Preface

The coming book “Physical Chemistry - an Introduction with New Concept and Numerous Experiments” will give an overview about important areas of physical chemistry. It is addressed to undergraduate students in courses where physical chemistry is required in support but also to beginners in mainstream courses.

Four special features of the book may be highlighted:

- The basic quantities and equations necessary for the qualitative and quantitative description of transformations of substances are introduced by using everyday experiences and particularly more than hundred demonstration experiments. The motivating power of fascinating experiments is made use of, because students often regard physical chemistry as very abstract and remote from everyday life.

- It seems that two thermodynamic quantities are especially difficult to understand: entropy and chemical potential – entropy $S$ as quantity associated to temperature $T$ and chemical potential $\mu$ as quantity associated to amount of substance $n$. The pair $S$ and $T$ is responsible for all kinds of heat effects, whereas the pair $\mu$ and $n$ controls all the processes involving substances such as chemical reactions, phase transitions or dispersal in space. Nevertheless, $S$ and $\mu$ are compatible with a layperson's perception. Therefore, the simplest way to introduce these central quantities – in addition to energy – to first-year students and even pupils without frightening mathematical apparatus is by firstly characterizing them by their typical and easily observable properties, i.e. by designing a kind of “wanted poster” for them. This phenomenological description is supported by a direct measuring procedure, a method normally used for the quantification of basic concepts such as length, time or mass. The proposed approach leads directly to practical results such as the prediction whether or not a reaction is spontaneously possible by using the chemical potential. Moreover, the chemical potential is key in dealing with physicochemical problems. Based on this central concept, it is possible to explore many other fields. The dependence of the chemical potential upon temperature, pressure and concentration is the “gateway” to the deduction of the mass action law, the calculation of equilibrium constants, solubilities, and many other data, the construction of phase diagrams and so on. An expansion of the concept to colligative phenomena, diffusion processes, surface effects, electrochemical processes, etc., is easily possible. Furthermore, the same tools allow us to solve problems even at the atomic and molecular level, that are usually treated by quantum statistical methods.

- This approach – directly via entropy and chemical potential – allows to eliminate other common thermodynamic quantities which are usually considered as indispensable: for example enthalpy, Helmholtz energy, Gibbs energy, activity, fugacity, and all their numerous descendents. Usage of these quantities is not excluded, but superfluous in most cases. An optimized calculus results in short calculations, which are intuitively predictable and can be checked easily.

- For understanding the basic ideas, only elementary mathematical knowledge is necessary (therefore, the concept can be easily adapted to all levels of education). For
many applications linear formulas are often sufficient. If required more sophisticated mathematical tools with detailed explanations are incorporated.

Further informations about the presented concept as well as instructions and video clips of the demonstration experiments can be found on our website www.job-foundation.org.

The text book was published in German by Vieweg+Teubner in October 2010. Publication in English, but also in Spanish and Chinese is planned in the near future.

The excerpt presents the table of contents of the coming book as well as the chapters 4 to 6 and 12 in the form of lecture notes. The text represents a preliminary version in process. Therefore, we would be very grateful for any contribution to the discussion or suggestion for corrections.

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1. **Introduction and First Basic Concepts**

After a short introduction to chemical dynamics, important basic concepts are introduced, such as
- substance and amount of substance,
- homogeneous and heterogeneous mixture including measures of composition (for example mole fraction, molar concentration),
- physical state (states of aggregation, state functions),
- transformation of substances (description by conversion formulas (reaction equations) and stoichiometric calculations).

1.1 Chemical dynamics  
1.2 Substances and basic substances  
1.3 Measurement and metricization  
1.4 Amount of substance  
1.5 Homogeneous and heterogeneous mixture, and measures of composition  
1.6 Physical state  
1.7 Transformation of substances

2. **Energy**

First, the conventional indirect way of defining energy is briefly presented. A much simpler way to introduce this quantity is characterizing it by its typical and easily observable properties using everyday experiences. This phenomenological description may be supported by a direct measuring procedure, a method normally used for the quantification of basic concepts such as length, time or mass. Subsequently, the law of energy conservation and different manifestations of energy like that in a stretched spring, a body in motion etc., are discussed. With the help of the concept of energy, pressure and momentum are introduced.

2.1 Introducing energy indirectly  
2.2 Direct metricization of energy  
2.3 Energy conservation  
2.4 Energy of a stretched spring  
2.5 Pressure  
2.6 Energy of a body in motion  
2.7 Momentum  
2.8 Energy of a raised body

3. **Entropy and Temperature**

In phenomenological description (comparable to a kind of “wanted poster”) the entropy appears as a kind of “stuff” which is distributed in space, can be stored or transferred, collected or distributed, soaked up or squeezed out, concentrated or dispersed. It is involved in all thermal effects and can be considered their actual cause. Without it, there would be no hot and no cold. It can be easily generated, if the required energy is available, but it cannot be destroyed. Actually, entropy can be easily recognized by these effects. This direct understanding of the quantity $S$ is deepened by a simplified molecular kinetic interpretation.
The Second Law can then be formulated without recourse to energy and temperature. On the contrary, the absolute temperature can be introduced via energy and entropy. The Third Law is also easily accessible, and heat pumps and heat engines are analyzed after this introduction, without discussing process cycles, gas laws, or energy conversion processes.

3.1 Introduction
3.2 Macroscopic properties of entropy
3.3 Molecular kinetic interpretation of entropy
3.4 Conservation and generation of entropy
3.5 Effects of increasing entropy
3.6 Entropy transfer
3.7 Direct metricization of entropy
3.8 Temperature
3.9 Examples of applications of entropy
3.10 Temperature as “thermal tension"
3.11 Energy for generation and exchange of entropy
3.12 Determining entropy calorimetrically
3.13 Heat pumps and heat engines
3.14 Entropy generation in an entropy flow

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 reactants and the products. This is illustrated by numerous experimental examples. The quantitative description can be simplified by defining a “chemical drive” \( A \) as the difference of these sums. In this context, a positive value of \( A \) means that the reaction proceeds spontaneously in the forward direction.

4.1 Introduction
4.2 Basic characteristics of the chemical potential
4.3 Competition between substances
4.4 Reference level and values of chemical potentials
4.5 Sign of the chemical potential
4.6 “Chemical drive” and application in chemistry
4.7 Direct measurement of chemical drive
4.8 Indirect metricization of chemical potential

5. Influence of Temperature and Pressure on Chemical Transformations

The chemical potential can be regarded as constant only in a first approximation. A more detailed approach considers the temperature and pressure dependence of \( \mu \). Often linear approaches to these dependencies suffice. If the corresponding coefficients are given, it is easily possible to predict the behavior when the substances involved are heated, compressed etc. The melting, boiling, sublimation points etc., can also be calculated. Only the pressure
coefficient of gases shows a strong pressure dependence; therefore, the linear approach is only valid in a small pressure range. For wider application, a logarithmic approach must be used.

5.1 Introduction
5.2 Temperature dependence of chemical potential and drive
5.3 Pressure dependence of chemical potential and drive
5.4 Simultaneous temperature and pressure dependence
5.5 Behavior of gases under pressure

6. **Mass Action and Concentration Dependence of the Chemical Potential**

The concept of mass action, its relation to the concentration dependence of the chemical potential (mass action equation), and subsequently, its relation to the chemical drive are discussed. An important application is the derivation of the “mass action law.”

6.1 The concept of mass action
6.2 Concentration dependence of chemical potential
6.3 Concentration dependence of chemical drive
6.4 The mass action law
6.5 Special versions of the mass action equation
6.6 Applications of the mass action law
6.7 Potential diagrams of dissolved substances

7. **Consequences of Mass Action: Acid-Base Reactions**

The concept of mass action is applied to acid-base reactions as one important example for chemical transformations. The quantity “proton potential” $\mu_p$ is introduced and its use for describing acid-base titrations is shown. Also, the mechanism of action of buffers and indicators is discussed.

7.1 Introduction
7.2 The acid-base concept according to BRØNSTED and LOWRY
7.3 Proton potential
7.4 Equation of proton level and protonation equation
7.5 Acid-base titrations
7.6 Buffers
7.7 Acid-base indicators

8. **Side Effects of Transformations of Substances**

Transformations of substances like reactions, phase transitions, distribution in space etc. are often accompanied by very striking side effects, such as smoldering and flashing, fizzling and cracking, bubbling and fuming. These side effects (which make chemistry so fascinating) can primarily be attributed to

- changes of volume,
- exchange and generation of entropy,
- changes of energy

during the processes. The quantitative description of these effects is the objective of this chapter.
8.1 Introduction
8.2 Volume demand
8.3 Volume changes associated with transformations
8.4 Entropy demand
8.5 Changes of entropy associated with transformations
8.6 Energy changes associated with transformations
8.7 Heat effects
8.8 Calorimetric measurement of chemical drives

9. Coupling

It is possible to act on a system of substances mechanically (by expansion and compression ...), thermally (by heating and cooling ...), and chemically (by addition of substances, reactions). All these actions are accompanied by energy changes as shown in the previous chapters. These energy changes can be combined into a single equation, the so-called “main equation.“ Important couplings like the equivalence of the temperature coefficient of $\mu$ and the negative molar entropy are easily deduced by special mathematical “flip rules.”

9.1 Main equation
9.2 Mechanical-thermal coupling
9.3 Coupling of chemical quantities
9.4 Further mechanical-thermal applications

10. Molecular Kinetic View of Dilute Gases

The general gas law is deduced from experimental observations (BOYLE-MARIOTTE’s law, law of CHARLES and GAY-LUSSAC, AVOGADRO’s principle). This is followed by an introduction to the kinetic model of gases. In order to derive the distribution of particle velocities in a gas (MAXWELL distribution), the concentration dependence (mass action equation) and additionally the energy dependence (excitation equation) of the chemical potential is used.

10.1 Introduction
10.2 General gas law
10.3 Molecular interpretation of the general gas law
10.4 Excitation equation and velocity distribution
10.5 Barometric formula and BOLTZMANN distribution

11. Substances with Higher Density

If one changes from dilute (ideal) gases to real gases with higher density, the interaction between the particles and the condensation phenomenon have to be considered. This results in the VAN DER WAALS equation. The simultaneous temperature and pressure dependence (Section 5.4) can be used to calculate the vapour pressure curve if the phase transition is formulated as a reaction and the equilibrium condition is taken into consideration. The complete phase diagrams of pure substances can be constructed similarly.

11.1 VAN DER WAALS equation
11.2 Condensation
11.3 Critical temperature
11.4 Boiling pressure curve (vapor pressure curve)
11.5 Complete phase diagram

12. Spreading of Substances

So far, the discussion of the chemical potential has concentrated primarily on chemical reactions and phase transitions. But another property of substances is also of great importance: their tendency to disperse in space. The phenomenon of diffusion is explained in this context. Further, the colligative properties like osmotic pressure, lowering of vapor pressure and freezing point, and raising of boiling point, are discussed.

12.1 Introduction
12.2 Diffusion
12.3 Indirect mass action
12.4 Osmosis
12.5 Lowering of vapor pressure
12.6 Lowering of freezing point and raising of boiling point
12.7 Colligative properties and determining molar mass

13. Homogeneous and Heterogeneous Mixtures

The change of the chemical potential of a substance in ideal and real solutions and the reason for spontaneous mixing or de-mixing are discussed. The quantitative description of real mixtures requires the introduction of an extra potential $\mu$. For the description of mixing processes, it is useful to assign an (average) chemical potential to a mixture of two components A and B (with the mole fractions $x_A$ and $x_B$), as is done for pure substances. In the case of homogeneous and heterogeneous mixtures, the concentration dependence of this average potential is different. This is shown and used for the discussion of phase reactions (miscibility gap, lever rule).

13.1 Introduction
13.2 Chemical potential in homogeneous mixtures
13.3 Extra potential
13.4 Chemical potential of homogeneous and heterogeneous mixtures
13.5 Mixing processes
13.6 More phase reactions

14. Two-Component Systems

The average chemical potential depends not only upon the composition, but also upon the temperature (and pressure). These dependencies and the fact that the phase with the lowest chemical potential at a given temperature (or pressure) will be stable, can be used to construct the phase diagrams of different mixtures.

14.1 Phase diagrams of two-component systems
14.2 Liquid-liquid phase diagrams (miscibility diagrams)
14.3 Solid-liquid phase diagrams (melting point diagrams)
14.4 Liquid-gaseous phase diagrams (vapor pressure and boiling point diagrams)
15. **Interface Phenomena**

In this chapter, we discuss how the properties of substances at interfaces are modified compared to those in the interior of the phase. For quantitative description, quantities like surface tension and surface energy have to be introduced. The Langmuir isotherm as simplest isotherm for the chemical adsorption (chemisorption) of a gas (or liquid) to a solid surface is deduced by kinetic interpretation of the adsorption equilibrium. Alternatively, it is derived by introduction of the chemical potential of free and occupied sites and consideration of the equilibrium condition.

15.1 Surface tension, surface energy
15.2 Surface effects
15.3 Adsorption at liquid surfaces
15.4 Adsorption at solid surfaces
15.5 Applications

16. **Basic Concepts of Kinetics**

The branch of physical chemistry called chemical kinetics is concerned with the temporal course of chemical reactions. After defining the fundamental quantities of rate and rate density of a reaction, different techniques for their measurement in slow and fast reactions are presented. Finally, the rate laws of first- and second-order reactions are discussed.

16.1 Introduction
16.2 Rate of a chemical reaction
16.3 Rate density
16.4 Measurement of the rate density
16.5 Rate laws for single-step reactions

17. **Kinetics of Complex Reactions**

Kinetic measurements show that the simple rate laws known from Chapter 16 are often not sufficient for a correct description of the temporal course of a reaction or the composition of a reaction mixture. Three fundamental types of complex reactions are discussed in this chapter.

17.1 Introduction
17.2 Balanced reactions
17.3 Parallel reactions
17.4 Consecutive reactions

18. **Theory of Reaction Rate**

First, the temperature dependence of reaction rates is described empirically by the Arrhenius equation. A more detailed view will be given by the collision theory and the transition state theory.

18.1 Temperature dependence of reaction rates
18.2 Collision theory
18.3 Transition state theory
18.4 Molecular interpretation of the transition state
19. Catalysis

The acceleration (or deceleration) of chemical reactions by addition of small amounts of a substance (catalyst or inhibitor) will be discussed. The kinetics of enzymes, the vitally essential biological catalysts, and also the technically important heterogeneous catalysis are presented in more detail.

19.1 Introduction
19.2 Mechanism of action of a catalyst
19.3 Enzyme kinetics
19.4 Heterogeneous catalysis

20. Transport Phenomena

Diffusion can play an important role for the kinetics of chemical reactions in solutions. Additionally, other transport phenomena such as internal friction and entropy conduction will be discussed.

20.1 Diffusion-controlled reactions
20.2 Rate of diffusion
20.3 Viscosity
20.4 Entropy conduction
20.5 Comparative survey of the transport phenomena

21. Electrolytic Solutions

A discussion of the chemical drive of solvation and hydration, respectively, leads to the introduction of the basic concepts of electrolytic dissociation and electric potential. Subsequently, the migration of ions as a special case of spreading of substances in space under the influence of electric fields is discussed. The ionic mobilities provide a link to conductivity and transport numbers.

21.1 Electrolytic dissociation
21.2 Electric potential
21.3 Ionic migration
21.4 Conductivity of electrolytic solutions
21.5 Concentration dependence of conductivity
21.6 Transport numbers

22. Electrode Reactions and GALVANI Voltage

The electrochemical potential $\tilde{\mu}$ and the electron potential $\mu_e$ are introduced to characterize processes in which charge-carrying substances are involved. This allows us to discuss the behavior of an electrode in contact with another metal and subsequently, its behavior in contact with an electrolyte resulting in the formation of an electrical double layer. Finally, redox reactions as well as the NERNST equation and its applications to different systems like redox electrodes, gas electrodes, membrane electrodes etc. are presented.

22.1 GALVANI voltage und electrochemical potential
22.2 Electron potential in metals and contact voltage
22.3 GALVANI voltage between metal and solution
22.4 Redox reactions
22.5 GALVANI voltage of half-cells
22.6 GALVANI voltage at interfaces of liquids
22.7 GALVANI voltage at membranes

23. Redox Potentials and Galvanic Cells

The correlation between the drive of the cell reaction and the cell voltage will be discussed. Different examples such as the DANIELL cell and technical applications such as dry batteries and fuel cells will be presented.

23.1 Measurement of redox potentials
23.2 Cell voltage
23.3 Technical applications of galvanic cells

Appendix
A1 Basic mathematical principles
A2 Tables
4. Chemical Potential

**Topic:** Chemical potential as measure of a general tendency of substances to transform, and as central concept of chemical dynamics.

### 4.1 Introduction

After our short excursion into thermodynamics, we will now turn to the chemical potential $\mu$ which—along with the amount of substance $n$—is the most important and far reaching concept in chemical dynamics.

**HERACLITUS** concluded from observations of his environment that “Everything flows—Nothing stands still ($\piάντα ρεῖ$).” Creation and decay are well known in the living world but there are also forces in inanimate nature which change the things around us more or less rapidly (Experiment 4.1):

- Bread dries out,
- Paper turns yellow,
- Iron rusts,
- Rocks weather,
- Butter or fat becomes rancid,
- Rubber becomes brittle,
- Copper gets a patina,
- Clay petrifies, and so on.

**Experiment 4.1:** Changes in the world of substances.


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.

Acrylic acid (propenoic 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 (Experiment 4.2). Thereby, the small acrylic acid molecules combine to form long chains:

...+ CH$_2$=CH + CH$_2$=CH... $\rightarrow$ ...–CH$_2$–CH–CH$_2$–CH–... .

**Experiment 4.2:** Aging of acrylic acid.

The transformation of pure substances such as the weathering of soda and Glauber’s salt in ambient air where the large colorless crystals become covered with a white powdery crust as they lose water,
Na₂CO₃·10 H₂O → Na₂CO₃·7 H₂O + 3 H₂O,  
Na₂SO₄·10 H₂O → Na₂SO₄ + 10 H₂O,

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

\[
\begin{align*}
\text{S|β} & \rightarrow \text{S|α} \\
\text{P|white} & \rightarrow \text{P|red}
\end{align*}
\]

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 sulphide is formed because the starting substances iron and sulphur 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 sulphur, the differences are very pronounced. For example, magnesium, when mixed with sulphur and ignited, explodes violently. In contrast, the last metal powder, gold, does not react with sulphur at all:

\[
\begin{align*}
\text{Mg} & \rightarrow \text{Zn} & \rightarrow \text{Fe} & \rightarrow \text{Cu} & \rightarrow \text{Au} \\
\text{explosive} & & \text{glaring} & \text{glowing} & \text{glimmering} & \text{nothing!}
\end{align*}
\]

On the basis of the violence of reaction, we arrive at the following sequence:

MgS < ZnS < FeS < CuS < AuS.

Obviously, magnesium sulphide is the easiest to produce meaning it has the weakest tendency to transform. Gold sulphide, on the other hand, seems to have a relatively strong tendency to transform. It is possible, however, to obtain various compounds of gold and sulphur 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 the tendency to transform and its quantitative description with the help of the 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, as well as
  - 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 A, 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, A → A*, or to react with other substances A’, A’’ …,

\[
A + A' + ... \rightarrow ... .
\]

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

\[
A|\alpha \rightarrow A|\beta
\]

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:

\[
A|\text{location 1} \rightarrow A|\text{location 2} .
\]

The chemical potential \( \mu \) is a measure of the strength of this tendency. We write \( \mu_A \) or \( \mu(A) \) to signify the potential of substance A. The greater \( \mu \), the more active or “bustling” the substance. The smaller \( \mu \), 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 \( \mu_A \), 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 A. In order to express these relations, we may write
\[ \mu_A(T, p, c \ldots, S \ldots) \quad \text{or} \quad \mu(A, T, p, c \ldots, S \ldots). \]

Experiment 4.3 illustrates how a substance reacts to a changed milieu. In this case, it is the change of solvent S.

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. Obviously, 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.

**Experiment 4.3:** Iodine in different milieu.

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 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 upwards (maybe balloons) are attached to the scale.

**Fig. 4.1:** Weight as model.

This behavior can also be expressed mathematically:

The left side wins, i.e. the objects \( A', A'' \ldots \) on the left side of the balance scale or seesaw are successful against the objects \( B', B'' \ldots \) on the right side in their attempt to sink downward if

\[ G(A') + G(A'') + \ldots > G(B') + G(B'') + \ldots. \]
Equilibrium is established when the sums of the weights on the left and right side of the scale are just equal,

\[ G(A^-) + G(A^{--}) + \ldots = G(B^-) + G(B^{--}) + \ldots . \]

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

\[ A^+ + A^{--} + \ldots \rightarrow B^- + B^{--} + \ldots , \]

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

\[ \mu(A^-) + \mu(A^{--}) + \ldots > \mu(B^-) + \mu(B^{--}) + \ldots \]

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

\[ \mu(A^-) + \mu(A^{--}) + \ldots = \mu(B^-) + \mu(B^{--}) + \ldots . \]

Fig. 4.2: Burning candle as example.

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

\[ 3 \mu(O_2) + 2 \mu((CH_2)) > 2 \mu(CO_2) + 2 \mu(H_2O). \]

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 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, a drop in the potential 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 doing so. We do not even have to bore a hole in the cup for the barrier to be overcome. A bent straw is already enough. When candle wax and air are put together, no fire occurs. The candle wick and flame work as a siphon or valve 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 upwards, 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 condi-
tions, 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 you need to look out for.

The adjoining figure 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 level 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.

There is a simple way out of this dilemma. The heights of mountains are not referred to the geocentre 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.

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

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 („Die chemische Affinität“, 1972, 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 1000 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:

\[
\begin{align*}
N_2 + 3 H_2 & \rightarrow 2 NH_3 \\
\mu: & \begin{array}{c}
0 \\
0.3 \cdot 2 \cdot (-16)
\end{array} & \begin{array}{c}
2.000 \\
2.2968
\end{array} & \Rightarrow (\mu(N_2) + 3 \mu(H_2) - 2 \mu(NH_3) = +32 \text{ kG}
\end{align*}
\]

N appears two times on the left as well as on the right side of the conversion formula, H, however, six times. Therefore, if the chemical potential of a substance is increased by a fixed, although arbitrary summand (say 1000 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. But 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 Chapter 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 \( \mu^\Theta \) to designate \( \mu \) values at standard conditions. Thus, it follows that (if E represents any arbitrary element in its most stable modification):

\[
\mu^\Theta(E) = 0.
\]

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 und \( \mu(E) \) correspondingly \( \frac{1}{2} \mu^\Theta(E_2) \).

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 can replace those of differences 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), $\mu(T, p, ...)$). 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:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>$\mu^\ominus$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pure substances</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>s</td>
</tr>
<tr>
<td>Graphite</td>
<td>C</td>
<td>graphite</td>
</tr>
<tr>
<td>Diamond</td>
<td>C</td>
<td>diamond</td>
</tr>
<tr>
<td>Water</td>
<td>H_{2}O</td>
<td>l</td>
</tr>
<tr>
<td>Water vapor</td>
<td>H_{2}O</td>
<td>g</td>
</tr>
<tr>
<td>Table salt</td>
<td>NaCl</td>
<td>s</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO_{2}</td>
<td>s</td>
</tr>
<tr>
<td>Marble</td>
<td>CaCO_{3}</td>
<td>s</td>
</tr>
<tr>
<td>Cane sugar</td>
<td>C_{12}H_{22}O_{11}</td>
<td>s</td>
</tr>
<tr>
<td>Paraffin wax</td>
<td>\approx(CH_{2})</td>
<td>s</td>
</tr>
<tr>
<td>Benzene</td>
<td>C_{6}H_{6}</td>
<td>l</td>
</tr>
<tr>
<td>Acetylene (ethyne)</td>
<td>C_{2}H_{2}</td>
<td>g</td>
</tr>
<tr>
<td><strong>In water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cane sugar</td>
<td>C_{12}H_{22}O_{11}</td>
<td>w</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH_{3}</td>
<td>w</td>
</tr>
<tr>
<td>Hydrogen(I)</td>
<td>H^{+}</td>
<td>w</td>
</tr>
<tr>
<td>Calcium(II)</td>
<td>Ca^{2+}</td>
<td>w</td>
</tr>
</tbody>
</table>

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 (cf. Section 1.6); modifications can be characterized by the relevant descriptions such as diamond, graphite, etc.

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 Sections 4.7 and 4.8.

**Dissolved substances.** The potential of a substance A changes if it is brought into another milieu for example by dissolving it. In this context, what matters is not only the type of the solvent but also the concentration of A. Therefore, the concentration $c$ of a dissolved substance, for which the tabulated value will be valid, must be specified in addition to $p$ and $T$.

We always assume water to be the solvent unless otherwise stated. The usual reference value is $1 \text{ kmol} \text{ m}^{-3} (= 1 \text{ mol} \text{ L}^{-1})$. For the symbol to describe the state we utilize the addition |w. There exist some peculiarities concerning the determination of these standard values (like in the case of gases) but we will discuss them in Section 6.2.

We can summarize:

$$
\mu^\Theta = \mu(p^\Theta, T^\Theta) \quad \text{for pure substances} \\
\mu^\Theta = \mu(p^\Theta, T^\Theta, c^\Theta) \quad \text{for dissolved substances}
$$

$T^\Theta, p^\Theta, c^\Theta$ indicate **standard temperature, standard pressure and standard concentration**.

**Zero-order approximation.** As long as the temperature does not vary by more than $\pm 10 \text{ K}$, and pressure and concentration do not fluctuate more than a power of ten, the changes of potential of substances of low molecular mass remain about $\pm 6 \text{ kG}$ 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 $\mu^\Theta$ 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

$$
\text{CO}_3^{2-} \rightarrow \text{C} + \frac{3}{2} \text{O}_2 + 2 \text{e}^- .
$$

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

$$
\mu^\Theta(\text{H}^+|w) = 0 .
$$
At first, this seems surprising because we know that the chemical potential of an element at standard conditions is zero, i.e. \( \mu^\Theta = 0 \). This is of course also valid for hydrogen, \( \mu^\Theta(H_2|g) = 0 \). That is why we expect that other states of hydrogen would show divergent \( \mu^\Theta \) 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:

\[
H_2|g \rightleftharpoons 2 H^+|w + 2 e^-
\]

with

\[
\mu^\Theta(H_2|g) = 2 \mu^\Theta(H^+|w) + 2 \mu^\Theta(e^-).
\]

When \( H_2 \) and \( H^+ \) are present at standard conditions and equilibrium has been established, the chemical potential of the electrons, \( \mu^\Theta(e^-) \), is supposed to be zero (the electron potential \( \mu(e^-) \), abbreviated \( \mu_e \), will be discussed in more detail in Chapter 22). Because \( \mu^\Theta(H_2|g) \) disappears by definition, it follows necessarily that in a state of equilibrium, \( \mu^\Theta(H^+|w) \) 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 \( \mu^\Theta = 0 \) (see also Table 4.3 at the end of this chapter or Table A2.1 in the appendix). This is for example valid for molecular hydrogen \( \mu^\Theta(H_2|g) = 0 \), while atomic hydrogen has a rather high positive potential \( \mu^\Theta(H|g) = +203 \) kG. This means that its tendency to transform into \( H_2 \) is very strong.

A look at Tables 4.3 and A2.1 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 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 vividly. In one instance, a small amount of the attractive orange crystals of tetrasulphur tetranitride \( S_4N_4 \) (\( \mu \approx +500 \) kG) explodes (like a cap for use in toy guns) when hit lightly with a hammer (Experiment 4.4). In the other, the easily produced black nitrogen triiodide \( NI_3 \) (\( \mu \approx +300 \) kG) decomposes in a dry state if touched by a feather or irradiated by a flash of light. It produces a sharp explosive sound (Experiment 4.5). Further examples would be heavy metal azides such as lead azide \( Pb(N_3)_2 \) (used as igniters) or silver azide \( AgN_3 \).
Experiment 4.4: Decomposition of $\text{S}_2\text{N}_4$ caused by a blow.  

Experiment 4.5: Decomposition of $\text{NI}_3$ caused by a flash light.

However, a positive $\mu$ does not always mean that the substance must be explosive. For example, benzene remains rather stable in spite of its $\mu^\Theta$ value of +125 kG. As discussed in Section 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:

| | $\text{CO}_2|_g$ | $\text{NO}_2|_g$ | $\text{ClO}_2|_g$ |
|---|---|---|---|
| $\mu^\Theta / \text{kG}$ | −394 | +52 | +123 |

The gas $\text{CO}_2$ with its strongly negative $\mu^\Theta$ value is stable and is spontaneously generated from carbon and oxygen, i.e., carbon is “combustible.” $\text{NO}_2$ with positive $\mu^\Theta$ is not formed spontaneously from $\text{N}_2$ and $\text{O}_2$, but is so stable that it is not dangerous to handle. Finally, $\text{ClO}_2$ has an even higher chemical potential and is extremely explosive.

A similar consideration can be used for solid oxides:

| | $\text{Al}_2\text{O}_3|_s$ | $\text{Fe}_2\text{O}_3|_s$ | $\text{Au}_2\text{O}_3|_s$ |
|---|---|---|---|
| $\mu^\Theta / \text{kG}$ | −1582 | −741 | +78 |

Aluminum and iron combine with oxygen to form their stable oxides, while solid $\text{Au}_2\text{O}_3$ must be handled carefully so that no oxygen separates from it.

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

| | $\text{MgS}|_s$ | $\text{ZnS}|_s$ | $\text{FeS}|_s$ | $\text{CuS}|_s$ | “$\text{AuS}”|_s$ |
|---|---|---|---|---|---|
| $\mu^\Theta / \text{kG}$ | −344 | −199 | −102 | −53 | > 0 |

The sequence deduced in Section 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 charac-
teristic such as the violence of reaction that is dependent upon different factors can only be considered evidence under comparable conditions.

4.6 “Chemical drive” and application in chemistry

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

$$A' + A'' + ... \rightarrow B' + B'' + ...$$

is possible when the following is valid:

$$\mu(A') + \mu(A'') + ... > \mu(B') + \mu(B'') + ... .$$

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

$$\mu(A') + \mu(A'') + ... - \mu(B') - \mu(B'') - ... > 0$$

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

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

the chemical drive $A$ of the process (reaction, phase transition, redistribution, etc.), in short, the drive, when it is clear that no non-chemical influences are participating. The unit for drive is “Gibbs,” as can be easily seen in the above definition.

Internationally, the quantity $A$ is 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 (International Union of Pure and Applied Chemistry) is $A$. So as to avoid confusion with other quantities labelled 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),
4. Chemical Potential

\[ U = \varphi_{\text{initial}} - \varphi_{\text{final}} \]

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 (light-bulb, resistor, diode, etc.).

The quantity \( A \) has a centuries old history under the name \textit{affinity}. The first table with values of this quantity was compiled by Louis-Bernard Guyton de Marveau in 1786. This was one 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, \( A > 0 \), “drives” a transformation as long as there are reactants available. A negative, \( A < 0 \), leads to a reaction in the opposite direction of the reaction arrow. \( A = 0 \) 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, ..., \( A_\alpha B_\beta C_\gamma \ldots \rightarrow v_A A + v_B B + v_C C + \ldots \), in which case the conversion number \( v_A \) is numerically equal to \( \alpha \), \( v_B \) to \( \beta \) etc.

For the strength of the tendency to decompose—the “drive to decompose” —we then obtain:

\[ A = \mu_{A,B,C,\ldots} - [v_A \mu_A + v_B \mu_B + v_C \mu_C + \ldots] \]

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:

\[ A = \mu_{A,B,C,\ldots} = \mu_{A,B,C,\ldots}^\oplus = \frac{v_A \mu_A^\oplus + v_B \mu_B^\oplus + v_C \mu_C^\oplus + \ldots}{0} \]

These circumstances were already anticipated and taken into consideration by our discussion in Section 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:

\[
\begin{align*}
\text{O}_3|_{\text{g}} & \rightarrow \frac{3}{2} \text{O}_2|_{\text{g}} \\
\mu^\oplus & : 163 > \frac{3}{2} \cdot 0 \text{ kG} \\
\Rightarrow & \quad A^\oplus = +163 \text{ kG}
\end{align*}
\]
In this case $\mathcal{A}^\Theta$ refers to the drive to decompose under standard conditions. The decomposition process is so slow, however, that ozone can be technically used despite of 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:

$$\mathcal{A}^\Theta(2 \text{ O}_3 \rightarrow 3 \text{ O}_2) = +326 \text{ kG},$$
$$\mathcal{A}^\Theta(\text{O}_3 \rightarrow \frac{3}{2} \text{ O}_2) = +163 \text{ kG}.$$

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 $\zeta$ values (Section 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:

$$A \rightarrow B \text{ is spontaneously possible if } \mu_A > \mu_B \text{ i.e. } \mathcal{A} > 0.$$

A suitable substance for an example is mercury iodide HgI$_2$, which appears in beautiful red and yellow modifications with somewhat different chemical potentials:

$$\text{HgI}_2|\text{yellow} \rightarrow \text{HgI}_2|\text{red}$$

$$\mu^\Theta: \quad -101.1 \quad > \quad -101.7 \quad \text{ kG}$$

$$\Rightarrow \quad \mathcal{A}^\Theta = +0.6 \text{ kG}$$

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. 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 side 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 $\Gamma^-$, is used. At first, the precipitate is sallow yellow, which immediately turns to orange and finally to deep red (left, in the figure).

**Experiment 4.6: Change of Modification of HgI$_2$.**

**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:

$$\text{H}_2\text{O}|s \rightarrow \text{H}_2\text{O}|l$$

$$\mu^\Theta: \quad -236.6 \quad > \quad -237.1 \quad \text{ kG}$$

$$\Rightarrow \quad \mathcal{A}^\Theta = +0.5 \text{ kG}$$
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.

Diamond should undergo a transition into graphite because it has a higher chemical potential:

\[
\begin{align*}
\text{C}_{\text{diamond}} & \rightarrow \text{C}_{\text{graphite}} \\
\mu^\Theta: & \quad 2.9 \quad > \quad 0 \quad \text{kG} \\
\Rightarrow & \quad \Delta^\Theta = +2.9 \text{ kG}
\end{align*}
\]

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 \(\Delta\) 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 \(\rightarrow\) liquid \(\rightarrow\) 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. If a few pieces of marble are put in hydrochloric acid, an aqueous solution of hydrogen chloride, HC\(_1\), a strong effervescence of carbon dioxide can be observed (Experiment 4.7).

**Experiment 4.7: Dissolution of marble in hydrochloric acid.**

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 HC\(_1\) 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.

\[
\begin{align*}
\text{CaCO}_3|s + 2 \text{H}^+|w & \rightarrow \text{Ca}^{2+}|w + \text{CO}_2|g + \text{H}_2\text{O}|l \\
\mu^\Theta: & \quad -1129 \quad 2 \quad 0 \quad -554 \quad -394 \quad -237 \quad \text{kG} \\
\Rightarrow & \quad \Delta^\Theta = +56 \text{ kG}
\end{align*}
\]

Another example is the development of hydrogen chloride gas when concentrated sulphuric acid reacts with table salt:
4. Chemical Potential

\[
\text{NaCl}_s + \text{H}_2\text{SO}_4|_l \rightarrow \text{HCl}_g + \text{NaHSO}_4|_s
\]

\[
\mu^\theta: \begin{array}{cccc}
-384 & -690 & -95 & -993 \\
\end{array} \begin{array}{c}
kG \\
\hline
-1074 > -1088
\end{array}
\]

\[\Rightarrow \text{A}^\theta = +14 \text{ kG}\]

For lack of better criteria, it is common to explain the fact that hydrogen chloride can be obtained from table salt and concentrated sulphuric 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 to the contrary: If gaseous hydrogen sulphide is made to flow over anhydrous, white copper sulphate, black copper sulphide is produced. This let us observe the reaction easily.

**Experiment 4.8:** Blackening of CuSO$_4$ by H$_2$S.

\[
\text{CuSO}_4|_s + \text{H}_2\text{S}_g \rightarrow \text{CuS}_s + \text{H}_2\text{SO}_4|_l
\]

\[
\mu^\theta: \begin{array}{cccc}
-661 & -33 & -53 & -690 \\
\end{array} \begin{array}{c}
kG \\
\hline
-694 > -743
\end{array}
\]

\[\Rightarrow \text{A}^\theta = +49 \text{ kG}\]

In this case, the weak, volatile acid H$_2$S displaces the strong, low volatile sulphuric acid H$_2$SO$_4$ from its salt (which contradicts both rules mentioned above).

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

\[
\text{Pb}^{2+}|_w + 2 \text{I}^-|_w \rightarrow \text{PbI}_2|_s
\]

\[
\mu^\theta: \begin{array}{cccc}
-24 & 2 \cdot (-52) & -174 \\
\end{array} \begin{array}{c}
kG \\
\hline
-128 > -174
\end{array}
\]

\[\Rightarrow \text{A}^\theta = +46 \text{ kG}\]

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 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.)
Precipitation expected (+), not expected (−):

<table>
<thead>
<tr>
<th></th>
<th>CO$_3^{2−}$</th>
<th>S$^{2−}$</th>
<th>I$^{−}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$^{2+}$</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>+</td>
<td>+</td>
<td>−</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
</tbody>
</table>

Table 4.2: Prediction of precipitation reactions.

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.

**Experiment 4.9:** Precipitation of Pb$^{2+}$, Zn$^{2+}$, Ba$^{2+}$ by S$^{2−}$.

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

**Experiment 4.10:** Carbide lamp.

$$\text{CaC}_2|_s + 2 \text{H}_2\text{O}|_l \rightarrow \text{Ca(OH)}_2|_s + \text{C}_2\text{H}_2|_g$$

$$\mu^\Theta: \begin{pmatrix} -65 \\ 2(-237) \end{pmatrix} -898 +210 \text{ kG}$$

$$\begin{pmatrix} -539 \\ > \end{pmatrix} -688$$

$$\Rightarrow \ A^\Theta = +149 \text{ kG}$$

The gas is produced when water is poured onto the carbide. Both of these substances have negative chemical potentials which might give the impression of the reaction running “uphill,” against the potential drop. But the very low chemical potential of calcium hydroxide on the product side makes sure that the chemical drive $A$ is generally positive, even though $\mu$(ethyne) is $> 0$.

**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 behavior of solutions 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 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:

\[
\begin{align*}
\text{C}_{12}\text{H}_{22}\text{O}_{11}|s & \rightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11}|w \\
\mu^\Theta: & \quad -1558 > -1565 \quad \text{kG} \\
\Rightarrow & \quad A^\Theta = +7 \text{ kG}
\end{align*}
\]

\(A^\Theta > 0\) means that the sugar dissolves by itself even in such a concentrated solution. Sugar dissolves easily, as we know from using it every day. The process becomes noticeable by the sugar cube shrinking in a glass of tea even when it is not touched (Experiment 4.11).

**Experiment 4.11:** Sugar cube in aqueous solution (or water).

An even more impressive version of this process is stacking sugar cubes into a tower on a plate with water in it. The tower dissolves into a pool in the plate.

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

\[
\begin{align*}
\text{NaCl}|s & \rightarrow \text{Na}^+|w + \text{Cl}^-|w \\
\mu^\Theta: & \quad -384 -262 -131 \quad \text{kG} \\
\Rightarrow & \quad A^\Theta = +9 \text{ kG}
\end{align*}
\]

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

\[
\begin{align*}
\text{I}_2|s & \rightarrow \text{I}_2|w \\
\mu^\Theta: & \quad 0 +16 \quad \text{kG} \\
\Rightarrow & \quad A^\Theta = -16 \text{ kG}
\end{align*}
\]

The chemical drive is strongly negative so the process can only run backwards 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 Chapter 6.

Even the solution 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:

\[
\begin{align*}
\text{NH}_3|g & \rightarrow \text{NH}_3|w \\
\mu^\Theta: & \quad -16 > -27 \quad \text{kG} \\
\Rightarrow & \quad A^\Theta = +11 \text{ kG}
\end{align*}
\]
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):

**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 so drastically that 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 Chapter 7).

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

\[
\text{CO}_2|_g \rightarrow \text{CO}_2|_w
\]

\[
\begin{align*}
\mu^\Theta: & \quad -394 \quad > \quad -386 \quad \text{kG} \\
\Rightarrow \quad A^\Theta & = -8 \text{ kG}
\end{align*}
\]

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 (Experiment 4.13).

**Experiment 4.13:** Effervescence of carbon dioxide.

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 $\mu^\Theta$ 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 $\mu^\Theta$ of the reactants and products. Let us take a closer look at the reaction of copper sulphate with hydrogen sulphide as an example (Fig. 4.4).

**Fig. 4.4:** Potential diagram for the reaction CuSO$_4$ + H$_2$S $\rightarrow$ H$_2$SO$_4$ + CuS under standard conditions: a) Levels of the potential for the substances involved and b) adding of the values of the potential in the initial and the final state of reaction.
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.

### 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 resulting substances, i.e., the drives \( \mathcal{A} = \sum_{\text{initial}} \mu_i - \sum_{\text{final}} \mu_j \) 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 \( \mathcal{A}_i \) 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 \( \mathcal{A}_i \) must then be converted to standard units.

Data in a SI coherent unit are desirable. G (Gibbs) is an example which has already been used 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 \( \mathcal{A}_i \) 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, 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 \( T = 273.16 \) K.

The cell in Figure 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.

**Fig. 4.5:** Cell representing a fixed value of drive \( \mathcal{A} \).

This example shows the solidification of supercooled heavy water (freezing point 276.97 K)

\[
\text{D}_2\text{O}_1 \rightarrow \text{D}_2\text{O}_s,
\]

which is embedded in airless light water and...
whose temperature is brought to 273.16 K. The transformation happens spontaneously if the D₂O 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

\[ A_l = 84 \text{ G}. \]

As we have already seen in the example of weight (Section 1.3), there are basically three agreements necessary for metricization. These are agreements about
a) sign,
b) sum,
c) unit

of the quantity \( A \) 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 Section 4.5: A process that runs forward spontaneously receives a positive value of drive \( A > 0 \), one that tends to run backward against the direction of the reaction arrow, receives a negative value \( A < 0 \), and a process that does neither is in equilibrium and has the value \( A = 0 \).

Now we need only think about creating sums (point b). Two or more transformations with the drives \( A', A'', A''' \ldots \) 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 \( A_{\text{total}} \) of the entire process, i.e. of the sequence of the coupled processes, is the sum of the drives of these processes:

\[ A_{\text{total}} = A' + A'' + A'''+ \ldots . \]

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 is 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:

\[
\begin{align*}
A + B + \ldots & \rightarrow C + D + \ldots + \underbrace{Z} \\
Z + \ldots + F + G & \rightarrow H + I + \ldots .
\end{align*}
\]

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 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 breathed air in it that contains carbon dioxide. In the process, the first two reactions are coupled by dissolved \( \text{CO}_2 \), the next by \( \text{HCO}_3^- \) and the last by \( \text{CO}_3^{2-} \).
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).

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

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,
4. Chemical Potential

\[ e^- + B^+ + C \rightarrow D + E. \]

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:

\[ \mathcal{A}_{\text{total}} = m \cdot \mathcal{A} + n \cdot \mathcal{A}_1 = 0 \quad \text{or} \quad \mathcal{A} = -\left( \frac{n}{m} \right) \cdot \mathcal{A}_1. \]

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. 4.7 a). Like those vehicles, it is possible to inversely couple \( m \) galvanic cells which represent a particular reaction with unknown \( \mathcal{A} \) to \( n \) cells based on a reaction with known drive such as the unit reaction \( (\mathcal{A}_1) \) so that equilibrium is established and the electric current in the circuit is zero (Fig. 4.7 b). As mentioned earlier, we achieve the inverse coupling through reverse poling, i.e., by interchanging the positive and the negative terminals.

**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.

The procedure can be simplified considerably. For example, it is possible to calibrate a sufficiently sensitive highly resistive galvanometer directly in the unit \( \mathcal{A}_1 \). 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
4. Chemical Potential

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 (Section 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) (Section 6.4), calorimetric (Section 8.8), electrochemical (Section 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 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 A, 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.

![Fig. 4.8: Hypothetical arrangement for measuring chemical potentials $\mu$.](image)

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 A, 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), then sent to the container on the right in the desired form of A (solid or liquid, warm or cold, pure or dissolved, etc.). One might say that the reactor transports substance A 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 $\mu_A$. 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 A 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 \( A \) to transform, 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 \( n \):

\[
\mu = \frac{W_{\rightarrow n}}{n}.
\]

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

\[
\mu = \frac{dW_{\rightarrow n}}{dn}.
\]

It is of course necessary to avoid or subtract all energy contributions due to side effects (for example, 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 \( A \)) runs spontaneously from left to right, it releases energy. In this case, \( W_{\rightarrow n} \), 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 \( \mu = \frac{dW_{\rightarrow n}}{dn} \) 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,” in a manner analogous to “Volt” for the electric potential difference as we have done in Section 4.5:

\[
1 \text{ Gibbs (G)} = 1 \text{ J mol}^{-1}.
\]

Naturally, the energy of the portions of the elements taken from the left are to be found in the substance \( A \) 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 Section 4.4). Only the additional quantity \( dW_{\rightarrow n} \), which we can identify with \( \mu dn \), matters. Together with substance \( A \), it is added to the system on the right and so increases its energy. We could use the increase \( dW \) of \( W \) to infer the value of \( dW_{\rightarrow n} = \mu dn \), 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 (Section 1.6), the energy \( W \) may change as a result of different processes, such as transfer or generation of entropy (see Section 3.11), increase or decrease of volume (Section 2.5), or by taking in other substances \( A', A'', A''', \ldots \) etc.
4. Chemical Potential

\[
dW = -p\,dV + TdS + \mu\,dn + \mu'\,dn' + \mu''\,dn'' + \ldots
\]

To avoid interferences caused by the different paths for energy transfer, we require \(S, V, n', n''\) to be held constant, i.e., \(dS, dV, dn', dn''\), \(= 0\), so that the related energy contributions vanish:

\[
dW = -p\,dV + TdS + \mu\,dn + \mu'\,dn' + \mu''\,dn'' + \ldots = (dW)_{S,V,n',n''}\ldots
\]

If we introduce \(\mu = dW_{,n}/dn\) into this equation, this yields

\[
\mu = \left(\frac{dW}{dn}\right)_{S,V,n',n''} = \left(\frac{\partial W}{\partial n}\right)_{S,V,n',n''}\ldots
\]

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 \(x, V, S, n', n''\ldots\) 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 Section 1.3 to indirectly determine the weight \(G\) of a body via the energy:

\[
G = \left(\frac{dW}{dh}\right)_v = \frac{(dW)_v}{dh}.
\]

Here, \(dW\) is the energy used to lift the object a small distance \(dh\). The index \(v\) 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

\[
G = \left(\frac{dW}{dh}\right)_{p,S,n}
\]

where, for consistency’s sake, we have changed the variable \(v\) to the momentum \(p = mv\). 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” or “force-like” quantity in the sense of HELMHOLTZ (see Section 2.7).
4. Chemical Potential

Table 4.3: Chemical potential $\mu$ and its temperature and pressure coefficients $\alpha$ and $\beta$ under standard conditions (298 K, 100 kPa, dissolved substances at 1 kmol m$^{-3}$).

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\mu^\ominus$ (kG)</th>
<th>$\alpha$ (kG K$^{-1}$)</th>
<th>$\beta$ (kG Pa$^{-1}$)</th>
<th>Substance</th>
<th>$\mu^\ominus$ (kG)</th>
<th>$\alpha$ (kG K$^{-1}$)</th>
<th>$\beta$ (kG Pa$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>s</td>
<td>0</td>
<td>-0.027</td>
<td>7.1</td>
<td>HCl</td>
<td>g</td>
<td>-95</td>
</tr>
<tr>
<td>NaCl</td>
<td>s</td>
<td>-384</td>
<td>-0.072</td>
<td></td>
<td>H$_2$SO$_4$</td>
<td>w</td>
<td>-690</td>
</tr>
<tr>
<td>NaHSO$_4$</td>
<td>s</td>
<td>-993</td>
<td>-0.113</td>
<td></td>
<td>Na$_2$SO$_4$</td>
<td>s</td>
<td>-1270</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>s</td>
<td>-856</td>
<td>-0.041</td>
<td></td>
<td>CuSO$_4$</td>
<td>s</td>
<td>-661</td>
</tr>
<tr>
<td>CaCO$_3$</td>
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<td>-0.093</td>
<td>36.9</td>
<td>CuS</td>
<td>s</td>
<td>-53</td>
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<tr>
<td>C$_{12}$H$<em>2$O$</em>{11}$</td>
<td>s</td>
<td>-1558</td>
<td>-0.392</td>
<td></td>
<td>H$_2$S</td>
<td>g</td>
<td>-33</td>
</tr>
<tr>
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<td>w</td>
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<td>0.053</td>
<td>-17.8</td>
<td>CaC$_2$</td>
<td>s</td>
<td>-65</td>
</tr>
<tr>
<td>Element</td>
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<td>most stable form</td>
<td>Pb$^{2+}$</td>
<td>w</td>
<td>-24</td>
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<td></td>
</tr>
<tr>
<td>H$_2$</td>
<td>g</td>
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<td></td>
<td>Zn$^{2+}$</td>
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<td>-147</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>g</td>
<td>203</td>
<td></td>
<td>Ba$^{2+}$</td>
<td>w</td>
<td>-561</td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td>g</td>
<td>0</td>
<td></td>
<td>CO$_3^{2-}$</td>
<td>w</td>
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<td></td>
</tr>
<tr>
<td>O$_3$</td>
<td>g</td>
<td>163</td>
<td></td>
<td>S$^{2-}$</td>
<td>w</td>
<td>86</td>
<td></td>
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<tr>
<td>C</td>
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<td></td>
<td>$\Gamma$</td>
<td>w</td>
<td>-52</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>diamond</td>
<td>2.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_2$I$_3$</td>
<td>s</td>
<td>300</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S$_4$N$_4$</td>
<td>s</td>
<td>500</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>l</td>
<td>125</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>g</td>
<td>-394</td>
<td>-0.214</td>
<td></td>
<td>PbCO$_3$</td>
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</tr>
<tr>
<td>NO$_2$</td>
<td>g</td>
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<td>-0.240</td>
<td></td>
<td>ZnCO$_3$</td>
<td>s</td>
<td>-731</td>
</tr>
<tr>
<td>ClO$_2$</td>
<td>g</td>
<td>123</td>
<td>-0.257</td>
<td></td>
<td>BaCO$_3$</td>
<td>s</td>
<td>-1135</td>
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<tr>
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<td>-0.051</td>
<td></td>
<td>PbI$_2$</td>
<td>s</td>
<td>-174</td>
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<tr>
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<td></td>
<td>ZnI$_2$</td>
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<td>-209</td>
</tr>
<tr>
<td>Au$_2$O$_3$</td>
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<td></td>
<td>BaI$_2$</td>
<td>s</td>
<td>-602</td>
</tr>
<tr>
<td>MgS</td>
<td>s</td>
<td>-344</td>
<td>-0.050</td>
<td></td>
<td>C$<em>{12}$H$</em>{22}$O$_{11}$</td>
<td>w</td>
<td>-1565</td>
</tr>
<tr>
<td>ZnS</td>
<td>s</td>
<td>-199</td>
<td>-0.059</td>
<td></td>
<td>Na$^+$</td>
<td>w</td>
<td>-262</td>
</tr>
<tr>
<td>FeS</td>
<td>s</td>
<td>-102</td>
<td>-0.060</td>
<td></td>
<td>Cl$^-$</td>
<td>w</td>
<td>-131</td>
</tr>
<tr>
<td>CuS</td>
<td>s</td>
<td>-53</td>
<td>-0.066</td>
<td></td>
<td>I$_2$</td>
<td>s</td>
<td>0</td>
</tr>
<tr>
<td>AuS</td>
<td>s</td>
<td>&gt;0</td>
<td></td>
<td></td>
<td>I$_2$</td>
<td>w</td>
<td>16</td>
</tr>
<tr>
<td>HgI$_2$</td>
<td>red</td>
<td>-101.7</td>
<td>-0.180</td>
<td></td>
<td>NH$_3$</td>
<td>g</td>
<td>-16</td>
</tr>
<tr>
<td>HgI$_2$</td>
<td>yel.</td>
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<td>-0.186</td>
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<td>w</td>
<td>-27</td>
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<td>H$^+$</td>
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<td></td>
<td></td>
<td>CO$_2$</td>
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<td>-386</td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>Substances</td>
<td>$\Sigma \mu$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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</table>

The table shows the chemical potential $\mu$ and its temperature and pressure coefficients $\alpha$ and $\beta$ for various substances under standard conditions (298 K, 100 kPa, dissolved substances at 1 kmol m$^{-3}$). The most stable form of each element is noted, along with the products of the reactions involving the substances.
5. Influence of Temperature and Pressure on Transformations

**Topic:** Influence of temperature and pressure upon the chemical potential and chemical drive and consequently, the behavior of substances.

### 5.1 Introduction

Until now, the tabular values we have used were the so-called standard values based upon room temperature and standard pressure (298 K and 100 kPa). For dissolved substances, the standard concentration is 1 kmol m$^{-3}$. Up to this point, our statements about the possibility of a transformation have been valid for these conditions only.

However, temperature and pressure often have a decisive influence on the chemical potential and therefore on the course of chemical processes. Water freezes in the cold and evaporates in the heat. Cooking fat melts in a frying pan and pudding gels while cooling, ice melts under the blades of ice-skates and butane gas (the fuel of a cigarette lighter) becomes liquid when compressed. The chemical potential $\mu$ is not a material constant, but depends upon temperature, pressure and a number of other parameters.

### 5.2 Temperature dependence of chemical potential and drive

**Introduction.** To begin, let us consider as a typical example the change with temperature in the chemical potential of table salt $\mu(\text{NaCl})$ (Fig. 5.1). For comparison, the graphic also shows the temperature dependence of the chemical drive of table salt to decompose into the elements $\mathcal{A}(\text{NaCl} \rightarrow \text{Na} + \frac{1}{2} \text{Cl}_2)$.

**Example:**

$\mu(\text{NaCl})$ and $\mathcal{A}(\text{NaCl} \rightarrow \text{Na} + \frac{1}{2} \text{Cl}_2)$

**Fig. 5.1:** Chemical potential of table salt and the chemical drive to decompose according to $\text{NaCl} \rightarrow \text{Na} + \frac{1}{2} \text{Cl}_2$ depending upon temperature (at constant pressure $p^\circ$).

It is striking that the chemical potential falls more and more steeply with increasing temperature. Except for a very few exceptions of dissolved substances (e.g. Ca$^{2+}$ in aqueous solution), all substances exhibit this behavior. The tendency of a substance to transform generally decreases when it is put into a warmer environment.
The chemical drive $A(T)$ which is calculated from the temperature dependent potentials, exhibits a noticeably more linear gradient than the $\mu(T)$ curves. Both curves intersect at the standard temperature $T^\oplus$ because the chemical potential of a substance at standard conditions corresponds to the drive to decompose into the elements (here sodium and chlorine).

The drop of potential appears, at first glance, to contradict the observation that reactions progress more readily and more quickly at higher temperatures than at lower ones. But it should be noted that a higher velocity does not necessarily mean a stronger chemical drive. This can also be caused by a smaller or even vanishing inhibition as is actually often the case in chemical reactions. The strong decrease of inhibition resulting from an increase of warming masks the mostly weak change to the drive $A$. Moreover, it should be remembered that $A$ is determined by the difference of the chemical potentials of the starting substances and the products, and *not* by the absolute levels of potentials. Since the potentials of the initial substances as well as of the products decrease as a result of an increase in temperature, the potential difference which is alone responsible for the reaction drive does not necessarily decrease. It can remain constant or even increase, as in our example.

**Temperature coefficient.** In order to describe the drop of potential with increasing temperature, we will be content with a simple approach at first. For example, if one wishes to show how the length $l$ of a rod changes with temperature, this can be done with the help of a temperature coefficient which tells us by how much the length increases when its temperature is changed by 1 K. The increase in length for a temperature increase from an initial value of $T_0$ to a value of $T$ can be described by a linear equation as long as $\Delta T = T - T_0$ is not too large:

$$l = l_0 + \varepsilon \cdot (T - T_0) .$$

The initial value is represented by $l_0$ and $\varepsilon$ represents the temperature coefficient.

To indicate the change of chemical potential as a result of warming, we proceed exactly in the same manner:

$$\mu = \mu_0 + \alpha \cdot (T - T_0) .$$

Here, $\mu_0$ characterizes the initial value of the chemical potential. This represents a value at arbitrarily chosen values of temperature $T_0$, pressure $p_0$ and concentration $c_0$ (in contrast to the standard value $\mu^\oplus$). However, standard values often serve as the initial values of a calculation, so that in special cases, $\mu_0 = \mu^\oplus$ but this is not necessarily the case. The temperature coefficient $\alpha$ represents the slope of the function $\mu(T)$ at the point $(T_0; \mu_0)$ (it is therefore strictly valid only for the reference temperature $T_0$), and is therefore almost always negative, as we have seen.

For the temperature dependence of the chemical drive $A$ of a transformation

$$B' + B'' + \ldots \rightarrow D' + D'' + \ldots$$

we obtain analogously:

$$A = A_0 + \alpha \cdot (T - T_0) .$$

The temperature coefficient $\alpha$ of the drive can be calculated by the same easy to remember
procedure as the drive itself:

\[
\alpha = \alpha(B) + \alpha(B') + \ldots - \alpha(D) - \alpha(D') - \ldots
\]

(Remember: \(A = \mu(B) + \mu(B') + \ldots - \mu(D) - \mu(D') - \ldots\)).

If we take room conditions as the starting point, the error is about 1 kG for low-molecular substances for \(\Delta T\) values of about ±100 K. This approximation remains useful for rough estimates up to \(\Delta T \approx 1000\) K and above, although \(\mu(T)\) falls sharply with rising temperature. This remarkable and (for applications) important circumstance is based upon the fact that it is not the potentials that are decisive in chemical processes, but the drives. When taking the difference \(A = \sum_{\text{initial}} \mu - \sum_{\text{final}} \mu\), the progressive contributions of the functions \(\mu(T)\) largely cancel.

If higher precision is desired, the approach can be easily improved by adding more terms to the equation:

\[
\mu = \mu_0 + \alpha \cdot \Delta T + \alpha' \cdot (\Delta T)^2 + \alpha'' \cdot (\Delta T)^3 + \ldots
\]

Of course, there are other possible approaches; reciprocals for instance, or logarithmic terms. However, we do not wish to go into mathematical refinements of this type here because it is astounding how far one can actually go with the linear approximation. It is our goal here to show this.

Table 5.1 shows the chemical potential \(\mu^\oplus\) as well as its temperature coefficient \(\alpha\) for some substances.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>(\mu^\oplus) kG</th>
<th>(\alpha) G K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>s</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>l</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>g</td>
<td>368.3</td>
</tr>
<tr>
<td>Graphite</td>
<td>C</td>
<td>graphite</td>
<td>0</td>
</tr>
<tr>
<td>Diamond</td>
<td>C</td>
<td>diamond</td>
<td>2.9</td>
</tr>
<tr>
<td>Iodine</td>
<td>I(_2)</td>
<td>s</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>I(_2)</td>
<td>l</td>
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<td>g</td>
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<td></td>
<td>I(_2)</td>
<td>w</td>
<td>16.4</td>
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<tr>
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<td>H(_2)O</td>
<td>s</td>
<td>−236.6</td>
</tr>
<tr>
<td></td>
<td>H(_2)O</td>
<td>l</td>
<td>−237.1</td>
</tr>
<tr>
<td></td>
<td>H(_2)O</td>
<td>g</td>
<td>−228.6</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH(_3)</td>
<td>l</td>
<td>−10.2</td>
</tr>
<tr>
<td></td>
<td>NH(_3)</td>
<td>g</td>
<td>−16.4</td>
</tr>
<tr>
<td></td>
<td>NH(_3)</td>
<td>w</td>
<td>−26.6</td>
</tr>
<tr>
<td>Calcium(II)</td>
<td>Ca(^{2+})</td>
<td>w</td>
<td>−553.6</td>
</tr>
</tbody>
</table>

**Table 5.1:** Chemical potential \(\mu\) and its temperature coefficient \(\alpha\) for some selected substances at standard conditions (298 K, 100 kPa, dissolved substances at 1 kmol m\(^{-3}\)).
Along with the already mentioned basic rule which states that the temperature coefficient $\alpha$ is (almost) always negative, another rule (which almost all substances follow) becomes apparent when the $\alpha$ values are compared for changes of state of aggregation. The temperature coefficient $\alpha$ of the chemical potential of a substance B becomes increasingly negative when the phase changes from solid to liquid and finally to the gaseous state. The jump corresponding to the second transition (represented by the sign $<<$) is considerably greater than the one corresponding to the first one. For a substance in an aqueous solution, $\alpha$ is mostly similar to that of the liquid state. The values scatter more strongly, though, so that we cannot easily fit $\alpha(B|w)$ into the other $\alpha$-values:

$$\alpha(B|g) << \alpha(B|l) < \alpha(B|s) < 0 \quad \alpha(B|w)$$

For clarification, we will single out the values for iodine at standard conditions given in G K$^{-1}$ from Table 5.1:

$$-260.7 << -150.4 < -116.1 < 0. \quad -137.2$$

(As we will see in Section 9.3, the temperature coefficient $\alpha$ corresponds to the negative molar entropy $S_m$, i.e., $\alpha = -S_m$. Anticipating this can help us to remember the two rules above more easily: First, in Chapter 3, we demonstrated that the molar entropy is always positive; the negative sign of the temperature coefficient easily results from this (the rare exceptions mentioned above will be discussed in detail in Section 8.4). Second, the fact that the molar entropy of a liquid is greater than that of a solid, and the molar entropy of a gas is much greater than that of a liquid (see Section 3.9), leads to the sequence above).

**Phase transition.** The chemical potential of gases therefore decreases especially fast with increase in temperature. Their tendency to transform decreases most strongly so that, by comparison to other states, the gaseous state becomes more and more stable. This only means that, as a result of temperature increase, all other states must eventually transform into the gaseous state. At high temperatures, gases possess the weakest tendency to transform and therefore represent the most stable form of matter.

We will use water to take a closer look at this behavior. Under standard conditions, the chemical potential of ice, water, and water vapor has the following values:

| $\mu^\circ / \text{kG}$ | $\text{H}_2\text{O}|s$ | $\text{H}_2\text{O}|l$ | $\text{H}_2\text{O}|g$ |
|------------------------|----------------|----------------|----------------|
|                        | $-236.6$       | $-237.1$       | $-228.6$       |

One sees here that under these conditions, ice melts, and water vapor condenses because water in its liquid state has the lowest chemical potential and therefore the weakest tendency to transform. However, this changes if the temperature is raised or lowered sufficiently. For easy calculation, we will consider a temperature change of $\pm 100$ K. The following results are obtained using the linear approach:

| $\alpha / \text{G K}^{-1}$ | $\text{H}_2\text{O}|s$ | $\text{H}_2\text{O}|l$ | $\text{H}_2\text{O}|g$ |
|---------------------------|----------------|----------------|----------------|
|                           | $-45$          | $-70$          | $-189$         |
| $\mu(398 \text{ K}) / \text{kG}$ | $-241$       | $-244$         | $-248$         |
| $\mu(198 \text{ K}) / \text{kG}$ | $-232$       | $-230$         | $-210$         |
We see that at 398 K (125 °C), the chemical potential of water vapor has the smallest value and that water vapor must result from the other forms, while at 198 K (−75 °), ice must develop. This result is represented graphically in Figure 5.2.

**Fig. 5.2:** Chemical potential of water in various states at 198 K, 298 K, and 398 K.

**Phase transition temperatures.** How to calculate the phase transition temperatures now appears obvious: If a substance like lead is solid at room temperature, this is because its chemical potential has its lowest value in the solid state. The potential of liquid lead has to exceed that of solid lead, otherwise, at room temperature, it would be liquid like mercury. We will now visualize this in a diagram (Fig. 5.3):

**Fig. 5.3:** Temperature dependence of the chemical potential of the solid and liquid phase of a substance (the lowest chemical potential for each is highlighted).

\(\mu(\text{Pb}|\text{s})\) as potential of an element at room temperature (and standard pressure) is equal to zero since this value has been arbitrarily chosen as the zero point of the \(\mu\) scale. Under these conditions, \(\mu(\text{Pb}|\text{l})\) must lie above this. The chemical potentials decrease with warming. This happens more quickly in the liquid state than in the solid (according to the sequence presented above: \(\alpha(\text{B}|\text{l}) < \alpha(\text{B}|\text{s}) < 0\)). For this reason, the curves must intersect at some point, say at the temperature \(T_{\text{sl}}\). This \(T_{\text{sl}}\) is the melting point of lead because below \(T_{\text{sl}}\), the most stable state of lead is the solid state, above \(T_{\text{sl}}\), however, the most stable state is the liquid state. In order to indicate the phase transition in question, the symbols for the corresponding states of aggregation are inserted as indices (see also the comment in Section 3.9).

We can calculate the temperature \(T_{\text{sl}}\). In order to do this we have to consider the melting process

\[\text{Pb}|\text{s} \rightarrow \text{Pb}|\text{l}.\]

\(T_{\text{sl}}\) is the temperature at which the chemical potentials of solid and liquid phase are equal,

\(\mu_{\text{s}} = \mu_{\text{l}}.\)

At this temperature, the two phases are in equilibrium. The temperature dependence of \(\mu\) is expressed by the linear approximation:

\[\mu_{\text{s},0} + \alpha_{\text{s}}(T_{\text{sl}} - T_0) = \mu_{\text{l},0} + \alpha_{\text{l}}(T_{\text{sl}} - T_0).\]

By transforming this we obtain

\[(\alpha_{\text{l}} - \alpha_{\text{s}})(T_{\text{sl}} - T_0) = \mu_{\text{s},0} - \mu_{\text{l},0} \]
and respectively

\[ T_{sl} = T_0 - \frac{\mu_{s,0} - \mu_{l,0}}{\alpha_s - \alpha_l} = T_0 - \frac{A_0}{\alpha}. \]

The derivation is somewhat shortened when the following equivalent of the first equation (\( \mu_s = \mu_l \))

\[ A = 0 \]

is used as a starting point for the existence of a state of equilibrium. If the temperature dependence of the chemical drive is taken into account, we have

\[ A_0 + \alpha \cdot (T_{sl} - T_0) = 0 \]

and therefore

\[ T_{sl} = T_0 - \frac{A_0}{\alpha}. \]

Of course, strictly speaking, our result is not accurate because our formula for temperature dependence is only an approximation. The smaller \( \Delta T (:= T_{sl} - T_0) \) is, the more exact the calculated value will be. The melting point of lead is actually 601 K. Based on the tabulated standard values (Table A2.1 in the Appendix), our calculation yields

\[ T_{sl} = 298 \text{ K} - \frac{0 - 2220}{(-64.8) - (-71.7)} \frac{G}{\text{G} \cdot \text{K}^{-1}} = 620 \text{ K}. \]

The result is surprisingly good for this rough approximation.

We will now complete our diagram by adding the chemical potential of lead vapor (Fig. 5.4).

**Fig. 5.4:** Temperature dependence of the chemical potentials of a substance as solid, melt, or vapor.

At room temperature, the chemical potential of vapor lies much higher than that of the liquid phase. However, with rising temperature, \( \mu(\text{Pb}|g) \) falls rather steeply, as is usual in all gases. At some temperature \( T_{lg} \) the potential of lead vapor intersects with that of liquid lead. When this temperature is exceeded, the melted lead undergoes a transition to vapor because now vapor is the most stable state. \( T_{lg} \) is nothing other than the boiling temperature of lead melt. The boiling temperature can be calculated in the same manner as the melting temperature, only now the potentials and their temperature coefficients for liquid and gaseous states will be used.

There are substances for which the chemical potential of the vapor is relatively low compared to that of the melt. The potential of the vapor can then intersect that of the solid below the
5. Influence of Temperature and Pressure on Chemical Changes

melting point. This means that there is no temperature (for a given pressure) at which the liquid phase exhibits the lowest chemical potential and is therefore stable. Such substances do not melt when warmed but transform immediately into the vapor state (Fig. 5.5). This phenomenon is called sublimation.

Fig. 5.5: Gradients of chemical potentials of all phases as a function of temperature for sublimation.

An excellent example of such a substance is frozen carbon dioxide which has the characteristic of vaporizing without melting. Because of this it is also called “dry ice.” Sublimation temperatures \( T_{sg} \) can be calculated based on the same procedure as above.

Other transitions can be dealt with in the same way. A good object for demonstration is the already mentioned mercury iodide:

| \( \mu^\Theta / \text{kG} \) | \( \text{HgI}_2|\text{yellow} \) | \( \text{HgI}_2|\text{red} \) |
|----------------|----------------|----------------|
| \( \alpha / \text{G K}^{-1} \) | \(-101.1\) | \(-101.7\) |
| \(-186\) | \(-180\) |

When heated, the temperature coefficient of the yellow form decreases more quickly than that of the red one because \( \alpha(\text{HgI}_2|\text{yellow}) < \alpha(\text{HgI}_2|\text{red}) < 0 \), so that above a certain temperature, \( \mu(\text{HgI}_2|\text{yellow}) \) falls below \( \mu(\text{HgI}_2|\text{red}) \), making the yellow form the more stable modification. The transition temperature (398 K or 125 °C) can be calculated just like the melting point of lead and can be easily verified by experiment (Experiment 5.1).

Experiment 5.1: Heating \( \text{HgI}_2 \) to above 398 K.

Reaction temperatures. Chemists are mostly interested in “real” chemical reactions. Because the temperature changes in gases have the strongest effect on their potentials, they are what shapes the behavior of reactions. Processes which produce more gas than is used up (so-called gas forming reactions) benefit from the strongly negative temperature coefficients \( \alpha \) of gases when the temperature rises. In contrast, the chemical drive of a gas binding reaction is weakened by a rise in temperature. Consider the example of thermal decomposition of silver oxide:

\[
2 \text{Ag}_2\text{O} |\text{s} \rightarrow 4 \text{Ag} |\text{s} + \text{O}_2 |\text{g}
\]

\[
\mu^\Theta: \ 2(-11.3) \quad 4\cdot0 \quad 0 \quad \text{kG} \quad \Rightarrow \quad \lambda^\Theta = -22.6 \text{ kG}
\]

\[
\alpha: \ 2(-121) \quad 4(-43) \quad -205 \quad \text{G K}^{-1} \quad \Rightarrow \quad \alpha = +135 \ \text{G K}^{-1}
\]

The decomposition does not take place at room temperature due to the negative drive. However, since a gas should be formed, we expect that this process begins at a high enough tem-
The minimum temperature $T_D$ for the decomposition of $\text{Ag}_2\text{O}$ is obtained from the condition that the combined chemical potentials of the initial and final substances must be equal and the chemical drive $\mathcal{A}$ changes its sign:

$$\mathcal{A} = \mathcal{A}_0 + \alpha \cdot (T_D - T_0) = 0.$$ 

In analogy to the equations above, we obtain for the decomposition temperature

$$T_D = T_0 - \frac{\mathcal{A}_0}{\alpha}.$$ 

Inserting the $\mathcal{A}^\Theta$ and $\alpha$ values which are calculated according to $\alpha = 2 \cdot \alpha_{\text{Ag}_2\text{O}} - 4 \cdot \alpha_{\text{Ag}} - \alpha_{\text{O}_2}$ results in $T_D \approx 465$ K.

When the blackish brown silver oxide is heated by a burner (Experiment 5.2), the generation of a gas is detectable by the slow blowing up of the balloon. Subsequently, the gas can be identified as oxygen with a glowing splint. White shiny silver metal remains in the test tube.

**Experiment 5.2: Annealing of silver oxide.**

![Schematic of a blast furnace](image)

The same procedure can be used, for example, to calculate how strongly a compound containing crystal water must be heated in a drying oven in order to dehydrate it. Industrially important processes such as smelting of iron ore in a blast furnace (Fig. 5.6) can also be captured descriptively.

**Fig. 5.6: Schematic of a blast furnace.**

If the technical details are left out, a blast furnace can be considered a chemical reactor where iron ore, coal, and oxygen are introduced and furnace gas and pig iron exit. If this process uses the minimum amount of coal (in the conversion formula simplistically represented by carbon) it cannot take place at room temperature due to its negative chemical drive.

$$\text{Fe}_2\text{O}_3|\text{s} + 3\text{C}|\text{graphite} \rightarrow 2\text{Fe}|\text{s} + 3\text{CO}|\text{s}$$

$$\mu^\Theta: \quad -741.0 \quad 3\cdot0 \quad 2\cdot0 \quad 3\cdot(-137.2) \quad \text{kG} \quad \Rightarrow \quad \mathcal{A}^\Theta = -329.4 \text{ kG}$$

$$\alpha: \quad -87 \quad 3\cdot(-6) \quad 2\cdot(-27) \quad 3\cdot(-198) \quad \text{G K}^{-1} \quad \Rightarrow \quad \alpha = +543 \text{ G K}^{-1}$$

However, a gas is formed, so we expect that the reaction should be possible at higher temperatures. If one wishes to find out if the 700 K in the upper part of the shaft of the furnace is hot enough, the drive must be approximated for this temperature according to

$$\mathcal{A} = \mathcal{A}_0 + \alpha \cdot (T - T_0).$$

With a value of $-111$ kG, the drive is noticeably less negative, i.e., the potential difference between the reactants and products has become smaller, but the reaction still cannot take
place. Again, the minimum temperature $T_R$ needed for the reaction can be approximated by an equation equivalent to the one above:

$$ T_R = T_0 - \frac{A_0}{\alpha}. $$

We therefore obtain a value for $T_R$ of $\approx 900$ K. Extra coal is needed for the furnace to reach this temperature ($\text{Fe}_2\text{O}_3 + 7 \text{C} + \text{O}_2 \rightarrow 2 \text{Fe} + 7 \text{CO}$).

Of course, all of these calculations depend upon access to the necessary data.

5.3 Pressure dependence of chemical potential and drive

**Pressure coefficient.** As previously stated, the value of the chemical potential of a substance depends not only upon temperature, but upon pressure as well. Moreover, the potential generally increases when the pressure increases (Fig. 5.7).

Fig. 5.7: Pressure dependence of the chemical potentials of a substance in solid, liquid or gaseous state.

In a small range of pressures, all the curves can be approximated as linear, comparable to the way in which we described the influence of temperature:

$$ \mu = \mu_0 + \beta \cdot (p - p_0). $$

$\mu_0$ is the starting value of the chemical potential for the initial pressure $p_0$. The pressure coefficient $\beta$ is almost always positive.

Analogously, the pressure dependence of the chemical drive $A$ of a transformation

$$ B' + B'' + ... \rightarrow D' + D'' + ... $$

results in

$$ A = A_0 + \beta \cdot (p - p_0), \quad \text{where} \quad \beta = \beta(B') + \beta(B'') + ... - \beta(D') - \beta(D'') - ... . $$

The linear approximation is useful for solid, liquid, as well as dissolved substances and for the drives of the corresponding transformations up to $\Delta p \approx 10^5$ kPa ($= 1000$ bar). For obtaining general approximations, it is useful even up to $10^6$ kPa ($= 10000$ bar). In the case of gases and the drives of transformations in which gases participate, $\Delta p/p < 10\%$ is considered acceptable because the slope $\beta$ of the corresponding curve changes relatively strongly with pressure. For greater ranges of pressure $\Delta p$, the mass action relation must be applied. We will be introduced to this in Section 5.5 (and Section 6.5).

Table 5.2 shows the $\beta$ values for the substances of Table 5.1.
Tab. 5.2: Chemical potential $\mu$ and its pressure coefficient $\beta$ for some selected substances at standard conditions (298 K, 100 kPa, dissolved substances at 1 kmol m$^{-3}$).

A rule similar to the one for temperature coefficients is valid for pressure coefficients. It is very useful for qualitative considerations:

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

To make this clear, we will again single out the values for iodine at standard conditions, this time given in $\mu$G Pa$^{-1}$:

$$0 < 51.5 < 60.3 << 24.8 \times 10^3.$$ 

$\approx 50$

Like any rule, this one has exceptions. For instance, $\beta$ for some ions in an aqueous solution is negative and sometimes—as in the case of water—$\beta$ in the solid state is greater than in the liquid state. This is exactly the opposite from what the rule would lead us to expect.

(In this case, as well, there is a relation to a molar quantity, namely the molar volume $V_m$: we have $\beta = V_m$ (compare Section 9.3). Because all molar volumes are basically positive, the pressure coefficient always has a positive sign (the very few exceptions and their cause will be discussed in detail in Section 8.2). The molar volume of a gas is far greater (by a factor of 1000) than that of the condensed phases (liquid and solid). On the other hand, the molar volume of a liquid phase is usually greater than that of the solid phase so that the sequence above results).

**Phase transition.** Raising the pressure generally causes the chemical potential to increase although, as already stated, the increase varies for the different states of aggregation. In the solid state, it is smallest and in the gaseous state, greatest. As a rule, the higher the pressure is, the more stable the solid state is compared to the others and the greater the tendency of the substance to undergo a transition to the crystalline state. Conversely, a pressure reduction re-
sults in a preference for the gaseous state.

Let us once more consider the behavior of water from this new viewpoint. The following table summarizes the necessary chemical potentials and pressure coefficients:

|        | H$_2$O|s | H$_2$O|l | H$_2$O|g |
|--------|--------|--------|--------|--------|
| $\mu^\Theta / kG$ | $-236.6$ | $-237.1$ | $-228.6$ |
| $\beta / 10^{-6} \mu G Pa^{-1}$ | $19.8$ | $18.1$ | $24.8 \cdot 10^3$ |

One sees that lukewarm water can boil at low pressure, although, at room conditions, $\mu$(H$_2$O|g) > $\mu$(H$_2$O|l), liquid water is the stable phase. If the pressure is lowered enough by pumping the air above the water out of a closed container, $\mu$(H$_2$O|g) will at some point fall below $\mu$(H$_2$O|l), because $\beta$ is especially great for the gaseous state. The reduction of pressure becomes noticeable by a strong decrease of chemical potential and the water begins to transform into water vapor by boiling (Experiment 5.3). But low pressure can also be created by using ice-water to cool a closed flask containing only hot water and water vapor (Experiment 5.4). In the process, a part of the vapor condenses, leading to a decrease in pressure.

**Experiment 5.3:** Boiling of lukewarm water at low pressure.  
**Experiment 5.4:** Causing warm water to boil by cooling.

**Phase transition pressure.** We shall take a closer look at a further example of the transition of a substance under pressure. Diamond is a high pressure modification of carbon which should never appear at normal pressure. The most stable modification of carbon, the one with the lowest chemical potential, is graphite which we know from pencils. A characteristic of graphite is that its chemical potential increases more strongly with pressure than the potential of diamond so that, at one point, $\mu$(C|graphite) should exceed $\mu$(C|diamond) making it possible for diamond to form (Fig. 5.8).

**Fig. 5.8:** Pressure dependence of the chemical potentials of graphite and diamond (the lowest chemical potential for each is again highlighted).

At normal pressure and room temperature, $\mu$(C|graphite) equals zero because this value has been arbitrarily set as the zero point of the $\mu$ scale. The $\mu(p)$ curve is steeper for graphite than for diamond. Therefore, the two curves must intersect at a pressure $p_{\alpha\beta}$, which we will call the transition pressure. The index $\alpha\beta$ indicates that
the transition of one modification $\alpha$ (here graphite) into another modification $\beta$ (here diamond) is considered. Below $p_{\alpha\beta}$, graphite is more stable, above it, diamond is more stable.

The pressure $p_{\alpha\beta}$ can be calculated because $p_{\alpha\beta}$ is the pressure for which

$$\mu_\alpha = \mu_\beta.$$  

The pressure dependence of $\mu$ is expressed by a linear relation:

$$\mu_{\alpha,0} + \beta_\alpha (p_{\alpha\beta} - p_0) = \mu_{\beta,0} + \beta_\beta (p_{\alpha\beta} - p_0),$$

resulting in

$$(\beta_\beta - \beta_\alpha) (p_{\alpha\beta} - p_0) = \mu_{\alpha,0} - \mu_{\beta,0}$$

and correspondingly

$$p_{\alpha\beta} = p_0 - \frac{\mu_{\alpha,0} - \mu_{\beta,0}}{\beta_\alpha - \beta_\beta} = p_0 - \frac{\mu_\alpha - \mu_\beta}{\beta}.$$  

The expression shows a great formal similarity to the one for determining a transformation temperature whether it applies to a phase change, a decomposition, or something else. Inserting the tabulated values results in $p_{\alpha\beta} \approx 14 \cdot 10^5$ kPa (= 14 000 bar). Strictly speaking, this result cannot be accurate because the linear relations only represent approximations. However, as a general tool for orientation, it is quite useful.

### 5.4 Simultaneous temperature and pressure dependence

There is nothing stopping us from expanding our ideas to transformations in which temperature and pressure change simultaneously. In this case the chemical potential can be expressed as follows:

$$\mu = \mu_0 + \alpha \cdot (T - T_0) + \beta \cdot (p - p_0).$$

Correspondingly, the chemical drive takes the form

$$A = A_0 + \alpha \cdot (T - T_0) + \beta \cdot (p - p_0).$$

The dependence of transition temperatures upon pressure can be described by these equations as well. Here is a familiar example representative of many others. Ice melts under high pressure (if it is not too cold). The chemical potential of ice is the same as that of ice-water ($\mu(\text{H}_2\text{O}|s) = \mu(\text{H}_2\text{O}|l)$) at 273 K (0 °C) and standard pressure. However, because of $\beta(\text{H}_2\text{O}|s) > \beta(\text{H}_2\text{O}|l)$, the value of $\mu(\text{H}_2\text{O}|s)$ increases above that of $\mu(\text{H}_2\text{O}|l)$ as the pressure increases, and the ice begins to melt. This is how a wire loop with a weight hanging from it slowly “melts” its way through a block of ice (Experiment 5.5). The process is supported by the high entropy conductivity of the steel wire (see Section 20.4).

**Experiment 5.5:** Ice melting under pressure.
As mentioned, water is among the few exceptions where $\beta$ in the solid state is greater than in the liquid state. This special characteristic of ice is responsible for the ability of a glacier to flow downward a few meters per day in a mountain valley like slow moving dough. Where the ice is under especially high pressure, it melts and becomes pliable so that it gradually moves around obstacles.

But a block of ice does not totally melt when compressed because it cools down during melting. The reason for the drop in temperature is that the entropy required for the phase transition solid $\rightarrow$ liquid is not supplied from outside (cp. Section 3.5). It has to be provided by the system itself, leading to a lowering of temperature. The chemical potentials increase because of the negative temperature coefficients $\alpha$. Because of $\alpha$(H$_2$O|l) $< \alpha$(H$_2$O|s) $< 0$, the effect is stronger in water than in ice. The potential difference due to excess pressure is compensated and the process of melting stops. Again, there is equilibrium between the solid and the liquid phase, but this time at a lower freezing point. Only when the pressure is further increased does the ice continue to melt until additional cooling balances the potentials again.

To illustrate this, let us take a look at Figure 5.9. If the pressure is increased, the chemical potentials of the solid and the liquid phase increase; but this increase is much more pronounced for solids than for liquids (because of $\beta$(B|s) $> \beta$(B|l) $> 0$). Thus the intersection point of the curves ($T_{sl}'$) shifts to the left, i.e. the freezing point is lowered by $\Delta T_{sl}$.

**Fig. 5.9:** Temperature dependence of the chemical potentials at different pressures and origin of lowering of freezing point.

It is easy to calculate the lowering of temperature in compressed ice, i.e. the freezing-point depression of water under pressure. The condition for equilibrium $\mu_s = \mu_l$ takes the following form:

$$\mu_{s,0} + \alpha_s \cdot (T - T_0) + \beta_s \cdot (p - p_0) = \mu_{l,0} + \alpha_l \cdot (T - T_0) + \beta_l \cdot (p - p_0) .$$

or in shortened form:

$$\mu_{s,0} + \alpha_s \cdot \Delta T + \beta_s \cdot \Delta p = \mu_{l,0} + \alpha_l \cdot \Delta T + \beta_l \cdot \Delta p .$$

If the freezing point of water at standard pressure ($T_0 = 273$ K) is chosen as the initial value, then $\mu_{s,0}$ and $\mu_{l,0}$ are equal and drop out of the expression. The following relation remains with the change in temperature $\Delta T$ as the only unknown:

$$\Delta T = -\frac{\beta_s - \beta_l}{\alpha_s - \alpha_l} \cdot \Delta p = -\frac{\beta}{\alpha} \cdot \Delta p .$$

For $\Delta p = 10^4$ kPa (100 bar), the lowering of the freezing point due to pressure results in $\Delta T = -0.67$ K.
However, for most substances, the melting temperature increases with increased pressure (because of $0 < \beta(B|s) < \beta(B|l)$) (see Fig. 5.10). Correspondingly, the shifts in potentials cause higher pressure to raise the boiling point and lower pressure to lower the boiling point (because of $0 < \beta(B|l) << \beta(B|g)$). This is also valid for water as we have seen in Experiments 5.3 and 5.4. Again, the change $\Delta T$ can be approximated with the formula derived above. The value of $\beta$ for boiling is roughly $10^4$ greater than for melting, whereas the $\alpha$ values do not vary so drastically. Therefore, even small changes of pressure are enough to noticeably shift the boiling point. To achieve a comparable change of the freezing point, much higher pressures are necessary. A pressure increase of about 10 kPa (0.1 bar) already results in a shift of the boiling point of water of about $+2.0$ K, while for a comparable change of the freezing point ($\Delta T = -2.0$ K), a pressure increase of more than $3 \cdot 10^4$ kPa (300 kbar) is necessary.

Fig. 5.10: Temperature dependence of the chemical potentials at different pressures and origin of lowering of freezing point and raising of boiling point.

We will close this section with a look at our “home planet.” The temperature increase towards the middle of the Earth (> 5000 K) causes the iron core to melt. The pressure which grows to $3.6 \cdot 10^8$ kPa, turns it into a solid again at the very center (Fig. 5.11) (standard melting and boiling points of iron are about 1809 K and 3340 K, respectively). This behavior clearly shows the great influence of temperature and pressure upon the chemical potential.

Fig. 5.11: Opposing effects of temperature and pressure in the Earth’s interior.

5.5 Behavior of gases under pressure

As already stated, the chemical potential of gases is especially sensitive to changes of pressure. For this reason, the pressure coefficient $\beta$ is greater by several powers of ten than those of solid or liquid substances. At the same time, $\beta$ itself is strongly dependent upon pressure. For these reasons, the linear approximation is only applicable to a narrow range of pressures ($\Delta p/p < 10\%$). This is far too limiting for most applications so a formula must be sought that spans a much wider range of pressures. A look at the tabulated values shows that $\beta$ has not only a large value but the same value for all gases at standard conditions. Apparently, the pressure coefficient $\beta$ of gases is a universal quantity. For given $T$ and $p$, it is the same for all
gases in all milieus. Moreover, it is directly proportional to the absolute temperature $T$ and indirectly proportional to the pressure $p$ of the gas in question. This remarkable fact can be expressed as follows:

$$\beta = \frac{RT}{p} \quad \text{where} \quad R = 8.314 \ \text{G K}^{-1}.$$

$R$ is a fundamental constant and is the same for all substances. It is called the “(general) gas constant” because it was first discovered in a law valid for gases (Section 10.2). The relation above is based upon the phenomenon called mass action in chemistry. We will go more deeply into this in the next chapter. (Note: $\beta$ corresponds here to the molar volume of a so-called ideal gas, as we will see in Section 10.2).

Inserting $\beta$ into the relation above yields the following equation:

$$\mu = \mu_0 + \frac{RT}{p} \cdot (p - p_0).$$

Those proficient in mathematics immediately see that there is a logarithmic relation between $\mu$ and $p$:

$$\mu = \mu_0 + RT \ln \frac{p}{p_0}.$$

The pressure coefficient $\beta$ of gases is nothing other than the derivative of the function $\mu(p)$ with respect to $p$. If we take the derivative with respect to $p$ of the function above, we retrieve the first equation.

For those interested in mathematics: The equation above can be transformed to result in

$$\mu - \mu_0 = \frac{RT}{p} \cdot (p - p_0) \quad \text{or} \quad \Delta \mu = \frac{RT}{p} \cdot \Delta p.$$

For very small (infinitesimal) changes, the relation is

$$d\mu = \frac{RT}{p} \cdot dp.$$

If we wish to calculate the change of the chemical potential from the initial value $\mu_0$ to the final value $\mu$ for a change of pressure from $p_0$ to $p$, we must integrate both sides (the concept of integration will be described in more detail in Appendix A1.3). The following elementary indefinite integral will serve well for this:

$$\int \frac{1}{x} \, dx = \ln x + C.$$

Inserting the limits results in:

$$\int_{\mu_0}^{\mu} d\mu = RT \int_{p_0}^{p} \frac{1}{p} \, dp,$$

and respectively,
We tend to consider a logarithm as unfamiliar and therefore complicated. This is unjustified. Basically, the relation is as simple as a linear one (cf. Appendix A1.1). In contrast to the linear approximation, this still relatively simple logarithmic formula spans the much wider range of pressures from between zero and $10^4$ kPa (100 bar). The range of validity will be discussed in more detail in Section 6.5.

Let us take a closer look at these relations using the example of butane (the fuel in a gas lighter) (Fig. 5.12). The $\mu(p)$ curve of gaseous butane shows the expected logarithmic relationship. Futhermore, we can see from the figure that, when compressed at room temperature, butane turns into liquid relatively easily. The so-called “boiling pressure” $p_{lg}$, i.e., the intersecting point of the potentials for the liquid and the gaseous phase, lies only a little above 200 kPa. This intersecting point characterizes the state of butane in a lighter at room temperature. However, further important information can be derived from the figure: The $\mu(p)$ curve for a liquid is an almost horizontal line (its slope is very small). For this reason, the chemical potential of condensed phases (liquids and solids) can be considered nearly independent of pressure in most cases.

Fig. 5.12: Pressure dependence of the chemical potential of butane in liquid and gaseous state at room temperature (298 K).

Furthermore, the chemical potential of a gas continues to decrease with falling pressure. The $\mu$ value approaches negative infinity if the pressure approaches zero.

This leads to the following remarkable conclusions. We can infer, for example, that calcium carbonate $\text{CaCO}_3$ cannot be stable if the $\text{CO}_2$ pressure in the surroundings falls to zero. In this case, the chemical potential of $\text{CO}_2$ would have the value $-\infty$. The reaction

$$\text{CaCO}_3|s \rightarrow \text{CaO}|s + \text{CO}_2|g$$

$$\mu^\Theta: \quad -1128.8 \quad -603.3 \quad -394.4 \quad \text{kG} \quad \Rightarrow \lambda^\Theta = -131.1 \text{ kG}$$

$$\alpha: \quad -93 \quad -38 \quad -214 \quad \text{G K}^{-1} \quad \Rightarrow \alpha = +159 \text{ G K}^{-1},$$

which cannot take place at standard conditions, would have a positive drive. The sum of potentials on the left would be higher than on the right. However, decomposition produces $\text{CO}_2$, so that the $\text{CO}_2$ pressure must rise in a closed system. The process continues until the $\text{CO}_2$ pressure has reached a value for which the chemical potentials on the left and right sides balance. This $\text{CO}_2$ pressure is called the decomposition pressure of calcium carbonate.

The decomposition pressure can be easily calculated. If the chemical potentials satisfy
we have equilibrium. We ignore the pressure dependence of solid substances because, in comparison to gases, it is smaller by three orders of magnitude. We only take the dependence for CO\textsubscript{2} into account:

\[
\mu_{\text{CaCO}_3} = \mu_{\text{CaO}} + \mu_{\text{CO}_2} ,
\]

This results in

\[
\frac{\mu_{\text{CaCO}_3,0} - \mu_{\text{CaO},0} - \mu_{\text{CO}_2,0}}{A_0} = RT \ln \frac{P}{P_0} .
\]

and

\[
\exp \frac{A_0}{RT} = \exp \left( \ln \frac{P}{P_0} \right)
\]
or, respectively,

\[
p = p_0 \exp \frac{A_0}{RT} .
\]

In order to calculate the decomposition pressure for a temperature different from standard temperature, the \(\mu\) values in the exponents only need to be converted to the new temperature. The linear formula for temperature dependence is generally good enough for this:

\[
p = p_0 \exp \frac{A_0 + \alpha(T - T_0)}{RT} .
\]

With the help of corresponding data, i.e. the standard values and the corresponding temperature coefficients from Table A2.1 in the Appendix, the \(p(T)\) curve can be determined (Fig. 5.13). This curve gives the decomposition pressure of calcium carbonate as a function of temperature:

\[
p = 100 \text{ kPa} \cdot \exp \frac{-1.311 \cdot 10^5 + 159 \cdot (T / K - 298)}{8.314 \cdot T / K} .
\]
12. Spreading of Substances

Topic: Spreading of substances and effects that result from it, indirect mass action and colligative effects such as osmosis, lowering of vapor pressure, etc.

12.1 Introduction

Until now, when we have considered the chemical potential we have primarily concentrated upon chemical reactions and phase transitions. However, there is another characteristic of substances that is almost as important. This is the tendency to spread out or disperse in space whether it is “empty” or filled with matter. This phenomenon can easily be illustrated by everyday processes. Mostly, substances migrate extremely slowly and in infinitesimally small amounts so that this migration remains imperceptible. However, there are many examples of spreading that are quite noticeable. When the aroma of freshly ground, unpacked coffee escapes over the course of a few days, when the water in a rain puddle evaporates in a few hours, when glue from a tube congeals in one minute or the ink from a felt pen dries within seconds, these are all examples of how mobile and volatile some substances can be. The following is an example that shows clearly how substances do not disappear but simply redistribute. A piece of zwieback stored for two or three days in a bread box or plastic bag together with fresh bread absorbs moisture and becomes soft and bendable while a slice of bread in a bag full of zwieback becomes hard and brittle from losing moisture to the dry zwieback (Experiment 12.1).

Experiment 12.1: A piece of zwieback stored with bread becomes soft and bendable. A slice of bread stored with zwieback becomes hard and brittle.

It is easy to follow the spreading of strong smelling or colored substances. The scent of a bouquet of lilacs, a peeled orange or the pungent odor of potent cheese quickly fill a whole room. The spreading of colored low-molecular chemicals such as potassium permanganate in a liquid, or better, in a gel (to hinder convection) happens so fast that it can readily be observed (Experiment 12.2). The vapor from a drop of bromine in a gas jar spreads quickly and fills the whole space inside it (Experiment 12.3).

Experiment 12.2: Spreading of KMnO₄ in agar gel (view from above on a thin layer of gel in a Petri dish).  
Experiment 12.3: Spreading of Br₂ in air.
Even crystallized, compact bodies are not impenetrable. Iron can be “carbonized” by annealing in charcoal powder at approx. 1000 °C. This means that the carbon atoms move into it. The changes of the grain structure at the border of the sample are visible to the naked eye as a dark area but they can be examined in more detail with a microscope. The iron can also be “decarbonized” by heating in an oxidizing flame or in a furnace in air (Experiment 12.4).

**Experiment 12.4:** “Carbonizing” and “decarbonizing” of iron (schematic representation).

These examples show that spreading (diffusion, dispersion …) of substances is a very general characteristic of matter. The migration of a substance from one place to another can be considered as a transformation

\[ B|\text{Origin} \rightarrow B|\text{Destination}, \]

so it is plausible that the chemical potential also controls this process. The transport of substances always follows the direction of the potential gradient. This means that the substance only moves spontaneously in one direction, the direction where the \( \mu \) value at the starting point is higher than at the destination (if no other forces play a role like centrifugal forces in a centrifuge or electrical forces in an electrolytic cell). In this case, a characteristic of \( \mu \) plays a decisive role that we have already been introduced to, namely its concentration dependency (compare Section 6.2): *The more diluted a substance is, the lower is its chemical potential and the chemical potential can be lowered to any degree if the dilution is strong enough.*

In the following, we will apply this statement to the spreading of substances and other phenomena related to it. Chapter 13 will deal with the special features that result when the rule mentioned above no longer applies which is the case at higher concentrations.

### 12.2 Diffusion

If a substance is mobile enough, it must distribute in an otherwise homogeneous material or space uniformly over the entire area. This is because at locations of lower concentrations, its chemical potential is lower causing the substance to move from locations of higher concentration into areas of lower concentration (Fig. 12.1). When several substances migrate in an area at the same time, this holds for every one of them. The substances strive intrinsically for homogeneous distribution. This is called *diffusion*.

**Fig. 12.1:** Flow of substance caused by an inhomogeneous distribution of the substance in an otherwise homogeneous area.

Although difference of concentration is by far the most important cause for diffusion, it is not the only cause. Other factors influencing the chemical potential can also play a role. It is entirely possible that at certain locations in inhomogeneous areas, a substance is enriched at the
cost of neighboring areas. This characteristic is applied in microscopy in order to color areas that would tend to preferentially absorb certain dyes (staining in histology). A dye more or less evenly applied distributes unevenly even without outside influence.

We shall now take a closer look at transport of matter. As we have already seen, the determining quantity is the chemical potential. The substance moves spontaneously only in the direction in which the potential falls. If the transfer of a substance B from position \( z_1 \) to position \( z_2 \) (Fig. 12.2) is formulated as a reaction, then:

\[
B|z_1 \rightarrow B|z_2 \quad \text{occurs spontaneously if} \quad \mu_B(z_1) > \mu_B(z_2).
\]

![Fig. 12.2: Determination of force \( F \) upon a small sample of amount \( n \) of a substance B in a gradient of chemical potential.](image)

The chemical drive \( A \) of this process is the corresponding potential difference,

\[
A = \mu_B(z_1) - \mu_B(z_2) = -\Delta \mu_B,
\]

and the conversion \( \Delta \xi \) is the amount of substance \( n_B \) transferred from position \( z_1 \) to position \( z_2 \). The potential gradient causes a force \( F \) that pushes the substance in the direction of the falling potential. \( F \) is easy to calculate if the energy \( W \) for transporting a small amount \( n_B \) from location \( z_1 \) to location \( z_2 \) is expressed first as expenditure for the reaction and then as that required for the displacement against the force \( F \). For this, let us consider that the potential \( \mu_B \) increases in the \( z \) direction and that the substance is transported “uphill” opposite to the potential gradient. The energy \( W \) is then \( > 0 \) while the chemical drive \( A \) is negative. \( F \) also counts as negative because it is oriented opposite to the positive \( z \) axis. In general, \( F \) depends upon the position \( z \). If the segment \( \Delta z = z_2 - z_1 \) is made small enough, \( F \) can be considered constant. As a consequence, we obtain:

\[
W = -A \cdot \Delta \xi = \Delta \mu \cdot n \quad \text{and} \quad W = -F \cdot \Delta z \quad \text{for small} \ \Delta z.
\]

When both equations are combined, we find

\[
F = -n \cdot \frac{\Delta \mu}{\Delta z}
\]

or more precisely

\[
F = -n \cdot \frac{d\mu}{dz}.
\]

It is fitting to call \( F \) diffusion force because \( F \) is the driving force behind the kind of transport called diffusion. In Chapter 20, which deals with transport phenomena, we will discuss the velocity of substance transport and the laws pertaining to it (section 20.2).

When we apply molecular kinetic considerations, diffusion tends to be conceptualized as a result of random motion of molecules and not as an effect of a directed force. When the boundaries of two areas of different concentrations of a substance B touch each other, a totally random movement of molecules occurs where, on average, more particles move from the concentrated area into the diluted area than vice versa. Random chance suffices to explain that B
gradually moves from areas of higher concentration into ones of lower concentration until it is evenly distributed. No special driving force is necessary for this. Actually, there is no discrepancy between the two models. The greater number of molecular collisions occurring at higher concentrations of the diffusing substance B must lead to a directed force at the transition to the area of lower concentration. This is the diffusion force $F$ calculated above.

Other phenomena already familiar to us also belong to the category of spreading. Water (Section 6.1), but also alcohol, ether, etc., evaporate into the air. They convert to a gaseous state although the chemical potential of liquid A is smaller below its boiling point than that of pure vapor. What makes this possible is the fact that the vapor is not pure but so diluted by air that $\mu(A|g) < \mu(A|l)$.

Any substance B dissolves in finite amounts in any other substance A (even if these amounts are immeasurably small) because when it is diluted enough, the chemical potential of the dissolved substance B falls below the fixed $\mu$ value of the non-dissolved solute of B, so that B begins to migrate away from it (Section 6.6).

Finally, the mass action law that is so important in chemistry can also be mentioned in this connection as long as it deals with an exchange of substances taking place between spatially separate areas. NERNST’s law of distribution, HENRY’s law of gas solubility, and even the vapor pressure formula of pure substances are all examples of this.

### 12.3 Indirect mass action

When a small amount $n_F$ of a foreign substance is dissolved in a liquid A, the chemical potential $\mu_A$ of this liquid will decrease at constant $p$ and $T$. In fact, it decreases in proportion to the mole fraction $x_F = n_F/(n_A + n_F) \approx n_F/n_A$ of the foreign substance, independent of the type of solute in question:

$$\mu_A = \tilde{\mu}_A - RT \cdot x_F$$  \hspace{1cm} \text{for} \hspace{1cm} x_F << 1 \hspace{1cm} \text{“colligative lowering of potential,”}$$

(the term “colligative” is explained at the end of this section). $\tilde{\mu}_A$ (pronounced “mu-A-pure”) designates the potential of A in its pure state ($x_A = 1$). Until now, we have ignored the “moderating influence” that the addition of a small amount of foreign substance can have upon another substance’s tendency to transform. An example would be the application of the mass action law when the solvent takes part in the reaction in question. The reason for this is that for dilute solutions, the contribution $-RTx_F$ is small compared to the concentration dependent contributions $\mu = -RT \ln c_t$ of the dissolved substances. The latter tend to $-\infty$ for decreasing concentration. In the mass action law which applies in the limit of strong dilution, the contribution $-RTx_F$ disappears, but the mass action terms $\tilde{\mu}$ do not; they actually increase without limit.

In order to describe the dependency of the chemical potential $\mu_B$ upon the composition (concentration $c_B$, partial pressure $p_B$, mole fraction $x_B$, etc.) of a substance B, chemists generally separate the potential $\mu_B$ into two parts: a fundamental component $\tilde{\mu}_B$ independent of concentration and a remainder that is dependent upon it. In the sense explained here, $\tilde{\mu}_B$ represents a
particular basic value. Only when this needs to be emphasized will we us the form $\mu_B^*$, otherwise we will stay with $\mu_B$.

The equation above for the lowering of potential is valid as long as the foreign substance or substances (there can be several different ones since their kind does not matter) dissolve molecularly but do not associate or dissociate, meaning they may not decompose into smaller components or form aggregates of several molecules. This remarkable relation, which is valid for all substances, is the indirect result of the mass action of the dissolved substances. Remember that mass action is independent of what kind of substances make up solvent A and solute F (see the mass action equations in chapter 6).

Note that the new equation holds only in the limit of a small amount of a foreign substance being added to the solvent. Admittedly, this change of potential is small. However, because substance A is highly concentrated, it can have significant effects, which we will look into in the next sections.

For the mathematically interested: In order to derive the equation above, we will refer back to the cross relation discussed in Section 9.3 known as $n-n$ coupling. When one substance tries to displace (or favor) another one, this happens reciprocally and with equal strength. The corresponding displacement coefficients are equal as can easily be shown by applying the flip rule (main equation: $dW = -pdV + TdS + \mu_A d\eta_A + \mu_F d\eta_F$):

$$\left(\frac{\partial \mu_A}{\partial n_F}\right)_{p,T,n_A} = -\left(\frac{\partial \mu_F}{\partial n_A}\right)_{p,T,n_F}.$$

Taking into account that $\mu_F$ is dependent upon $c_F$ and $c_F$ is dependent upon $n_A$, $\mu_F(c_F(n_A))$, which means that we have to apply the chain rule in order to calculate the derivative on the right, the result is:

$$\left(\frac{\partial \mu_A}{\partial n_F}\right)_{p,T,n_A} = -\left(\frac{\partial \mu_F}{\partial c_F}\right)_{p,T} \left(\frac{\partial c_F}{\partial n_A}\right)_{p,T,n_F}.$$

When we started examining the phenomenon called mass action, we chose the situation where the concentration coefficient $\gamma$ of the chemical potential at low concentrations $c$ is a universal quantity (Section 6.2). When applied to substance F, this means:

$$\left(\frac{\partial \mu_F}{\partial c_F}\right)_{p,T} = \gamma = \frac{RT}{c_F}.$$

Now, $c_F = n_F/V$ is indirectly dependent upon $n_A$ even at a constant $n_F$, because $V = n_A V_A + n_F V_F$. Since $n_F \ll n_A$, the contribution $n_F V_F$ to the volume $V$ can be ignored and $V_A$ can be considered equal to the volume demand of the pure substance A and therefore independent of $n_A$. When we take the derivative of $c_F = n_F/(n_A V_A)$ with respect to $n_A$,

$$\left(\frac{\partial c_F}{\partial n_A}\right)_{p,T,n_F} = -\frac{n_F}{n_A^2 V_A} = -\frac{n_F}{n_A V_A} = -\frac{c_F}{n_A},$$

and insert the result further above, we obtain:
The derivative is not dependent upon \( n_F \), meaning that, with increasing amount \( n_F \), \( \mu_A \) decreases linearly with constant slope from the initial value \( \mu_A^* \):

\[
\mu_A = \mu_A^* - \frac{RT}{n_A} \cdot n_F \approx \mu_A^* - RT \cdot x_F.
\]

Figure 12.3 shows the chemical potential \( \mu(x) \) as a function of \( x \) within the entire range from \( x = 0 \) to 1. The solid curve illustrates the logarithmic relation considered the ideal case. If the mole fraction is reduced by a power of ten each time, the chemical potential always decreases by the same value: the decapotential \( \mu_d \) of 5.7 kG at room temperature. As already stated (and derived above), all \( \mu(x) \) curves must show the same slope \( RT \) for \( x \approx 1 \) that is \( x_F \approx 0 \). We will go more deeply into this subject in Section 13.2.

Fig. 12.3: Dependence of chemical potential upon mole fraction \( x \).

“Colligative lowering of potential” leads to several effects: development of osmotic pressure, lowering of vapor pressure of a solution (compared with the pure solvent), raising of its boiling point and lowering of its freezing point. These effects are determined solely by the mole fraction of the foreign substances, i.e., the number of dissolved particles (“assemblies of atoms”) and not their chemical nature, size and form. For this reason, the term colligative properties is used (from the Latin colligare „to assemble“). An aqueous solution with a mole fraction of glucose of 0.001 corresponds quite well to a urea solution with the same mole fraction for all the properties just mentioned (osmotic pressure, vapor pressure, freezing point and boiling point). However, each type of particle in the solution must be treated as an individual substance. For example, the cations and anions in an electrolyte solution need to be counted separately. For a solution of table salt with \( x_{NaCl} = 0.001 \), \( x_F = x_{Na^+} + x_{Cl^-} = 2 \cdot x_{NaCl} = 0.002 \); this is so because NaCl is fully dissociated into the \( Na^+ \) and \( Cl^- \) ions. In a calcium chloride solution, we even have \( x_F = x_{Ca^{2+}} + x_{Cl^-} = 3 \cdot x_{CaCl_2} = 0.003 \).

### 12.4 Osmosis

When two solutions with different concentrations of a substance B are separated by a thin wall that only allows solvent A to pass through (a so-called semipermeable membrane, Fig. 12.4), solvent A will migrate through this membrane from the more diluted solution (with respect to B) to the one of higher concentration. In this case, one of the solutions can be composed of the pure solvent for which \( c_B = 0 \). In the solution having a higher concentration of B, substance A appears more strongly diluted due to its solution partner B. This means that the concentration of solvent is smaller and because of this, its chemical potential \( \mu_A \) is also smaller. Thus, the chemical drive for this process called osmosis is the difference of potential generated by different concentrations of foreign substances.
The biological membranes surrounding living cells are also semipermeable. They allow water and molecules of comparable size through while holding back enzymes and proteins inside cells. In biology, osmotic exchange of water represents a ubiquitous phenomenon. It is responsible for the effect that juice is “drawn out” from strawberries that are sugared (Experiment 12.5) or that cherries swell up and burst after a long rain.

**Experiment 12.5:** Juice “extraction” from sugared fruit.

In the first case, water migrates out through the peel into the concentrated, therefore water-poor, sugar solution. In the second case, water flows inward, because the water is more diluted there. Another good example of the first effect would be salted slices of white radish (Experiment 12.6). Immediately, juice begins to drip out of the stack with the salted slices. The second effect can also be demonstrated on a raw decalcified egg in water, which is cautiously placed in water (Experiment 12.7). After a while, the egg has swollen considerably.

**Experiment 12.6:** Juice “extraction” from slices of salted radish.

**Experiment 12.7:** Swelling of a decalcified egg in water.

A gradual excess pressure results from the flow of solvent A into the concentrated solution. The chemical potential $\mu_A$ also gradually increases so that the potential gradient decreases. The process stops when $\mu_A$ on the right and on the left of the wall becomes equal (or when the
12. Flow of Substances

Substance A completely disappears from one side. The resulting excess pressure is called *osmotic pressure*.

We will now take a closer look at osmosis. We consider a vessel containing an amount $n_A$ of a liquid A. When a small amount $n_B$ of a foreign substance is dissolved in it, the chemical potential $\mu_A$ of the solvent decreases (“colligative potential lowering”):

$$
\mu_A = \mu_A^0 - RT \cdot x_B \quad \text{for} \quad x_B \ll 1.
$$

Let us imagine the container connected to another one by a wall that is permeable only for the solvent (Fig 12.5). The liquid in the second container is in its pure state.

**Fig. 12.5:** Experiment illustrating osmotic pressure. The riser pipe on the left serves as manometer.

The potential gradient causes this liquid to flow through the wall into the solution. This flow can be suppressed by compensating for the loss of potential by raising the pressure on the solution. The chemical potential grows with increasing pressure (compare section 5.3):

$$
\mu_A = \mu_A^0 - RT \cdot x_B + \beta_A \cdot \Delta p.
$$

where the pressure coefficient $\beta_A$ corresponds to the molar volume $V_A$ of the pure solvent (compare Section 9.3). The following is then valid for the osmotic equilibrium:

$$
\dot{\mu}_A - RT \cdot x_B + V_A \cdot \Delta p = \mu_A \quad \text{and respectively,} \quad -RT \cdot x_B + V_A \cdot \Delta p = 0.
$$

The simple arrangement in Figure 12.5 shows the pressure working against the flow of solvent into the solution as a result of the gravitational pressure of the column of solution in the riser pipe on the left. This pressure is produced by the osmosis itself as the pure solvent moves through the semipermeable wall into the solution. In the process, the difference of level between the two riser pipes gradually becomes greater until eventually, the gravitational pressure compensates for the effect of osmotic pressure. This means that osmotic equilibrium has been established. The osmotic pressure $p_{\text{osm}} = \rho gh$ can be easily calculated from the resulting rise $h$ of the column of liquid, the density $\rho$ of the solution, and the gravitational acceleration $g$.

With the help of a carrot and a riser pipe with a funnel shaped end, it is easy to construct an experiment to prove the existence of osmotic pressure (Experiment 12.8). For this purpose, the inside of the carrot is hollowed out in a cylindrical form and filled with a colored saturated calcium chloride solution. Then the riser pipe is attached. The cell membranes in the carrot act as the semipermeable wall. After a short time, one observes a continuous rise of the solution in the riser pipe.
**Experiment 12.8:** Experimental demonstration of osmotic pressure.

We have \( x_B = n_B/(n_A + n_B) \approx n_B/n_A \) for a diluted solution because the amount \( n_B \) of solute is so small compared to the amount \( n_A \) of the solvent, that it can be ignored. Multiplying the equation above by \( n_A \) yields:

\[
-RT \cdot n_B + n_A V_A \cdot p_{\text{osm}} = 0. 
\]

If \( V \approx n_A V_{m,A} \) indicates the volume of liquid (ignoring the small amount \( n_B V_{m,B} \) of foreign substance), then the osmotic pressure \( p_{\text{osm}} \) results in:

\[
p_{\text{osm}} = n_B \frac{RT}{V} \quad \text{VAN’T HOFF’s equation.}
\]

At room temperature \((T = 298 \, \text{K})\), a solution of an arbitrary non-electrolyte with a concentration of 0.01 kmol m\(^{-3}\) results in an osmotic pressure of 250 kPa (= 2.5 bar). This would be enough to raise the column of liquid more than 25 meters. Even at very small concentrations, osmotic pressure is of such a magnitude that it is easy to measure with sufficient precision.

VAN’T HOFF’s equation is very similar to the general gas law. In fact, both equations can be interpreted in the same way. Here we need to keep in mind that the forces of attraction between the A particles keep the liquid together (compare section 11.1, keyword “cohesion pressure”). The contribution of the external pressure \( p \) is comparatively small. The B particles that drift far away from each other and scarcely influence each other cause a pressure like that of a thin gas. However, in this case the pressure is not compensated by the container walls but by the cohesion of the A particles. When the osmotic pressure \( p_{\text{osm}} \) is higher than the external pressure—a condition that is often attained—the liquid A behaves as if it were under negative pressure. If we calculate the potential \( \mu_A \) of the liquid for a pressure reduced by \( p_{\text{osm}} \) and keep in mind that for dilute solutions \( V \approx n_A V_{m,A} \) and \( n_B/n_A \approx x_B \), we again end up with the equation above. This demonstrates that both descriptions are equivalent:

\[
\mu_A - \beta_A \cdot p_{\text{osm}} = \mu_A - V_A \frac{n_B RT}{V} = \mu_A - x_B RT. 
\]

If the dilute solution contains several types of particles which cannot penetrate the membrane, we have

\[
p_{\text{osm}} = n_F \frac{RT}{V} = c_F RT, 
\]

where \( n_F \) as well as \( c_F \) are the sum of the amounts of substance and the sum of concentrations of all types of particles, respectively. \( c_F \) is called the osmolarity of the solution. Since the total number of dissolved particles must be taken into account when calculating the osmolarity, the number of ions that form an ionic substance must also be considered. For example, the osmolarity of an aqueous solution of the salt CaCl\(_2\) with a concentration \( c \) is three times higher than this concentration. Correspondingly, the osmotic pressure of the solution of this salt is three times that of a solution of a non-electrolyte with the same concentration.
As we have mentioned at the beginning, osmotic phenomena play an essential role in biological processes. They have great importance for the balance of water in living organisms and influence the form of their cells. The osmolarity $c_F$ of cell liquid in human red blood cells, for example, is approximately 300 mol m$^{-3}$. In this case, we can apply Van’t Hoff’s law only with reservations due to this relatively high concentration. However, for body temperature, an osmotic pressure of $p_{osm} = 300 \text{ mol m}^{-3} \cdot 8.3 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 310 \text{ K} = 770 \text{ kPa}$ can be at least estimated. If red blood cells were to be suspended in pure water, they would have to withstand about 8 times normal atmospheric pressure. In fact, they swell up and burst long before this point (Fig. 12.6 a). On the other hand, if red blood cells are put into contact with an aqueous saline solution that has a much higher osmotic pressure than 770 kPa, the water in the cells will flow out and they will shrink (the membranes of red blood cells are almost impenetrable for Na$^+$, Fig. 12.6 c). Only if the osmotic pressure is the same inside the red blood cells and the surrounding solution (which is the case for blood plasma) do the cells keep their normal shape (figure, part b).

In reverse osmosis, an external excess pressure is exerted upon the side of the concentrated solution that is higher than the osmotic pressure $p_{osm}$ of this solution. This causes the solvent’s molecules to be “forced” in the direction opposite to the osmotic effect. They are forced through the semipermeable membrane and into the more diluted solution where they are enriched. This procedure is used in desalinization of sea water as well as wine processing.

12.5 Lowering of vapor pressure

A pure liquid A is assumed to be in equilibrium with its vapor at a pressure of $p_{lg}$ (initial situation: $\mu_{A|l} = \mu_{A|g}$). The vapor pressure of A is lowered if a low-volatile foreign substance B is dissolved in it (Fig. 12.7).

Fig. 12.7: Formation of equilibrium between a solution of a foreign substance B in a liquid A and the pure vapor phase of A.

Qualitatively, this can be understood immediately. Adding B dilutes liquid...
A|l, thereby lowering its chemical potential $\mu_{A|l}$. The dissolved substance B should have low volatility so it contributes nothing to the vapor A|g and the potential $\mu_{A|g}$ remains unchanged. Because $\mu_{A|l}$ is now lower than $\mu_{A|g}$, the vapor has to condense on the surface of the solution thereby causing the pressure to fall.

Also the quantitative discussion is not difficult. The process continues until equality of potentials is regained, $\mu_{A|l} = \mu_{A|g}$. For this purpose, reducing the pressure by a small amount $\Delta p$ is sufficient. The chemical potential $\mu_{A|g}$ of the vapor falls steeply with decreasing pressure because of its high pressure coefficient, $\beta_{A|g} \gg \beta_{A|l}$, whereas the change of the potential $\mu_{A|l}$ is so small that it can be neglected. If we consider the “colligative potential lowering” $-RTx_B$ caused by B we obtain for the equilibrium condition:

$$\mu_{A|g} = \mu_{A|g} + \beta_{A|g} \cdot \Delta p = \mu_{A|l} - RT \cdot x_B = \mu_{A|l}.$$  

We act on the assumption that $\mu_{A|l} = \mu_{A|g}$, therefore these contributions cancel each other out. Because we also have $\beta_{A|g} = V_{A|g} = RT/p$ (see section 9.3), the equation can be simplified according to:

$$RT \frac{\Delta p}{p} = -RT \cdot x_B,$$

$p$ corresponds in this context to the vapor pressure $p_{lg}$ of the pure solvent. If it is important to emphasize this fact, we add the symbol $\bullet$ and write $p_{lg}$ instead of $p_{lg}$. For the “lowering of vapor pressure” $\Delta p_{lg}$ we obtain a relation that was discovered empirically in 1890 by François Marie RAOUULT:

$$\Delta p_{lg} = -x_B \cdot p'_{lg},$$  

RAOULT’s law.

But let us have a look at Fig. 12.8 for illustration:

**Fig. 12.8: Dependence of the chemical potential upon pressure, and lowering of vapor pressure.**

At the intersection of the potentials for pure solvent and pure vapor, there is equilibrium between the liquid and its vapor phase at the vapor pressure $p_{lg}$. A dissolved substance of low volatility lowers the chemical potential of the solvent by $-RTx_B$ (“colligative potential lowering” according to the distance between the both nearly horizontal straight lines), but leaves that of the vapor unchanged. Thus, the intersection of the curves $(p'_{lg})$ shifts to the left. This means that the vapor pressure is lowered by $\Delta p (\Delta p < 0!)$. With the aid of the “slope triangle” drawn in the figure the slope $\beta_{A|g}$ of the potential curve for pure vapor results in

$$\beta_{A|g} = \frac{-RTx_B}{\Delta p}.$$
Considering that $\beta_{A|g} = V_{A|g} = RT/p$ and solving the equation for $\Delta p$ results in RAOUlt’s law. Whether one prefers the first pure mathematical or the second more geometrical derivation is a question of personal preference.

The simple setup can serve as a demonstration experiment (Experiment 12.9). The vapor pressure of ether in the gas washing bottle with added oleic-acid decreases in comparison to that of pure ether. This is shown by the level of liquid in the pressure gauge.

**Experiment 12.9:** Comparison of the vapor pressures of ether and an ether-oleic acid mixture

12.6 **Lowering of freezing point and raising of boiling point**

A frozen liquid $A$ melts more easily when a substance $B$ that is soluble in the liquid but not in the solid is added (Fig. 12.9).

**Fig. 12.9:** Melting of a frozen liquid in a solution.

At the normal freezing point $T_{sl}$ of the liquid $A$, the chemical potentials for the solid and the liquid state are equal ($\mu_{A|s} = \mu_{A|l}$). If a foreign substance is dissolved in the liquid phase, the chemical potential of this phase decreases so that it falls below that of the solid phase which then begins to melt. The entropy required for the phase transition solid $\rightarrow$ liquid is not added from outside but has to be brought up by the system itself. Therefore, the entire mixture cools down and the chemical potentials rise due to their negative temperature coefficients. However, because the temperature coefficient for a liquid is smaller than for a solid ($\alpha_{A|l} < \alpha_{A|s} < 0$), $\mu_{A|l}$ grows faster with decreasing temperature than does $\mu_{A|s}$. This causes the temperature gradient to disappear again at a certain lower temperature and the melting process stops.

An illustration (Fig. 12.10) explains this phenomenon:

**Fig. 12.10:** Temperature dependence of chemical potentials, lowering of freezing point as well as raising of boiling point. The lowering of potential of solvent $A$ by $-RTx_B$ caused by the foreign substance $B$ is compensated at the freezing point by a lowering and at the boiling point by a raising of temperature.

When the chemical potential for the pure solvent as well as for the pure solid are drawn as functions of temperature, the intersection of the two curves yields the freezing point $T_{sl}$. The dissolved substance lowers the chemical potential of the liquid but does not influence
the solid phase. The intersection of the curves ($T_{sl}^{'}$) is therefore shifted to the left. This means that the freezing point is lowered by $\Delta T_{sl}$ ($\Delta T_{sl} < 0$).

In the following calculation we again assume a re-established equilibrium. This time it is between the liquid and solid phases, $\mu_{A,l} = \mu_{A,s}$. Because the changes in temperature $T$ we are interested in are mostly small we can assume a linear dependence of the chemical potential upon $T$. At constant pressure, we obtain the following result (keep in mind that in this case the freezing point is the reference point for the temperature coefficients):

$$\mu_{A,l} = \mu_{A,l}^{*} - RT_{sl} \cdot x_{B} + \alpha_{A,l} \cdot \Delta T = \mu_{A,s}^{*} + \alpha_{A,s} \cdot \Delta T = \mu_{A,s}^{*}$$

Again the basic values cancel each other out, $\mu_{A,l}^{*} = \mu_{A,s}^{*}$. When the equation is solved for $\Delta T$ or more detailed $\Delta T_{sl}$, the freezing point depression results in:

$$\Delta T_{sl} = -\frac{RT_{sl} \cdot x_{B}}{\alpha_{A,s} - \alpha_{A,l}}$$

Here, the temperature coefficient corresponds to the negative molar entropy of the substance (compare section 9.3). Subsequently, the difference $S_{A,l}^{*} - S_{A,s}^{*}$ can be summarized as the molar entropy of fusion $\Delta_{sl}S_A$ of the pure solvent (at freezing point) (compare Section 11.5):

$$\Delta T_{sl} = -\frac{RT_{sl} \cdot x_{B}}{\Delta_{sl}S_A}$$

Like the lowering of vapor pressure, the lowering of freezing point is directly proportional to the mole fraction $x_{B}$ of dissolved substance. The additional character $\ast$, which symbolizes that the labeled quantity applies to the pure substance can be omitted if misunderstandings are not possible.

For example, in an aqueous non-electrolyte solution with a mole fraction of $x_{B} = 0.01$, $\Delta T_{sl}$ is about $-1$ K. An example from everyday life is shown in Experiment 12.10: When rum, schnaps or whisky is poured over ice, it will become noticeably colder than $0 \degree C$.

**Experiment 12.10:** “Whisky on the rocks” as example for lowering of freezing point.

A prime example of an application of freezing point depression is, however, the melting effect of road salt.

In contrast to the freezing point, the boiling point of a solution is raised as demonstrated in Experiment 12.11. A saturated solution of table salt begins to boil at a noticeable higher temperature than tap water.

**Experiment 12.11:** Raising of boiling point of a a saturated solution of table salt.
Correspondingly, the position of the equilibrium between liquid and vapor is shifted to a higher temperature in Figure 12.10. However, this raising of boiling point is much smaller than the lowering of freezing point which can be attributed to the different slopes of the curves representing the potentials. These, in turn, are determined by the molar entropies, which naturally leads to the steepest drop for the gaseous state of the solvent.

A consideration similar to that for lowering the freezing point leads to the equation for raising the boiling point:

\[ \Delta T_{lg} = \frac{RT_{lg} \cdot x_B}{a_{Ag} - a_{Al}} \]

and correspondingly:

\[ \Delta T_{lg} = \frac{RT_{lg}^* \cdot x_B}{\Delta_{lg}S_A} \]

where \( \Delta_{lg}S_A \) now represents the molar entropy of vaporization \( (S_{Ag} - S_{Al}) \) at the boiling point.

In summary, when a low-volatile foreign substance is dissolved in a liquid, the potential of the pure vapor, which is then higher than that of the solution, can be lowered in two ways. First, by lowering the pressure (Section 12.5), and second, by raising the temperature.

### 12.7 Colligative properties and determining molar mass

The four phenomena just described (osmosis, lowering of vapor pressure, lowering of freezing point, and raising of boiling point) have a common feature: they are all dependent upon the indirect mass action of dissolved substances, i.e., the lowering of the chemical potential by mixing in small amounts of foreign substances. These so-called colligative phenomena depend solely upon the mole fraction of these foreign substances and therefore the number of dissolved particles. However, what type of substances they are is unimportant.

Because of this peculiarity, the colligative properties can be used to determine the amount of substance \( n_B \) of a sample of an unknown substance \( B \) and therefore, if the mass \( m_B \) of the sample is known, also the molar mass \( M_B = m_B/n_B \). Let us take a quick look at this by considering the example of lowering of freezing point. \( x_B \approx n_B/n_A \) is valid at high dilution and because of \( n_A = m_A/M_A \) we have \( x_B \approx n_B \cdot M_A/m_A \). The quotient \( n_B/m_A \) corresponds to the molality \( b_B \) (compare Section 1.5). Inserting these expressions in the equation above for the freezing point depression results in

\[ \Delta T_{dl} = -K_f \cdot \frac{n_B}{m_A} = -K_f \cdot b_B \quad \text{with} \quad K_f = -\frac{RT_{df}M_A}{\Delta_{df}S_A}, \]

a coefficient called “cryoscopic constant” which is only dependent from pressure and type of solvent. \( K_f \) corresponds to the lowering of freezing point which is obtained from 1 mol of dissolved substance in 1 kg of solvent. At such high concentrations the equation above can only
be an approximation. For measuring the temperature changes at low concentrations with a sufficient precision, it is advisable to use solvents with $K_f$ values as high as possible. Table 12.1 shows the “cryoscopic constants” of some solvents.

**Table 12.1:** Cryoscopic and ebullioscopic constants of some solvents (from: CRC Handbook of Chemistry and Physics, 89th edition (2008)).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$T_{sl}$ K</th>
<th>$K_f$ K kg mol$^{-1}$</th>
<th>$T_{lg}$ K</th>
<th>$K_b$ K kg mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>273.2</td>
<td>1.86</td>
<td>373.1</td>
<td>0.51</td>
</tr>
<tr>
<td>Benzene</td>
<td>278.6</td>
<td>5.07</td>
<td>353.2</td>
<td>2.64</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>279.7</td>
<td>20.8</td>
<td>353.9</td>
<td>2.92</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>299.1</td>
<td>42.2</td>
<td>434.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Campfor</td>
<td>452.0</td>
<td>37.8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

There are analogous relations and applications for the raising of boiling point:

$$
\Delta T_{lg} = +k_c \cdot \frac{n_a}{m_A} = +k_c \cdot b_B \quad \text{with} \quad k_c = \frac{RT_{lg} M_A}{\Delta_{lg} S_A}.
$$

The “ebullioscopic constant” $K_b$ that corresponds to $K_f$ is positive and, because of its higher denominator ($\Delta_{lg} S_A > \Delta_{sl} S_A$), it is (in absolute terms) smaller than $K_f$ (compare Table 12.1). For this reason, the change of temperature here is smaller than for lowering of freezing point and therefore more difficult to measure. Finally, the molar mass $M_B$ results from the equations above by solving for $n_B$ and calculation according to $M_B = m_B / n_B$.

Development of osmotic pressure can also be used in determining amounts of substances and thereby molar masses. The principle of this method, which is also known as osmometry, is to measure the pressure in a solution of known molality. The advantage of this method compared to the other methods using colligative properties is that it is much more sensitive. For instance, an aqueous solution of cane sugar with a concentration of 0.01 mol kg$^{-1}$ exhibits a raising of boiling point of 0.005 K and a lowering of freezing point of 0.02 K. However, the osmotic pressure is 25 kPa (0.25 bar) which can be measured both easily and precisely. Because of its sensitivity, osmometry is useful particularly for the investigation of macromolecular substances such as synthetic polymers, proteins or enzymes having molar mass between $10^4$ and $10^6$ g mol$^{-1}$. The lowering of the freezing point is commonly used in medicine for determining the total osmolality of aqueous solutions such as blood serum or urine.

The gas law also belongs to the colligative properties but often it is not mentioned in this context. It can be used for the same purposes. The vacuum appears here in the role of the solvent, whereas the gas pressure corresponds to the osmotic pressure.

**Topic:** Concentration dependence of \( \mu \) and the most important applications.

### 6.1 The concept of mass action

It has been known for a long time that the amounts of reacting substances can play an important role in the drive of chemical reactions. In 1799, the French chemist Claude-Louis Berthollet was the first to point out this influence and discuss it using many examples. Contrary to the prevailing concept of that time, he stated that it is not necessarily the case that a reaction must completely take place whenever a substance B displaces another substance C in a compound,

\[
B + CD \rightarrow C + BD
\]

(even if there is a great excess of B), but that an equilibrium is established which is dependent upon the amounts of the substances involved. The stronger B is bonded to D, and the greater the amounts of unbound B in the reaction chamber compared to substance C, the more BD should form at the cost of CD and vice versa.

Based upon this finding, we can conclude that the tendency \( \mu \) of substances to transform is not only dependent upon the types of those substances, but also upon their amounts \( n \): The greater the amount of a substance (or the mass proportional to it) in the reaction chamber, the higher its expected potential \( \mu \) should be. Closer scrutiny of this effect which is known as mass action shows that, in this case, the quantity \( n \) itself is unimportant. It is \( n \) in relation to the volume \( V \) in which a substance is distributed, meaning its concentration \( c = n/V \), that is important. If B or C, or both, participate as pure substances in a reaction, meaning at fixed concentrations, their amounts \( n_B \) and \( n_C \) have no influence upon the state of equilibrium and therefore, upon the amounts of BD and CD formed. How much or how little of a substance is present in this case, is apparently not decisive but rather how densely or loosely it is distributed in the space. This means that the more cumulative and concentrated the application, the more intense the effect. In other words, the mass of a substance is not decisive for mass action, but its “massing”, its “density” in a space: not the amount, but the concentration. Cato Maximilian Guldberg and Peter Waage of Norway called attention to this in the year 1864.

Thus, the tendency to transform and therefore the chemical potential of substances increases according to how strongly concentrated they are. Conversely, the chemical potential goes down when the concentration of a substance decreases. We will use an example from everyday life to illustrate this. According to the values of the chemical potentials, pure water vapor must condense at room conditions:

\[
\begin{align*}
H_2O|g & \rightarrow H_2O|l \\
\mu^\Theta/kG: & \quad -228.6 \quad > \quad -237.1 \quad \Rightarrow \Delta \mu^\Theta = -8.5 \text{ kG}
\end{align*}
\]
However, if the vapor is diluted by air, the value of its potential decreases below that of liquid water. It can then undergo a phase transition to the gaseous state. It evaporates. \( \mu(H_2O|g) < \mu(H_2O|l) \) is required for wet laundry, wet dishes and wet streets to dry (if no other causes such as direct sunlight play a role).

### 6.2 Concentration dependence of chemical potential

**Concentration coefficient.** The influence of concentration \( c \) upon the tendency \( \mu \) of a substance to transform can basically be described by a linear relation like it was done in the last chapter to describe the influence of temperature \( T \) and pressure \( p \). As long as \( \Delta c = c - c_0 \) is small enough we have:

\[
\mu = \mu_0 + \gamma \cdot (c - c_0)
\]

for \( \Delta c << c \).

Mass action is an effect which superposes with other less important influences which we will address later and all of which contribute to the concentration coefficient \( \gamma \): \( \gamma = \gamma' + \gamma'' + \ldots \). The symbol \( \times \) above a term will be used here and in the following to denote the quantities dependent upon mass action when it is desirable to distinguish them from similar quantities of different origins. Mass action appears most noticeably at small concentrations where the other influences recede more and more until they can be totally neglected, \( \gamma' \gg \gamma'', \gamma''', \ldots \). If one wishes to investigate this effect as directly as possible, experiments should be carried out with strongly diluted solutions \( c << c^\Theta = 1 \text{ kmol m}^{-3} \).

The temperature coefficient \( \alpha \) and the pressure coefficient \( \beta \) (except for the latter in the case of gases) are not only different from substance to substance but also vary according to type of solvent, temperature, pressure, concentration, etc. In short, they depend upon the overall consistency of the milieu they are in. In contrast, the concentration coefficient \( \gamma \) related to mass action is a universal quantity. At the same \( T \) and \( c \), it is the same for all substances in every milieu. It is directly proportional to the absolute temperature \( T \) and inversely proportional to concentration \( c \) of the substance in question and has the same basic structure as the pressure coefficient \( \beta \) of gases:

\[
\gamma = \gamma = \frac{R T}{c} \quad \text{for} \quad c << c^\Theta \quad \text{where} \quad R = 8.314 \text{ G K}^{-1}.
\]

Because the quantity \( T \) is in the numerator, we can conclude that the mass action gradually loses importance with a decrease of temperature and eventually disappears at 0 K.

**Mass action equations.** If we insert the second equation into the first one, we obtain the following relation

\[
\mu = \mu_0 + \frac{RT}{c} \cdot (c - c_0) \quad \text{for} \quad \Delta c << c << c^\Theta.
\]

Analogous to the considerations about the pressure coefficient \( \beta \) of gases (Section 5.5), a logarithmic relation between \( \mu \) and \( c \) is the result:
\[ \mu = \mu_0 + RT \ln \frac{c}{c_0} \quad \text{for } c, c_0 \ll c^\Theta \] (mass action equation 1).

We will return to the term “mass action equation” below.

As already mentioned, precise measurements show that the relation above is not strictly adhered to. At higher concentrations, values depart quite noticeably from this relation. If we gradually move to lower concentrations, the differences become smaller. The equation here expresses a so-called “limiting law” which strictly applies only when \( c \to 0 \). For this reason, we have added the requirement for a small concentration \( (c, c_0 \ll c^\Theta) \) to the equation.

In practice, this relation serves as a useful approximation up to rather high concentrations. In the case of electrically neutral substances, deviations are only noticeable above 100 mol m\(^{-3}\). For ions, deviations become observable above 1 mol m\(^{-3}\), but they are so small that they are easily neglected if accuracy is not of prime concern. For practical applications let us remember that:

\[ \mu \approx \mu_0 + RT \ln \frac{c}{c_0} \quad \text{for } c < \begin{cases} 100 \text{ mol m}^{-3} & \text{for neutral substances,} \\ 1 \text{ mol m}^{-3} & \text{for ions.} \end{cases} \]

However, it is precisely for standard concentration \( c^\Theta = 1000 \text{ mol m}^{-3} = 1 \text{ mol L}^{-1} \) (the usual reference value), that the logarithmic relation is not satisfied for any substance. Still, this concentration is used as the usual starting value for calculating potentials, and we write:

\[ \mu = \tilde{\mu} + RT \ln \frac{c}{c^\Theta} = \tilde{\mu} + RT \ln c \quad \text{for } c \ll c^\Theta \] (mass action equation 1’).

**Basic value.** Here, \( c_r \) is the relative concentration. \( \tilde{\mu} \), intended as the basic value (at fixed concentration \( c^\Theta \)) has been chosen so that the equation gives the right results at low values of concentration. In contrast to the mass action equation 1, the initial value of \( \mu \) is no longer real, but fictitious. Note that the basic value \( \mu \) of a dissolved substance \( B \) depends upon pressure \( p \) and temperature \( T \), \( \tilde{\mu}_B(p, T) \). This distinguishes it from the standard value \( \mu^\Theta_B = \tilde{\mu}_B(p^\Theta, T^\Theta) \) already known to us. The term \( RT \ln c_r = \mu \) is also called the mass action term.

In its first or second version, this law describes mass action formally as a characteristic of the chemical potential. We assign to these equations a name in order to refer to them more easily. In fact, we will assign the same name to all relations of this type (there are several more of them), “mass action equations.” As expected, the tendency of a substance to transform increases with its concentration. This does not happen linearly, though, but logarithmically. We obtain the following graph for the dependence of the chemical potential of a dissolved substance upon its concentration (Fig. 6.1):

Fig. 6.1: Dependence of the chemical potential upon concentration.

For small concentrations, the measured curve approximates the dotted logarithmic function very well while, at higher concentrations, the two diverge noticeably. Depending upon the type of substance, the actual curves can run above or below the logarithmic ones. Keep in mind that the basic value $\mu^\circ$ of the chemical potential of the dissolved substance coincides with the logarithmic approximation and not with the measured function!

Decapotential. The logarithmic initial part of the $\mu(c)$ curve, which theoretically extends to $-\infty$, is the same for all substances in every type of milieu. If the concentration increases one decade (a factor of ten), the chemical potential always increases by the same amount $\mu_d$, the so-called “decapotential” (which is still dependent upon temperature $T$):

$$\mu \rightarrow \mu + \mu_d \quad \text{for} \quad c \rightarrow 10c, \quad \text{as long as} \quad c \ll c^\Theta.$$

In order to calculate the $\mu_d$ value at room temperature, we only need to go back to the first of our mass action equations and to insert $c = 10c_0$:

$$\mu = \mu_0 + RT \ln \frac{10c_0}{c_0}$$

$$\mu_d = RT \ln 10 = 8.314 \text{ G K}^{-1} \cdot 298 \text{ K} \cdot \ln 10 = 5.708 \text{ kG}.$$

It is helpful to remember the value $\mu_d \approx 5.7 \text{ kG}$ (approximately $\approx 6 \text{ kG}$) in order to quickly estimate the influence of a change of concentration of a substance upon the level of its potential or vice versa.

In summary, when the concentration $c$ of a substance increases to 10 times its initial value at room temperature, its chemical potential $\mu$ increases by 6 kG. It does not matter,

- what substance it is,
- what it is dissolved in,
- how often this step is repeated (assuming that the concentration remains small enough).

Practical examples. To obtain a better impression of the order of magnitude of the potentials, we will look at a concrete example. We have chosen $\mu(c)$ for ethanol (Fig. 6.2).

Fig. 6.2: Dependence upon concentration of the chemical potential of ethanol in water at 298 K.
The basic value of the potential of dissolved ethanol (in water) has been added to the graph. This value lies only about 0.1 kG above the actual \(\mu\) value at standard concentration. The basic value of pure ethanol has also been included (the peculiarities in the case of basic values of (nearly) pure substances will be discussed later).

Using the newly derived relations, we will again take a closer look at evaporation. When the vapor is diluted by air, say, by a factor of 100 (by two orders of magnitude), its potential goes down by around \(2 \cdot 5.7 \text{ kG} = 11.4 \text{ kG}\) to about \(-240.0 \text{ kG}\). At that point, \(\mu(\text{H}_2\text{O}|\text{g})\) actually lies below the value for liquid water and evaporation takes place. At a concentration of \(\gamma/\gamma_0\), the air is already so moist that it cannot absorb any more water. It is said to be saturated. A concentration of \(\gamma/\gamma_0\) means about 1.5 orders of magnitude below the concentration of pure vapor. Therefore, the water vapor potential lies about \(1.5 \times 5.7 \text{ kG} = 8.6 \text{ kG}\) below the value for pure vapor. At \(-237.2 \text{ kG}\), it is at about the same level as that of liquid water and the drive to evaporate disappears. Even a little higher concentration leads to condensation and the excess water precipitates as dew.

**6.3 Concentration dependence of chemical drive**

We can now use what we have learned to easily show how shifts in concentration affect the chemical drive to react. Observe the following reaction

\[
B + C + ... \rightarrow D + E + ...
\]

between dissolved substances, meaning a homogeneous reaction. The drive results in

\[
A = [\mu_B + \mu_C + ...] - [\mu_D + \mu_E + ...].
\]

If all the substances are present in small concentrations, we can apply the mass action equation for all of them:

\[
A = \left[\hat{\mu}_B + RT \ln c_r(B) + \hat{\mu}_C + RT \ln c_r(C) + ...\right] - \left[\hat{\mu}_D + RT \ln c_r(D) + \hat{\mu}_E + RT \ln c_r(E) + ...\right].
\]

The terms of the equation can be sorted a bit

\[
A = \left[\hat{\mu}_B + \hat{\mu}_C + ... - \hat{\mu}_D - \hat{\mu}_E - ...ight] + \left[RT \ln c_r(B) + \ln c_r(C) + ... - \ln c_r(D) - \ln c_r(E) - ...\right]
\]

and the final result is

\[
A = \hat{A} + RT \frac{c_r(B) \cdot c_r(C) \cdot ...}{c_r(D) \cdot c_r(E) \cdot ...}.
\]

We have applied the rules for logarithms (“log rules”) (cp. Appendix A1.1), more precisely the rule (A1.2): \(\log(x/y) = \log x - \log y\).

The result is \(\hat{A} = \hat{\mu}_B + \hat{\mu}_C + ... - \hat{\mu}_D - \hat{\mu}_E - ...\) for the basic value \(\hat{A}\). It expresses the (hypothetical) drive when all reaction partners have the standard concentration of 1 kmol m\(^{-3}\).

\[
RT \frac{c_r(B) \cdot c_r(C) \cdot ...}{c_r(D) \cdot c_r(E) \cdot ...} = \hat{A}
\]

in turn, represents the mass action term.
We will explain the influence of concentration shifts upon the chemical drive using the example of decomposing cane sugar,

\[ \text{Sac}_{w} + \text{H}_2\text{O}_{l} \rightarrow \text{Glc}_{w} + \text{Fru}_{w}. \]

Sac is the abbreviation for cane sugar (sucrose, C\(_{12}H_{22}O_{11}\)), Glc and Fru represent the isomeric monosaccharides grape sugar (glucose, C\(_{6}H_{12}O_{6}\)) and fruit sugar (fructose, C\(_{6}H_{12}O_{6}\)). From the chemical potentials, we obtain the following for the drive \( A \):

\[
A = \mu(\text{Sac}) + \mu(\text{H}_2\text{O}) - \mu(\text{Glc}) - \mu(\text{Fru})
\]

\[
= \tilde{\mu}(\text{Sac}) + RT \ln \frac{c(\text{Sac})}{c^o} + \tilde{\mu}(\text{H}_2\text{O}) - \tilde{\mu}(\text{Glc}) - RT \ln \frac{c(\text{Glc})}{c^o} - \tilde{\mu}(\text{Fru}) - RT \ln \frac{c(\text{Fru})}{c^o}.
\]

We cannot apply the mass action equation to water because its concentration lies far outside the equation’s range of validity, \( c(\text{H}_2\text{O}) \approx 50 \text{ kmol m}^{-3} \). The potential curves for high \( c \) values are very flat, and the \( c(\text{H}_2\text{O}) \) value in dilute solutions does not differ significantly from the concentration for pure water so it is not only possible to replace the actual \( \mu(\text{H}_2\text{O}) \) value with that of pure water but that is what we must do. We will indicate the potential for the pure solvent (in this case water) similarly to the basic potentials of dissolved substances \( \tilde{\mu} : \tilde{\mu}(\text{H}_2\text{O}) \).

In general, solvents of dilute solutions can be approximated well by pure substances. Therefore, we obtain for the drive of the decomposition of cane sugar:

\[
\mu^{\Theta}/\text{kG:} \quad -1565 \quad -237 \quad -917 \quad -916 \quad \Rightarrow A^{\Theta} = +31 \text{ kG}.
\]

A brief comment about how to write arguments and indexes: \( \mu(\text{H}_2\text{O}), c(\text{H}_2\text{O}) \) ... and \( \mu_{\text{H}_2\text{O}}, c_{\text{H}_2\text{O}} \) ... are treated as equivalent forms. In the case of long names of substances or substance formulas with indexes (such as H\(_2\)O) or an accumulation of indexes, the preferred way of writing is the first one, otherwise, for the sake of brevity, the second.

For the more general reaction

\[
\nu_B[B] + \nu_C[C] + ... \rightarrow \nu_D[D] + \nu_E[E] + ...
\]

we correspondingly obtain

\[
A = \left[ \nu_B \mu_B + \nu_C \mu_C + ... - \nu_D \mu_D + \nu_E \mu_E + ...ight].
\]

If the concentration dependence of the chemical potential is taken into account, it results in

\[
A = \left[ \nu_B \tilde{\mu}_B + \nu_B RT \ln c_r(B) + \nu_C \tilde{\mu}_C + \nu_C RT \ln c_r(C) + ...ight] - \left[ \nu_D \tilde{\mu}_D + \nu_D RT \ln c_r(D) + \nu_E \tilde{\mu}_E + \nu_E RT \ln c_r(E) + ...ight].
\]

We can rearrange

\[ \mathcal{A} = \left[ v_B \bar{\mu}_B + v_C \bar{\mu}_C + \ldots - v_D \bar{\mu}_D - v_E \bar{\mu}_E - \ldots \right] + RT \left[ v_B \ln c_r(B) + v_C \ln c_r(C) + \ldots - v_D \ln c_r(D) - v_E \ln c_r(E) - \ldots \right] \]

and obtain

\[ \mathcal{A} = \tilde{\mathcal{A}} + RT \ln \frac{c_r(B)^{k_B} \cdot c_r(C)^{k_C} \ldots}{c_r(D)^{n_D} \cdot c_r(E)^{n_E} \ldots} \cdot \]

Here, additionally the logarithm rule (A1.3) has been applied: \( \log(x^a) = a \cdot \log(x) \).

Let us now take another look at a concrete example. For this, we choose the reaction of \( \text{Fe}^{3+} \) ions with \( \Gamma^- \) ions:

\[ 2 \text{Fe}^{3+} |w + 2 \Gamma^- |w \rightarrow 2 \text{Fe}^{2+} |w + \Gamma^- |w \]

Therefore, the conversion numbers are: \( v_{\text{Fe}^{3+}} = -2 \), \( v_{\Gamma^-} = -2 \), \( v_{\text{Fe}^{2+}} = +2 \) und \( v_{\Gamma^-} = +1 \). Insertion into the formula above results in:

\[ \mathcal{A} = \tilde{\mathcal{A}} + RT \ln \frac{c_r(\text{Fe}^{3+})^2 \cdot c_r(\Gamma^-)^2}{c_r(\text{Fe}^{2+})^2 \cdot c_r(\Gamma^-)^2} \]

However, the concentrations do not remain constant during a reaction. They change in the course of the reaction. If there is only one substance at the beginning, its concentration decreases continuously to the benefit of the product. Using the simplest reaction possible, we will discuss the transformation of a substance B into a substance D:

\[ B \rightarrow D. \]

An example would be the transition of \( \alpha \)-D-glucose into the isomeric \( \beta \)-D-glucose in aqueous solution. These are two stereoisomers of glucose \( C_6H_{12}O_6 \), i.e. the isomers do not differ in the structure (unlike the structural isomers described in Section 1.2) but only in the spatial placement of substituents with the same bond structure. In our case the position of the OH group at the first C atom (characterized by \( * \)) is different. This OH group was formed by the ring closure thereby making the first C atom chiral as well, since its four bonds lead to four different groups.

\[ \alpha \text{-D-Glc}|w \rightarrow \beta \text{-D-Glc}|w \]

(The transition takes place via the open-chain form, but its concentration is so small that it can be ignored.)

We obtain for the drive of the transformation at standard conditions:
The two substances are optically active, i.e. the plane of linearly polarized light is rotated when the light passes through their solutions. Pure α-D-glucose shows an angle of rotation of +112°, pure β-D-glucose, however, one of +18.7°. Therefore, a polarimeter can be used to observe the change in the solution’s angle of rotation. When crystals of pure α-D-glucose are dissolved in water, the specific rotation of the solution decreases gradually from an initial value of +112° to a value of +52.7°.

In Section 1.7, the extent of conversion (extent of reaction) $\xi$ was introduced as a measure of the progress of a reaction. The amounts $n_i$ and therefore the concentrations $c_i$ of the substances involved change with increasing $\xi$. Starting with the initial values $n_{i,0}$ and $c_{i,0}$, respectively, we obtain:

$$n_i = n_{i,0} + v_i \xi \quad \text{and} \quad c_i = c_{i,0} + v_i \cdot \xi / V .$$

The drive $\mathcal{A}$ of a reaction changes along with the concentrations $c_i$. If one assumes a concentration of $c_0$ of the initial substance B as well as an absence of the product D at the beginning of the reaction, the concentration of D after a certain period of time will be $\xi / V$, that of B $c_0 - \xi / V$. Therefore, the following relation for the dependence of the drive upon the extent of conversion is obtained:

$$\mathcal{A} = \mathcal{A} + RT \ln \left( \frac{c_0 - \xi / V}{c_0} / c_0 \right) = \mathcal{A} + RT \ln \left( \frac{c_0 - \xi / V}{\xi / V} \right) .$$

For the sake of simplicity, we will now relate the extent of conversion $\xi$ to the maximum possible value $\xi_{\text{max}}$. This value is reached when one of the initial substances (here only one) is entirely consumed, i.e. its concentration disappears. In this case, the numerator $c_0 - \xi / V$ equals 0, a fact that results in $c_0 = \xi_{\text{max}} / V$. Dividing numerator and denominator by $c_0$ yields:

$$\mathcal{A} = \mathcal{A} + RT \ln \frac{1 - \xi / \xi_{\text{max}}}{\xi / \xi_{\text{max}}} .$$

Because we will use the quotients $\xi / V$ und $\xi / \xi_{\text{max}}$ frequently we assign to them their own symbol and name:

$$c_\xi := \frac{\xi}{V} \quad \text{“density of conversion”},$$
$$\alpha_\xi := \frac{\xi}{\xi_{\text{max}}} \quad \text{“degree of conversion.”}$$

The index $\xi$ is added for clarification to avoid confusion with the molar concentration $c_i$ and the temperature coefficient $\alpha_i$ of the chemical potential. For the drive we obtain correspondingly:

$$\mathcal{A} = \mathcal{A} + RT \ln \frac{c_0 - c_\xi}{c_\xi} \quad \text{and} \quad \mathcal{A} = \mathcal{A} + RT \ln \frac{1 - \alpha_\xi}{\alpha_\xi} .$$
With a standard value of \( \mathcal{A}^\Theta = 1.25 \) kG for the transition of \( \alpha \)-D- into \( \beta \)-D-glucose at room temperature, a characteristic S shaped curve is obtained for the dependence of chemical drive upon extent of conversion \( \xi \) (Fig. 6.3).

**Fig. 6.3:** Dependence of chemical drive \( \mathcal{A} \) upon the degree of conversion \( \alpha_\xi \) for the transition of \( \alpha \)-D glucose into \( \beta \)-D glucose in an aqueous solution at room temperature.

At the beginning of the reaction, meaning for \( \alpha_\xi = 0 \), \( \mathcal{A} \) equals \( +\infty \). \( \mathcal{A} \) decreases during the reaction and, at an \( \mathcal{A} \) dependent \( \xi \) value, finally reaches a value of zero (equilibrium point). When all the initial substance has been used up, meaning at \( \alpha_\xi = 1 \), \( \mathcal{A} \) takes a final value of \( -\infty \).

The mathematical relation becomes rather complicated for reactions with a complex stoichiometry such as the reaction of Fe\(^{3+}\) ions with I\(^-\) ions mentioned above. For better overview, it would be advisable in this case to create a table (Tab. 6.1). For each substance involved, the table lists in the first row the standard value of its chemical potential for calculating the drive of the reaction under standard conditions. In the following, we assume that at the beginning of the reaction, Fe\(^{3+}\) and I\(^-\) both have a concentration of \( c_0 \) and that Fe\(^{2+}\) und I\(_2\) are absent. The concrete values of the initial concentrations of the substances follow in the next row. Finally, the formulas for the concentrations at an arbitrary time \( t \) are listed which can be calculated by using the stoichiometry of the reaction. \( c_\xi \) is the density of conversion:

\[
2 \text{ Fe}^{3+} + 2 I^- \rightarrow 2 \text{ Fe}^{2+} + I_2
\]

\[
\mu^\Theta: \quad 2\cdot(-4.7) \quad 2\cdot(-51.6) \quad 2\cdot(-78.9) \quad 16.4 \ \text{kG} \quad \Rightarrow \mathcal{A}^\Theta = +28.8 \ \text{kG}
\]

| \( c_0 \) | \( 0.001 \) | \( 0.001 \) | \( 0 \) | \( 0 \) | kmol m\(^{-3}\) |
| \( c_\xi \) | \( c_0 - 2c_\xi \) | \( c_0 - 2c_\xi \) | \( 2c_\xi \) | \( c_\xi \) |

Tab. 6.1: Collection of data relevant for a concrete reaction

If we insert the expressions for the concentrations \( c_\xi \) into the equation above, we obtain for the drive of the reaction:

\[
\mathcal{A} = \mathcal{A} + RT \ln \left( \frac{[c_0 - 2c_\xi/c^\Theta] \cdot [(c_0 - 2c_\xi/c^\Theta)]^2}{[(2c_\xi/c^\Theta)^2] \cdot [(c_\xi/c^\Theta)]} \right) = \mathcal{A} + RT \ln \left( \frac{(c_0 - 2c_\xi)^4}{4c_\xi^3 \cdot c^\Theta} \right).
\]

The density of conversion \( c_\xi \) reaches its maximum value if \( c_0 - 2c_\xi \) in the numerator vanishes, meaning \( c_0 = 2c_{\xi,\text{max}} \). If we also consider the relationship \( \alpha_\xi = c_\xi/c_{\xi,\text{max}} (= \xi/\xi_{\text{max}}) \) the equation above can be written as follows:

\[
\mathcal{A} = \mathcal{A} + RT \ln \left( \frac{2(1-\alpha_\xi)^4 c_\Theta}{\alpha_\xi^3 \cdot c^\Theta} \right).
\]

Despite the more complex stoichiometry of the reaction and the correspondingly more complicated calculations, we obtain again the typical S shaped curve (Fig. 6.4).

**Fig. 6.4:** Dependence of drive $\mathcal{A}$ upon the degree of conversion $\alpha_f$ for the reaction $2 \text{Fe}^{3+} + 2 \text{I}^- \rightarrow 2 \text{Fe}^{2+} + \text{I}_2$ in an aqueous solution at room temperature (at initial concentrations of $\text{Fe}^{3+}$ and $\text{I}^-$ of $0.001 \text{ kmol m}^{-3}$).

Let us remind ourselves of the criteria for a transformation which we were introduced to in Chapter 4: A reaction takes place spontaneously as long as drive $\mathcal{A}$ is positive. At $\mathcal{A} = 0$, there is equilibrium. A negative drive forces a reaction backwards against the direction the reaction arrow points in.

Here are some important consequences for the reaction process:

- Every homogeneous reaction begins spontaneously (if the concentrations of the reaction products are equal to zero at the beginning, we start with $\mathcal{A} = +\infty$).
- At a certain extent of conversion, the reaction ceases to change the ratio of reactants to products. We can also say that equilibrium is established.
- Equilibrium can be reached from both sides, meaning from the side of the initial substances as well as from the side of the reaction products.

In equilibrium, neither the forward reaction nor the backward reaction take place spontaneously. Macroscopically speaking, there is no more transformation and the composition of the reaction mixture remains constant. However, forward and backward reactions do continue to occur at the microscopic level between the particles. These happen at identical rates though, so that the transformations in the two directions compensate for each other. In this case, one speaks traditionally of a *dynamic equilibrium*, an equality of forward and backward “forces” although one means a *kinetic equilibrium*, an equality of forward and backward reaction rates. We will go into this in more detail later on in Section 17.2.

### 6.4 The mass action law

What is commonly known as the *mass action law* as defined by Guldberg and Waage, is a consequence of a combination of the mass actions of individual substances participating in a reaction. Let us, once again, consider a reaction in a homogeneous solution

$$\text{B} + \text{C} + \ldots \rightleftharpoons \text{D} + \text{E} + \ldots .$$

*Equilibrium* is established when there is no longer any potential gradient and the drive $\mathcal{A}$ disappears. Therefore:

$$\mathcal{A} = \mathcal{A} \circ + RT \ln \frac{c_r(B) \cdot c_r(C) \cdots}{c_r(D) \cdot c_r(E) \cdots} = 0.$$
Consequently, we obtain

\[ \hat{A} = -RT \ln \frac{c_i(B) \cdot c_i(C) \cdots}{c_i(D) \cdot c_i(E) \cdots} \]

or by applying the logarithm rules (Appendix A1.1)

\[ \hat{A} = RT \ln \frac{c_i(D) \cdot c_i(E) \cdots}{c_i(B) \cdot c_i(C) \cdots} . \]

When we divide by \( RT \) and take the antilogarithm, we finally obtain

\[ \hat{K} = \left( \frac{c_i(D) \cdot c_i(E) \cdots}{c_i(B) \cdot c_i(C) \cdots} \right)_{\text{eq.}} \quad \text{with} \quad \hat{K} := \exp \frac{\hat{A}}{RT} . \]

This equation characterizes the relationship between concentrations in **equilibrium** which has been referred to by the index \( \text{eq.} \) and shows a possible form of the mass action law for the reaction. The quantity \( \hat{K} \) which is called the **equilibrium constant** of the reaction is so named because it does not depend upon the concentration of the substances. A more precise name, however, would be **equilibrium number** because \( \hat{K} \) is a number and it is not constant but dependent upon temperature, pressure, solvent, etc. The index \( \circ \) which is actually superfluous, has been inserted in order to emphasize that \( \hat{K} \) is to be formed from \( \hat{A} \) (and not from \( \mathcal{A}! \)).

For the more general reaction between dissolved substances

\[ |v_B|B + |v_C|C + \cdots \rightleftharpoons v_D D + v_E E + \cdots \]

we obtain entirely appropriately

\[ \hat{K} = \left( \frac{c_i(D)^{v_D} \cdot c_i(E)^{v_E} \cdots}{c_i(B)^{v_B} \cdot c_i(C)^{v_C} \cdots} \right)_{\text{eq.}} . \]

Conventionally, the relative concentrations \( c \) are replaced by \( c / c^\Theta \) and the fixed standard concentration \( c^\Theta \) is combined with the equilibrium number \( \hat{K} \) to form the new equilibrium constant \( \hat{K} \) (\( \kappa \)“dimension factor”):

\[ \hat{K} = \kappa \hat{K} , \quad \text{where} \quad \kappa = (c^\Theta)^{v_c} \quad \text{with} \quad v_c = v_B + v_C + \cdots + v_D + v_E + \cdots . \]

\( v_c \) is the sum of the conversion numbers of dissolved substances, more precisely, those substances which show a dependence of the chemical potential upon concentration \( c \); this is indicated by the index \( c \). If the chemical potentials of all substances involved are concentration dependent, this fact can be emphasized by writing \( \hat{K}_c \) and \( \hat{K}_e \). In our first example, the conversion numbers are \(-1\) for the initial substances \( B, C, \ldots \) and \(+1\) for the products \( D, E, \ldots \). As stated above, \( \hat{K}_e \) is always a number while the conventional constant \( \hat{K} \) has the unit \( \text{(mol m}^{-3})^\kappa \). Only when \( v_c \) happens to be 0, are \( \hat{K}_c \) and \( \hat{K} \) identical. \( \hat{K} \) is the more convenient quantity for formulating the mass action law,

\[ \hat{K} = \hat{K}_c = \left( \frac{c_D \cdot c_E \cdots}{c_B \cdot c_C \cdots} \right)_{\text{eq.}} , \]
while, for general considerations, $\tilde{K}$ is preferred since its dimension is the same for all reactions.

Here is an example of what has been said. With the help of table A2.1 in the Appendix, we will determine the *acidity constant* of acetic acid (CH$_3$COOH), abbreviated to HAc, in an aqueous solution, i.e., the equilibrium constant for the *dissociation* of acetic acid in water

$$\text{HAc}\warrow \rightleftharpoons \text{H}^+\warrow + \text{Ac}^-\warrow$$

\[
\mu^\Theta/\text{kG}: \begin{array}{ccc}
-396.46 & 0 & -369.31 \\
\Rightarrow \quad \nu_1 = -27.15 \text{ kG}
\end{array}
\]

or the equilibrium constant for the *proton transfer* from acetic acid to water in BRONSTED’s sense (this will be discussed in more detail in the next chapter)

$$\text{HAc}\warrow + \text{H}_2\text{O}|l \rightleftharpoons \text{H}^+\warrow + \text{Ac}^-\warrow$$

\[
\mu^\Theta/\text{kG}: \begin{array}{ccc}
-396.46 & -237.14 & -237.14 & -369.31 \\
\Rightarrow \quad \nu_2 = -27.15 \text{ kG}
\end{array}
\]

In both cases, the chemical drive has the same value meaning that the equilibrium numbers calculated by using this value are identical: $K^\Theta = \exp(\Delta^\Theta/RT) = 1.74 \cdot 10^{-5}$ (at 298 K and 100 kPa). Because the dimension factors $\kappa = (c^\Theta)\nu$ are equal ($\nu_1 = -1 + 1 + 1 = +1 = \nu_2$, since the solvent water is treated as pure substance and therefore does not appear in the sum $\nu_2$ of conversion numbers), this is also valid for the equilibrium constants $K^\Theta = 1.74 \cdot 10^{-5} \text{ kmol m}^{-3}$. In the first case, the mass action law is written numerically as

$$\tilde{K}_1 = \frac{c_i(\text{H}^+) \cdot c_i(\text{Ac}^-)}{c_i(\text{HAc})}$$

and in the conventional way as

$$\tilde{K}_1 = \frac{c(\text{H}^+) \cdot c(\text{Ac}^-)}{c(\text{HAc})} = \kappa \tilde{K}_1$$

In the second case, when we take into account that the solvent water has to be treated as a pure substance, we obtain for the mass action law

$$\tilde{K}_2 = \frac{c_i(\text{H}_2\text{O}^+) \cdot c_i(\text{Ac}^-)}{c_i(\text{HAc})}$$

and written in the conventional way,

$$\tilde{K}_2 = \frac{c(\text{H}_2\text{O}^+) \cdot c(\text{Ac}^-)}{c(\text{HAc})} = \kappa \tilde{K}_2$$

We have to keep in mind that $\text{H}^+\warrow$ and $\text{H}_2\text{O}^+\warrow$ are merely two different notations for the same kind of particle. From now on, we will avoid the rather cumbersome index eq. as long as it is clear from the relation, as in this example, that we are dealing with the equilibrium composition.
The mass action law’s range of validity is the same as that of the mass action equations (from which it is derived). The smaller the concentrations, the more strictly the law applies. At higher concentrations, deviations occur as the result of molecular or ionic interactions.

The magnitude of the equilibrium number determined according to

$$\bar{A} = RT \ln \bar{K}$$

is a good qualitative indication for how a reaction proceeds. The more strongly positive $\bar{A}$ is, the greater $\bar{K}$ ($\bar{K} \gg 1$) is. In this case, the end products dominate in the equilibrium composition. Because of the logarithmic relation, even small changes to $\bar{A}$ lead to noticeable shifts in the position of equilibrium. On the other hand, if $\bar{A}$ is strongly negative, $\bar{K}$ approaches zero ($\bar{K} \ll 1$) and the initial substances dominate in the equilibrium composition. At the same time, this also means that, even for negative $\bar{A}$, a small amount of the initial substance is still converted into the end products because $\bar{K}$ has a small yet finite value. When $\bar{A} \approx 0$ and therefore $\bar{K} \approx 1$, the initial substances and end products are present in comparable amounts in equilibrium. (Keep in mind, however, that in all three cases discussed, $\bar{A} = 0$! since we have equilibrium.)

With the help of the equilibrium number or the conventional equilibrium constant, the equilibrium composition of a mixture which has formed by spontaneous transformation of given amounts of initial substances can be quantitatively determined. If, for example, pure $\alpha$-D-glucose at the concentration $c_0 = 0.1 \text{ kmol m}^{-3}$ is dissolved in water, one can use a polarimeter to observe a continuous change to the angle of rotation until a constant value is finally achieved. This can be ascribed to the partial transition of $\alpha$-D-glucose into $\beta$-D-glucose (remember the discussion further above). If we indicate the concentration of $\beta$-D-glucose in equilibrium by the density of conversion $c_\xi$, we obtain in equilibrium

$$\bar{K} = \kappa \cdot \exp \frac{\bar{A}}{RT} = \frac{c_\xi}{c_0 - c_\xi}.$$

The dimension factor $\kappa$ equals 1 because of $\nu_c = 0$. The equilibrium constant at room temperature can be calculated by use of the standard value $\bar{A}^\circ = 1.25 \text{ kG}$ (see Section 6.3):

$$K^\circ = \exp \frac{1.25 \cdot 10^3 \text{ G}}{8.314 \text{ G K}^{-1} \cdot 298 \text{ K}} = 1.66.$$

Solving for $c_\xi$ results in:

$$c_\xi = \frac{K^\circ \cdot c_0}{K^\circ + 1} = \frac{1.66 \cdot 0.1 \text{ kmol m}^{-3}}{1.66 + 1} = 0.0624 \text{ kmol m}^{-3}.$$

According to this, the state of equilibrium shows that 37.6 % of all dissolved molecules are $\alpha$-D-glucose molecules and 62.4 % are $\beta$-D-glucose molecules.

The mathematical relations become rather complicated for reactions with a more complex stoichiometry. If we like to determine for example the equilibrium composition in the case of the reaction
2 Fe$^{3+}$|w + 2 I$^-$|w $\rightarrow$ 2 Fe$^{2+}$|w + I$_2$|w

caracterized by the table above, we obtain

$$\tilde{K} = \kappa \cdot \exp \left( \frac{\tilde{A}}{RT} \right) = \frac{4c_\xi^3}{(c_0 - 2c_\xi)^4}$$

with the dimension factor $\kappa = (c^\Theta)^{-1} = 1 \text{ kmol}^{-1} \text{ m}^3$ (because of $v_\xi = -2 - 2 + 2 + 1 = -1$). Because the value of $\tilde{A}$ is positive and relatively high ($\tilde{A} = +29 \text{ kG}$), we have $K^\Theta >> 1$, i.e. we can expect that the end products dominate in the equilibrium composition. For more detailed data we have to solve the equation above for $c_\xi$. Because a higher degree polynomial is involved, a numerical technique using appropriate mathematical software or a graphical approach are advisable. The equilibrium point can be determined from the figure in Section 6.3: $\alpha_\xi = c_\xi/c_{\xi,max} \approx 0.79$. The concentrations of the substances in the equilibrium mixture are therefore $c(\text{Fe}^{3+}) \approx 0.21 \text{ mol m}^{-3}$ and $c(\Gamma) \approx 0.21 \text{ mol m}^{-3}$ for the initial substances and $c(\text{Fe}^{2+}) \approx 0.79 \text{ mol m}^{-3}$ and $c(\text{I}_2) \approx 0.39 \text{ mol m}^{-3}$ for the final products, respectively.

We can also use the equation $\tilde{A} = RT \ln \tilde{K}$ the other way around to experimentally determine the basic drive $\tilde{A}$ of a reaction. In order to do this, it suffices to first calculate the equilibrium number $\tilde{K}$ and then to derive $\tilde{A}$ from it. At first glance, this looks amazingly easy, but the reaction can be so strongly inhibited that the concentrations being determined do not correspond to equilibrium values. This obstacle can be overcome, though, by adding a catalyst (compare to Section 19.2). As long as the added amount remains small, the position of equilibrium does not change and we can directly use the equilibrium values obtained in the equation above. Once the basic drive is known, the drive for any other concentration can be calculated provided that its values lie within the range of validity of the mass action equations.

### 6.5 Special versions of the mass action equation

Until now, we have described mass action by using functions in which the concentrations $c$ or, more exactly, the ratios $c/c_0$ or $c/c^\Theta$ appear as arguments. Instead of $c$, it would be possible to introduce any other measure of composition as long as it is proportional to concentration. This is almost always the case at small $c$ values. We will highlight two of these measures here because they are of greater importance.

When the pressure of a gas is increased, the concentration of the gas particles also increases because they are compressed into a smaller volume. If the temperature remains unchanged, the concentration grows proportionally to the pressure: $c \sim p$, or

$$\frac{c}{c_0} = \frac{p}{p_0}.$$  

As a result, the concentration ratio in the mass action equation for gases can be replaced by the pressure ratio:

$$\mu = \mu_0 + RT \ln \frac{p}{p_0}$$  

for $p, p_0 << 10 p^\Theta$  (mass action equation 2).
This equation is precise enough to be applied to pressures up to about $10^2$ kPa (1 bar). It also lends itself to estimates up to $10^3$ or even $10^4$ kPa. In anticipation of this, we have applied the equation above to treating the pressure dependence of the chemical potential of gases (Section 5.5).

The mass action equation 2 can be generalized somewhat. In the case of gaseous mixtures, one imagines that each component B, C, D, ... produces a partial pressure which is independent of its partners in the mixture. This corresponds to the pressure that the gaseous components would have if they alone were to fill up the available volume. The total pressure $p$ of the gaseous mixture is simply equal to the sum of the partial pressures of all the components present (DALTON’s law):

$$p_{\text{total}} = p_B + p_C + p_D + ...$$

(as well as $c_{\text{total}} = c_B + c_C + c_D + ...$).

If a gas is compressed, the concentrations of all the components and the partial pressures increase. This is exactly as if the gases were separate from each other. The formula $c \sim p$ is valid even when $p$ represents only a partial pressure of a gas and not the total pressure. Hence, the equation $c/c_0 = p/p_0$ as well as the mass action equation remain correct if we take $c$ to be the partial concentration and $p$ the partial pressure of a gas in a mixture.

In closing, we will once more into the problem of the starting or reference values when calculating potentials. Normally, the standard pressure $p^\Theta = 100$ kPa is chosen as the initial value for pressure although at this pressure, the chemical potential $\mu$ already deviates somewhat from the value the mass action equation yields. In order to have the results remain correct at low pressures, the true $\mu$ value at standard pressure cannot be inserted. Instead, a fictitious value which varies from it somewhat must be used (this is analogous to the procedure used for concentrations). This fictitious value that is valid for standard pressure can be found in tables and then used to calculate the potentials at any other, not too high pressure. This special value is also called the basic value $\hat{\mu}$, which should be indicated again by the index $^\circ$ placed above the symbol:

$$\mu = \hat{\mu} + RT \ln \frac{p}{p^\Theta} = \hat{\mu} + RT \ln p_r \quad \text{for } p << p^\Theta \quad \text{(mass action equation 2')},$$

where $p_r$ is the relative pressure. In contrast to this, all the $\mu$ values in the mass action equation 2 are real.

Another much used measure of composition is mole fraction $x$. As long as the content of a substance in a solution is small, concentrations and mole fractions are proportional to each other: $c \sim x$ for small $c$. In turn, this means

$$\frac{c}{c_0} = \frac{x}{x_0}.$$

Hence, $x/x_0$ can replace the concentration ratio $c/c_0$ in the mass action equation:

$$\mu = \mu_0 + RT \ln \frac{x}{x_0} \quad \text{for } x, x_0 << 1 \quad \text{(mass action equation 3')}.$$
6.6 Applications of the mass action law

Disturbance of equilibrium. One way to disturb a pre-existing equilibrium would be to add a certain amount of one of the starting substances to the reaction mixture. Gradually, a new equilibrium would be established where the new equilibrium concentrations differ from the original ones. However, in all, the above relation

$$K = \frac{c(D)^{n_D} \cdot c(E)^{n_E} \cdot \ldots}{c(B)^{n_B} \cdot c(C)^{n_C} \cdot \ldots}$$

remains fulfilled.

As an example, we consider the equilibrium in aqueous solution between iron hexaquo complex cations and thiocyanate anions on the one hand and the blood red iron thiocyanate complex on the other which can be described in the following simplified manner:

$$[\text{Fe(H}_2\text{O)}_6\text{]}^{3+}|w + 3 \text{SCN}^-|w \rightleftharpoons [\text{Fe(H}_2\text{O)}_3\text{(SCN)}_3]|w + 3 \text{H}_2\text{O}|l.$$

If the blood red solution is diluted with water, the concentration and therefore also the chemical potential of the dissolved substances decreases for all substances by the same amount. This is indicated by an arrow placed above the formulas of the substances:

$$\downarrow [\text{Fe(H}_2\text{O)}_6\text{]}^{3+}|w + 3 \text{SCN}^-|w \rightleftharpoons [\text{Fe(H}_2\text{O)}_3\text{(SCN)}_3]|w + 3 \text{H}_2\text{O}|l.$$

The potential of water remains nearly unchanged because of its high excess. At the beginning, the sum of potentials on both sides is equal. Afterwards, the equilibrium is disturbed because the decrease on the left side is four times stronger than that on the right side. The complex decomposes, its potential decreases, whereas the potential of the substances on the left side increases. The reaction takes place (easily observable by the fading of the red color) until the equilibrium is again established. The pale orange color of the resulting solution is caused by the iron hexaquo complex.

If Fe$^{3+}$ or SCN$^-$ solutions are added to the pale orange dilute iron thiocyanate solution, it will turn red again in both cases (Experiment 6.1).

**Experiment 6.1:** Iron(III) thiocyanate equilibrium.

By adding excess iron (III) ions, their concentration in the solution and therefore also their potential increases; the reaction runs backwards and correspondingly the color deepens again to blood red. This can be illustrated again by arrows above the chemical formulas.

$$\uparrow [\text{Fe(H}_2\text{O)}_6\text{]}^{3+}|w + 3 \text{SCN}^-|w \rightleftharpoons [\text{Fe(H}_2\text{O)}_3\text{(SCN)}_3]|w + 3 \text{H}_2\text{O}|l.$$

Adding excess thiocyanate ions shows the same result: the pale orange solution turns red again. But one should keep in mind, that together with the dissolved substances, water is also added which results in dilution. For achieving the desired effect, the added solutions of Fe$^{3+}$ and SCN$^-$ should therefore not be too thin.
We can get the same results in a somewhat more cumbersome manner if we write down the mass action law and take into consideration that numerator and denominator must increase or decrease by the same factor in order to preserve equilibrium (water as solvent is treated as pure substance; therefore, it does not appear in the formula):

\[
\hat{K} = \frac{c_r([\text{Fe(H}_2\text{O})_6\text{SCN}])}{c_r([\text{Fe(H}_2\text{O})_6]^3) \cdot c_r(\text{SCN}^-)^1}.
\]

Diluting with water for example lowers the concentration of the complex, but also the concentrations of the free ions. Therefore, the denominator would decrease much faster than the numerator. Because the quotient has to remain constant and equal to \(\hat{K}\), the numerator must decrease as well: the equilibrium is displaced towards the reactant side.

**Homogeneous gas equilibria.** To obtain homogeneous gas equilibria

\[
|v_B|B + |v_C|C + ... \rightleftharpoons v_D + v_E + ...
\]

we can derive the equilibrium number analogously to the homogeneous solution equilibria, but instead of the mass action equation 1', we refer to the mass action equation 2'. To indicate that partial pressures \(p\) replace concentrations \(c\) usually the symbol \(\hat{K}_p\) is used instead of simply \(\hat{K}\):

\[
\hat{K}_p = \frac{p_r(D)^{v_D} \cdot p_r(E)^{v_E} \cdot ...}{p_r(B)^{v_B} \cdot p_r(C)^{v_C} \cdot ...}.
\]

To convert into the conventional equilibrium constant \(\hat{K}_p\) a dimension factor must again be taken into account:

\[
\hat{K}_p = \kappa \hat{K}_p, \quad \text{where} \quad \kappa = (\rho^\Theta)^{v_p} \quad \text{with} \quad v_p = v_B + v_C + ... + v_D + v_E + ....
\]

As an example, let us consider the synthesis of ammonia:

\[
\text{N}_2|g + 3 \text{H}_2|g \rightleftharpoons 2 \text{NH}_3|g
\]

\[
\mu^\Theta/\text{kG:} \quad 0 \quad 3.0 \quad 2.165 \quad \Rightarrow \mu^\Theta = +33.0 \text{ kG}.
\]

With the standard value of the chemical drive of around +33 kG, the corresponding equilibrium number at room temperature is

\[
\hat{K}_p^\Theta = \frac{p_r(\text{NH}_3)^2}{p_r(\text{N}_2) \cdot p_r(\text{H}_2)^3} = \exp \frac{\mu^\Theta}{RT} = \exp \frac{33 \cdot 10^3 \text{ G}}{8.314 \text{ G} \text{K}^{-1} \cdot 298 \text{ K}} = 6.1 \cdot 10^5.
\]

The conventional equilibrium constant is

\[
K_p^\Theta = \frac{p(\text{NH}_3)^2}{p(\text{N}_2) \cdot p(\text{H}_2)^3} = K_p^\Theta \cdot (100 \text{ kPa})^{-2} = 61 \text{ kPa}^{-2}
\]

with \(v_p = -1 - 3 + 2 = -2\).

In general, we notice that, depending upon the quantity used to describe the composition and its standard value (\(c^\Theta = 1000 \text{ mol m}^{-3}\), \(\rho^\Theta = 100 \text{ kPa} \ldots\)), the same substance yields different basic values \(\hat{K}_c\), \(\hat{K}_p\) \ldots and therefore different equilibrium numbers \(\hat{K}_c\), \(\hat{K}_p\) \ldots for the same
reaction. This is indicated by the varying indexes. Normally, we use $\mu_c$ for dissolved substances and $\mu_p$ for gases. If there is no index, we simply imagine what it is supposed to be.

**Decomposition equilibria.** As yet we have only considered homogeneous equilibria, i.e. equilibria in which all participating substances are in the same phase. Next we will discuss heterogeneous equilibria in which the substances are in different phases. Heterogeneous gas reactions in which solid phases are involved will be our first topic. We start with a process which is also industrially important, the calcination of limestone.

In the case of the decomposition reaction of calcium carbonate described by

$$
\text{CaCO}_3|s \rightleftharpoons \text{CaO}|s + \text{CO}_2|g
$$

\[\mu^\Theta /\text{kG}: -1129 \quad -603 \quad -394 \Rightarrow A^\Theta = +132 \text{ kG}\]

in a closed system, two pure solid phases (CaCO$_3$ und CaO) and a gas phase are in equilibrium. The mass action equation 2’ is applied for the gas carbon dioxide. But how can we take pure solid substances (or pure liquids) B into account? In the case of these substances, the mass action term $RT\ln c(B)$ is omitted, i.e., $\mu(B) = \mu^\circ(B)$; the pure solid substance does not appear in the mass action law. In a dilute solution, this is also valid for the solvent which can be treated as a pure substance (see Section 6.3).

The equilibrium number $K_p^\circ$ for the decomposition of carbonate is therefore equal to

$$
K_p^\circ = p_1(\text{CO}_2) \quad \text{with} \quad K_p^\circ = 1.3 \cdot 10^{-23} \text{ at } 298 \text{ K}.
$$

The conventional equilibrium constant results in

$$
K_p = p(\text{CO}_2).
$$

The equilibrium constant is identical to the decomposition pressure, i.e., the pressure of carbon dioxide at equilibrium, and hence not dependent on the amounts of the solid substances. Even though the pure solid substances do not appear in the mass action law, they have to be present for establishing equilibrium. Like the equilibrium constant, the decomposition pressure depends, however, on temperature (see also Section 5.5).

When the calcium carbonate is, however, heated in an open system like a lime kiln, the gas escapes into the surroundings, equilibrium is not established and all of the carbonate decomposes.

The decomposition of crystalline hydrates etc. can be described in the same way.

**Phase transitions.** The approach can not only be applied to heterogeneous chemical reactions but also to transitions where the state of aggregation changes. The evaporation of water represents an example for a phase transition where a gas participates. The equilibrium number $K_p^\circ$ for the equilibrium between liquid water and water vapor in a closed system,

$$
\text{H}_2\text{O}|l \rightleftharpoons \text{H}_2\text{O}|g
$$

\[\mu^\Theta /\text{kG}: -237.1 \quad -228.6 \Rightarrow A^\Theta = -8.5 \text{ kG},\]

results in

$$\hat{K}_p = p_r(H_2O|g) \quad \text{with} \quad K^\Theta_p = 3.24 \cdot 10^{-2} \text{ at } 298 \text{ K.}$$

Liquid water as pure liquid does not appear in the equation. The corresponding conventional equilibrium constant is

$$\hat{K}_p = p(H_2O|g) = p_{lg}(H_2O).$$

Hence, the equilibrium constant represents the vapor pressure of water, i.e., the pressure of water vapor in equilibrium with liquid water at the temperature considered.

We will discuss phase transitions in more detail in chapter 10.

**Solubility of ionic solids.** Our next topic is heterogeneous solution equilibria. A substance submerged in a liquid will generally begin to dissolve. The extremely low chemical potential $\mu$ of this substance in the pure solvent rises rapidly—remember that $\mu \to -\infty$ for $c \to 0$—with increasing dissolution and therefore concentration. The process stops when the chemical potential of the substance in the solution is equal to that of the solid, i.e. equilibrium is established. We then refer to the solution as saturated, i.e. the solution contains as much dissolved material as possible under given conditions (temperature, pressure, such as standard conditions).

If the substance dissociates when dissolved, such as a salt in water

$$\text{AB}|s \rightleftharpoons A^+|w + B^-|w$$

the products of the dissociation compensate together for the dissolution drive of the salt AB:

$$\mu(\text{AB}) = \mu(A^+) + \mu(B^-).$$

The mass action law for the dissolution process, here the transition from solid state to dissolved, $s \to d$, is

$$\hat{K}_{sd} = c_r(A^+) \cdot c_r(B^-)$$

with

$$\hat{K}_{sd} = \exp \frac{\Delta_{sd}}{RT} = \exp \frac{\hat{\mu}(\text{AB}) - \hat{\mu}(A^+) - \hat{\mu}(B^-)}{RT},$$

as long as some undissolved AB is present. Here the mass action term for a pure solid and therefore also the denominator in the equation above have been omitted. Thus, the product of the relative concentrations of the ions in a saturated solution is constant under given conditions. In chemistry, the value $\hat{K}_{sd}$ usually receives its own name, solubility product. (This is commonly indicated by the index $\text{sp}(\hat{K}_{sp})$, but for the sake of consistency we will use $sd$). If a substance dissociates into several ions, then $\hat{K}_{sd}$ consists of the corresponding number of factors.

If the concentration of one of the ions, e.g. $c(A^+)$, increases, the concentration of the second, $c(B^-)$, must decrease in order to maintain equilibrium. This means that the substance AB pre-

Precipitates from the solution. As an example, we consider a saturated table salt solution in which solid NaCl is in equilibrium with its ions in the solution (Experiment 6.2):

\[
\text{NaCl}_s \rightleftharpoons \text{Na}^+|w + \text{Cl}^-|w
\]

\[
\mu^\Theta /\text{kG}: -384.1 \quad -261.9 \quad -131.2 \quad \Rightarrow \mu^\Theta = 9.0 \text{ kG}.
\]

Consequently, the equilibrium number \( K_{sd}^\Theta \) at room temperature is 37.8. The heterogeneous equilibrium can be described by the solubility product:

\[
\hat{K}_{sd} = c_i(\text{Na}^+) \cdot c_i(\text{Cl}^-).
\]

For the concentration \( c_{sd} = c(\text{Na}^+) = c(\text{Cl}^-) = c^\Theta \sqrt{K_{sd}^\Theta} \) of the saturated solution at 298 K, we obtain the value 6.1 kmol m\(^{-3}\) that corresponds—better than expected—to the measured value of 5.5 kmol m\(^{-3}\).

**Experiment 6.2:** Adding Na\(^+\) or Cl\(^-\) to a saturated NaCl solution.

When Na\(^+\) ions (in the form of sodium hydroxide solution) or Cl\(^-\) ions (in the form of hydrochloric acid) are added to the saturated solution, NaCl precipitates. Consequently, adding compounds which have an ionic species in common with the salt under consideration, affects its solubility.

In the case of readily soluble salts we can only indicate general trends due to the strong ion-ion interaction in concentrated electrolyte solutions especially if multivalent ions are involved. However, quantitative statements can be made in the case of slightly soluble compounds. As an example, let us consider lead(II) iodide:

\[
PbI_2|s \rightleftharpoons Pb^{2+}|w + 2 I^-|w
\]

\[
\mu^\Theta /\text{kG}: -173.6 \quad -24.4 \quad 2(-51.6) \quad \Rightarrow \mu^\Theta = -46.0 \text{ kG}
\]

with \( K_{sd}^\Theta = 8.6 \cdot 10^{-9} \) at room temperature. The mass action law for the solution equilibrium is

\[
\hat{K}_{sd} = c_i(\text{Pb}^{2+}) \cdot c_i(\text{I}^-)^2.
\]

We can calculate the saturation concentration \( c_{sd} \) of this salt from the numerical value for the solubility product at 298 K. In our example, the stoichiometry of equilibrium results in two I\(^-\) ions being produced for one Pb\(^{2+}\) ion. In contrast to the case of table salt, we now have

\[
c(\text{Pb}^{2+}) = c_{sd} \quad \text{and} \quad c(\text{I}^-) = 2c_{sd}.
\]

Insertion results in

\[
\hat{K}_{sd} = (c_{sd} / c^\Theta) \cdot (2c_{sd} / c^\Theta)^2 = 4c_{sd}^3 / (c^\Theta)^3
\]

and the saturation concentration at 298 K is

\[
c_{sd} = \sqrt[3]{K_{sd}^\Theta / 4c^\Theta} = \sqrt[3]{8.6 \cdot 10^{-9} / 4 \text{ kmol m}^{-3}} = 1.3 \cdot 10^{-3} \text{ kmol m}^{-3}.
\]

It is now possible to estimate the effect of adding one of the ions. Let us add enough of a concentrated NaI solution to the saturated lead iodide solution so that the I\(^-\) concentration will be
equal to 0.1 kmol m$^{-3}$. Now, with the extra iodide ions present, the concentration of lead ions results in:

$$c(\text{Pb}^{2+}) = \frac{K_{\text{sd}}}{(c(I^-)/c^{\Theta})^2} = \frac{8.6 \cdot 10^{-6}}{0.01} \text{ kmol m}^{-3} = 8.6 \cdot 10^{-7} \text{ kmol m}^{-3}.$$  

As expected, adding I$^-$ drastically decreases the lead concentration as expected. But “too much of a good thing” can be bad because a too big excess of I$^-$ results in the formation of soluble complexes, e.g. PbI$_2$ + I$^- \rightarrow$ PbI$_3$. This effect too could be calculated with the help of our approach.

The solubility of certain slightly soluble compounds can be controlled by different means as well, for example by the pH value. We shall conclude this section by discussing the following interplay between the precipitation and the dissolution processes: The following interplay between the precipitation and the dissolution process shall terminate this section: When a potassium dichromate solution is added to a barium chloride solution (Experiment 6.3), a yellow precipitate of slightly soluble barium chromate is formed according to

$$2 \text{ Ba}^{2+} |w + \text{Cr}_2\text{O}_7^{2-} |w + \text{H}_2\text{O} |l \rightleftharpoons 2 \text{ BaCrO}_4 |s + 2 \text{ H}^+ |w .$$

To be more precise, the concentrations of the initial substances decrease, i.e., barium chromate precipitates until equilibrium is established.

The precipitate dissolves after addition of hydrochloric acid. The concentration of H$^+$ ions and therefore their chemical potential increase. For re-establishing the equilibrium, BaCrO$_4$ has to dissolve:

$$\uparrow \uparrow \uparrow \quad 2 \text{ Ba}^{2+} |w + \text{Cr}_2\text{O}_7^{2-} |w + \text{H}_2\text{O} |l \rightleftharpoons 2 \text{ BaCrO}_4 |s + 2 \text{ H}^+ |w .$$

If, on the other hand, the H$^+$ ions which are released during precipitation are removed in the filtrate by adding sodium acetate (Ac$^- + \text{H}^+ \rightarrow \text{HAc}$), their chemical potential decreases. Consequently, more BaCrO$_4$ has to precipitate.

The same result can be obtained by considering the mass action law:

$$\hat{K} = \frac{c_r(\text{H}^+)^2}{c_r(\text{Ba}^{2+})^2 \cdot c_r(\text{Cr}_2\text{O}_7^{2-})} .$$

By adding H$^+$ the numerator increases so that the denominator must also increase in order for the quotient to remain constant and equal to $\hat{K}$. However, the concentrations $c_r(\text{Ba}^{2+})$ and $c_r(\text{Cr}_2\text{O}_7^{2-})$ can only increase when the precipitate BaCrO$_4$ dissolves.

**Experiment 6.3: Precipitation of Ba$^{2+}$ with Cr$_2$O$_7^{2-}$**

**Solubility of gases.** Next we will discuss the dissolution behavior of gases. If a gas B is brought into contact with a liquid (or solid), it diffuses within it until the chemical potential of the gas inside is as high as outside. The potential of B in the solution is described by the mass action equation 1’$. In the gas phase, however, it is described by the mass action equation 2’$. The equilibrium number $\hat{K}_{gld}$ or, more briefly, $\hat{K}_{gld}$ turns out to be

\[ \hat{K}_{gd} = \frac{c_r(B)}{p_r(B)}. \]

Take into account that in this case, \( \hat{K} \) corresponds to neither \( \hat{K}_c \) nor \( \hat{K}_p \), but represents a so-called “mixed” constant \( \hat{K}_{pc} \). Like the mass action equations themselves, this equation is only valid as long as the concentration \( c \) in the solution and the pressure \( p \) outside it are small. Written in the conventional way, the equilibrium constant is

\[ \hat{K}_{gd} = \frac{c(B)}{p(B)}. \]

In 1803, the English chemist William Henry empirically discovered this relation which states that the solubility of a gas at constant temperature is proportional to its partial pressure above the solution (Henry’s law). Therefore, \( \hat{K}_{gd} \) is also known as the Henry constant \( \hat{K}_H \).

Let us take a look at the solubility of oxygen in water:

\[ \begin{align*} \text{O}_2|\text{g} & \rightleftharpoons \text{O}_2|\text{w} \\ \mu^\Theta/kG: \ 0 & \rightleftharpoons A^\Theta = -16.4 \text{ kG.} \end{align*} \]

In this case, the standard value of the chemical drive is \(-16.4 \text{ kG}\). The equilibrium number at room temperature is equal to

\[ \hat{K}_{gd} = \frac{c_r(\text{O}_2)}{p_r(\text{O}_2)} = 1.3 \cdot 10^{-3}, \]

while the conventional equilibrium constant results in

\[ K_{gd} = \frac{c(\text{O}_2)}{p(\text{O}_2)} = \hat{K}_{gd} \cdot 1 \text{ kmol m}^{-3} = 1.3 \cdot 10^{-5} \text{ mol m}^{-3} \text{ Pa}^{-1}. \]

The partial pressure of \( \text{O}_2 \) in air is about 20 kPa. For the \( \text{O}_2 \) concentration in air-saturated water at 298 K, we obtain

\[ c_r(\text{O}_2) = K_{gd} \cdot p(\text{O}_2) = 1.3 \cdot 10^{-5} \text{ mol m}^{-3} \text{ Pa}^{-1} \cdot 20 \cdot 10^3 \text{ Pa} = 0.26 \text{ mol m}^{-3}. \]

Concentration of \( \text{O}_2 \) in bodies of water, a factor of prime importance for biological processes, can be estimated in this way.

**Distribution equilibria.** Relations that can be dealt with in a theoretically similar way would be, for example, systems where a third substance B (possibly iodine) is added to two practically immiscible liquids such as water/ether. Iodine is soluble in both liquid phases (’) and (’’). Substance B disperses between these phases until its chemical potential is equal in both. The equilibrium number \( \hat{K}_{d-d} \) is then:

\[ \hat{K}_{dd} = \frac{c_r(B)'}{c_r(B)}. \]

where

\[ \hat{K}_{dd} = \exp \frac{\hat{A}}{RT} = \exp \frac{\mu(B') - \mu(B)}{RT}. \]
Conventionally, we obtain
\[ \tilde{K}_{\text{dd}} = \frac{c(B)''}{c(B)'}. \]

In the case of small concentrations, the ratio of equilibrium concentrations (or mole fractions, etc.) of the dissolved substance in two liquid phases is a (temperature dependent) “constant” (Nernst’s distribution law). The constant \( \tilde{K}_{\text{dd}} \) is also called Nernst’s distribution coefficient \( K_N \).

Distribution equilibria play a significant role in separating the substances in a mixture by the process of extraction. The laboratory procedure called “extraction by shaking” (extracting a substance from its solution) by using another solvent in which the substance dissolves much better, is based on such equilibria. This method can be used to completely remove iodine from water by repeatedly extracting it with ether. Partition chromatography is based upon the same principle. A solvent acts as the stationary phase in the pores of a solid carrier material (paper for example) and a second solvent (with the substance mixture to be separated) flows past it in the form of a mobile phase. This is known as a mobile solvent. The more soluble a substance is in the stationary phase, the longer it will remain there and the more strongly its movement along this phase will slow down. Eventually a separation occurs in the mixture originally applied at a point.

**Influence of temperature.** The equilibrium numbers (and constants) we have considered so far are valid only under certain conditions (mostly standard conditions at 298 K and 100 kPa). If the value of \( K_N \) at an arbitrary temperature is of interest, then the \( RT \) term as well as the temperature dependence of chemical drive \( \mathcal{A} \) need to be taken into account. We refer here to the linear approximation introduced in Section 5.2:
\[ \mathcal{A} = A_0 + \alpha(T - T_0). \]

Insertion into the equation above yields the following result for the equilibrium number at a temperature \( T \)
\[ \tilde{K}(T) = \exp\left(\frac{\mathcal{A}(T_0) + \alpha(T - T_0)}{RT}\right). \]

When the temperature is increased \( (\Delta T > 0) \), \( \tilde{K}(T) \) can increase or decrease relative to the initial value \( \tilde{K}(T_0) \) depending upon the values of \( \mathcal{A}(T_0) \) and \( \alpha \) which are typical for a particular reaction. In the first case, the equilibrium composition shifts to benefit the products and in the second case, it shifts to benefit the initial substances. The equilibrium constant can be influenced by the choice of temperature. This is of potentially great importance for large-scale technical reactions as well as for environmentally relevant ones.

**6.7 Potential diagrams of dissolved substances**

Energy must be used in order to transfer matter from a state of low \( \mu \) value to a state of high \( \mu \) value. Therefore, the potential \( \mu \) can be regarded as a kind of energy level the matter is on. This is why matter with a high chemical potential is often called *energy rich* and matter with low potential, *energy poor*. These terms are not to be considered absolute in themselves but
only in relation to other substances with which the substance in question can reasonably be compared.

When the amount $n$ of a dissolved substance in a given volume is continuously increased, the potential $\mu$ of the substance also increases. While at first, small changes $\Delta n$ in the amount of substance are enough to cause a certain rise in potential $\Delta \mu$, later on increasingly large amounts are necessary for this. As long as the concentration is not too high, the mass action equation remains valid. This means that the concentrations (or when the volume remains constant, the amount), must always increase by the same factor $\beta$ if $\mu$ is to increase by the same amount. $n$ therefore increases exponentially along with the chemical potential $\mu$.

Relative to the same increase of potential $\Delta \mu$, the solution takes up the more of the substance to be dissolved the more it already contains. Hence, the “capacity” for this substance increases with the amount already present—perhaps somewhat different from what one might expect. The capacity $B$ of a substance, the so-called substantial capacity, is defined by the following equation:

$$B = \frac{dn}{d\mu}.$$

A well known example of the quantity $B$ is the so-called buffering capacity, meaning the capacity $B_p$ of a given amount of a solution for hydrogen ions. We will go into in greater detail in Section 7.6. If the region being dealt with is homogeneous, $B$ can logically be related to the volume:

$$b = \frac{B}{V}.$$

In contrast to $B$, we will call $b$ the substantial capacity density.

If the substantial capacity $B$ of a finite volume $V$ of solution is plotted against the chemical potential $\mu$ (Fig. 6.5, part a), the area under the $B(\mu)$ curve from $-\infty$ to the actual potential $\mu$ represents the amount $n$ of the substance in this volume. The relation becomes clearer if the axes are exchanged and the curve then appears as a two-dimensional outline of a container filled to the level $\mu$ with the amount of substance $n$ (Fig. 6.5, part b). Finally, if $\sqrt{B/\pi}$ is plotted instead of $B$, the resulting curve can be thought of as the outline of a rotationally symmetrical chalice (Fig. 6.5, part c). In this case as well, $n$ is the volume of the container filled up to the level $\mu$. In the following we will make use of this image because it is not only vivid, but also has the advantage of reducing the width of otherwise very wide curves, making them easier to draw.

The area under the curve of a continuous function $f(x)$ in the interval $[a;b]$ is calculated by

$$F = \int_{a}^{b} f(x)dx$$

(cp. Appendix A1.2). The volume of a body created by rotating the area in the diagram about the $x$-axis can be calculated analogously:

\[ V = \pi \int_{a}^{b} f(x)^2 \, dx. \]

Such bodies are also called solids of revolution.

**Fig. 6.5:** a) Plotting the substantial capacity \( B \) as a function of chemical potential \( \mu \), b) exchanging axes, and c) solid of revolution having the same content.

As long as the mass action equations are valid, it is easy to express \( n \) as a function of \( \mu \). To do so, we solve the equation \( \mu = \hat{\mu} + RT \ln(c/e^\Theta) \) with \( c = n/V \) for \( n \) and obtain:

\[ \frac{\mu - \hat{\mu}}{RT} = \ln \frac{n}{Ve^\Theta} \]

or

\[ n = Ve^\Theta \cdot \exp \left( \frac{\mu - \hat{\mu}}{RT} \right). \]

The substantial capacity is the derivative with respect to \( \mu \), for constant \( Ve^\Theta \) and \( \hat{\mu} \):

\[ B = \frac{Ve^\Theta}{RT} \cdot \exp \left( \frac{\mu - \hat{\mu}}{RT} \right) = \frac{n}{RT}. \]

In order to obtain the substantial capacity \( B = \frac{dn}{d\mu} \), we must take the derivative of the equation above with respect to \( \mu \). Remember the following derivative which we will use in a moment:

\[ y = \exp(x) \quad \Rightarrow \quad \frac{dy}{dx} = \exp(x). \]

We also will need the chain rule, which is one of the most important differentiation rules (cp. Appendix A1.2):

\[ \frac{dy}{dx} = \frac{dy}{dz} \cdot \frac{dz}{dx}. \]
One can simply remember that the derivative of the composite function is the product of the derivative of the outer function and the derivative of the inner function.

This may look somewhat difficult at first so we will use our example to demonstrate this approach

\[ y = a \cdot \exp \frac{x-b}{RT}. \]

The inner function is:

\[ z = \frac{x-b}{RT} = \frac{x}{RT} - \frac{b}{RT}. \]

For the derivative, we obtain

\[ \frac{dz}{dx} = \frac{1}{RT}, \]

because the second term is not dependent upon \( x \), therefore resulting in zero. Further,

\[ y = a \cdot \exp(z) \]

is the outer function and

\[ \frac{dy}{dz} = a \cdot \exp(z) \]

is its derivative. We must keep in mind that constant factors remain unchanged in the process of differentiation. According to the chain rule, the total derivative results in

\[ \frac{dy}{dx} = \frac{dy}{dz} \cdot \frac{dz}{dx} = a \cdot \exp(z) \cdot \frac{1}{RT} = \frac{a}{RT} \cdot \exp \frac{x-b}{RT}. \]

As a consequence, \( B \), like \( n \), depends exponentially upon \( \mu \). In this case, the container whose curve we are interested in has the form of an “exponential horn” which is open at the top.

The substantial capacity density \( \delta \) can be easily calculated from \( B \):

\[ \delta = \frac{B}{V} = \frac{c^\circ}{RT} \cdot \exp \frac{\mu - \hat{\mu}}{RT} = \frac{c}{RT}. \]

Like \( B \) and \( n \), \( \delta \) depends exponentially on \( \mu \).

We will take a closer look at this approach using the example of glucose (Fig. 6.6). In its solid and pure state, glucose has a chemical potential which is not subject to mass action. For this reason, it is represented as a horizontal line in the potential diagram. Because, as previously stated, glucose occurs in two forms, \( \alpha \) and \( \beta \), two potential levels lying close together should actually be drawn in. However, for the sake of simplicity, only one is represented here.
In the dissolved state and depending upon concentration or amount, we have an entire band of potential values. Instead of the band, we will use the $B(\mu)$ curve as it is described for the general case in Figure 6.5 to express this dependence. Alternatively, we can use the $b(\mu)$ curve, which looks identical to it. The radius of the rotationally symmetrical chalice equals $\sqrt{b/\pi}$. Therefore, the content up to a chosen level corresponds to the quantity of glucose present there relative to the volume of solution. This means it is equal to the total concentration of glucose. At small concentrations, the radius increases exponentially with rising $\mu$; for high concentrations, this is only approximate. We do not need to distinguish between the $\alpha$ and the $\beta$ forms because an equilibrium rather quickly develops between the two isomers. The basic value of the potential (at a concentration of 1000 mol m$^{-3}$) applies to this equilibrium mixture.

The content of the chalice has been drawn to this arbitrarily chosen potential level. We will also generally choose this fill level for other substances. The value in a living organism would be considerably lower, though.

**Fig. 6.6:** Potential diagram of glucose.

If the amount of dissolved glucose were to be continuously increased, and the fill level of the chalice raised to the level of the solid glucose, the glucose would begin to crystallize. The glucose would begin to run over the rim of the chalice, so to speak. If, on the other hand, glucose were present as excess solid, it would need to dissolve for as long as it would take for all the crystals to disappear or until the potential in the solution increased to the level of the chalice rim in the drawing. One might say that in this state, the glucose solution is saturated relative to the solid.