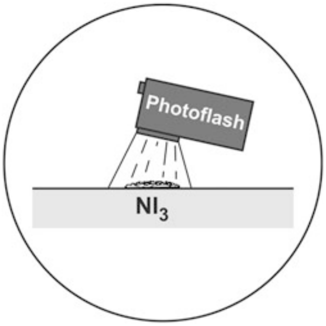
If we use values of chemical potentials in the following, they are valid for room conditions and for dissolved substances of concentrations of 1 kmol $m^{-3}$ (= 1 mol $L^{-1}$) where water is the usual solvent. Elements in their usual, stable state receive, as agreed, the value $\mu^\ominus = 0$ (see also Table 4.3 at the end of this chapter or Sect. A.2.1 in the Appendix). This is for example valid for molecular hydrogen $\mu^\ominus(H_2|g) = 0$, while atomic hydrogen has a rather high positive potential $\mu^\ominus(H|g) = +203\,\text{kG}$. This means that its tendency to transform into $H_2$ is very strong.

A look at Table 4.3 and Sect. A.2.1 in the Appendix shows something remarkable. Most of the potential values are *negative*. A substance with negative chemical potential can be produced spontaneously from the elements because it has a weaker tendency to transform than the elements it is produced from. However, this also means that most substances do not tend to decompose into their elements but, in

**Experiment 4.4** *Decomposition of $S_4N_4$*: A small amount of tetrasulfur tetranitride explodes (like a cap for use in toy guns) when hit lightly with a hammer.



**Experiment 4.5** *Decomposition of $NI_3$*: Nitrogen triiodide decomposes in a dry state if touched by a feather or irradiated by a flash of light thereby producing a sharp explosive sound. The produced iodine can be easily identified by the cloud of violet smoke.



contrast, tend to be produced from them. Therefore, most of the substances we deal with are *stable*; they do not decompose.

If, on the other hand, the potential is positive, the substance will tend to decompose into its elements. Such a substance is *unstable*, thus eluding preparation or is *metastable* at best, i.e., in principle a spontaneous decomposition is possible, but there exists an inhibition. If the inhibition can be overcome, e.g., by supplying energy or by making use of a catalyst, it is very common for the substance to react violently, especially when the value of $\mu$ is very large.

This behavior can be demonstrated quite impressively by means of the attractive orange crystals of tetrasulfur tetranitride $S_4N_4$ ($\mu^\ominus \approx +500$ kG) (Experiment 4.4).

Further examples would be heavy metal azides such as lead azide $Pb(N_3)_2$ (used in detonators to initiate secondary explosives) or silver azide $AgN_3$. Furthermore, the easily produced black nitrogen triiodide $NI_3$ ($\mu^\ominus \approx +300$ kG) tends to decompose into its elements as well (Experiment 4.5).

However, a positive $\mu$ does not always mean that the substance must be explosive. For example, benzene remains rather stable in spite of its $\mu^\ominus$ value of +125 kG. As discussed in Sect. 4.3, a positive $\mu$ value is a necessary but not sufficient condition for a spontaneous decomposition of a substance into its elements to take place. Therefore, we cannot simply assume that just because there is a possibility of transformation, it will take place within a certain span of time, be it years, millennia, or millions of years.

Comparing analogous substances shows best how the level of the chemical potential affects their properties. Here are three examples:

| | $CO_2$\|g | $NO_2$\|g | $ClO_2$\|g |
|---|---|---|---|
| $\mu^\ominus$(kG) | −394 | +52 | +123 |

The gas $CO_2$ with its strongly negative $\mu^\ominus$ value is stable and spontaneously produced from carbon and oxygen, i.e., carbon is "combustible." $NO_2$ with positive $\mu^\ominus$ is not formed spontaneously from $N_2$ and $O_2$, but is so stable that it is not dangerous to handle. Finally, $ClO_2$ has an even higher chemical potential and is extremely explosive.

A similar consideration can be used for solid oxides:

| | $Al_2O_3$\|s | $Fe_2O_3$\|s | $Au_2O_3$\|s |
|---|---|---|---|
| $\mu^\ominus$(kG) | −1,582 | −741 | +78 |

Aluminum and iron combine with oxygen to form their stable oxides, while solid $Au_2O_3$ must be handled carefully so that no oxygen separates from it.

The category of metal sulfides also contains similarly composed substances that are appropriate for comparison:

| | MgS\|s | ZnS\|s | FeS\|s | CuS\|s | "AuS"\|s |
|---|---|---|---|---|---|
| $\mu^\ominus$(kG) | −344 | −199 | −102 | −53 | >0 |

The sequence deduced in Sect. 4.1 from the violence of the reactions of formation actually runs parallel with the values of the chemical potentials. However, be careful: A vague characteristic such as the violence of reaction that is dependent upon different factors can only be considered evidence under comparable conditions.

## 4.6 Applications in Chemistry and Concept of Chemical Drive

**Concept of Chemical Drive** The most important application for the chemical potential $\mu$ is that it enables us to predict whether a transformation of substances can happen spontaneously or not. As we have seen, a chemical reaction

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

is possible when the following is valid:

$$\mu(\mathrm{B}) + \mu(\mathrm{B}') + \ldots > \mu(\mathrm{D}) + \mu(\mathrm{D}') + \ldots .$$

If we wish to find out if a previously unknown process can run spontaneously, it is enough to find the corresponding $\mu$ values in appropriate tables and then to compare the potentials on the right and left side of the conversion formula. Spontaneously, processes only run "downhill," meaning from left to right, when the sum of the $\mu$ values on the left is greater than on the right.

The condition for a spontaneous process results in

$$\mu(\mathrm{B}) + \mu(\mathrm{B}') + \ldots - \mu(\mathrm{D}) - \mu(\mathrm{D}') - \ldots > 0$$

after rearrangement of the formula above. The summation of the variables can be presented in a shorter form by using the sigma sign, $\sum$. We summarize:

$$\text{reactants} \rightarrow \text{products is spontaneously possible if } \sum_{\text{initial}} \mu_i - \sum_{\text{final}} \mu_j > 0$$

That means that how a reaction runs has less to do with the levels of the potentials themselves than with the potential difference between the substances in their initial and final state. Therefore, it is convenient to introduce this difference as an independent quantity. We will call the quantity

$$\mathcal{A} = \sum_{\text{initial}} \mu_i - \sum_{\text{final}} \mu_j \tag{4.3}$$

the *chemical drive* $\mathcal{A}$ of the process (reaction, phase transition, redistribution, etc.), in short, the *drive*, when it is clear that no nonchemical influences are participating. The unit for drive is "Gibbs," as can be easily seen in the above definition.

Internationally, the quantity $\mathcal{A}$ is usually called *affinity*. The origin of this name reaches back into antiquity. However, it is, unfortunately, a bad indicator of the characteristic it describes (see below). The symbol recommended by IUPAC (**I**nternational **U**nion of **P**ure and **A**pplied **C**hemistry) is $A$. So as to avoid confusion with other quantities labeled by the letter $A$, such as area, we shall use another font (like $\mathcal{A}$).

The name *chemical tension* for $\mathcal{A}$ would be appropriate as well when taking into consideration that the quantities electric potential $\varphi$ and electric tension $U$ (voltage),

$$U = \varphi_{\text{initial}} - \varphi_{\text{final}},$$

are similarly related both conceptually and formally as chemical potential and drive. $U$ describes the (electric) drive for a charge transfer between two points. The simplest case of this would be between the input and output of a two-terminal electronic component (lightbulb, resistor, diode, etc.).

The quantity $\mathcal{A}$ has a centuries-old history under the name *affinity*. The first table with values of this quantity was compiled by Louis-Bernard Guyton de Morveau in 1786. This was hundred years before the concept of chemical potential was created.

At that time, people had very different ideas about the causes of substance transformations. The closer the "relationship (affinity)" of two substances, the stronger the driving force for them to bond. This was the main reason for using this name. Substance A might displace substance B from a compound BD, if it had a closer relationship or affinity to D than B. It might also occur that if A was already loosely bound to a partner C, it would then be free for a new partnership: AC + BD → AD + BC. The German writer and polymath Johann Wolfgang von Goethe was inspired by this idea in his novel "The Elective Affinities" of 1809 in which he transferred this concept to human relationships.

A positive drive, $\mathcal{A} > 0$, "drives" a transformation as long as there are reactants available. A negative, $\mathcal{A} < 0$, leads to a reaction in the opposite direction of the reaction arrow. $\mathcal{A} = 0$ means no drive, therefore, a standstill where equilibrium is established. Here are some examples:

**Decomposition of a Substance into Its Elements** We have already encountered one type of reaction, namely the decomposition of a compound $A_\alpha B_\beta C_\gamma \ldots$ into the elements that make it up, A, B, C, …:

$$A_\alpha B_\beta C_\gamma \ldots \rightarrow \nu_A A + \nu_B B + \nu_C C + \ldots\ ,$$

in which case the conversion number $\nu_A$ is numerically equal to $\alpha$, $\nu_B$ to $\beta$, etc. For the strength of the tendency to decompose—the "drive to decompose"—we then obtain:

$$\mathcal{A} = \mu_{A_\alpha B_\beta C_\gamma \ldots} - [\nu_A \mu_A + \nu_B \mu_B + \nu_C \mu_C + \ldots].$$

Having arbitrarily set the potentials of the elements (in their most stable modification) under standard conditions equal to zero the expression in brackets disappears and the drive to decompose corresponds to the chemical potential of the substance:

$$\mathcal{A} = \mu_{A_\alpha B_\beta C_\gamma \ldots} - \underbrace{\left[\nu_A \cdot \mu_A^\ominus + \nu_B \cdot \mu_B^\ominus + \nu_C \cdot \mu_C^\ominus + \ldots\right]}_{0} = \mu_{A_\alpha B_\beta C_\gamma \ldots}.$$

These circumstances were already anticipated and taken into consideration by our discussion in Sect. 4.5. As a concrete example, we will consider the decomposition of ozone $O_3$. This tends to transform into oxygen gas $O_2$, which we can see easily by comparing the potentials:

$$\begin{array}{llcll} & \underline{O_3|g} & \underline{\rightarrow} & \underline{{}^3\!/_2\, O_2|g} & \\ \mu^\ominus(\text{kG}): & 163 & > & {}^3\!/_2 \times 0 & \Rightarrow \mathcal{A}^\ominus = +163\ \text{kG}. \end{array}$$

In this case $\mathcal{A}^\ominus$ refers to the drive to decompose under standard conditions. The decomposition process is so slow, however, that ozone can be technically used despite its limited stability. We just have to produce it fast enough to compensate for its decomposition.

Here is an anomaly that one can easily stumble over: We obtain different values for the drive to decompose of ozone depending upon which formula is being used to describe the process:

$$\mathcal{A}^{\ominus}(2\,O_3 \rightarrow 3\,O_2) = +326\,\text{kG},$$
$$\mathcal{A}^{\ominus}(O_3 \rightarrow {}^3\!/_2\,O_2) = +163\,\text{kG}.$$

Basically, only the sign of $\mathcal{A}$ matters, and it is the same in both cases. Still it seems strange that there appear to be different values of the drive for the same process. The first process, however, differs from the second one in the same way that a harnessed team of two horses differs from just one harnessed animal. We expect that the team will be twice as strong as the single one. This is also true for reactions. Just as with the $\xi$ values (Sect. 1.7), it is always important to indicate the conversion formulas that one is referring to.

**Transitions** Another simple case is the transition of one substance into another one:

$B \rightarrow D$ is spontaneously possible if $\mu_B > \mu_D$, i.e., $\mathcal{A} > 0$.

A suitable substance for an example is mercury iodide $HgI_2$, which appears in beautiful red and yellow modifications with somewhat different chemical potentials:

$$\begin{array}{lcccl} & \underline{HgI_2|\text{yellow}} & \underline{\rightarrow} & \underline{HgI_2|\text{red}} & \\ \mu^{\ominus}(\text{kG}): & -101.1 & > & -101.7 & \Rightarrow \mathcal{A}^{\ominus} = +0.6\,\text{kG}. \end{array}$$

Because of the yellow modification's higher (not as strongly negative) tendency to transform, it must change into the red form. That this is actually the case is shown by Experiment 4.6.

*Phase transitions* such as melting and vaporization of substances can be treated in the same way. Such processes can also be formulated like reactions. An example of this is melting of ice:

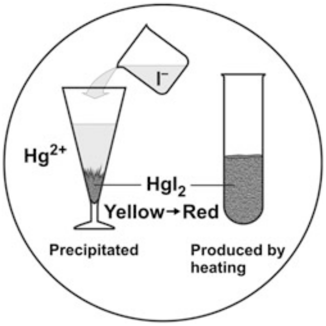
$$\begin{array}{lcccl} & \underline{H_2O|s} & \underline{\rightarrow} & \underline{H_2O|l} & \\ \mu^{\ominus}(\text{kG}): & -236.6 & > & -237.1 & \Rightarrow \mathcal{A}^{\ominus} = +0.5\,\text{kG}. \end{array}$$

We have used the tabulated values valid for a temperature of 298 K or 25 °C. Therefore, a positive drive can be expected that allows ice to melt under these conditions. For given conditions, the phase with the lowest chemical potential is stable.

Therefore, diamond should undergo a transition into graphite because it has a higher chemical potential:

$$\begin{array}{lcccl} & \underline{C|\text{diamond}} & \underline{\rightarrow} & \underline{C|\text{graphite}} & \\ \mu^{\ominus}(\text{kG}): & +2.9 & > & 0 & \Rightarrow \mathcal{A}^{\ominus} = +2.9\,\text{kG}. \end{array}$$

**Experiment 4.6** *Change of modification of $HgI_2$*: Within an hour, a spoonful of yellow $HgI_2$ powder (produced by heating the red form in an oil bath or drying oven to over 125 °C) becomes spotted with red. These spots get larger and grow together to become uniformly red (*right*, in the figure). The process takes place within seconds when the poorly soluble $HgI_2$, precipitated out of a $Hg^{2+}$ solution by addition of $I^-$, is used. At first, the precipitate is sallow yellow, which immediately turns to orange and finally to deep red (*left*, in the figure).



However, this does not happen at room temperature because the process is much too inhibited. The reason is that for the carbon atoms to form a graphite lattice, the very strong bonds of the carbon atoms in the diamond must be broken and this is just about impossible at room temperature. In this context let us once again recall that a potential drop from the left to the right side and therewith a positive value of the chemical drive $\mathcal{A}$ merely tells us that the process *can* proceed spontaneously in this direction in principle, but it does not signify that the process will actually run. Changes in the states of aggregation, gas → liquid → solid, take place largely without inhibition and therefore almost immediately due to a high mobility of the individual particles in participating gases or liquids, as soon as the potential gradient has the necessary sign for a spontaneous process. On the other hand, an unstable state in a solid body can be "frozen" and stay like that for thousands or even millions of years.

**Reactions of Substances in General** When several substances participate in a reaction, the decision about whether or not a process can take place is not more difficult to make.

We can take the reaction of marble with hydrochloric acid, an aqueous solution of hydrogen chloride, HC1, as first example (Experiment 4.7).

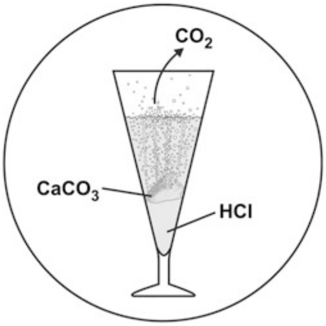
Therefore, we conclude that the reaction drive has to be positive. Indeed, we arrive at this result if we calculate the value of the drive by using the tabulated potential values (assuming an acid concentration of 1 kmol $m^{-3}$). In doing so we have to consider that HC1 is a strong acid and is entirely dissociated into hydrogen and chloride ions, $H^+$ and $Cl^-$. The $H^+$ ions are responsible for the reaction, while the $Cl^-$ ions remain more or less inactive.

$$\underline{\mathrm{CaCO_3|s} + 2\,\mathrm{H^+|w} \rightarrow \mathrm{Ca^{2+}|w} + \mathrm{CO_2|g} + \mathrm{H_2O|l}}$$

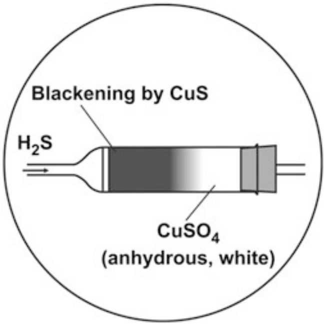
$$\mu^\ominus(\mathrm{kG}):\ \underbrace{-1{,}129 \qquad 2\times 0}_{-1{,}129} \quad > \quad \underbrace{-554 \qquad -394 \qquad -237}_{-1{,}185} \qquad \Rightarrow \mathcal{A}^\ominus = +56\ \mathrm{kG}.$$

Another example is the development of hydrogen chloride gas when concentrated sulfuric acid reacts with table salt:

**Experiment 4.7**
*Dissolution of marble in hydrochloric acid*: If a few pieces of marble are put in hydrochloric acid, a strong effervescence of carbon dioxide can be observed.



**Experiment 4.8**
*Blackening of $CuSO_4$ by $H_2S$*: If gaseous hydrogen sulfide is made to flow over anhydrous, white copper sulfate, black copper sulfide is produced. This let us observe the reaction easily.



$$\begin{array}{lcccccl}
 & \mathrm{NaCl|s} + \mathrm{H_2SO_4|l} & \rightarrow & \mathrm{HCl|g} + \mathrm{NaHSO_4|s} & & \\
\hline
\mu^{\ominus}(\text{kG}): & \underbrace{-384 \qquad -690}_{-1{,}074} & > & \underbrace{-95 \qquad -993}_{-1{,}088} & & \Rightarrow \mathcal{A}^{\ominus} = +14\ \text{kG}.
\end{array}$$

For lack of better criteria, it is common to explain the fact that hydrogen chloride can be obtained from table salt and concentrated sulfuric acid by use of a rule that states that a less volatile acid displaces a higher volatile acid from its salts. In the case of dissolving marble in hydrochloric acid, also a stronger acid displaces a weaker one. These rules are often satisfied, but they are less than reliable. Experiment 4.8 shows an example that contradicts both rules:

$$\begin{array}{lcccccl}
 & \mathrm{CuSO_4|s} + \mathrm{H_2S|g} & \rightarrow & \mathrm{CuS|s} + \mathrm{H_2SO_4|l} & & \\
\hline
\mu^{\ominus}(\text{kG}): & \underbrace{-661 \qquad -33}_{-694} & > & \underbrace{-53 \qquad -690}_{-743} & & \Rightarrow \mathcal{A}^{\ominus} = +49\ \text{kG}.
\end{array}$$

In this case, the weak, volatile acid hydrogen sulfide displaces the strong, low volatile sulfuric acid from its salt.

It is also easy to predict the production of a low soluble precipitate from its ionic components when two solutions are combined:

$$\begin{array}{lccccc} & \mathrm{Pb^{2+}|w} & + \; \mathrm{2\,I^{-}|w} & \rightarrow & \mathrm{PbI_2|s} & \\ \hline \mu^{\ominus}(\mathrm{kG}): & \underbrace{-24 \qquad\qquad 2\times(-52)}_{-128} & & > & -174 & \Rightarrow \mathcal{A}^{\ominus} = +46\ \mathrm{kG}. \end{array}$$

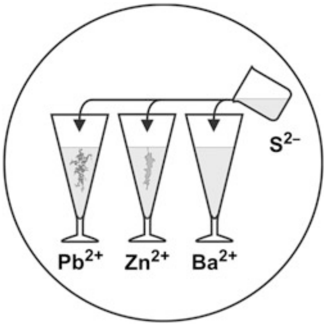
Lead iodide must precipitate out of an aqueous solution containing $Pb^{2+}$ and $I^-$ ions. Many other precipitation reactions can be predicted according to the same pattern. When solutions containing $Pb^{2+}$, $Zn^{2+}$, or $Ba^{2+}$ are mixed with those that contain $CO_3^{2-}$, $S^{2-}$, or $I^-$ ions, precipitation can be expected (based on calculations similar to that for lead iodide) only in those instances that are marked with a plus sign in Table 4.2.

To save some calculation, the chemical potential of the possible precipitates and the combined potential of the ions forming them are included in Table 4.3 at the end of the chapter. The predicted result can be easily proven in a demonstration experiment, for example, by using $S^{2-}$ (Experiment 4.9). Reactions with $CO_3^{2-}$ or $I^-$ can be carried out correspondingly. Because ionic reactions in particular are hardly inhibited in solutions and therefore usually proceed quickly if the potential gradient has the correct sign, they are especially well suited for comparing predictions with experimental results.

As discussed, a reaction always runs in the direction of a potential drop. This might give the impression that substances with a positive potential cannot ever be produced by normal reactions of stable substances (with negative $\mu$). The production of ethyne (acetylene) with a high positive chemical potential from calcium

**Table 4.2** Prediction of precipitation reactions.

| | $CO_3^{2-}$ | $S^{2-}$ | $2I^-$ |
|---|---|---|---|
| $Pb^{2+}$ | + | + | + |
| $Zn^{2+}$ | + | + | – |
| $Ba^{2+}$ | + | – | – |



**Experiment 4.9** *Precipitation of sulfides*: When a solution containing $S^{2-}$ ions is mixed with solutions that contain $Pb^{2+}$, $Zn^{2+}$, or $Ba^{2+}$ ions, precipitation only takes place in the first two cases.

carbide and water, both substances with a negative potential, shows that this is not the case (Experiment 4.10).

$$\begin{array}{lccccl} & \mathrm{CaC_2|s} + 2\,\mathrm{H_2O|l} & \rightarrow & \mathrm{Ca(OH)_2|s} + \mathrm{C_2H_2|g} & & \\ \hline \mu^{\ominus}(\mathrm{kG}): & \underbrace{-65 \qquad 2\times(-237)}_{-539} & > & \underbrace{-898 \qquad +210}_{-688} & & \Rightarrow \mathcal{A}^{\ominus} = +149\ \mathrm{kG}. \end{array}$$

The very low chemical potential of calcium hydroxide on the product side makes sure that the chemical drive $\mathcal{A}$ is generally positive, even though $\mu(\text{ethyne})$ is $> 0$. In earlier times, the gas extracted from this reaction was used to power miners' lamps and bicycle lights because of its bright flame. It is still used today for welding because of its high combustion temperature.

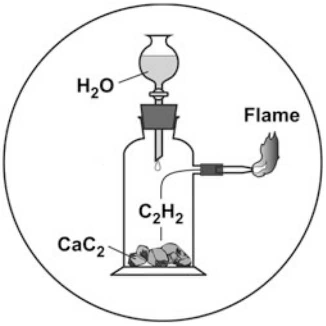
**Dissolution Processes** Dissolving substances in a solvent can also be described with the help of the concept of potentials. Whether a substance dissolves easily or not in water, alcohol, benzene, etc., is a result of the difference of its chemical potential in the pure and dissolved state. A first impression of the dissolution behavior of substances is all that will be given in this section. Chapter 6 will discuss how solubility can actually be calculated or estimated.

For dissolving for example cane sugar in water (more exactly: in a solution which already contains 1 kmol m$^{-3}$ of sugar, which is about 340 g per liter!) we obtain:

$$\begin{array}{lcccl} & \mathrm{C_{12}H_{22}O_{11}|s} & \rightarrow & \mathrm{C_{12}H_{22}O_{11}|w} & \\ \hline \mu^{\ominus}(\mathrm{kG}): & -1{,}558 & > & -1{,}565 & \Rightarrow \mathcal{A}^{\ominus} = +7\ \mathrm{kG}. \end{array}$$

$\mathcal{A}^{\ominus} > 0$ means that the sugar dissolves by itself even in such a concentrated solution. Sugar dissolves easily, as we know from using it every day (Experiment 4.11).

Table salt also dissolves easily in water, as we know. The reason for this is that in an aqueous medium (even at a concentration of 1 kmol m$^{-3}$), the chemical potential



**Experiment 4.10** *Carbide lamp*: When water is dripped onto some lumps of calcium carbide a vigorous generation of gas can be observed. The produced gaseous ethyne burns with a bright and sooty flame.

of the $Na^+$ and $Cl^-$ ions together is noticeably lower than when it is a salt in solid form.

$$\begin{array}{lccccl} & \mathrm{NaCl|s} & \rightarrow & \mathrm{Na^+|w} + \mathrm{Cl^-|w} & & \\ \hline \mu^\ominus(\mathrm{kG}): & -384 & & \underbrace{-262 \quad -131} & & \\ & -384 & > & -393 & & \Rightarrow \mathcal{A}^\ominus = +9\ \mathrm{kG}. \end{array}$$

For contrast, let us consider the dissolution behavior of iodine.

$$\begin{array}{lcccl} & \mathrm{I_2|s} & \rightarrow & \mathrm{I_2|w} & \\ \hline \mu^\ominus(\mathrm{kG}): & 0 & < & +16 & \Rightarrow \mathcal{A}^\ominus = -16\ \mathrm{kG}. \end{array}$$

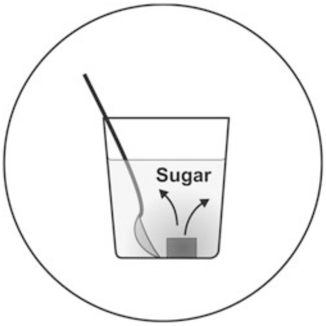
The chemical drive is strongly negative so the process can only run backward spontaneously. Solid iodine would precipitate from a solution with a concentration of 1 kmol $m^{-3}$. However, this does not mean that iodine is not at all soluble in water. Increasing the dilution decreases the potential of iodine in water so that the drive can become positive when the dilution is high enough. More about this in Chap. 6.

Even the dissolution behavior of gases can be easily described in this way. For our first example, we choose ammonia as the gas and water as the solvent:

$$\begin{array}{lcccl} & \mathrm{NH_3|g} & \rightarrow & \mathrm{NH_3|w} & \\ \hline \mu^\ominus(\mathrm{kG}): & -17 & > & -27 & \Rightarrow \mathcal{A}^\ominus = +10\ \mathrm{kG}. \end{array}$$

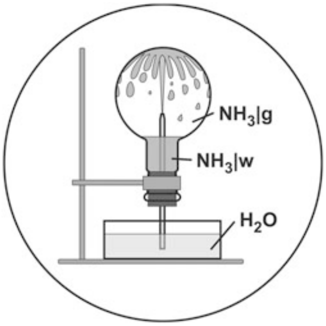
Consequently, ammonia is very easily dissolved in water. An impressive way of showing this excellent solubility is with a so-called fountain experiment (Experiment 4.12).

The situation is different with carbon dioxide, which is much less soluble in water.

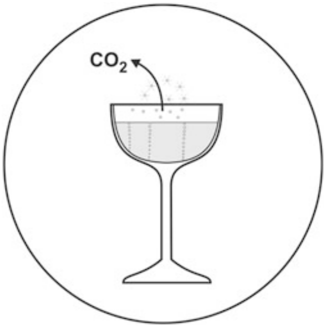


**Experiment 4.11** *Dissolution of a sugar cube*: The process becomes noticeable by the shrinking of the sugar cube in a glass of tea even when it is not touched. An even more impressive version of this process is stacking sugar cubes into a tower on a shallow plate and then pouring some water colored with a few drops of food dye onto the plate. The water immediately begins to move up the tower and make it collapse after a short while.

**Experiment 4.12** *Ammonia fountain*: $NH_3$ gas dissolves so readily in water that just a few drops are enough to decrease the pressure in the flask filled with gas so drastically that more water is drawn upward into it in a strong jet. If a few drops of the acid–base indicator phenolphthalein are added to the water, the solution turns pink just as soon as it enters the flask (more in Chap. 7).



**Experiment 4.13** *Effervescence of carbon dioxide*: Carbonated liquids such as champagne or mineral water are filled into bottles under excess pressure. When the pressure is reduced such a liquid releases carbon dioxide bubbles.



$$\begin{array}{lccc} & CO_2|g & \rightarrow & CO_2|w \\ \hline \mu^{\ominus}(\text{kG}): & -394 & > & -386 \end{array} \qquad \Rightarrow \mathcal{A}^{\ominus} = -8\ \text{kG}.$$

Therefore, it tends to bubble out of an aqueous solution (Experiment 4.13).

Ammonia and carbon dioxide are both very voluminous in their gaseous states, so their appearance or disappearance in dissolving or escaping is very noticeable.

**Potential Diagrams** Rather than merely comparing numerical values we gain an even clearer picture of the process of substance transformations if we enter the $\mu^{\ominus}$ values into a diagram that charts the potentials, a so-called *potential diagram*. Such a diagram lets us see the drop in the potential that "drives" the process particularly well if in each case we add up the values of the chemical potentials $\mu^{\ominus}$ of the reactants and products. Let us take a closer look at the reaction of copper sulfate with hydrogen sulfide as an example (Fig. 4.4).

Up until now, we have considered the chemical potential in the roughest (zero-order) approximation as a constant. In doing so, we have neglected the dependencies of temperature, pressure, concentration, etc. We will deal with these influences in the next chapters and discuss the consequences for the behavior of substances. But for now we will discuss how the tendency of substances to transform can be quantified.

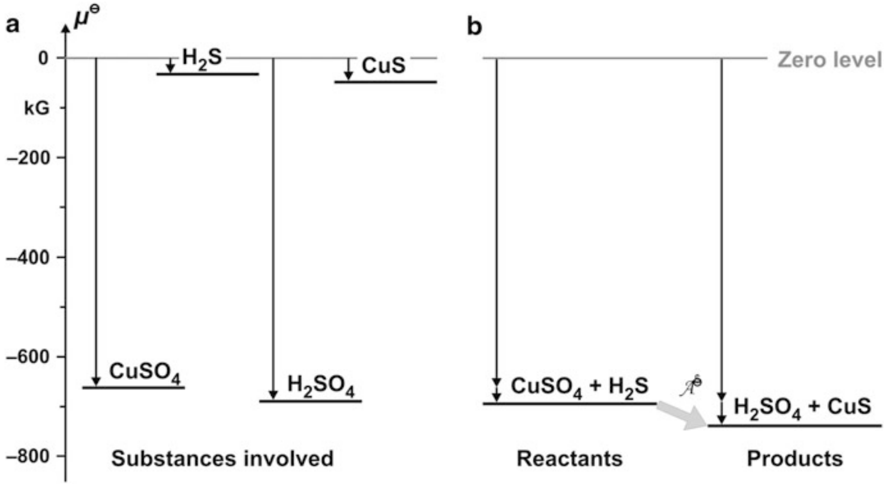


**Fig. 4.4** Potential diagram for the reaction $CuSO_4 + H_2S \rightarrow H_2SO_4 + CuS$ under standard conditions: (**a**) Levels of the potential for the substances involved, (**b**) Adding of the values of the potential in the initial and the final state of reaction.

## 4.7 Direct Measurement of Chemical Drive

The usual methods do not measure the chemical potentials of substances themselves, but only the difference between the sums of the potentials of the initial substances and the final products, i.e., the drives $\mathcal{A} = \sum \mu_{\text{initial}} - \sum \mu_{\text{final}}$ of chemical transformations. In other words, $\mathcal{A}$ is the basic quantity from which we derive the chemical potential $\mu$. This is also true for electric circuits where only the difference of electric potentials $\varphi$ between two points, i.e., the voltage $U = \varphi_{\text{initial}} - \varphi_{\text{final}}$, can be measured, and not the potentials themselves. If an arbitrary zero point is selected, the potentials can be derived.

The chemical drive $\mathcal{A}$ can be measured both directly and indirectly just as other quantities can. However, the direct method has the advantage of not being dependent upon other physical quantities. This means that the meaning of the quantity $\mathcal{A}$ can be comprehended directly. A disadvantage is that some reference standard, a well-reproducible process that represents the unit $\mathcal{A}_\text{I}$ of the drive, must be chosen. Reference standards (etalons) for the units of length and mass are, for example, the original meter and original kilogram made of platinum or a platinum alloy which are kept in Paris. Values of chemical drives initially measured as multiples of $\mathcal{A}_\text{I}$ must then be converted to standard units.

Data in a SI coherent unit are desirable. G (Gibbs) is an example which has already been presented here. There is a trick that can be used so that preliminary values do not have to be remembered. We do not assign a value of 1 to the drive $\mathcal{A}_\text{I}$ of the process which has been chosen as the unit of the chemical drive. Rather, we take a value which comes as close as possible to the value in Gibbs. For instance,

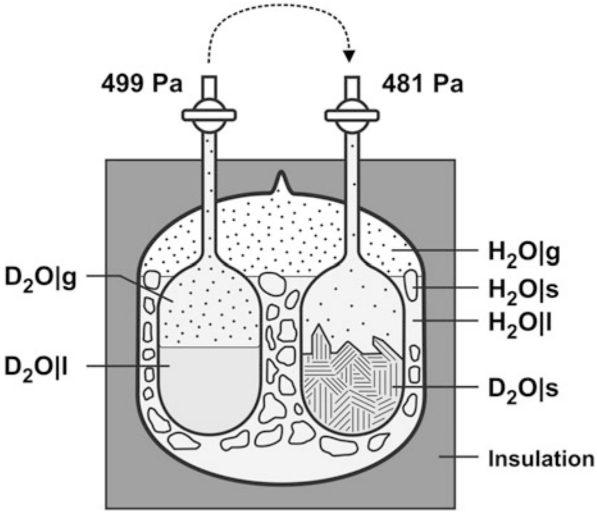


**Fig. 4.5** Cell representing a fixed value of chemical drive $\mathcal{A}$.

the temperature unit K (Kelvin) has been defined in this way and the temperature span of 1 K as closely approximated to the older unit 1 °C as possible. In this case, the temperature of a "triple point cell" (a cell where liquid water, water vapor, and solid ice are coexisting) is given the exact value $T = 273.1\underline{6}\,\mathrm{K}$.

The cell in Fig. 4.5 represents a fixed value of chemical drive just as the original meter and the original kilogram in Paris represent fixed length and mass values. This example shows the solidification of supercooled heavy water (freezing point 276.97 K),

$$D_2O|l \rightarrow D_2O|s,$$

which is embedded in airless light water and whose temperature is brought to 273.16 K. The transformation happens spontaneously if the $D_2O$ vapor is allowed to move from the container on the left to the one on the right. Expressed in SI coherent units, the drive is

$$\mathcal{A}_I = 84\ \mathrm{G}.$$

As we have already seen in the example of weight (Sect. 1.3), there are basically three agreements necessary for metricization. These are agreements about

(a) Sign,
(b) Sum,
(c) Unit

of the quantity $\mathcal{A}$ which serves as the measure of the drive of a chemical transformation. We have just discussed how to introduce a unit (point c) in detail. Quite a bit was also said about the sign (point a) in Sect. 4.5: A process that runs forward spontaneously receives a positive value of drive $\mathcal{A} > 0$, one that tends to run backward against the direction of the reaction arrow, receives a negative value $\mathcal{A} < 0$, and a process that does neither is in equilibrium and has the value $\mathcal{A} = 0$.

Now we need only think about creating sums (point b). Two or more transformations with the drives $\mathcal{A}, \mathcal{A}', \mathcal{A}'' \ldots$ are coupled to each other—it does not matter how—so that they have to take place together. We make the agreement that the drive $\mathcal{A}_{\text{total}}$ of the entire process, i.e., of the sequence of the coupled processes, is the sum of the drives of these processes:

$$\mathcal{A}_{\text{total}} = \mathcal{A} + \mathcal{A}' + \mathcal{A}'' + \ldots \; .$$

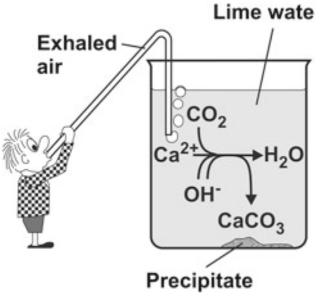
There exist a number of methods for achieving a coupling of two or more chemical processes. Here are some of them:

(a) *Chemically* through shared intermediate substances,
special case: *enzymatically* through enzyme substrate complexes,
(b) *Electrically* through electrons as the intermediate substance,
(c) *Mechanically* through cylinders, pistons, gears, etc.

*Chemical* coupling is the most common kind of coupling. Almost all reactions are made up of such coupled sub-steps. A strict synchronization and a close coupling are forced when, under the chosen experimental conditions, the *intermediate substance* Z no longer freely appears in noticeable quantities, i.e., just as Z is formed it is consumed by the next reaction:

$$\begin{array}{rcl} A + B + \ldots \rightarrow C + D + \ldots + & \boxed{\begin{array}{c} Z \\ Z \end{array}} & + \ldots + F + G \rightarrow H + I + \ldots \; . \end{array}$$

Both processes can only take place simultaneously or they have to rest simultaneously, i.e., the substance Z couples them rigidly like wheels in a clock or a gear. The short-lived intermediate substances are usually not noticed, so we can only guess what they might be. They can be quite exotic and we should not necessarily give them the status of proper substances. A simple example of a sequence of chemically coupled reactions for which the intermediate substances are well known is the precipitation of limestone from lime water that occurs when we blow exhaled air in it that contains carbon dioxide. In the process, the first two reactions are coupled by dissolved $CO_2$, the next by $HCO_3^-$, and the last by $CO_3^{2-}$.



$$\begin{aligned}
CO_2|g &\rightarrow \boxed{CO_2|w} && \mathcal{A}_1\\
OH^-|w + \boxed{CO_2|w} &\rightarrow \boxed{HCO_3^-|w} && \mathcal{A}_2\\
OH^-|w + \boxed{HCO_3^-|w} &\rightarrow \boxed{CO_3^{2-}|w} + H_2O|l && \mathcal{A}_3\\
Ca^{2+}|w + \boxed{CO_3^{2-}|w} &\rightarrow CaCO_3|s && \mathcal{A}_4\\
\mathcal{A}_{total} &= \mathcal{A}_1 + \mathcal{A}_2 + \mathcal{A}_3 + \mathcal{A}_4
\end{aligned}$$

*Enzymatic* coupling is an important special case of chemical coupling. This process has been developed to a high degree of perfection in biochemical reactions. For example, the innumerable reactions taking place in living cells are connected in this way which leads to the metabolism driving all other processes. Thereby reactions are interlocked like the wheels of a clock so that one transformation can drive many others.

Unfortunately, it is difficult to imitate the procedure with chemical equipment, and laboratory chemistry does not offer much room for systematic interlocking of various reactions. The coupling of a reaction with the chosen unit reaction required for measuring a drive is fundamentally possible but very difficult to realize with chemical methods.

*Electrical* coupling which makes use of reversible galvanic cells presents a much more flexible example. Theoretically, any chemical transformation can be used to transport electric charge from one terminal to another in a galvanic cell. After all, practically all substances contain electrons and therefore allow for dividing each transformation into a partial process which supplies electrons and another which consumes electrons. This can be accomplished in many different ways.

Let us select a general reaction

$$B + C \rightarrow D + E.$$

Theoretically, we can divide the reaction into two spatially separated partial processes where a sufficiently mobile ion $B^+$ is to act as the shared reaction partner. So as to keep the electrons from migrating along with the $B^+$ ions, we place a wall between them that is permeable only for ions. Gauze electrodes on both sides of the wall which will not hinder the migration of $B^+$ are used for the conduction of the electrons. In the simplest case, the wall is solid and the dissolved substances are located in a suitable trough (Fig. 4.6).

In order for substance B to go from left to right, it must be stripped of its surplus electrons,

$$B \rightarrow B^+ + e^-,$$

which accumulate on the electrode on the left, while they are in short supply on the one on the right because they are being consumed there,

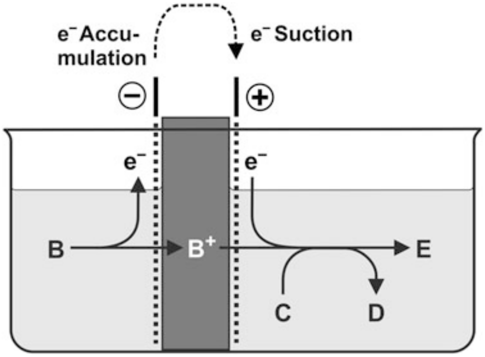


**Fig. 4.6** Coupling of two reactions that are spatially separated by electrons that serve as shared reaction partner.

$$e^- + B^+ + C \rightarrow D + E.$$

As a result, an electric "tension," a voltage, is developed between the electrodes. The experimental arrangement thus represents nothing but a galvanic cell in which the entire reaction can only proceed when the electrons are allowed to flow from the cell's terminal on the left to the one on the right. Chapter 23 will go more deeply into how such cells are constructed.

Ideally, transport of charge and chemical transformation are closely coupled. By connecting two or more such cells in series, the reactions in the cells are coupled so that they only run forward or backward as a unit. Their drives add up. For simplicity's sake, it is assumed that the reactions are formulated so that the conversion number of electrons is $\nu_e = 1$. When the terminals of a cell in such a series connection are switched, the drive of this cell is given a negative sign—like a weight on the opposite side of a scale.

It is also possible to couple reactions *mechanically*. However, this method succeeds only when conducted as a thought experiment and therefore we will not discuss it any further here.

Drive $\mathcal{A}$ of a transformation can be measured by the same procedure that we explained when discussing weights. All we need to do is couple $m$ specimens of the reaction to be measured inversely to as many specimens $n$ of the unit reaction (or a reaction with a known drive) required to achieve equilibrium. In other words, the drive of the entire process is made to disappear:

$$\mathcal{A}_{\text{total}} = m \cdot \mathcal{A} + n \cdot \mathcal{A}_{\text{I}} = 0 \text{ or } \mathcal{A} = -(n/m) \cdot \mathcal{A}_{\text{I}}. \tag{4.4}$$

By applying this method it is in principle possible to measure the quantity $\mathcal{A}$ with as much precision as we desire. We can illustrate the procedure with the example of oppositely coupled vehicles (Fig. 4.7a). Like those vehicles, it is possible to inversely couple $m$ galvanic cells which represent a particular reaction with

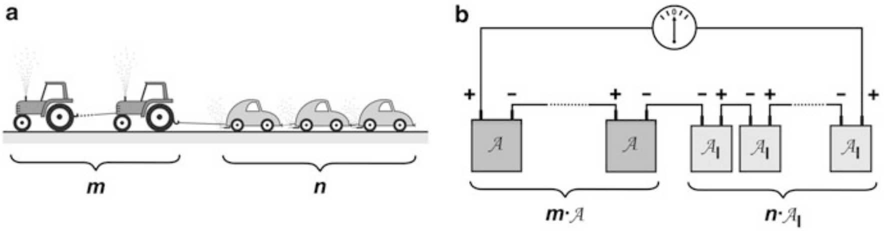


**Fig. 4.7** Comparison of (**a**) the tractive forces of vehicles with (**b**) the measurement of chemical drive $\mathcal{A}$ by means of electric coupling of reactions.

unknown $\mathcal{A}$ to $n$ cells based on a reaction with known drive such as the unit reaction ($\mathcal{A}_\mathrm{I}$) so that equilibrium is established and the electric current in the circuit is zero (Fig. 4.7b). As mentioned earlier, we achieve the inverse coupling through reverse poling, i.e., by interchanging the positive and the negative terminals.

The procedure can be simplified considerably. For example, it is possible to calibrate a sufficiently sensitive highly resistive voltmeter directly in the unit $\mathcal{A}_\mathrm{I}$. For this purpose one merely needs to connect the instrument to the two open terminals of various cell chains which consist of an increasing number of “unit cells.” The pointer deflections are marked and in this way we construct a scale suitable for the measurement of unknown $\mathcal{A}$ values. The procedure is similar to the calibration of a spring balance by utilizing a number of different weights or even to the calibration of the ice calorimeter directly in entropy units (Sect. 3.7).

On the chosen scale, the chemical potential $\mu$ is nothing else than the drive of a substance to decompose into its elements. Therefore, $\mu$ can be measured using analogous methods if the reaction is chosen suitably.

In addition to the *direct* methods for determining chemical drives and potentials, respectively, there are numerous *indirect* methods that are more sophisticated and therefore more difficult to grasp, yet more universally applicable. These include chemical (using the mass action law) (Sect. 6.4), calorimetric (Sect. 8.8), electrochemical (Sect. 23.2), spectroscopic, quantum statistical, and other methods to which we owe almost all of the values that are available to us today. Just as every relatively easily measured property of a physical entity that depends upon temperature (such as its length, volume, electrical resistance, etc.) can be used to measure $T$, every property (every physical quantity) which depends upon $\mu$ can be used to deduce $\mu$ values.

## 4.8 Indirect Metricization of Chemical Potential

In order to increase our understanding, we will consider a method which allows—in principle—the $\mu$ values of substances to be determined rather directly and in a way that approaches the way most commonly used. Figure 4.8 shows a theoretically

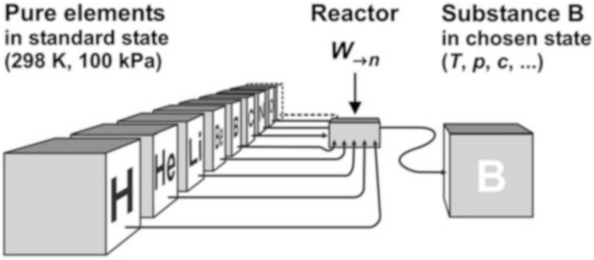


**Fig. 4.8** Hypothetical arrangement for measuring chemical potentials $\mu$.

possible setup for measuring $\mu$ which gives the values directly in the scale used by us. This method is indirect because the energy $W_{\rightarrow n}$, which is used for forming a small amount $n$ of the substance B, is measured. Almost everything we are doing is associated with some kind of energy "turnover," so it is not easy to separate the energy contribution $W_{\rightarrow n}$, which serves exactly this purpose, from the other energy contributions which only accompany the process.

The containers on the left in the figure contain the elements in their normal stable states at 298 K and 100 kPa. In order to produce substance B, the correct proportions of these elements are supplied to a continuously working reactor. They are transformed there (the details of this process are not necessary for a first understanding) and then sent to the container on the right in the desired form of B (solid or liquid, warm or cold, pure or dissolved, etc.). One might say that the reactor transports substance B from a state on the left, where it is broken down into its elementary components with the potential 0, to a state on the right with a potential of $\mu_B$. Whereas the matter on the left exists in a state which is identical for all substances to be formed, the matter on the right appears in a *specific form* and in a *specific milieu*. The form is determined by the selection of B with its fixed constituents and their arrangement; the milieu on the other hand is defined by temperature, pressure, concentration, type of solvent, etc. Energy is required to transform matter; as a rule the more complex and complicated the rearrangement the more energy is needed. We might say that matter will "resist" such change. This results in a more or less strong tendency to return to the old or even another state while releasing the consumed energy.

Let us recapitulate: The stronger the "drive" of a substance B to transform, here in particular the drive of the substance to decompose into the elements (in their standard state),

- The more difficult it is for the substance to be formed against its "drive,"
- The greater the amount of $W_{\rightarrow n}$ necessary to achieve this.

$W_{\rightarrow n}$ grows in proportion to the amount of substance $n$ formed (as long as $n$ remains small), so $W_{\rightarrow n}$ itself is not to be used as a measure of the tendency to transform and therefore of the chemical potential $\mu$, but rather $W_{\rightarrow n}$ divided by $n$:

$$\mu = W_{\to n}/n. \tag{4.5}$$

The accumulation of substance B in a container gradually changes the milieu of this substance and therefore its potential. For this reason, it is required that amount $n$ and energy $W_{\to n}$ are kept small in order to keep the disturbance small. This can be symbolized by $\mathrm{d}n$ and $\mathrm{d}W_{\to n}$. $\mu$ itself results as a quotient of both quantities:

$$\mu = \mathrm{d}W_{\to n}/\mathrm{d}n. \tag{4.6}$$

It is of course necessary to avoid or subtract all energy contributions due to side effects (e.g., as a result of friction, lifting, entropy transfer, acceleration, production of other substances, solvents, or mixing partners, etc.). If, on the other hand, the process (the transport of substance B) runs spontaneously from left to right, it releases energy. In this case, $W_{\to n}$ and therefore $\mu$ are negative but apart from that our considerations remain essentially the same.

The unit for chemical potential which results from the equation $\mu = \mathrm{d}W_{\to n}/\mathrm{d}n$ is J mol$^{-1}$. Since we constantly deal with values of the chemical potential, we are justified in giving this unit its own name, "Gibbs," abbreviated G, in a manner analogous to "Volt" for the electric potential difference as we have done in Sect. 4.5:

$$1\ \text{Gibbs(G)} = 1\ \text{J}\,\text{mol}^{-1}.$$

Naturally, the energy of the portions of the elements taken from the left is to be found in the substance B formed from them. We do not have to worry about these contributions since they drop out when calculating the drive of a transformation of substances. This is so because, as is always the case in chemistry, the elements are conserved (see Sect. 4.4). Only the additional quantity $\mathrm{d}W_{\to n}$ which we can identify with $\mu\mathrm{d}n$, matters. Together with substance B, it is added to the system on the right and so increases its energy. We could use the increase $\mathrm{d}W$ of $W$ to infer the value of $\mathrm{d}W_{\to n} = \mu\mathrm{d}n$, even if we did not know anything of the existence of the reactor or even if it did not exist at all.

Like the volume of water in a bathtub (Sect. 1.6), the energy $W$ may change as a result of different processes, such as transfer or generation of entropy (see Sect. 3.11), increase or decrease of volume (Sect. 2.5), or by taking in other substances B′, B″, … etc.:

$$\mathrm{d}W = \underbrace{-\,p\mathrm{d}V}_{\mathrm{d}W_{\to V}} + \underbrace{T\mathrm{d}S}_{\mathrm{d}W_{\to S}} + \underbrace{\mu\mathrm{d}n}_{\mathrm{d}W_{\to n}} + \underbrace{\mu'\mathrm{d}n'}_{\mathrm{d}W_{\to n'}} + \underbrace{\mu''\mathrm{d}n''}_{\mathrm{d}W_{\to n''}} + \ldots\ .$$

To avoid interferences caused by the different paths for energy transfer, we require $S$, $V$, $n'$, $n''$, … to be held constant, i.e., $\mathrm{d}S$, $\mathrm{d}V$, $\mathrm{d}n'$, $\mathrm{d}n''$, … $= 0$, so that the related energy contributions vanish:

$$\mathrm{d}W = \underbrace{-p\mathrm{d}V}_{0} + \underbrace{T\mathrm{d}S}_{0} + \underbrace{\mu\mathrm{d}n}_{\mathrm{d}W_{\to n}} + \underbrace{\mu'\mathrm{d}n'}_{0} + \underbrace{\mu''\mathrm{d}n''}_{0} + \ldots = (\mathrm{d}W)_{S,V,n',n''\ldots}.$$

If we introduce $\mu = \mathrm{d}W_{\to n}/\mathrm{d}n$ into this equation, this yields

$$\mu = \frac{(\mathrm{d}W)_{S,V,n',n''}}{\mathrm{d}n} = \left(\frac{\mathrm{d}W}{\mathrm{d}n}\right)_{S,V,n',n''\ldots} = \left(\frac{\partial W}{\partial n}\right)_{S,V,n',n''\ldots}. \tag{4.7}$$

This equation already shows some similarity to Gibbs's approach. When Josiah Willard Gibbs introduced the quantity $\mu$ in 1876 which we now call chemical potential, he addressed experts in his field. Students who are not used to work with such expressions may feel repelled by equations of this type. The expression in the middle means that we should consider $W$ a function of $n$, $W = f(n)$. We can consider this function to be given by a computational formula with $W$ as the dependent variable and $n$ the independent variable. $V$, $S$, $n'$ $n''$ … are constant parameters.

Here is an example from school mathematics. In the equation of a parabola $y = ax^2 + bx + c$, $W$ corresponds to $y$, $n$ to $x$. $V$, $S$, $n'$, $n''$, … correspond to the parameters $a$, $b$, $c$. To find $\mu$, we must take the derivative of $W = f(n)$ with respect to $n$, just as we take the derivative of $y = ax^2 + bx + c$ with respect to $x$ in order to find the slope of the function, i.e., $y' = 2ax + b$.

On the other hand, the expression on the right using the symbol $\partial$ assumes that $W$ is to be considered a function of *all* the variables in the denominator and the index, $W = g(V, S, n, n', n'', \ldots)$. Since all these quantities, except for the one in the denominator, are kept constant when we take the derivative, there is no difference to the result.

Remember the formula which we used in Sect. 1.3 to indirectly determine the weight $G$ of a body via the energy:

$$G = \left(\frac{\mathrm{d}W}{\mathrm{d}h}\right)_{\upsilon} = \frac{(\mathrm{d}W)_{\upsilon}}{\mathrm{d}h}.$$

Here, $\mathrm{d}W$ is the energy used to lift the object a small distance $\mathrm{d}h$. The index $_{\upsilon}$ means that the velocity is to be kept constant. When we considered this example, we neglected the fact that the energy $W$ of the body could also vary with its entropy $S$ (such as through friction) or with the amount $n$ of one of the substances it is made out of. To exclude these possibilities, we write

$$G = \left(\frac{\mathrm{d}W}{\mathrm{d}h}\right)_{p,S,n},$$

where, for consistency's sake, we have changed the variable $\upsilon$ to the momentum $p = m\upsilon$. Written in this form, we must gain the impression that the weight $G$ is a quantity that cannot be grasped and dealt with without the benefit of advanced mathematics and thermodynamics. The same happens when we try to understand the chemical potential as the partial derivative of special energy forms. That is why we prefer to introduce the chemical potential by characterizing it phenomenologically and by direct metricization. Once we have understood what the quantity $\mu$ means and which properties it has, it should be possible to follow the definition given by Gibbs. In concluding, we should once more bring to mind that $\mu$ like $G$ is not an energy but rather corresponds to a “force,” more precisely a “force-like” quantity in the sense of Helmholtz (see Sect. 2.7).

**Table 4.3** Chemical potential $\mu$ (and its temperature and pressure coefficients $\alpha$ and $\beta$ which we will get to know in the next chapter) under standard conditions (298 K, 100 kPa, dissolved substances at 1 kmol m$^{-3}$).

| Substance | $\mu^{\ominus}$(kG) | $\alpha$ (kG K$^{-1}$) | $\beta$ (μG Pa$^{-1}$) | Substance | $\mu^{\ominus}$(kG) | $\alpha$ (kG K$^{-1}$) | $\beta$ (μG Pa$^{-1}$) |
|---|---|---|---|---|---|---|---|
| Fe\|s | 0 | −0.027 | 7.1 | HCl\|g | −95 | | |
| NaCl\|s | −384 | −0.072 | | $H_2SO_4$\|l | −690 | | |
| $NaHSO_4$\|s | −993 | −0.113 | | $Na_2SO_4$\|s | −1,270 | | |
| $SiO_2$\|s | −856 | −0.041 | | $CuSO_4$\|s | −661 | | |
| $CaCO_3$\|s | −1,129 | −0.093 | | CuS\|s | −53 | | |
| $C_{12}H_{22}O_{11}$\|s | −1,558 | −0.392 | | $H_2S$\|g | −33 | | |
| $C_2H_2$\|g | 210 | −0.201 | $24.8 \times 10^3$ | $CaC_2$\|s | −65 | | |
| $Ca^{2+}$\|w | −554 | 0.053 | −17.8 | $OH^-$\|w | −157 | | |
| Element | 0 | Most stable form | | $Pb^{2+}$\|w | −24 | | |
| $H_2$\|g | 0 | | | $Zn^{2+}$\|w | −147 | | |
| H\|g | 203 | | | $Ba^{2+}$\|w | −561 | | |
| $O_2$\|g | 0 | | | $CO_3^{2-}$\|w | −528 | | |
| $O_3$\|g | 163 | | | $S^{2-}$\|w | 86 | | |
| C\|graphite | 0 | | | $I^-$\|w | −52 | | |
| C\|diamond | 2.9 | | | | | Substances | $\Sigma\mu$ |
| $NI_3$\|s | 300 | | | $PbCO_3$\|s | −625 | $Pb^{2+} + CO_3^{2-}$ | −552 |
| $S_4N_4$\|s | 500 | | | $ZnCO_3$\|s | −731 | $Zn^{2+} + CO_3^{2-}$ | −675 |
| $C_6H_6$\|l | 125 | | | $BaCO_3$\|w | −1,135 | $Ba^{2+} + CO_3^{2-}$ | −1,089 |

(continued)

**Table 4.3** (continued)

| Substance | $\mu^\ominus$(kG) | $\alpha$ (kG K$^{-1}$) | $\beta$ (μG Pa$^{-1}$) | Substance | $\mu^\ominus$(kG) | $\alpha$ (kG K$^{-1}$) | $\beta$ (μG Pa$^{-1}$) |
|---|---|---|---|---|---|---|---|
| $CO_2$\|g | −394 | −0.214 | Combustible | PbS\|s | −98 | $Pb^{2+} + S^{2-}$ | 62 |
| $NO_2$\|g | 52 | −0.240 | Incombust. | ZnS\|s | −199 | $Zn^{2+} + S^{2-}$ | −61 |
| $ClO_2$\|g | 123 | −0.257 | Incombust. | BaS\|s | −456 | $Ba^{2+} + S^{2-}$ | −475 |
| | | parent element | | $PbI_2$\|s | −174 | $Pb^{2+} + 2I^-$ | −128 |
| $Al_2O_3$\|s | −1,582 | −0.051 | Oxidizes | $ZnI_2$\|s | −209 | $Zn^{2+} + 2I^-$ | −251 |
| $Fe_2O_3$\|s | −741 | −0.087 | Rusts | $BaI_2$\|s | −602 | $Ba^{2+} + 2I^-$ | −665 |
| $Au_2O_3$\|s | 78 | −0.130 | Stable | $C_{12}H_{22}O_{11}$\|w | −1,565 | | |
| MgS\|s | −344 | −0.050 | | $Na^+$\|w | −262 | | |
| ZnS\|s | −199 | −0.059 | | $Cl^-$\|w | −131 | | |
| FeS\|s | −102 | −0.060 | | $I_2$\|s | 0 | | |
| CuS\|s | −53 | −0.066 | | $I_2$\|w | 16 | | |
| AuS\|s | >0 | | | $NH_3$\|g | −16 | | |
| $HgI_2$\|red | −101.7 | −0.180 | | $NH_3$\|w | −27 | | |
| $HgI_2$\|yellow | −101.1 | −0.186 | | $CO_2$\|w | −386 | | |
| $H^+$\|w | 0 | | | $H_2O$\|s | −236.6 | −0.045 | 19.7 |
| | | | | $H_2O$\|l | −237.1 | −0.070 | 18.1 |
| | | | | $H_2O$\|g | −228.6 | −0.189 | $24.8 \times 10^3$ |