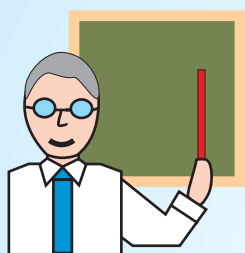


Excerpt from:

Physical Chemistry

Part 1: Fundamentals of Matterdynamics



- an introduction with new concept
and numerous experiments -

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Preface

The lecture gives an overview about important branches 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 lecture may be highlighted:

- ❖ The basic quantities and equations necessary for the qualitative and quantitative description of changes of substances are introduced by using everyday experiences and particularly numerous demonstration experiments. In this way the motivating power of fascinating experiments is utilised, because students often regard physical chemistry as very abstract and not useful for everyday life.
- ❖ It seems that two thermodynamic quantities are especially difficult to understand: the entropy S and the chemical potential μ . But in fact, both quantities are compatible with a layperson's perception. Therefore, they are introduced by a phenomenological description and direct measuring procedure, in the same way as the basic quantities length, time or mass. The chemical potential has a key position in dealing with chemical problems. Starting from this central quantity, it is possible to explore many other fields. Its dependence upon temperature, pressure and concentration leads directly to construction of phase diagrams, deduction of the mass action law, calculation of equilibrium constants, solubilities, and many other data. An expansion of the concept to diffusion processes, colligative phenomena, surface effects, electrochemical processes, etc., is easily possible. Furthermore, the same tools can be used 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 considered usually 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 controllable.
- ❖ For understanding the basic ideas, only elementary mathematical knowledge is necessary (therefore, the concept can also be easily adapted to all levels of education). For many applications linear formulas are often sufficient. Otherwise it is easy to incorporate more sophisticated mathematical tools if required.

Further informations about the presented concept and descriptions of demonstration experiments as well as video films can be found via internet at **www.job-foundation.org**.

The corresponding text book is scheduled for publication (at first in German) by Vieweg+Teubner in autumn 2010.

The excerpt presents the table of contents of the first part of the lecture notes dealing with chemical thermodynamics as well as the chapters 3 to 5 and 11. The text represents a preliminary version in process. Therefore, we would be very grateful for any contribution to the discussion or suggestion for corrections.

Contents

1. Introduction and First Fundamental Terms

After a short introduction in the area of matterdynamics, important fundamental terms are explained, like

- substance and amount of substance,
- homogeneous and heterogeneous mixture including measures of concentration (for example mole fraction, molar concentration),
- physical state (states of matter, but also volume, pressure, and temperature (discussed in detail in the next chapter (section 2.8))),
- changes of substances (description by reaction equations and stoichiometric calculations),
- work and energy (including volume work and first law).

- 1.1 Matterdynamics
- 1.2 Substances and basic substances
- 1.3 Amount of substance
- 1.4 Homogeneous and heterogeneous mixtures and measures of concentration
- 1.5 Physical state
- 1.6 Changes of substances
- 1.7 Energy

2. Entropy and Temperature

In the phenomenological description the entropy appears as a kind of “stuff” which is distributed in space, can be enclosed or passed on, 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, the entropy can be easily recognized by these effects. This straightforward understanding of the quantity S is deepened by a simplified molecular kinetic interpretation.

The second law can 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 engines and heat pumps are analysed shortly after this introduction, without discussing working cycles, gas laws or energy conversion processes.

- 2.1 Preliminary considerations
- 2.2 Macroscopic properties of entropy
- 2.3 Molecular kinetic interpretation of entropy
- 2.4 Conservation and generation of entropy
- 2.5 Effects of increasing entropy
- 2.6 Entropy transfer
- 2.7 Direct measurement of entropy
- 2.8 Temperature
- 2.9 Examples of applications of entropy
- 2.10 Temperature as “thermal tension”
- 2.11 Energy for producing and exchanging entropy
- 2.12 Heat pumps and heat engines
- 2.13 Entropy creation in an entropy flow

3. Chemical Potential

Also in the case of the chemical potential μ , used as a measure of the tendency of a substance to change, only a few properties are necessary for a complete description, and they are easy to grasp and illustrated by everyday examples. By means of these properties, and after choosing an convenient reference level, it is possible to derive quantitative scales of μ values (at first at room conditions). A first application in chemistry is the prediction of possible reactions by comparing the sum of potentials in the initial and the final state, which is illustrated by numerous experimental examples. The treatment can be simplified by definition of a “chemical drive” \mathcal{A} as the difference of these sums. In this context a positive value of \mathcal{A} means that the reaction proceeds voluntarily in a forward direction.

- 3.1 Introduction
- 3.2 Measurement and metrization: Weight as model
- 3.3 Main characteristics of the chemical potential
- 3.4 Competition between substances
- 3.5 Reference level and values of chemical potentials
- 3.6 Sign of the chemical potential
- 3.7 “Chemical drive” and application in chemistry
- 3.8 Direct measurement of chemical drive
- 3.9 Indirect metrization of chemical potential

4. Influence of Temperature and Pressure on Chemical Changes

The chemical potential can be regarded to be constant only in a zero approximation. A more detailed approach considers the temperature and pressure dependence of μ . But often linear approaches are sufficient. If the corresponding coefficients are given it is easily possible to predict the behaviour when the considered substances 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 region. For a more expanded application a logarithmic approach has to be used.

- 4.1 Introduction
- 4.2 Temperature dependence of chemical potential and drive
- 4.3 Pressure dependence of chemical potential and drive
- 4.4 Simultaneous temperature and pressure dependence
- 4.5 Behaviour of gases under pressure

5. 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 explained. A very important application is the derivation of the “mass action law.”

- 5.1 The concept of mass action
- 5.2 Concentration dependence of chemical potential
- 5.3 Concentration dependence of chemical drive
- 5.4 The mass action law
- 5.5 Special versions of the mass action equation

- 5.6 Applications of the mass action law
- 5.7 Potential diagrams of dissolved substances

6. Consequences of Mass Action: Acid-Base Reactions

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

- 6.1 Introduction
- 6.2 The acid-base concept according to BRØNSTED and LOWRY
- 6.3 Proton potential
- 6.4 Equation of level and protonation equation
- 6.5 Acid-base titrations
- 6.6 Buffers
- 6.7 Acid-base indicators

7. Side Effects of Chemical Changes

Changes of substances like reactions, transformations, distribution in space etc. are often accompanied by very striking side effects. It smolders and flashes, fizzes and cracks, bubbles and fumes. These side effects (which make chemistry so fascinating) can primarily be attributed to

- volume changes,
- entropy exchange,
- energy exchange

during the considered chemical changes. The quantitative description of these effects is the objective of this chapter.

- 7.1 Introduction
- 7.2 Volume demand
- 7.3 Volume changes associated with chemical changes
- 7.4 Entropy demand
- 7.5 Entropy changes associated with chemical changes
- 7.6 Energy exchanges associated with chemical changes
- 7.7 Heat effects
- 7.8 Calorimetric measurement of chemical drives

8. Coupling

It is possible to act on a substantial system 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 to a single equation, the so-called “main equation.” Important couplings like the equivalence of the temperature coefficient of μ and the negative molar entropy are easily deduced by special “flip rules.”

- 8.1 Main equation
- 8.2 Mechanical-thermal coupling
- 8.3 Coupling of chemical quantities
- 8.4 Further mechanical-thermal applications

9. Molecular Kinetic View of Thin Gases

At first the ideal gas law is deduced from experimental observations (BOYLE-MARIOTTE's law, CHARLES's law, 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 the concentration dependence (mass action equation) and additionally the energy dependence (excitation equation) of the chemical potential is used.

- 9.1 Introduction
- 9.2 Ideal gas law
- 9.3 Molecular interpretation of ideal gas law
- 9.4 Excitation equation and velocity distribution
- 9.5 Barometric formula and BOLTZMANN distribution

10. Changeover to Substances with Higher Density

If one changes from thin (ideal) gases to real gases with higher density, the interaction between the particles and finally the condensation phenomenon has to be considered. This results in the VAN DER WAALS equation. The simultaneous temperature and pressure dependence (chapter 4.4) can be used to calculate the vapour-pressure curve if the phase transition is formulated as a reaction and the equilibrium condition is considered. In a similar way the complete phase diagrams of pure substances can be constructed.

- 10.1 VAN DER WAALS equation
- 10.2 Condensation
- 10.3 Critical temperature
- 10.4 Vapour-pressure curve
- 10.5 Complete phase diagram

11. Flow of Substances

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

- 11.1 Introduction
- 11.2 Diffusion
- 11.3 Indirect mass action
- 11.4 Osmosis
- 11.5 Lowering of vapour pressure
- 11.6 Freezing-point depression and boiling-point elevation
- 11.7 Colligative properties and determining molar mass

12. 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 demixing is discussed. The quantitative description of real mixtures requires the introduction of an extra potential $\bar{\mu}^+$.

For the description of mixing processes it is useful to assign a (average) chemical potential to a mixture of two components A and B (with the mole fractions x_A and x_B), just like in the case of pure substances. The different concentration dependence of this average potential in the case of homogeneous and heterogeneous mixtures is shown and used for the discussion of phase reactions (miscibility gap, lever rule).

12.1 Introduction

12.2 Chemical potential in homogeneous mixtures

12.3 Extra potential

12.4 Average chemical potential of homogeneous and heterogeneous mixtures

12.5 Mixing processes

12.6 More phase reactions

13. Two-Component Systems

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

13.1 Phase diagrams of two-component systems

13.2 Liquid-liquid phase diagrams (miscibility diagrams)

13.3 Solid-liquid phase diagrams (melting point diagrams)

13.4 Liquid-gaseous phase diagrams (vapour pressure and boiling point diagrams)

3. Chemical Potential

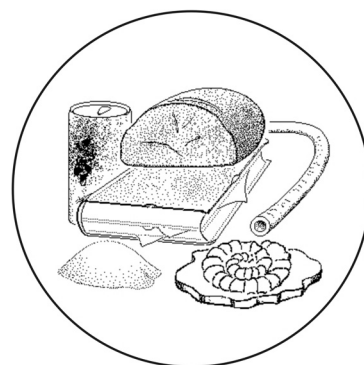
Topic: Chemical potential as measure of a general tendency of matter to change, and as central concept of chemical dynamics.

3.1 Introduction

After our short excursion into thermodynamics, we will now turn to the *chemical potential* μ 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 (πάντα ρεῖ)". Creation and decay are well known in the living world but there are forces in inanimate nature which change the things around us as well:

- Bread dries
- Paper yellows
- Iron rusts
- Stones weather
- Butter or fat becomes rancid
- Rubber embrittles
- Copper gets a patina
- Clay turns into stone, and so on.



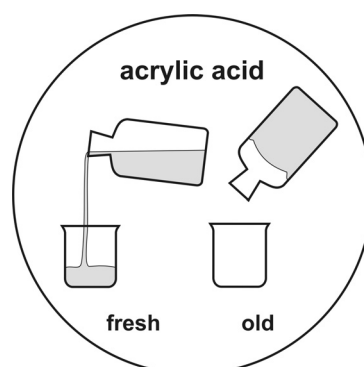
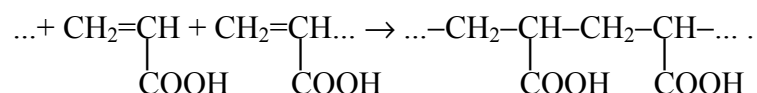
Experiment: Changes in the world of substances

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:

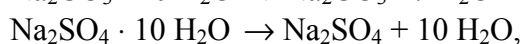
- Bread in a plastic bag;
- Tinned food in an unopened can;
- Chemicals in a sealed bottle.

Experiment: Aging of acrylic acid (propenoic acid)

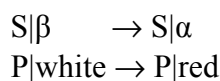
Acrylic acid as pure substance is a water-clear liquid strongly smelling of vinegar. If left to stand alone in a completely sealed container, it will change by itself after some time into a colourless and odourless rigid glass. Thereby, the small acrylic acid molecules combine to long chains:



The modification of pure substances such as the weathering of soda and Glauber salt in ambient air where the large colourless crystals become covered with a white powdery crust as they lose water,

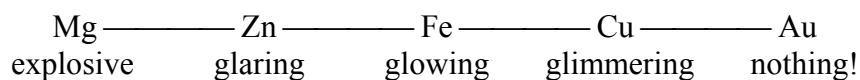


the slow transition of the almost colourless monoclinic β -sulphur into the yellow rhombic α -sulphur, or that of the low-molecular white phosphorus into the high-molecular red phosphorus,



shows that it is not an interaction between reaction partners that is the motor for the change of substances, but that the substances tend to change by themselves. This means that each and every individual substance has a "*tendency to change*." This tendency to change is certainly not the same for all substances, and it has no particular "goal." One might say that all substances are "driven to change" 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 processes of change are inhibited, and not because the drive for them does not exist.

From the transformation of the white into the red phosphorus mentioned above, it can be concluded that the white type has the stronger tendency to change and forces the formation of the red type against its own tendency to change. Similarly, we can imagine that iron sulphide is formed because the starting substances iron and sulphur together have a stronger tendency to react 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, virtually does not react with sulphur:



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



Obviously, magnesium sulphide is the easiest to produce since it has the weakest tendency to react. Gold sulphide, on the other hand, seems to have a relatively strong tendency to react. 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 react exceeds that of Au + S combined.

We will now go more deeply into the meaning of the tendency to change and its quantitative description with the help of the chemical potential. But first we will discuss briefly the definition of physical quantities in general.

3.2 Measurement and Metrization: Weight as Model

Measuring means to determine the value of a quantity. The length of a table, the height of a mountain, the diameter of the Earth's orbit, the distances of atoms in a crystal lattice are all calculated with different methods. Length, distance, width, thickness, circumference; these are all different names for quantities that we consider a similar type. They all fall under the *category* of length. Length is used in everyday life as a *metric* term, meaning a term used to quan-

tify a certain observable characteristic. *Values* are wholes, fractions or multiples of a chosen unit. A distance of ten steps or twenty minutes needs no explanation. More accurate agreements of units are necessary for people working in trades, engineering and the sciences, i.e. they have to be more exact in specifying what quantities and units should be used and how numbers should be allocated. The procedure used to assign a quantity to a concept (typically using the same name), and thus construct the quantity, shall be called *metrization*. The determination of values of this quantity will be called *measurement*.

Most physical quantities are formed by *indirect metrization* or explained by so-called *derived terms*. This means that there is a rule about how they should be calculated from previously known and defined quantities. For instance, the density (more precisely: mass density) ρ of a homogenous body is defined as the quotient of mass m and volume V , $\rho = m/V$.

A very different procedure for defining quantities is the *direct metrization* of a concept or a property. It is a procedure we have already used in our introduction to entropy but without emphasizing it. This approach is used for quantities which are considered basic concepts such as length, duration, mass, etc., and the other quantities such as area, volume, speed, etc., are derived from them. However, it is by no means limited to these basic quantities.

A simple example for the metrization of a property is to introduce a measure for what is commonly known as *weight* G . This example is chosen because it has many parallels to the chemical potential. When we talk about a larger or smaller (positive) G of an object in everyday language, we are expressing how strongly it tends to sink downward. Basically, there are three characteristics necessary to determine a measure for weight:

- a) *Sign*. We will consider the weight of something that sinks downward when let go as positive, $G > 0$. Consequentially, a balloon flying upward will have a negative weight, $G < 0$, as will a piece of wood surfacing after being thrown into water. Something that hovers in air has a weight of $G = 0$.
- b) *Sum*. If we put two things with the weights G_1 and G_2 together so that they can only rise or fall as a unit (for example, if they are put together onto a scale), we assume that the weights add up: $G_{\text{total}} = G_1 + G_2$.
- c) *Unit*. In order to represent the unit γ of weight, something that has an unchanging weight (when appropriate precautions are taken) is suitable (e.g. the international prototype of the kilogram which is made from an alloy of platinum and iridium and kept in Paris).

As used here, the weight G of an object is not a constant property. It depends upon the milieu the object is in. A striking example of this is a block of wood H which tends upward when under water W, $G(H|W) < 0$, but tends downward in air L, $G(H|L) > 0$. In the first step, we will consider the surroundings as unchangeable so that G is a constant. In the second step, we can investigate what changes occur when different surroundings are taken into account.

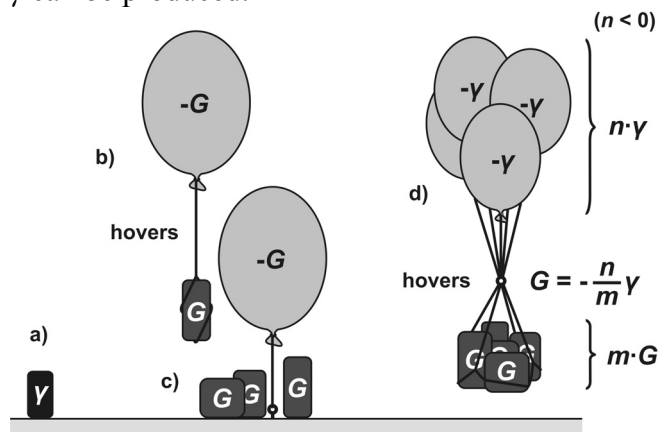
The few, roughly sketched agreements about

- a) sign,
- b) sum,
- c) unit

are sufficient to apply direct metrization to the concept of *weight*. This means that it can be assigned a measure G without referring to other quantities. *Measuring* the weight G of an object means determining how much heavier it is than the object representing the weight unit γ .

Direct measurement means that the value is determined by direct comparison with the unit and not by calculation from other measured quantities. This can be done even without the help of a scale.

At first an object has to be chosen which represents the weight unit γ (point (a) in the following figure). An important further step is the duplication of a weight. This means having an object D with an unknown weight G , and looking for other objects D', D'', D'''... with the same weight. In order to do this, an object B is created, maybe a balloon, with the weight $-G$. Checking the weight of B can be done by testing whether B and D both hover when they are attached to each other (point (b)). B helps to find the objects D', D'', D'''... (point (c)). In the same way, duplicates E', E'', E'''... and F', F'', F'''..., of the positive or negative weight unit γ can be produced.

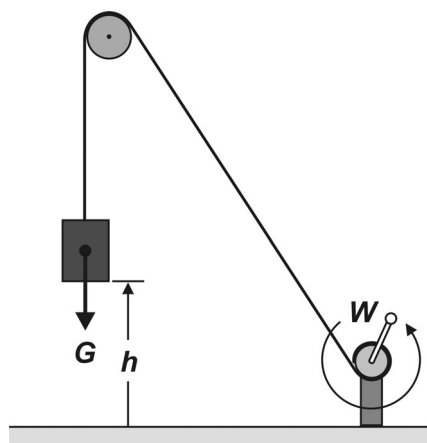


The value of G can be determined by making a bundle that hovers ($G_{\text{total}} = 0$) out of the objects D', D'', D'''... and E', E'', E'''... or F', F'', F'''... (point (d)). If m is used to indicate the number of things in the bundle with the weight G , and the positive or negative n is the number of duplicates with the weight $+\gamma$ or $-\gamma$ in the hovering bundle, then the following is valid:

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

Every real number can be approximated through the quotients of two whole numbers so this method can, in principle, be used to measure the quantity G with any desired degree of accuracy. This method of measurement can be simplified when a suitable set of weights is available. Weights with negative weight can be set aside when a balance scale can be used. This is because an object needs only to be put on the left side of the scale for the right side to show negative weight. These are all technical details that are important for application but unimportant for basic understanding.

In addition to the direct method of metrization, there are also indirect ones. For example, the weight of an object can be determined through its energy W (which is used for working against the object's tendency to fall) by raising it the distance h . The energy W expended at



the hoist in order to raise the block the height h is a measurable quantity, just as h is. The greater the weight, the more energy W is needed, so that it is possible to find the weight by determining W . Because W is proportional to the height h through which the body has been lifted (if h is small), W itself is not suitable as a measure of the weight. However, the quotient $G = W/h$ is. The unit of weight J/m can be obtained by using the unit Joule (J) for the energy, and the unit meter (m) for the height. The unit of weight γ mentioned above, which is represented by an object, is also measurable in this way so that the old scale can be related to the new one.

W and h are no longer proportional when the distance h (measured from the ground) is no longer small relative to the Earth's radius. The weight (the tendency to fall downward) decreases because gravity lessens at high altitudes. By setting $G = \Delta W / \Delta h$ where ΔW means the extra energy needed due to the small increase Δh , the definition of the quantity G can be extended to include this case. In order to indicate in the formula that the differences ΔW and Δh are considered small, the symbol for difference Δ is replaced by the differential symbol d and written as

$$G = \frac{dW}{dh} \quad \text{or more detailed:} \quad G(h) = \frac{dW(h)}{dh}.$$

For the sake of simplicity, although it is not completely mathematically sound, we want to consider differentials to be very small differences. This will be sufficient for all the applications we have in mind.

If the function $y = f(x)$ is known, the differential quotient $dy/dx = df(x)/dx$ at an arbitrary point x can be calculated by taking the derivative of this function with respect to x . Elementary mathematics provides the necessary rules for the simplest cases of finding the derivative $y' = f'(x)$. There are, however, software tools that do all of this work. Note in the expression above on the left, that W and G appear in the role of the variables y and y' while on the right, they appear in the role of the functional symbols f and f' . It is actually a common but not fully correct terminology to use the same letters for both cases, which should not cause serious mistakes if one is careful.

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

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

The replacement of the straight differential symbol d by the curved ∂ means that in forming the derivative, only the quantities in the denominator (in this case h) are to be treated as variable while the others appearing as argument (in this case only v) are to be kept constant. The constant v , and therefore $dv = 0$, means that the increase of energy dW is to be considered the result of a vertical displacement of dh and not of a change of velocity.

There is another notation which is preferred in thermodynamics and matterdynamics where the dependent variable is in the numerator (in this case W) and the independent variables appear in the denominator and in the index (in this case h and v). The variable that is held constant is added to the expression of the derivative as an index:

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

We see that defining G through energy becomes increasingly complex, the more generally one attempts to grasp the concept. Therefore, we introduce the quantities entropy and chemical potential by direct metrization. In this chapter our focus is upon chemical potentials. Our

knowledge about the most important characteristics of weight can help us to understand the method for defining or measuring the quantity μ .

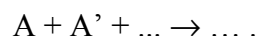
3.3 Main characteristics of the chemical potential

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.

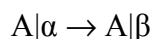
In order to do this, we compile the most important characteristics of the chemical potential into a short outline, a kind of “wanted poster” which we will subsequently go into more deeply.

- The tendency of a substance
 - to *react* with other substances,
 - to *transform* into another state,
 - to *redistribute* in space,
 can be expressed by one and the same quantity – its chemical potential μ .
- The magnitude of this tendency, meaning the numerical value of μ , 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, transformation, redistribution*, etc. can only proceed voluntarily if the tendency for the process is more pronounced in the initial state than in the final state.

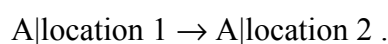
We can assume that a substance, let us call it A, has a more or less pronounced tendency to *change*. This means a tendency to *decompose* into its elementary (or other) components, to *rearrange* itself into some isomer, $A \rightarrow A^*$, or to *react* with other substances $A', A'' \dots$,



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



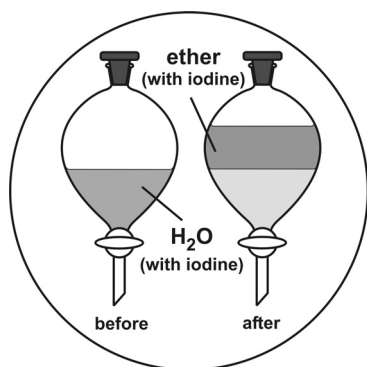
are driven by the same tendency to change. This also holds for the tendency of a substance to redistribute in space. This means its tendency to migrate to another location or to move into a neighbouring region:



The *chemical potential* μ is a measure of the magnitude of this tendency. We write μ_A or $\mu(A)$ to signify the potential of substance A. The greater μ , the more active or “driven” the substance. The smaller μ , the more passive or “phlegmatic” it is.

As stated above, the magnitude of the drive to change and with it, the numerical value of μ_A , depends, on the one hand, upon the nature of the substance. The nature of a substance is thereby determined by its chemical composition, characterised by the empirical molecular formula, but also by its state of aggregation, crystalline structure etc. Hence, liquid water and water vapour or diamond and graphite have different potentials under otherwise identical conditions, i.e. they have to be treated as different substances. The magnitude of the drive to change depends, on the other hand, upon the *milieu* in which the substance is situated. The milieu means the totality of parameters necessary to clearly characterise the surrounding of A such as temperature T , pressure p , concentration c , the type of solvent S, type and proportions of mixtures, etc. In order to express these relations, we write

$$\mu_A(T, p, c \dots, S \dots) \quad \text{or} \quad \mu(A, T, p, c \dots, S \dots).$$



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

Experiment: Iodine in different milieu

Iodine dissolved in water (left side) separates out when it is shaken with ether (right side). The ether floats on top of the specifically heavier, now colourless layer of water. The brown colour 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.

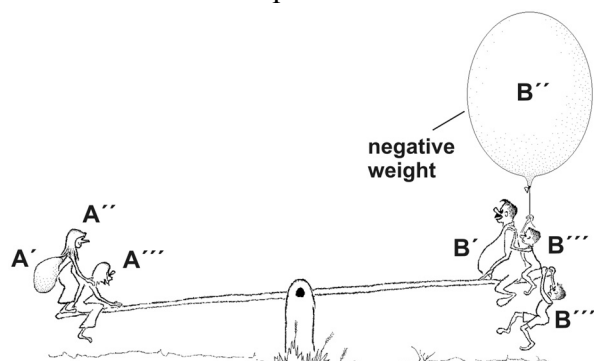
We will discuss the influence of the milieu in more detail in the following chapters.

An important characteristic of a substance's tendency to change is that it is *not* dependent upon the partner it reacts with or what products result. μ 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.

3.4 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 change 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 reaction equation.

An image commonly used for this competition is the relationship between things on the right and left pans of an equal-arm balance (or seesaw). 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 bal-



poons) are attached to the scale. This behaviour can also be expressed formally:

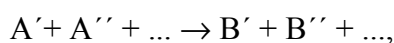
The left side wins, i.e. the objects A', A'' ... on the left side of a balance scale or seasaw are successful against the objects B', B'' ... on the right side in their attempt to sink downward if

$$G(A') + G(A'') + \dots > G(B') + G(B'') + \dots,$$

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

$$G(A') + G(A'') + \dots = G(B') + G(B'') + \dots$$

The statements made here for weights corresponds completely to the role of chemical potentials in substance conversion. It makes no difference whether it is a reaction between several substances or a transformation of a substance into another state, or just a change of location. The direction in which such a process progresses, for example the reaction

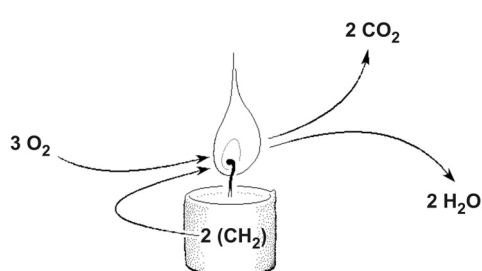


depends solely upon the sums of the chemical potentials μ of all the substances on either side. The substances on the left side prevail in their attempt to react if

$$\mu(A') + \mu(A'') + \dots > \mu(B') + \mu(B'') + \dots,$$

equilibrium rules if the sum of the “driving forces“ of the substances on both sides is the same and no particular direction is preferred:

$$\mu(A') + \mu(A'') + \dots = \mu(B') + \mu(B'') + \dots$$



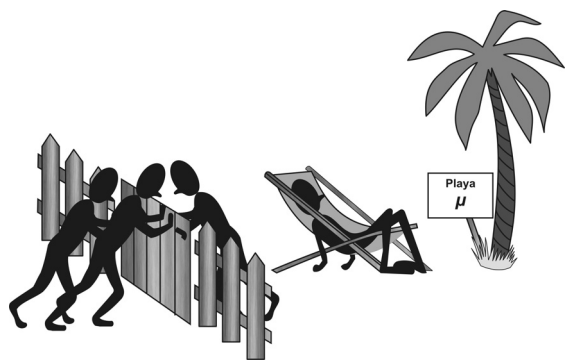
For example, a candle burns because the starting substances combined (in this case atmospheric oxygen and paraffin wax, formula $\approx(\text{CH}_2)$) have a higher chemical potential than the products (in this case, carbon dioxide and water vapour):

$$3 \mu(\text{O}_2) + 2 \mu((\text{CH}_2)) > 2 \mu(\text{CO}_2) + 2 \mu(\text{H}_2\text{O}).$$

Therefore, each realisable reaction is comparable to a kind of scale which allows the comparison of chemical potentials or their sums, respectively. But the measurement is often impossible due to any inhibitions, i.e. the scale “is jammed.” If there is a potential drop from the left to the right side, that only means that the process *can* proceed in this direction in principle; however, it does not mean that the process will actually run. Therefore, a potential drop is a necessary but not sufficient condition for the reaction considered. This is not really surprising. An apple tends 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 don't 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 environment. Without them, we would end up as carbon dioxide, water, nitrogen and ashes in the sea of oxygen in which we live.

If a conversion tends to run in one direction, this does not mean that the opposite direction is impossible, it just does not happen *spontaneously*. Sand trickles downward by itself. A mole can shovel it upwards, though, or a desert wind can form it into high sand dunes, but the sand

does not move in this direction on its own. Hydrogen and oxygen have a strong tendency to react to water. The reverse process never runs by itself at room conditions, but can be forced to do so in an electrolytic cell. Predicting substance changes 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.

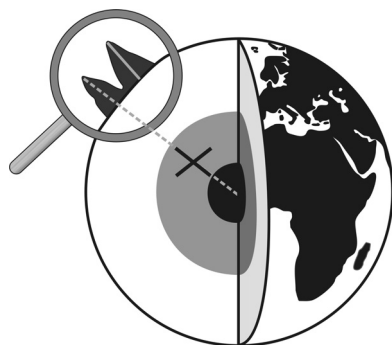


The adjoining figure concludes this section. Despite its anthropomorphic viewpoint, it is useful as an image of the general behaviour of substances:

More active, more “driven” substances are converted 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 greatest “laxness.”

3.5 Reference point and values of chemical potentials

Up to now, what we have been missing in order to make concrete predictions are the μ 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.



However, the heights of mountains are not referred to the geocentre but to the sea level. Everyday temperatures are not referred to absolute zero, but are given as Celsius temperatures based upon the freezing point of water. It is similarly practical to choose a convenient level of reference for the values of the chemical potential because differences of μ can be determined much more precisely than absolute values. Moreover, because we only need to compare potential values or their sums, it doesn't matter what the unit is at

first. The μ 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 E. WIBERG („Die chemische Affinität“, 1972, p. 164) to honour 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.

Next we enter into the question what reference states are suitable for the measurement of potential differences. It is useful to refer to the conventional basic materials in chemistry, the elements, as long as we exclude transformations of elements, i.e. nuclear reactions. The val-

ues 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 use of chemical reactions. Because it is not possible to transform one element into another by chemical means, however, the values of the various elements themselves are not related to each other. This means that the reference level for any element could in principle be chosen arbitrarily. Because the quantity of each element does not change, i.e. an equal number of chemical symbols appears on each side of a reaction equation, this has no effect upon the potential differences being observed and measured. Let us have a look at the synthesis of ammonia from nitrogen and hydrogen as example:

$$\begin{array}{rcll} \text{N}_2 + 3 \text{H}_2 & \rightarrow & 2 \text{NH}_3 & \\ \mu: & \begin{array}{ccc} 0 & 3 \cdot 0 & 2 \cdot (-16) \end{array} & \Rightarrow & (\mu(\text{N}_2) + 3 \mu(\text{H}_2) - 2 \mu(\text{NH}_3) = +32 \text{ kG} \\ & \begin{array}{ccc} 0 & 3 \cdot 2000 & 2 \cdot 2968 \end{array} & \Rightarrow & (\mu(\text{N}_2) + 3 \mu(\text{H}_2) - 2 \mu(\text{NH}_3) = +32 \text{ kG} \end{array}$$

N appears two times on the left as well as on the right side of the reaction equation, H, however, six times. If we increase the chemical potential of a substance, e.g. for every H in the molecular formula, by a fixed, but arbitrarily chosen summand, here 1000 kG, then the summand is cancelled by the calculation of the difference and we obtain the same value as in the line above. The same applies for nitrogen. This means, that the reference level for any element could in principle be chosen arbitrarily as mentioned. But for the sake of simplicity the value 0 is allocated to 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, O₂ or O₃ etc. As an easily reproducible reference state, we will choose the state in which the element in question appears in its “pure form“ and in its natural isotope composition under *standard conditions* (meaning 298 K and 100 kPa, as discussed in Chapter 2) in its most stable modification. 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. The μ values under standard conditions are generally labelled by μ^\ominus . Therefore, the following is valid (E means an arbitrary element in its most stable modification):

$$\boxed{\mu^\ominus(\text{E}) = 0}.$$

In the case of elements E like H, N, O, Cl etc., which occur at standard conditions normally in the form of diatomic gases, 1 mol E simply means $\frac{1}{2}$ mol E₂ und $\mu(\text{E})$ analogously $\frac{1}{2} \mu^\ominus(\text{E}_2)$.

Hence, the state of matter, in which the substances are decomposed into the elements under standard conditions represents the “zero level“ of the potential scale, comparable to the average sea level as the zero level in calculating elevations. Analogously, the specification of Celsius temperatures can replace that of differences of absolute temperature if melting ice was chosen as reference state.

The chemical potential μ of an arbitrary pure substance itself depends upon temperature and pressure (and possibly other parameters), $\mu(T, p, \dots)$. 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* μ^\ominus , i.e., for 298 K and 100 kPa. In the following table we find such standard values for some common substances:

Substance	Formula	μ^\ominus kJ
<i>pure substances</i>		
Iron	Fe s	0
Graphite	C graphite	0
Diamond	C diamond	+3
Water	H ₂ O l	−237
Water vapour	H ₂ O g	−229
Table salt	NaCl s	−384
Quartz	SiO ₂ s	−856
Marble	CaCO ₃ s	−1129
Cane sugar	C ₁₂ H ₂₂ O ₁₁ s	−1558
Paraffin wax	≈(CH ₂) s	+4
Benzene	C ₆ H ₆ l	+125
Acetylene (ethyne)	C ₂ H ₂ g	+210
<i>in Water</i>		
Cane sugar	C ₁₂ H ₂₂ O ₁₁ w	−1565
Ammonia	NH ₃ w	−27
Hydrogen(I)	H ⁺ w	0
Calcium(II)	Ca ²⁺ w	−554

Be careful: The potential value 0 for iron does not mean that iron has no “tendency to change,” but only that we have used its potential value as the zero level to base the values of the potential of other iron-containing substances upon.

The choice 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 colours, but these substances have almost no effect upon the chemical potential of its main component, CaCO₃. However, in order to specify the potential μ of a substance, an empirical molecular formula must be known which shows how it is composed of the elements, and which would then be binding for all calculations. This is why the 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 vapour or diamond and graphite have different potentials at the same temperature and pressure. In order that the μ values are unambiguously given the aggregation state of the substance concerned is added to the formula by a vertical line and the abbreviations s for solid, l for liquid and g for gaseous; modifications can be characterised for example by their names like diamond etc.

Because we are interested in a first basic knowledge of the chemical potential, we consider the values at the moment as given, just as we would consult a table when we are interested in the mass density or in the electric conductivity of a substance. Some measuring methods will be discussed in Section 3.8 and 3.9.

The potential of a substance A changes if it is brought in another milieu for example by solving it. It depends not only on the nature of the solvent but also on the concentration of A. Therefore, the concentration c of a dissolved substance, for which the tabulated values 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 $1 \text{ kmol m}^{-3} = 1 \text{ mol L}^{-1}$. In the case of a solute, the solvent used can be labelled in the same manner as above; for water the abbreviation w is chosen. There exist some peculiarities concerning the determination of these standard values (like in the case of gases) but we will discuss them in Chapter 5.

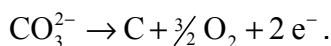
We can summarise:

$$\begin{array}{ll} \mu^\ominus = \mu(p^\ominus, T^\ominus) & \text{for pure substances} \\ \mu^\ominus = \mu(p^\ominus, T^\ominus, c^\ominus) & \text{for dissolved substances} \end{array} \quad \left[\begin{array}{l} T^\ominus = 298 \text{ K} \\ p^\ominus = 100 \text{ kPa} \\ c^\ominus = 1 \text{ kmol m}^{-3} \end{array} \right]$$

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

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 remain about $\pm 6 \text{ kJ}$ in general. Therefore, we can consider the μ values to be constant, at least very roughly. This precision is often sufficient for us so that we can use the μ^\ominus values found in tables. It is unnecessary to worry about temperature, pressure and concentration dependencies of the potentials at the moment. We will only start dealing in more detail with these influences in the following chapters. The approximation used here is a kind of zero-order approximation.

Ions can be assigned a chemical potential as well. If the ions are decomposed into the elements, a positive or negative amount n_e of electrons remains beside the neutral elements, for example



The amount of electrons has to be conserved in chemical processes like that of the elements, i.e., the electrons can be treated as a kind of additional element. They would obtain a value $\mu^\ominus = 0$ in a given reference state like all elements. However, electrons in a free state play no role in chemistry. Therefore, a value for $\mu^\ominus(\text{e}^-)$ has been arbitrarily chosen so that the most commonly appearing type of ion H^+ (in an aqueous solution w and at standard conditions) receives the μ^\ominus value of zero:

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

This seems surprising at first view because we know that the chemical potential of an element under standard conditions is zero, i.e. $\mu^\ominus = 0$. This is of course also valid for hydrogen, $\mu_{\text{H}_2}^\ominus = 0$. Therefore, we expect that other states of hydrogen have other μ^\ominus values. But let us have a

look at the system hydrogen gas/hydrogen ion, which is capable of providing electrons without inhibitions at suitable conditions:



with

$$\underbrace{\mu_{\text{H}_2}^\ominus}_{0_{\text{def.}}} = 2 \underbrace{\mu_{\text{H}^+}^\ominus}_0 + 2 \underbrace{\mu_{\text{e}^-}^\ominus}_{0_{\text{def.}}}.$$

When H_2 and H^+ are regarded under standard conditions and equilibrium rules, then the chemical potential of the electrons, $\mu_{\text{e}^-}^\ominus$, is supposed to be zero. Because $\mu_{\text{H}_2}^\ominus$ disappears by definition, $\mu_{\text{H}^+}^\ominus$ also has to be zero in equilibrium.

3.6 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} ($= 1 \text{ mol L}^{-1}$) where water is the usual solvent. Elements in their usual, stable state receive, as agreed, the value $\mu = 0$. This is for example valid for molecular hydrogen $\mu^\ominus(\text{H}_2|\text{g}) = 0$, while atomic hydrogen has a rather high positive potential $\mu^\ominus(\text{H}|\text{g}) = +203 \text{ kG}$. This means that its tendency to transform into H_2 is very strong.

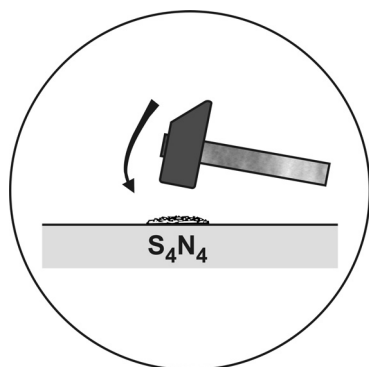
A look at the table at the end of the chapter shows something remarkable. Most of the potential values are *negative*. A substance with negative chemical potential can be produced voluntarily from the elements because it has a weaker tendency to change than the elements it is produced from. However, 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* and therefore difficult to prepare or metastable at best, i.e. in principle the decomposition is voluntarily possible but there exists an inhibition. If the inhibition is overcome e.g. by energy supply or by use of a catalyst, the substance reacts violently, especially when the value of μ is very large.

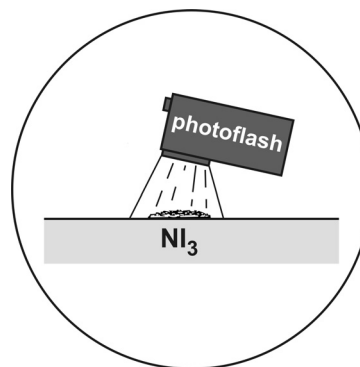
This behaviour can be demonstrated very well by two experiments. First, a small amount of the attractive orange crystals of tetrasulphur tetranitride S_4N_4 ($\mu \approx +500 \text{ kG}$) explodes (like a cap) when hit lightly with a hammer. Second, the easily produced black nitrogen triiodide NI_3 ($\mu \approx +300 \text{ kG}$) decomposes in a dry state if touched by a feather or hit by a flash of light. It produces a sharp explosive sound. Further examples would be heavy metal azides such as lead azide $\text{Pb}(\text{N}_3)_2$ (used as igniters) or silver azide AgN_3 .

However, a positive μ does not always mean that the substance must be explosive. For example, benzene remains rather stable in spite of its μ value of $+125 \text{ kG}$. As discussed in Section 3.4 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.

Experiment: Decomposition of S_4N_4 caused by a blow



Experiment: Decomposition of Nl_3 caused by a flash light



Comparing analogous substances shows best how the level of the chemical potential effects behaviour. Here are three examples:

	$CO_2 g$	$NO_2 g$	$ClO_2 g$
μ^\ominus / kG	-394	+52	+123

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

A similar consideration can be used for solid oxides:

	$Al_2O_3 s$	$Fe_2O_3 s$	$Au_2O_3 s$
μ^\ominus / kG	-1582	-741	+78

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

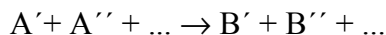
The category of metal sulphides contains similarly composed substances that are good for comparison:

	$MgS s$	$ZnS s$	$FeS s$	$CuS s$	" AuS " $ s$
μ^\ominus / kG	-344	-199	-102	-53	> 0

The sequence deduced in Section 3.1 from the intensity of the reactions of formation actually runs parallel with the values of the chemical potentials. However, be careful: A vague characteristic such as the intensity of reaction that is dependent upon different factors can only be considered evidence under comparable conditions.

3.7 “Chemical drive” and application in chemistry

The most important application for the chemical potential μ is that it enables us to predict whether a change of substances happens voluntarily or not. As we have seen, a chemical reaction



is possible when the following is valid:

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

If we wish to find out if a previously unknown process can run voluntarily, it is enough to find the corresponding μ values in the tables and then to compare the potentials on the right and left side of the reaction equation. Voluntarily, processes only run “downhill,” meaning from left to right, when the sum of the μ values on the left is greater than on the right.

The condition for a voluntary process results in

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

after conversion of the equation above. The summation of the variables can be presented in a shorter form by using the sigma sign, Σ . We summerise:

$\text{reactants} \rightarrow \text{products} \quad \text{is voluntarily possible if} \quad \sum_{\text{initial}} \mu - \sum_{\text{final}} \mu \quad \text{is positive} \quad .$

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 states. Therefore, it is convenient to introduce this difference as an independent quantity. We will call the quantity

$\mathcal{A} = \sum_{\text{initial}} \mu - \sum_{\text{final}} \mu$

the *chemical drive* of the process (reaction, transformation, redistribution, etc.), in short, the *drive*, when it is clear that no non-chemical influences are participating.

Internationally, the capital \mathcal{A} usually stands for *affinity*. The origins of this reach back into antiquity. This name is, unfortunately, a bad indicator of the characteristic it describes (see below). A recommended symbol is A (IUPAC). So as to avoid confusion with other quantities labeled by the letter A , such as area, we shall use \mathcal{A} .

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

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

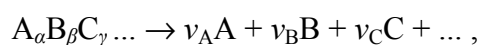
are similarly related both conceptually and formally. U describes the (electric) drive for a charge transfer between two points. The simplest case of this would be between the input and output of an electronic component (light-bulb, resistor, diode, etc.).

The quantity \mathcal{A} has a centuries old history under the name *affinity*. The first table with values of this quantity was compiled by 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 changes. The closer the “relationship” 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: $AC + BD \rightarrow AD + BC$. GOETHE was inspired by this idea in his novel “The Elective Affinities“ of 1809 in which he transferred this concept to human relationships.

The unit for drive is ”Gibbs,“ as can be easily seen in the above definition equation. A positive drive, $\mathcal{A} > 0$, ”drives“ a chemical change as long as there are reactants available. A negative, $\mathcal{A} < 0$, leads to a reaction in the opposite direction of the reaction arrow. $\mathcal{A} = 0$ means no drive, therefore, a standstill where equilibrium rules. Here are some examples:

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



the stoichiometric number ν_A being equal to α , ν_B to β etc.

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

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

Because we have arbitrarily set the potentials of the elements (at room conditions) equal to zero the expression in squared parentheses disappears and the drive of the decomposition corresponds to the chemical potential of the substance:

$$\mathcal{A} = \mu_{A_\alpha B_\beta C_\gamma \dots} - \underbrace{[\nu_A \cdot \mu_A^\ominus + \nu_B \cdot \mu_B^\ominus + \nu_C \cdot \mu_C^\ominus + \dots]}_0 = \mu_{A_\alpha B_\beta C_\gamma \dots}.$$

This fact was qualitatively considered in the discussion in Section 3.6. 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:

$$\begin{aligned} O_3|g &\rightarrow \frac{3}{2} O_2|g \\ \mu^\ominus: \quad 163 &> \frac{3}{2} \cdot 0 \quad \text{kG} \\ \Rightarrow \quad \mathcal{A}^\ominus &= +163 \text{ kG} \end{aligned}$$

\mathcal{A}^\ominus means the drive of decomposition under standard conditions.

The process is so slow, however, that we can make use of ozone despite its limited stability. We just have to produce it fast enough to compensate for its decomposition.

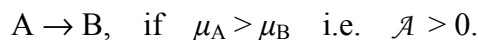
Here is an anomaly that one can easily stumble over: We obtain different values for the drive of decomposition of ozone depending upon which formula is being used to describe the process:

$$\begin{aligned} \mathcal{A}^\ominus(2 O_3 \rightarrow 3 O_2) &= +326 \text{ kG} \\ \mathcal{A}^\ominus(O_3 \rightarrow \frac{3}{2} O_2) &= +163 \text{ kG} \end{aligned}$$

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

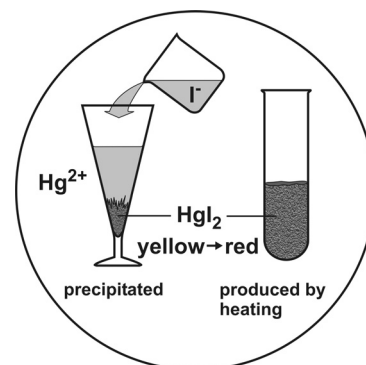
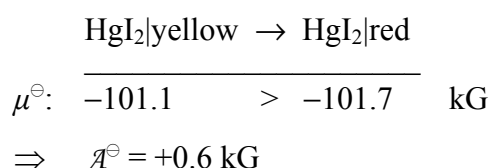
differs from just one harnessed animal. We expect that the team will be twice as strong as the single one. This is also true for reactions. Just as with the ξ values (Section 1.6), it is always important to give the chemical reaction equations that one is referring to.

Transformations. A simple case is also the transformation of one substance into another one:



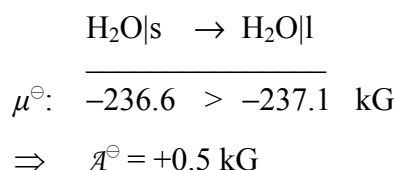
A suitable substance for an example is mercury iodide HgI_2 , which appears in beautiful red and yellow modifications with somewhat different chemical potentials:

Experiment: Modification transformation of HgI_2



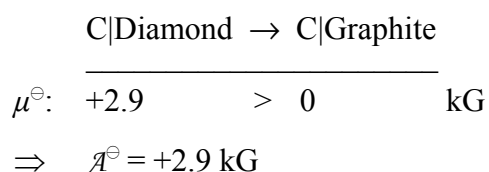
Because of the yellow modification's higher (not as strongly negative) tendency to transform, it must change into the red form. This is actually the case: Within an hour, a spoonful of yellow HgI_2 powder (produced by heating the red form in an oil bath or drying oven to over 125°C) becomes spotted with 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 precipitate, formed out of a Hg^{2+} solution by addition of I^- , is used. At first the precipitation is a sallow yellow, which immediately turns to orange and finally to deep red (left, in the figure).

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



We have used the tabulated values valid for a temperature of $298,15 \text{ K}$ or 25°C . Therefore, a positive drive can be expected that allows ice to melt under these conditions. For a given condition, the phase with the lowest chemical potential is stable.

Also diamond should transform into graphite because it has a higher chemical potential:



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

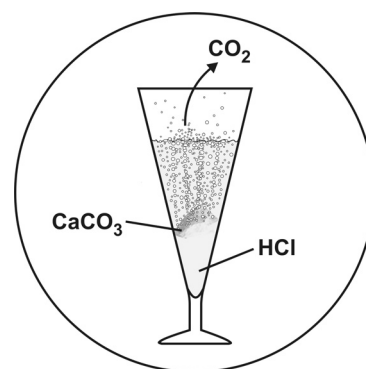
temperature. In this context we should remember that a potential drop from the left to the right side and therewith a positive value of the drive only means that the process *can* proceed in this direction in principle, but it does not mean that the process will actually run. Changes of states of aggregation, gas \rightarrow liquid \rightarrow solid, take place almost immediately and just about uninhibitedly due to high mobility of the individual particles in participating gases or liquids, as soon as the potential gradient has the necessary sign for this. 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 hydrochloric acid, an aqueous solution of hydrogen chloride, HCl, is poured over marble, foam develops that contains carbon dioxide. Therefore, we expect that the reaction drive is positive. Indeed, this can be shown by using the tabulated potential values (assuming an acid concentration of 1 kmol m^{-3}). We have also to consider that HCl 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.

Experiment: Dissolution of marble in hydrochloric acid

$$\begin{array}{rcccccc} \text{CaCO}_3|\text{s} + 2 \text{H}^+|\text{w} & \rightarrow & \text{Ca}^{2+}|\text{w} + \text{CO}_2|\text{g} + \text{H}_2\text{O}|\text{l} \\ \hline \mu^\ominus: & -1129 & 2 \cdot 0 & & -554 & -394 & -237 & \text{kG} \\ & \underbrace{\hspace{1.5cm}} & & & \underbrace{\hspace{1.5cm}} & & & \\ & -1129 & & > & -1185 & & & \\ \Rightarrow & \mathcal{A}^\ominus = +56 \text{ kG} & & & & & & \end{array}$$



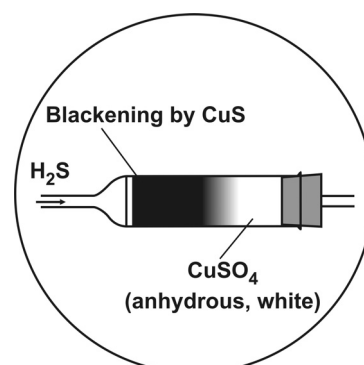
Another example is the development of hydrogen chloride gas when concentrated sulphuric acid reacts with table salt.

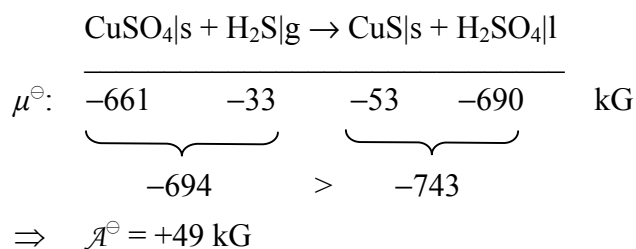
$$\begin{array}{rcccccc} \text{NaCl}|\text{s} + \text{H}_2\text{SO}_4|\text{l} & \rightarrow & \text{HCl}|\text{g} + \text{NaHSO}_4|\text{s} \\ \hline \mu^\ominus: & -384 & -690 & & -95 & -993 & & \text{kG} \\ & \underbrace{\hspace{1.5cm}} & & & \underbrace{\hspace{1.5cm}} & & & \\ & -1074 & & > & -1088 & & & \\ \Rightarrow & \mathcal{A}^\ominus = +14 \text{ kG} & & & & & & \end{array}$$

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

Experiment: Blackening of CuSO_4 by H_2S

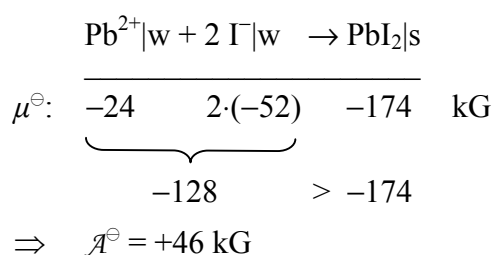
If gaseous hydrogen sulphide is led over anhydrous, white copper sulphate, black copper sulphide is produced:





In this case, the weak, volatile acid H_2S displaces the strong, low volatile sulphuric acid H_2SO_4 from its salt.

It is also easy to predict the production of low soluble precipitate from its ionic components when two solutions are combined. This is because ionic reactions in solutions proceed almost uninhibitedly and almost right away if the potential gradient has the correct sign.

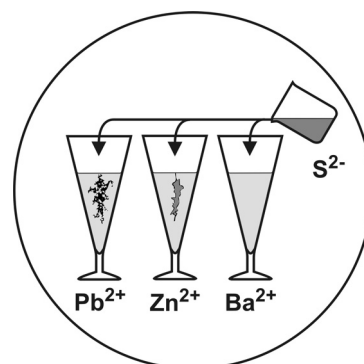


Lead iodide must precipitate out of an aqueous solution containing Pb^{2+} and I^- ions. Many other precipitation reactions can be predicted according to the same pattern. When solutions containing Pb^{2+} , Zn^{2+} or Ba^{2+} are mixed with ones containing CO_3^{2-} , S^{2-} or I^- -ions, precipitation can be expected only in the cases marked with plus signs. To save some calculation, the chemical potential of the possible precipitates and the combined potential of the ions forming it are included in the table at the end of the chapter.

Precipitation expected (+), not expected (–):

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

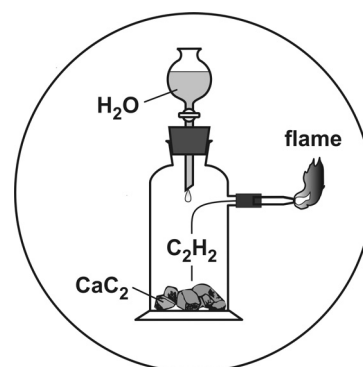
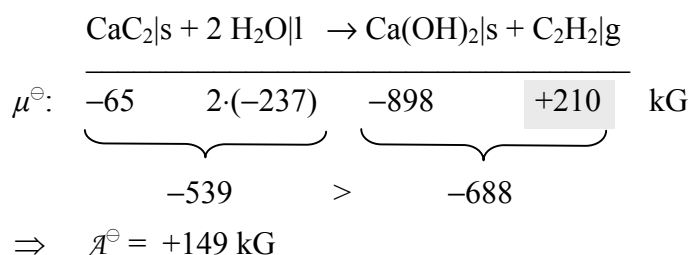
The predicted result can be easily proven in a demonstration experiment, for example by using S^{2-} . Reactions with CO_3^{2-} or I^- can be carried out correspondingly.



Experiment: Precipitation of Pb^{2+} , Zn^{2+} , Ba^{2+} by S^{2-}

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 μ). The production of ethyne (acetylene) with a high positive chemical potential from calcium carbide and water shows that this is not the case. 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.

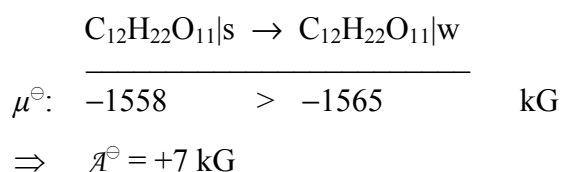
Experiment: Carbide lamp



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 “up-hill,” against the potential gradient. But the very low chemical potential of calcium hydroxide on the product side makes sure that the drive is generally positive, even though $\mu(\text{ethyne})$ is > 0 .

Solution behaviour. 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 behaviour of solutions of substances is all that will be given in this section. Chapter 5 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:



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

“Experiment”: Sugar cube in aqueous solution (or water)

The process becomes noticeable by the sugar cube shrinking even when it is not touched. 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.

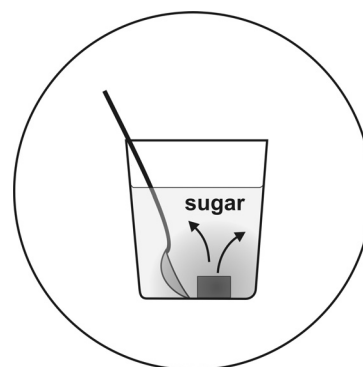
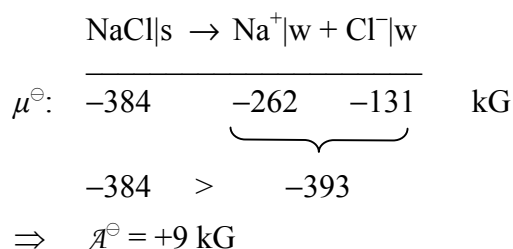


Table salt also dissolves easily in water, as we know. The reason for this is that in an aqueous environment (even at a concentration of 1 kmol m^{-3}), the chemical potential of the Na^+ and Cl^- ions is noticeably lower than when it is a salt in solid form.

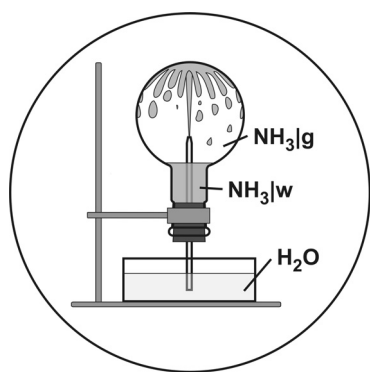


For contrast, let us consider the solution behaviour of iodine.

$$\begin{array}{l} \text{I}_2|\text{s} \rightarrow \text{I}_2|\text{w} \\ \hline \mu^\ominus: \quad 0 \quad < \quad +16 \quad \text{kG} \\ \Rightarrow \quad \mathcal{A}^\ominus = -16 \text{ kG} \end{array}$$

The drive is strongly negative so the process can only voluntarily run backwards. 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 5.

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



$$\begin{array}{l} \text{NH}_3|\text{g} \rightarrow \text{NH}_3|\text{w} \\ \hline \mu^\ominus: \quad -16 \quad > \quad -27 \quad \text{kG} \\ \Rightarrow \quad \mathcal{A}^\ominus = +11 \text{ kG} \end{array}$$

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

Experiment: Ammonia fountain

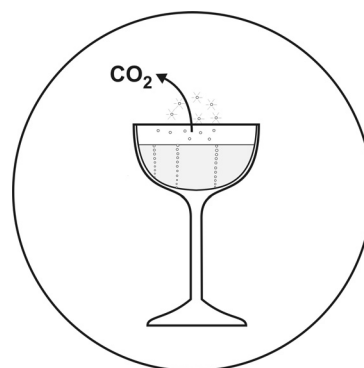
NH_3 gas dissolves so readily in water that just a few drops are enough to decrease the pressure in the flask so drastically that water is drawn upward into it in a strong jet.

The situation is different with carbon dioxide,

$$\begin{array}{l} \text{CO}_2|\text{g} \rightarrow \text{CO}_2|\text{w} \\ \hline \mu^\ominus: \quad -394 \quad > \quad -386 \quad \text{kG} \\ \Rightarrow \quad \mathcal{A}^\ominus = -8 \text{ kG} \end{array}$$

which is much less soluble in water.

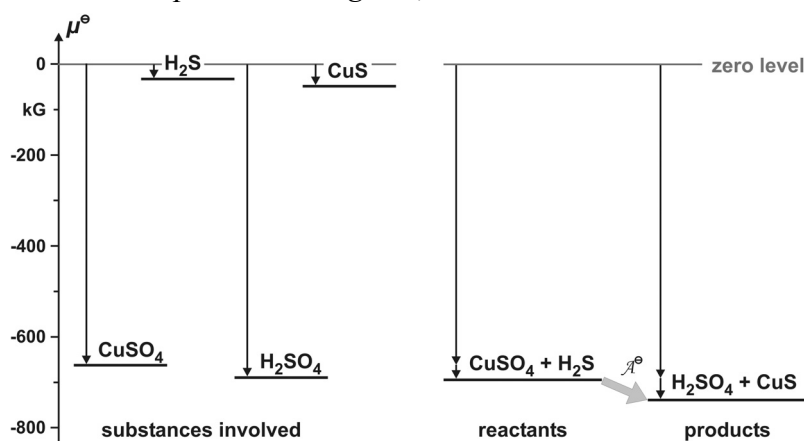
“Experiment”: “Bubbling” of carbon dioxide.



Carbonated liquids such as champagne or mineral water are packaged under excess pressure. The carbon dioxide produces bubbles when the pressure is reduced.

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

The description of the changes, not only by comparing the numerical values, but also by using a so-called *potential diagram*, is even more demonstrative. The potential drop which



“drives” the process can be demonstrated most suitably if the sums of the chemical potentials μ^\ominus of the reactants and products are plotted. This is shown for the reaction of copper sulphate with hydrogen sulphide as an example. On the left side of the figure we find the potential levels of the substances involved, on the right side

the sums of the values of the reactants and products, respectively.

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 behaviour of substances. But before we discuss how the tendency to change of substances can be quantified.

3.8 Direct measurement of chemical drive

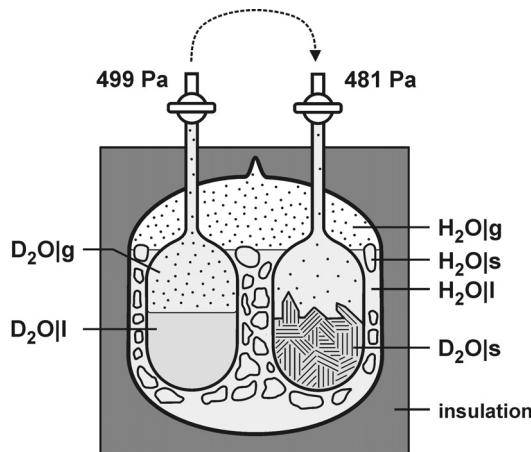
The usual methods do not measure the chemical potentials of a substance itself, but only the difference between the sums of the potentials of the initial substances μ_{initial} and the resulting substances μ_{final} , i.e., the drive $\mathcal{A} = \sum_{\text{initial}} \mu - \sum_{\text{final}} \mu$ of a chemical conversion. In other words, \mathcal{A} is

the basic quantity from which we derive the chemical potential. This is also true of electric circuits where only the difference of potentials 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.

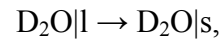
The drive \mathcal{A} can be measured both directly and indirectly just as other quantities can be. However, the direct method has the advantage of not being dependent upon other physical quantities. This means that the meaning of the quantity \mathcal{A} can be comprehended directly. A disadvantage is that some repeatable process that represents the unit \mathcal{A}_1 of the drive must be chosen. “Embodied” units of length and mass are, for example, the original meter and original kilogram made of platinum or a platinum alloy which are deposited in Paris. Values of chemical drives initially measured as multiples of \mathcal{A}_1 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}_1 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 pure water, steam, and ice are coexisting) is given the exact value $T = 273.16$ K.



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



which is imbedded in airless light water and whose temperature is brought to 273.16 K. The transformation happens voluntarily and by itself if the D_2O vapour is allowed to move from the container on the left to the one on the right. Expressed in SI coherent units, the drive is

$$\mathcal{A} = 84 \text{ G.}$$

As we have already seen in the example of weight, there are basically three agreements necessary for metrization. These are agreements about

- sign,
- sum,
- unit

of the quantity \mathcal{A} which serves as the measure of the drive of a chemical conversion. 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 3.7: A process that runs forward voluntarily receives a positive value of drive $\mathcal{A} > 0$, one that tends to run backward against the direction of the reaction arrow, receives a negative value $\mathcal{A} < 0$, and a process that does neither has found equilibrium and has the value $\mathcal{A} = 0$.

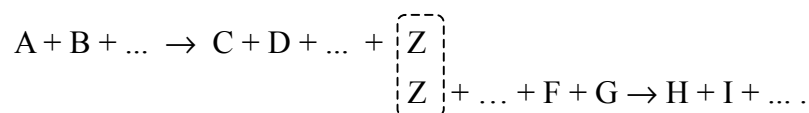
Now we need only think about creating sums (point b). Two or more conversions with the drives $\mathcal{A}', \mathcal{A}'', \mathcal{A}''' \dots$ are coupled to each other – it does not matter how – so that they can take place together. We make the agreement that the drive $\mathcal{A}_{\text{total}}$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

$$\mathcal{A}_{\text{total}} = \mathcal{A}' + \mathcal{A}'' + \mathcal{A}''' + \dots$$

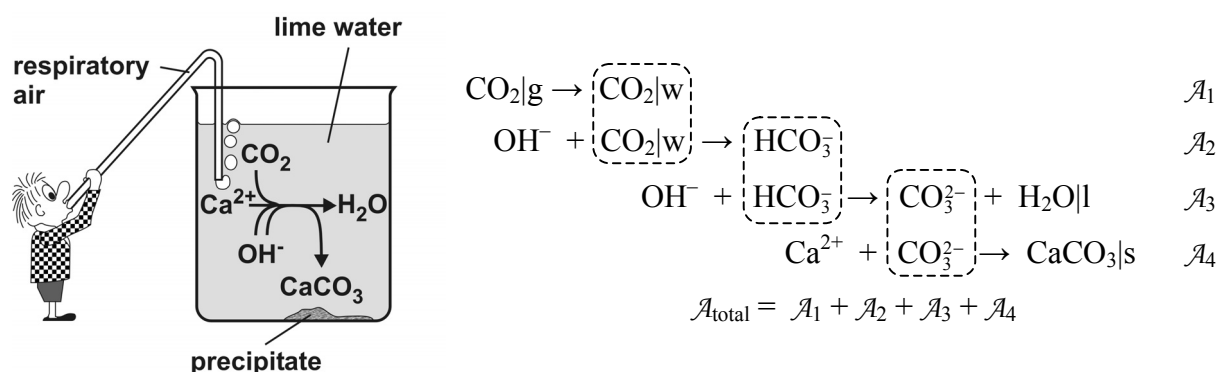
There exist a number of methods for achieving a coupling of two or more chemical processes. Here are some of them:

- chemically* through shared intermediate substances,
special case: *enzymatically* through enzyme substrate complexes,
- electrically* through electrons as the intermediate substance,
- mechanically* through cylinders, pistons, gears, etc.

Chemical coupling is the most common kind of coupling. Almost all conversions are made up of such coupled partial stages. A strict synchronization and a close coupling is forced when, under the chosen test conditions, the *intermediate substance* Z no longer freely appears in noticeable quantities, i.e. as soon as Z is created it is used up by the next reaction:



Both processes can only take place jointly or they have to rest jointly, i.e., they are fixed coupled through the shared substance Z 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 where the intermediate substances are well known is the precipitation of limestone from lime water by blowing carbon dioxide of breath into it. The first two reactions are coupled by dissolved CO_2 , the next by HCO_3^- and the last by CO_3^{2-} .

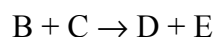
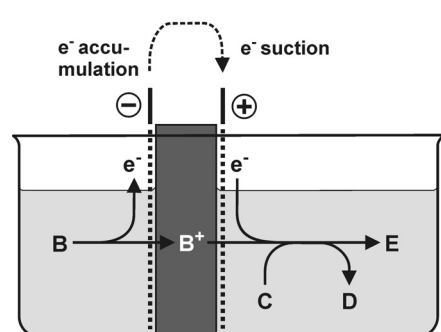


Enzymatic coupling is an important special case of chemical coupling. This process has been developed to a high degree of perfection in biochemical reactions. For example, the innumerable reactions taking place in animal cells are connected in this way which leads to the metabolism driving all other 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.

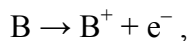
Electrical coupling which makes use of reversible galvanic cells is much more flexible. Theoretically, any chemical conversion can be used to transport electric charge from one pole to another in a galvanic cell. Because practically all substances contain electrons each substantial change can be subdivided in a partial process which supplies electrons and another which consumes electrons – in many different ways.

Let us consider the following reaction:



Theoretically, we can subdivide the reaction in two – also spatially - separated processes in which a sufficiently mobile ion B^+ act as shared reaction partner. The dividing wall is only permeable for B^+ ions so that the electrons can not migrate with the ions. This type of ionic conductor exists in solid or liquid state. Electrodes are used for the conduction of the electrons. In the sim-

pliest case the wall is solid and the dissolved substances are located in a suitable container. In order for substance B to go from left to right, it must be stripped of its surplus electrons:



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,



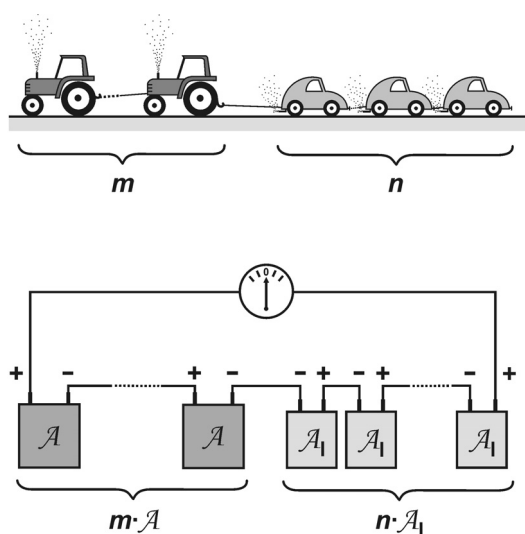
Subsequently, an electric tension is developed between the electrodes. The experimental arrangement represents nothing else than a galvanic cell in which the entire reaction can only proceed when the electrons are allowed to flow from the cell's pole on the left to the one on the right. Part 3 of the book will go more deeply into how such cells are constructed.

Ideally, transport of charge and chemical conversion 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. It is assumed that for simplicity's sake, the reactions are formulated so that the amount of electrons converted is $\nu_e = 1$. When the poles 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.

In addition, reactions can be *mechanically* coupled. This works well only in thought experiments and therefore will not be gone into here.

The drive \mathcal{A} of a conversion can be measured in the same way that we discussed for weights. All we need to do is couple the reaction to be measured inversely to as many specimens of the unit reaction (or a reaction with known drive) that equilibrium is achieved, i.e. the drive of the entire process disappears:

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



The quantity \mathcal{A} can, in principle, be measured as precisely as we wish by using this method. We can demonstrate the procedure in an example of oppositely coupled vehicles. Analogously, m galvanic cells which represent a given reaction with unknown \mathcal{A} can be coupled in opposition to n cells based on a reaction with known drive like the unit reaction (\mathcal{A}_1) so that equilibrium rules, i.e., the electric current in the circuit is zero.

Because the chemical potential μ is nothing else than the drive for decomposition of a substance into its elementary constituent parts it can be measured with exactly the same methods.

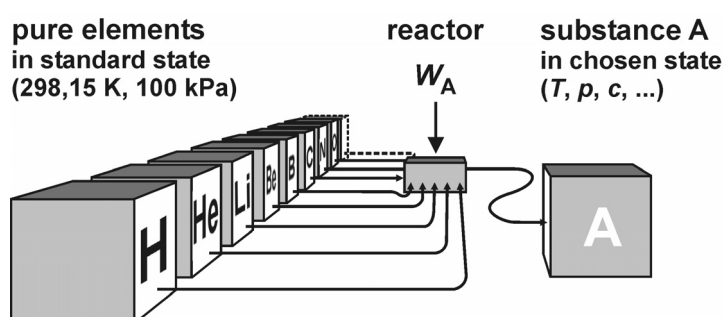
The procedure can be simplified considerably. It is for example possible to calibrate a sufficiently sensitive highly resistive galvanometer directly in the unit \mathcal{A}_1 . For this purpose one has only to connect the instrument with the two open terminals of various cell chains consisting of

an increasing number of “unit cells.” The related pointer deflections are marked, in this way constructing a division scale suitable for the measurement of unknown \mathcal{A} values. The procedure is comparable to the calibration of a spring balance with different weights or to the calibration of the ice calorimeter directly in entropy units (Section 3.7).

Alongside the *direct* methods shown here for determining drives, there are numerous *indirect* methods that are more sophisticated and therefore more difficult to grasp but are more universally applicable. These include chemical (using the mass action law) (Section 5.4), calorimetric (7.8), electrochemical, spectroscopic, quantum statistical, and other methods to which we owe almost all of the values we have at our disposal today.

3.9 Indirect metrization of chemical potential

In order to increase our understanding, we will consider a method which allows – in principle – the μ values of substances to be determined rather directly and in a way that approaches the way most commonly used. The following figure shows a theoretically possible setup for measuring μ which gives the values directly in the scale used by us. This method is indirect because the energy W_A which is used for forming a small amount n_A 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_A , which serves exactly this purpose, from the other energy contributions which only accompany the process.



The containers on the left in the figure contain the elements in their normal stable states at 298,15 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 converted there, 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 to its elementary components with the potential 0, to a state on the right with a potential of μ_A . The stronger the “drive” for a conversion of the substance A, in this case the drive for decomposition in the elements in their normal state,

- the more difficult it is for the substance to be formed against its “drive,”
- the greater the amount of W_A necessary to achieve this.

W_A grows in proportion to the amount of substance n_A formed (as long as n_A stays small), so W_A itself is not to be used as a measure of conversion drive or the chemical potential μ_A , but rather W_A divided by n_A :

$$\mu_A = W_A/n_A$$

The accumulation of substance A in a container gradually changes the environment there for substance A and its potential. For this reason, it is required that the amount n_A and energy W_A

are kept small in order to keep the disturbance small. This can be symbolized by dn_A and dW_A . μ_A itself results as a quotient of both quantities:

$$\mu_A = dW_A/dn_A.$$

It is of course necessary to avoid or subtract all energy conversions and transfers due to side effects (for example, as a result of friction, lifting, heat transfer, acceleration, production of other substances, solvents or mixing partners, etc.).

If, on the other hand, the process (the transport of substance A) runs voluntarily from left to right, it releases energy.

The unit for chemical potential which results from the equation above is J/mol. 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 3.5:

$$1 \text{ Gibbs (G)} = 1 \text{ J/mol.}$$

At this point it should be reiterated that the chemical potential is itself *not* work but corresponds to a “force” or “strength.” Again, the weight G can be used for comparison. The tendency of a body to fall can be defined by the lifting work W relative to the distance h through which the body has been lifted, $G = W/h$ (unit : J/m = N (Joule/ Meter = Newton)).

The equation above already shows similarity to GIBBS’s approach. W. GIBBS was addressing his colleagues in 1876 when he introduced the quantity μ , which is known today as the chemical potential. He assumed they would have the knowledge of mathematics and physics necessary for understanding it. He defined the potential μ by a formal rule that is shown in a modern form in the following equation, which can be found in many textbooks of physical chemistry:

$$\mu = \left(\frac{\partial W}{\partial n} \right)_{V, S, n', n'' \dots}$$

n represents the amount of substance in question, $n', n'' \dots$ is the amount of each partner in the mixture, W is the energy, V is the volume, and S is the entropy of the body which, for simplicity’s sake, is homogenous, weightless and resting.

For the unpracticed, however, it is quite difficult to understand what this equation is expressing. That is why we prefer the introduction of the chemical potential by phenomenological characterization and direct metrization. Now, looking back, after one has understood what the quantity μ means, and what characteristics it has, GIBBS definition becomes understandable.

Table: Chemical potential μ and its temperature and pressure coefficients α and β under standard conditions (298,15 K, 100 kPa, ions in aqueous solution at 1 kmol m⁻³)

Substance	μ^\ominus	α	β	Substance	μ^\ominus	α	β
	kG	kG K ⁻¹	$\mu\text{G Pa}^{-1}$		kG	kG K ⁻¹	$\mu\text{G Pa}^{-1}$
Fe s	0	-0.027	7.1	HCl g	-95		
NaCl s	-384	-0.072		H ₂ SO ₄ w	-690		
NaHSO ₄ s	-993	-0.113		Na ₂ SO ₄ s	-1270		
SiO ₂ s	-856	-0.041		CuSO ₄ s	-661		
CaCO ₃ s	-1129	-0.093	36.9	CuS s	-53		
C ₁₂ H ₂₂ O ₁₁ s	-1558	-0.392	217	H ₂ S g	-33		
C ₂ H ₂ g	210	-0.201	24.8·10 ³	CaC ₂ s	-65		
Ca ²⁺ w	-554	0.053	-17.8	OH ⁻ w	-157		
Element	0	most stable form		Pb ²⁺ w	-24		
H ₂ g	0			Zn ²⁺ w	-147		
H g	203			Ba ²⁺ w	-561		
O ₂ g	0			CO ₃ ²⁻ w	-528		
O ₃ g	163			S ²⁻ w	86		
C Graph.	0			I ⁻ w	-52		
C Diam.	2.9					Substances	$\Sigma\mu$
NI ₃ s	300			PbCO ₃ s	-625	Pb ²⁺ + CO ₃ ²⁻	-552
S ₄ N ₄ s	500			ZnCO ₃ s	-731	Zn ²⁺ + CO ₃ ²⁻	-675
C ₆ H ₆ l	125			BaCO ₃ s	-1135	Ba ²⁺ + CO ₃ ²⁻	-1089
CO ₂ g	-394	-0.214	combustible incombustible incombustible	PbS s	-98	Pb ²⁺ + S ²⁻	62
NO ₂ g	52	-0.240		ZnS s	-199	Zn ²⁺ + S ²⁻	-61
ClO ₂ g	123	-0.257 parent element		BaS s	-456	Ba ²⁺ + S ²⁻	-475
Al ₂ O ₃ s	-1582	-0.051	oxidises rusts stable	PbI ₂ s	-174	Pb ²⁺ + 2 I ⁻	-128
Fe ₂ O ₃ s	-741	-0.087		ZnI ₂ s	-209	Zn ²⁺ + 2 I ⁻	-251
Au ₂ O ₃ s	78	-0.130		BaI ₂ s	-602	Ba ²⁺ + 2 I ⁻	-665
MgS s	-344	-0.050		C ₁₂ H ₂₂ O ₁₁ w	-1565		
ZnS s	-199	-0.059		Na ⁺ w	-262		
FeS s	-102	-0.060		Cl ⁻ w	-131		
CuS s	-53	-0.066		I ₂ s	0		
AuS s	>0			I ₂ w	16		
HgI ₂ red	-101.7	-0.180		NH ₃ g	-16		
HgI ₂ yel.	-101.1	-0.186		NH ₃ w	-27		
H ⁺ w	0			CO ₂ w	-386		
				H ₂ O s	-236.6	-0.045	19.8
				H ₂ O l	-237.1	-0.070	18.1
				H ₂ O g	-228.6	-0.189	24.8·10 ³

4. Influence of Temperature and Pressure on Chemical Changes

Topic: The influence of temperature and pressure on the chemical potential and drive and therefore the behaviour of substances.

4.1 Introduction

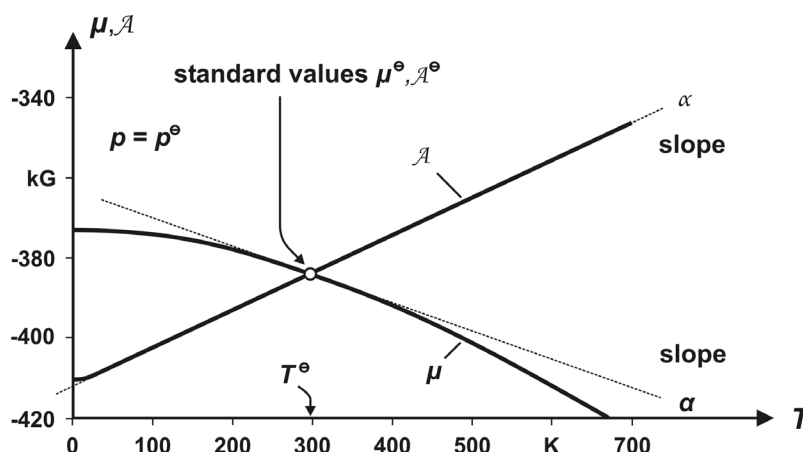
Until now, the tabular values we have used were the so-called standard values based upon room temperature and standard pressure (298 K and 100 kPa). For dissolved substances, the standard concentration is 1 kmol m^{-3} . Up to this point, our statements about the possibility of a chemical change have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

However, temperature and pressure often have a decisive influence upon the chemical potential and thereby, upon 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 μ is not a material constant, but depends upon temperature, pressure, etc.

4.2 Temperature dependence of chemical potential and drive

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

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



It is striking that the chemical potential *falls* more and more steeply with *increasing temperature*. Except for a very few exceptions of dissolved substances (f.e. Ca^{2+} in aqueous solution), all substances exhibit this behaviour. The tendency of a substance to change generally decreases when it is put into a warmer environment.

The chemical drive $\mathcal{A}(T)$ which is calculated from the temperature dependent potentials, exhibits a noticeably more linear gradient than the $\mu(T)$ curves.

The decline in 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 be caused by a smaller or even vanishing inhibition as is actually the case in chemical reactions. The strong decrease of inhibition resulting from an increase of warming masks the mostly weak change to the drive \mathcal{A} . Moreover, it should be remembered that \mathcal{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 of 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.

In order to describe the decrease of potential, 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:

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

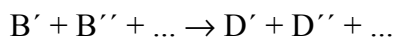
The initial value is represented by l_0 and ε represents the temperature coefficient.

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, μ_0 characterises 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 μ^\ominus). But standard values often serve as the initial values of a calculation, so that in special cases, $\mu_0 = \mu^\ominus$. The *temperature coefficient* α represents the slope of the function $\mu(T)$ at the point $(T_0; \mu_0)$, and is therefore almost always *negative*, as we have seen.

For the temperature dependence of the drive \mathcal{A} of a chemical change



we obtain analogously:

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

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

$$\alpha = \alpha(B') + \alpha(B'') + \dots - \alpha(D') - \alpha(D'') - \dots .$$

(Remember that $\mathcal{A} = \mu(B') + \mu(B'') + \dots - \mu(D') - \mu(D'') - \dots$).

If we take standard room conditions as starting point, the error is about 1 kJ for low-molecular substances for ΔT values of about ± 100 K. This approach 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 which are decisive in chemical processes, but the drives. When taking the difference $\mathcal{A} = \sum_{\text{initial}} \mu - \sum_{\text{final}} \mu$, 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:

$$\mu = \mu_0 + \alpha \cdot \Delta T + \alpha' \cdot (\Delta T)^2 + \alpha'' \cdot (\Delta T)^3 + \dots$$

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 approach. It is our goal here to show this.

The following table shows the chemical potential μ as well as its temperature coefficient α for some substances at standard conditions (298 K, 100 kPa, dissolved substances at 1 kmol m⁻³):

Substance	Formula	μ^\ominus kJ	α G/K
Iron	Fe s	0	-27.3
	Fe l	5.3	-35.6
	Fe g	368.3	-180.5
Graphite	C Graphite	0	-5.7
Diamond	C Diamond	2.9	-2.4
Iodine	I ₂ s	0	-116.1
	I ₂ l	3.3	-150.4
	I ₂ g	19.3	-260.7
	I ₂ w	16.4	-137.2
Water	H ₂ O s	-236.6	-44.8
	H ₂ O l	-237.1	-70.0
	H ₂ O g	-228.6	-188.8
Ammonia	NH ₃ l	-10.2	-103.9
	NH ₃ g	-16.4	-192.8
	NH ₃ w	-26.6	-111.3
Calcium(II)	Ca ²⁺ w	-553.6	+53.1

Along with the already mentioned basic rule which states that the temperature coefficient α is (almost) always negative, another rule (which almost all substances follow) becomes apparent when the α -values are compared for phase transformations. The temperature coefficient α 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, α is mostly similar to that of the liquid state. The values scatter more strongly, though, so that we cannot easily fit $\alpha(\text{B}|w)$ into the other α -values:

$$0 > \alpha(\text{B|s}) > \alpha(\text{B|l}) \gg \alpha(\text{B|g})$$

$$\longleftarrow \alpha(\text{B|w}) \longrightarrow$$

For clarification, we will single out the values for iodine at standard conditions given in $\text{G}\cdot\text{K}^{-1}$ from the table above:

$$-260,7 < -150,4 < -116,1 < 0.$$

$$-137,2$$

(As we will see in Chapter 8, the temperature coefficient α corresponds to the negative molar entropy S_m , i.e., $\alpha = -S_m$. Anticipating this can help with remembering the rules more easily: First, in Chapter 2, we demonstrated that the molar entropy is always positive; the negative sign of the temperature coefficient easily results from this. 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, leads to the sequence above (see Section 2.9)).

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 behaviour. Under standard conditions, the chemical potential of ice, water, and water vapour has the following values:

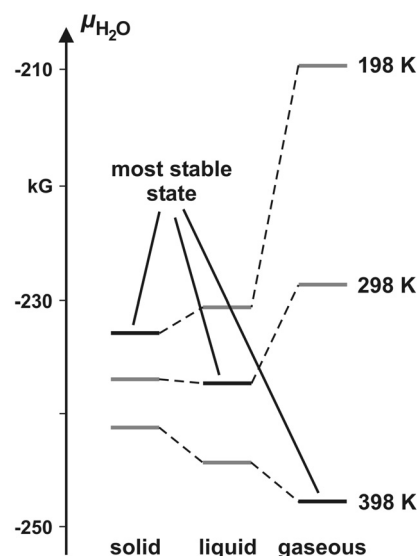
	$\text{H}_2\text{O s}$	$\text{H}_2\text{O l}$	$\text{H}_2\text{O g}$
μ^\ominus / kG	-236.6	-237.1	-228.6

One sees here that under these conditions, ice melts, and water vapour condenses because water in its liquid state has 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 $\pm 100 \text{ K}$. The following results are obtained using the linear approach:

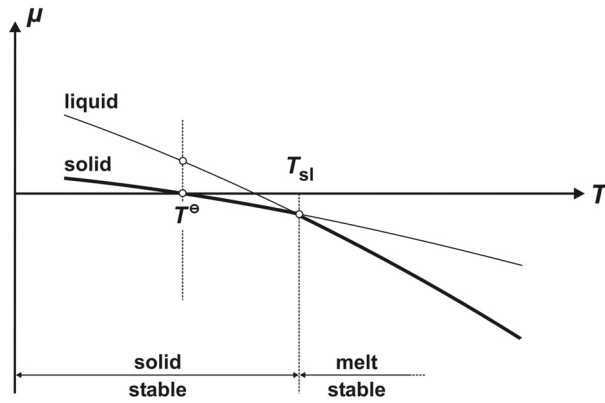
	$\text{H}_2\text{O s}$	$\text{H}_2\text{O l}$	$\text{H}_2\text{O g}$
$\alpha / \text{G}\cdot\text{K}^{-1}$	-45	-70	-189
$\mu(398 \text{ K}) / \text{kG}$	-241	-244	-248
$\mu(198 \text{ K}) / \text{kG}$	-232	-230	-210

We see that at 398 K (125°C), the chemical potential of water vapour has the smallest value and that water vapour must result from the other forms, while at 198 K (-75°), ice must develop. This result is represented graphically in the figure on the right.

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



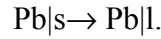
is highlighted):



$\mu(\text{Pb}|s)$ 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 μ -scale. Under these conditions, $\mu(\text{Pb}|l)$ must lie above this. The chemical potentials decrease with warming. This happens more quickly in the liquid state than in the solid. For this reason, the curves must intersect at some point, say at the temperature T_{sl} . This T_{sl} is the *melting point* of lead because be-

low T_{sl} , the most stable state of lead is the solid state, above T_{sl} , however, it is the liquid state. In order to indicate the phase transformation in question, the symbols for the corresponding aggregation states are inserted.

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



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

$$\mu_s = \mu_l.$$

At this temperature, the two phases are in equilibrium. The temperature dependence of μ is expressed by the linear formula:

$$\mu_{s,0} + \alpha_s(T_{sl} - T_0) = \mu_{l,0} + \alpha_l(T_{sl} - T_0).$$

By transforming this we obtain

$$(\alpha_l - \alpha_s)(T_{sl} - T_0) = \mu_{s,0} - \mu_{l,0}$$

and respectively

$$T_{sl} = T_0 - \frac{\mu_{s,0} - \mu_{l,0}}{\alpha_s - \alpha_l} = T_0 - \frac{\mathcal{A}_0}{\alpha}.$$

The derivation is somewhat shortened when the following equivalent of the first equation

$$\mathcal{A} = 0$$

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

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

and therefore

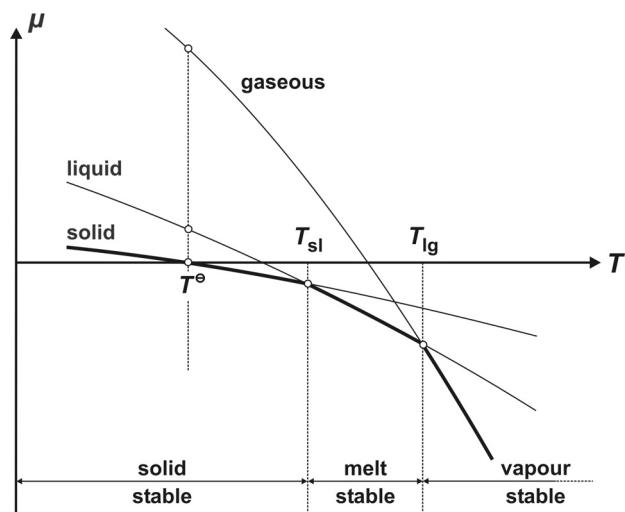
$$T_{sl} = T_0 - \frac{\mathcal{A}_0}{\alpha}.$$

Of course, strictly speaking, our result is not accurate because our formula for temperature dependence is only an approximation. The smaller ΔT ($:= T_{sl} - T_0$) is, the more exact the calculated value will be. The melting point of lead is actually 601 K. Based on the tabulated

standard values, our calculation yields

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

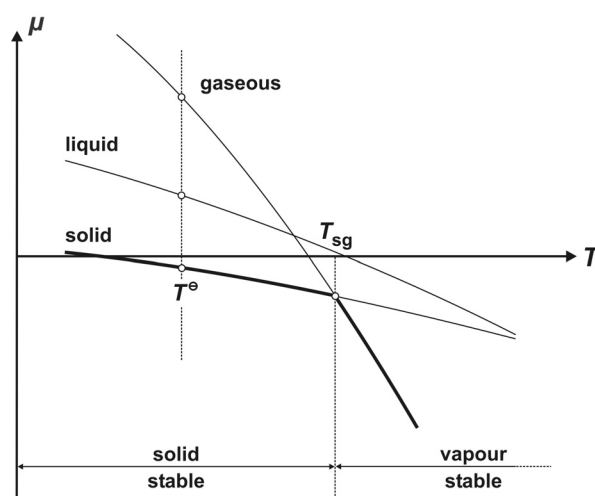
The result is surprisingly good for this rough approximation.



We will now complete our diagram by adding the chemical potential of lead vapour. At room temperature, the chemical potential of vapour lies much higher than that of the liquid phase. However, with rising temperature, $\mu(\text{Pb}|\text{g})$ falls rather steeply, as is usual in all gases. At some temperature T_{lg} the potential of lead vapour intersects with that of liquid lead. When this temperature is exceeded, the melted lead transforms into vapour because now vapour 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 vapour is relatively low compared to that of the melt. The potential of the vapour can then intersect that of the solid below the 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 vapour state. This phenomenon is called *sublimation*. An excellent example of such a substance is frozen carbon dioxide which has the characteristic of vaporising 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.

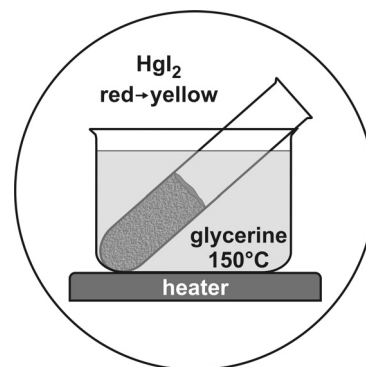


Other transformations can be dealt with in the the same way. A good object for demonstration is the already mentioned mercury iodide:

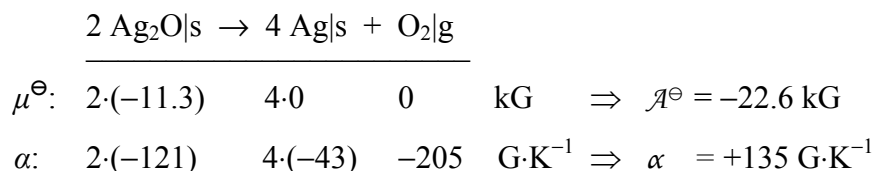
	HgI ₂ yellow	HgI ₂ red
μ^\ominus / kJ	-101.1	-101.7
$\alpha / \text{G} \cdot \text{K}^{-1}$	-186	-180

Experiment: Heating HgI_2 to above 398 K

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 temperature of transformation (398 K or 125°C) can be calculated just like the melting point of lead and can be easily verified by experiment.



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 behaviour of conversions. Processes which produce more gas than is used up (so-called *gas forming* reactions) benefit from the strongly negative temperature coefficients α of gases when the temperature rises. In contrast, the chemical drive of a *gas binding* reaction is weakened by the rise in temperature. Consider the example of thermal decomposition of silver oxide:



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 temperature. The minimum temperature T_D for the decomposition of Ag_2O 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:

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

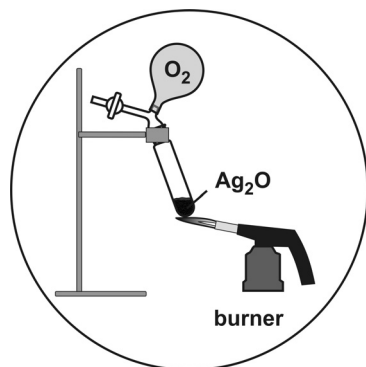
In analogy to the equations above, we obtain

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

Inserting the \mathcal{A}^\ominus and α 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 $T_D \approx 465 \text{ K}$.

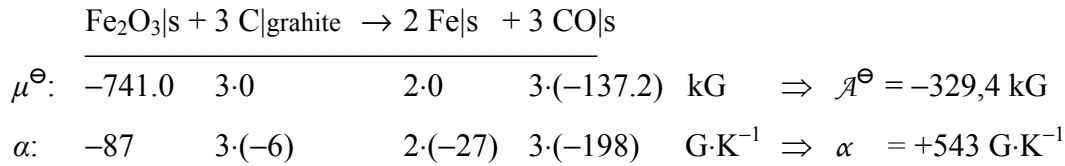
Experiment: Annealing of Ag_2O

When the blackish brown silver oxide is heated by a burner, the oxygen that forms can be demonstrated with a glowing splint. White shiny silver metal remains in the test tube.



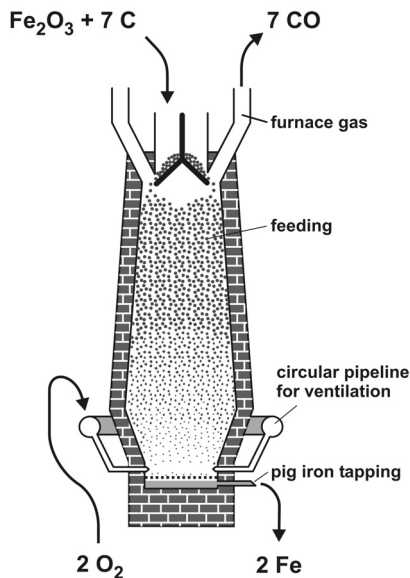
The same procedure can be used, for example, to calculate how strongly a compound containing crystal water must be heated in a drying oven in order to dehydrate it. Industrially important processes such as smelting of iron ore in a blast furnace can also be made accessible to a description. If the technical 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 reaction equation simplistically represented by carbon)



it cannot take place at room temperature due to its negative chemical drive. 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 according

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



for this temperature. 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 needed can be approximated by an equivalent to the equation above:

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

We therefore obtain a value for T_R of $\approx 900 \text{ K}$. Extra coal is needed for the furnace to reach this temperature.

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

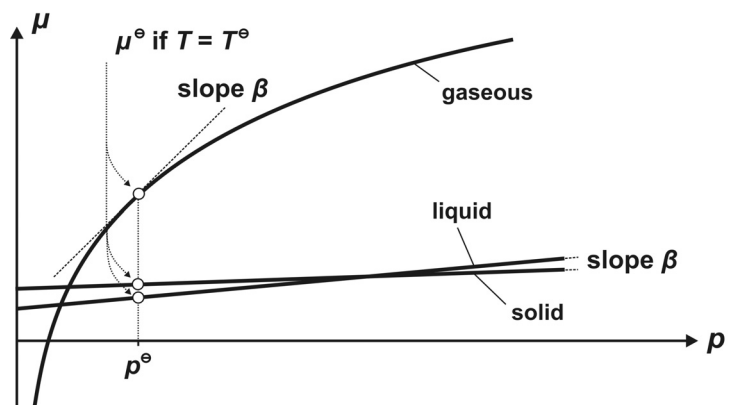
4.3 Pressure dependence of chemical potential and drive

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*.

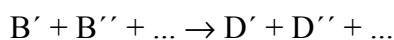
In a small range of pressures, all the curves can be approximated as linear, comparable to how we described the influence of temperature:

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

μ_0 is the starting value of the chemical potential for the initial pressure p_0 . The pressure coefficient β is almost always *positive*.



Analogously, the pressure dependence of drive \mathcal{A} of a reaction



results in

$$\boxed{\mathcal{A} = \mathcal{A}_0 + \beta \cdot (p - p_0)} \quad , \quad \text{where} \quad \beta = \beta(B') + \beta(B'') + \dots - \beta(D') - \beta(D'') - \dots$$

The linear approach is useful for solid, liquid, but also dissolved substances and for the drives of the corresponding conversions 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 reactions in which gases participate, $\Delta p/p < 10\%$ is considered acceptable because the slope β of the corresponding curve changes relatively strongly with pressure. For greater ranges of pressure Δp , the mass action relation must be applied. We will be introduced to this in Section 4.5.

The following table shows the β values for the substances of the table above.

Substance	Formula	μ^\ominus kJ	β $\mu\text{G}\cdot\text{Pa}^{-1}$
Iron	Fe s	0	7.1
	Fe g	368.3	$24.8 \cdot 10^3$
Graphite	C Graphite	0	5.5
Diamond	C Diamond	2.9	3.4
Iodine	I ₂ s	0	51.5
	I ₂ l	3.3	60.3
	I ₂ g	19.3	$24.8 \cdot 10^3$
Water	H ₂ O s	-236.6	19.8
	H ₂ O l	-237.1	18.1
	H ₂ O g	-228.6	$24.8 \cdot 10^3$
Ammonia	NH ₃ l	-10.2	28.3
	NH ₃ g	-16.5	$24.8 \cdot 10^3$
	NH ₃ w	-26.6	24.1

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

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

$$\longleftarrow \beta(B|w) \longrightarrow$$

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

$$0 < 51,5 < 60,3 \lll 24,8 \cdot 10^3.$$

(In this case, as well, there is a relation to a molar quantity, namely the molar volume V_m . Therefore, we have $\beta = V_m$ (compare Chapter 8). Because all molar volumes are basically positive, the pressure coefficient always has a positive sign. 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).

Like any rule, this one has exceptions. For instance, the β for some ions in an aqueous solution is negative and sometimes – as in the case of water – the β 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.

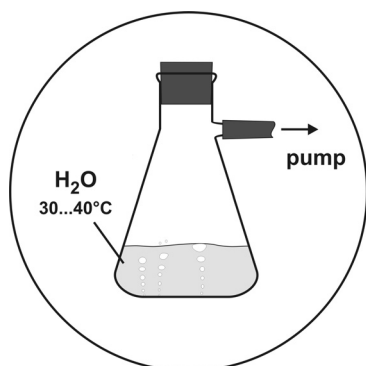
Raising the pressure generally causes the chemical potential to increase although, as already stated, the increase varies for the different states of aggregation. In the solid state, it is smallest and in the gaseous state, greatest. As a rule, the higher the pressure is, the more stable the solid state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

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

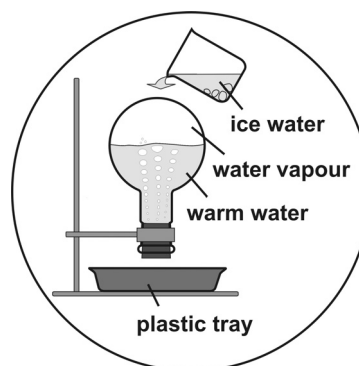
	H ₂ O s	H ₂ O l	H ₂ O g
μ^\ominus / kJ	-236.6	-237.2	-228.6
$\beta / 10^{-6} \mu\text{G}\cdot\text{Pa}^{-1}$	19.8	18.1	24.8·10 ³

One sees that lukewarm water can boil at low pressure, although, at room conditions, $\mu(\text{H}_2\text{O}|g) > \mu(\text{H}_2\text{O}|l)$, liquid water is the stable phase. If the pressure is lowered enough by pumping the air above the water out of a closed container, $\mu(\text{H}_2\text{O}|g)$ will fall below $\mu(\text{H}_2\text{O}|l)$, at some point because β 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 vapour by boiling. But low pressure can also be created by using ice-water to cool a closed flask containing only hot water and steam. In the process, a part of the vapour condenses, leading to a decrease in pressure.

Experiment: Boiling of warm water at low pressure

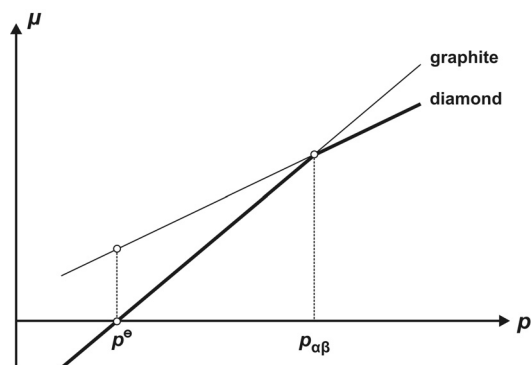


Experiment: Boiling by cooling



We shall take a closer look at a further example of the transformation 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, $\mu(\text{C}|\text{graphite})$ should exceed $\mu(\text{C}|\text{diamond})$ making it possible for diamond to form.



At normal pressure and room temperature, $\mu(\text{C}|\text{graphite})$ equals zero because this value has been arbitrarily set as the zero point of the μ 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 transformation pressure. The index $\alpha\beta$ indicates that the transformation of a modification α (here graphite) into another modification β (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 μ 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

$$p_{\alpha\beta} = p_0 - \frac{\mu_{\alpha,0} - \mu_{\beta,0}}{\beta_{\alpha} - \beta_{\beta}} = p_0 - \frac{\mathcal{A}_0}{\beta}.$$

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 $p_{\alpha\beta} \approx 14 \cdot 10^5 \text{ kPa}$ ($= 14\,000 \text{ bar}$). 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.

4.4 Simultaneous temperature and pressure dependence

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

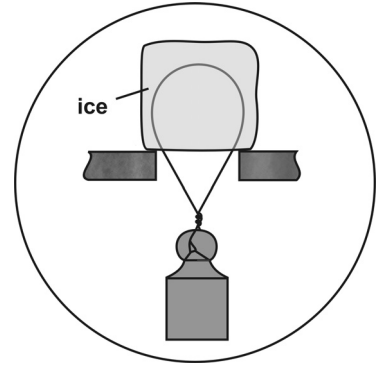
$$\mu = \mu_0 + \alpha \cdot \Delta T + \beta \cdot \Delta p.$$

Correspondingly, the chemical drive takes the form

$$\mathcal{A} = \mathcal{A}_0 + \alpha \cdot \Delta T + \beta \cdot \Delta p.$$

But also the dependence of transformation temperatures from pressure can be determined by these equations. Here is a familiar example representative of many others. Ice melts under high pressure (if it is not too cold). By nature, the potential of ice equals that of ice-water

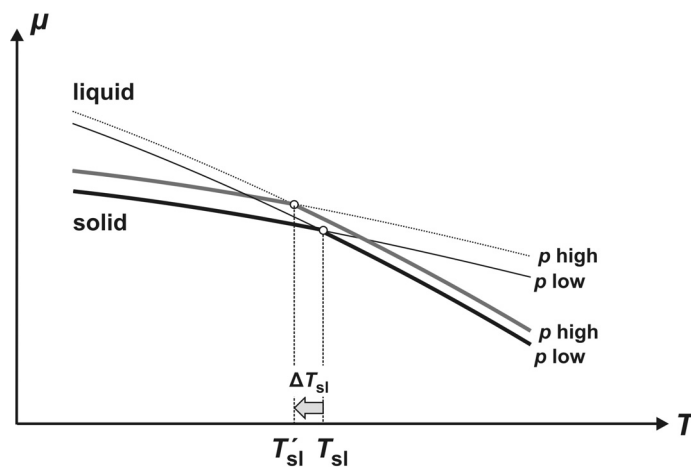
$(\mu(\text{H}_2\text{O}|s) = \mu(\text{H}_2\text{O}|l))$ at 273 K (0°C) and standard pressure. However, because of $\beta(\text{H}_2\text{O}|s) > \beta(\text{H}_2\text{O}|l)$, the value of $\mu(\text{H}_2\text{O}|s)$ exceeds that of $\mu(\text{H}_2\text{O}|l)$ as the pressure increases, and the ice 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: Ice melting under pressure

As mentioned, water is among the few exceptions where β 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 chemical potentials increase because of the negative temperature coefficients α . Because of $0 > \alpha(\text{H}_2\text{O}|s) > \alpha(\text{H}_2\text{O}|l)$, 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 melting 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 have a look at the figure on the left. If the pressure is increased, the chemical potential of the solid phase as well as that of the liquid phase increase; but this increase is much more pronounced for the solid state than for the liquid one (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 the amount ΔT_{sl} .

It is easy to calculate the lowering of temperature in compressed ice which is nothing else than the freezing-point depression of water under pressure. The condition for equilibrium $\mu_s = \mu_l$ takes the following form:

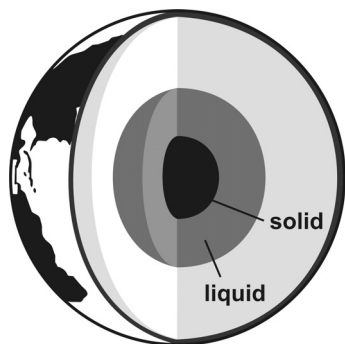
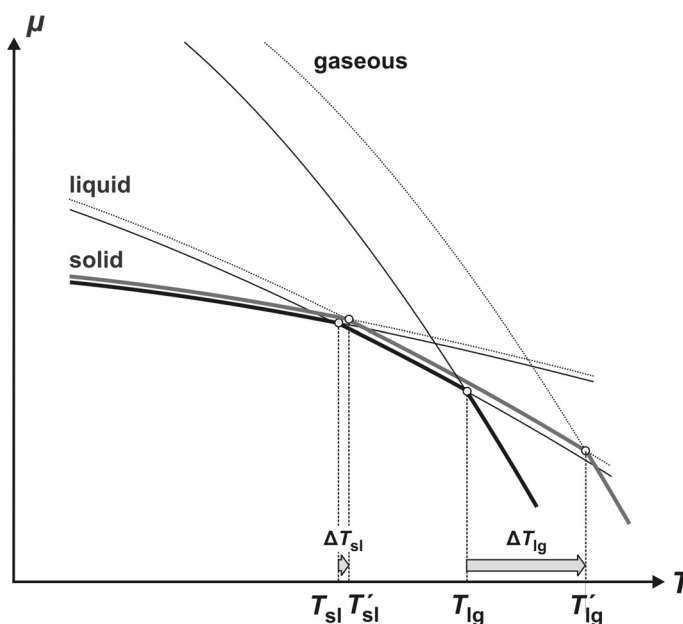
$$\mu_{s,0} + \alpha_s \cdot \Delta T + \beta_s \cdot \Delta p = \mu_{l,0} + \alpha_l \cdot \Delta T + \beta_l \cdot \Delta p.$$

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:

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

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 under pressure (because of $\beta(B|l) > \beta(B|s) > 0$) (see the figure on the right). Correspondingly, the shifts in potentials cause higher pressure to raise the boiling point and a lower pressure to lower the boiling point (because of $\beta(B|g) \gg \beta(B|l) > 0$). This is also valid for water as we have seen in experiments above. Again, the change ΔT can be approximated with the formula derived above. The value of β for evaporation is roughly 10^4 greater than for melting, whereas the α 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 melting 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 melting point ($\Delta T = -2.0$ K), a pressure increase of more than $3 \cdot 10^4$ kPa (300 kbar) is necessary.



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 (standard melting and boiling points of iron are about 1809 K and 3340 K, respectively). This behaviour clearly shows the great influence of temperature and pressure upon the chemical potential.

4.5 Behaviour 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 is greater by several powers of ten than those of solid or liquid substances. At the same time, β 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 β has not only a large value but the same value for all gases at standard conditions. Apparently, the pressure coefficient β 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:

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

R is a fundamental constant and is the same for all substances. It is called the universal gas constant because it was first discovered in a law valid for gases (Section 9.2). The relation above is based upon the phenomenon called *mass action* in chemistry. We will go more deeply into this in the next chapter. (Mentioned in passing: β corresponds here to the molar volume of a so-called ideal gas as we will see in Section 9.1).

Inserting β into the relation above yields the following equation:

$$\mu = \mu_0 + \frac{RT}{p} \cdot \Delta p .$$

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

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

The pressure coefficient β 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

$$\Delta\mu = \frac{RT}{p} \cdot \Delta p .$$

For small (infinitesimal) changes, the relation is

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

If we wish to calculate the change of the chemical potential from the initial value μ_0 to the final value μ for a change of pressure from p_0 to p , we must integrate both sides. The following elementary indefinite integral will serve well for this:

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

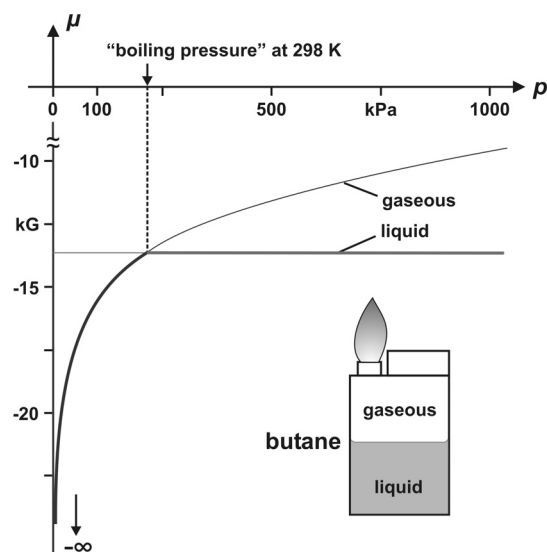
Inserting the limits results in:

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

and respectively,

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

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 4.5.

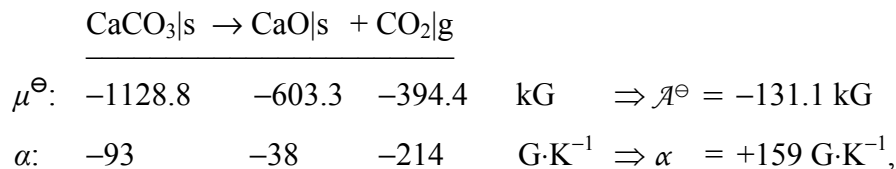


Let us take a closer look at these relations using the example of butane (the fuel in a gas lighter). The $\mu(p)$ curve of gaseous butane shows the expected logarithmic relationship. Furthermore, we can see from the figure that, when compressed at room temperature, butane turns into liquid relatively 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 characterises 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.

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

This leads to the following remarkable conclusions. We can infer, for example, that calcium carbonate CaCO_3 cannot be stable if the CO_2 pressure in the environment falls to zero. In this case, the chemical potential of CO_2 would have the value $-\infty$. The reaction



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 CO_2 , so that the CO_2 pressure must rise in a closed system. The process continues until the CO_2 pressure has reached a value for which the chemical potentials on the left and right sides balance. This CO_2 pressure is called the *decomposition pressure* of calcium carbonate.

The decomposition pressure can be easily calculated. If the chemical potentials satisfy

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

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_2 into account:

$$\mu_{\text{CaCO}_3,0} = \mu_{\text{CaO},0} + \mu_{\text{CO}_2,0} + RT \ln \frac{p}{p_0}.$$

This results in

$$\underbrace{\mu_{\text{CaCO}_3,0} - \mu_{\text{CaO},0} - \mu_{\text{CO}_2,0}}_{\mathcal{A}_0} = RT \ln \frac{p}{p_0}.$$

and

$$\exp \frac{\mathcal{A}_0}{RT} = \exp \left(\ln \frac{p}{p_0} \right)$$

or, respectively,

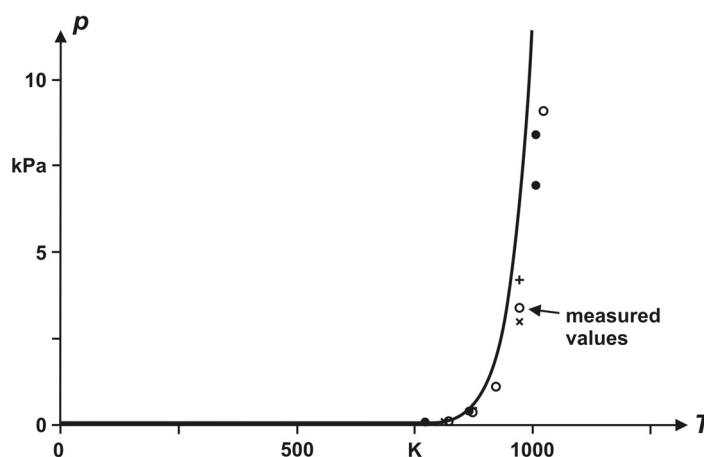
$$p = p_0 \exp \frac{\mathcal{A}_0}{RT}.$$

In order to calculate the decomposition pressure for a temperature different from standard temperature, the μ 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:

$$p = p_0 \exp \frac{\mathcal{A}_0 + \alpha(T - T_0)}{RT}.$$

With the help of corresponding data, the $p(T)$ curve can be determined. This curve gives the decomposition pressure as a function of temperature:

$$p = 100 \text{ kPa} \cdot \exp \frac{-1.311 \cdot 10^5 + 159 \cdot (T / \text{K} - 298)}{8.314 \cdot T / \text{K}}.$$

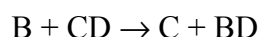


5. Mass Action and Concentration Dependence of the Chemical Potential

Topic: Concentration dependence of μ and the most important applications.

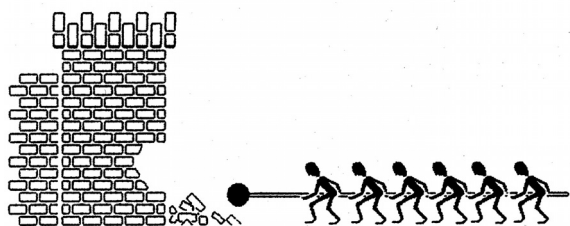
5.1 The concept of mass action

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 a reaction must not necessarily take place fully if a substance B displaces another substance C in a compound,



(even if there is a great excess of B), but that an *equilibrium* forms 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 μ of substances to change 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 μ 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



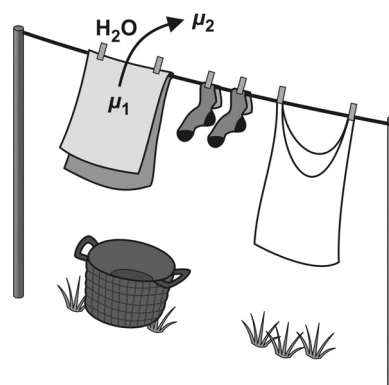
in the space. This means that the more cumulative and concentrated the application, the more intense the effect. In other words, the *mass* of a substance is not decisive for mass action, but its “massing”, its “*density*” in a space: not the *amount*, but the *concentration*. Cato Maximilian GULDBERG and Peter

WAAGE of Norway brought our attention to this in the year 1864.

Thus, the chemical potential of substances and the tendency to change 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 vapour must condense at room conditions:

$$\begin{array}{l} \text{H}_2\text{O|g} \rightarrow \text{H}_2\text{O|l} \\ \mu^\ominus: -228.6 > -237.1 \text{ kG} \\ \Rightarrow \mathcal{A}^\ominus = -8.5 \text{ kG} \end{array}$$

However, if the vapour is diluted by air, the value of its potential decreases below that of liquid water. It can then convert to the gaseous state. It *evaporates*. $\mu(\text{H}_2\text{O|g}) < \mu(\text{H}_2\text{O|l})$ is required for wet laundry, wet dishes and wet streets to dry.



5.2 Concentration dependence of chemical potential

The influence of concentration c upon the tendency μ of a substance to change 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 . $\Delta c = c - c_0$ must be small enough:

$$\mu = \mu_0 + \gamma \cdot \Delta c \quad \text{for } \Delta c \ll c.$$

Mass action is an effect which is covered up by other less important influences which will be gone into later on and which all contribute to the *concentration coefficient* γ : $\gamma = \overset{\times}{\gamma} + \gamma' + \gamma'' + \dots$. The symbol \times above a term will be used here and in the following to denote the quantities dependent upon mass action when these should be distinguished from similar quantities with other origins. Mass action appears most noticeably at small concentrations where the other influences recede more and more until they can be totally neglected, $\overset{\times}{\gamma} \gg \gamma', \gamma'', \dots$. If one wishes to investigate this effect most easily, experiments can be done with strongly diluted solutions $c \ll c^\ominus$ ($= 1 \text{ kmol m}^{-3}$).

The temperature coefficient α and the pressure coefficient β (except 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 entire composition of the *milieu* they are in. In contrast, the concentration coefficient $\overset{\times}{\gamma}$ 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 β of gases:

$$\boxed{\gamma = \overset{\times}{\gamma} \equiv \frac{RT}{c}} \quad \text{for } c \ll c^\ominus \quad \text{where } R = 8.314 \text{ G K}^{-1}.$$

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.

If we insert the second equation into the first one, we obtain the following relation

$$\mu = \mu_0 + \frac{RT}{c} \cdot \Delta c \quad \text{for } \Delta c \ll c \ll c^\ominus.$$

Analogous to the treatment of the pressure coefficient β of gases, a logarithmic relation between μ and c results:

$$\mu = \mu_0 + RT \ln \frac{c}{c_0} \quad \text{for } c, c_0 \ll c^\ominus \quad (\text{mass action equation 1}).$$

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 $c \rightarrow 0$. For this reason, we have added the requirement for a small concentration ($c, c_0 \ll c^\ominus$) 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:

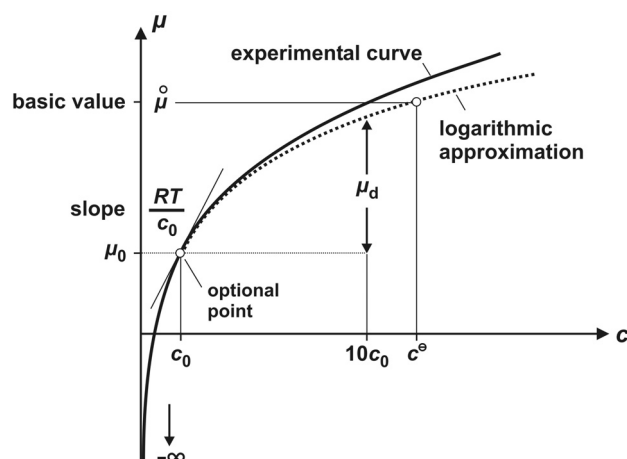
$$\mu \approx \mu_0 + RT \ln \frac{c}{c_0} \quad \text{for } c < \begin{cases} 100 \text{ mol m}^{-3} & \text{for neutral substances,} \\ 1 \text{ mol m}^{-3} & \text{for ions.} \end{cases}$$

However, it is precisely for *standard concentration* $c^\ominus = 1000 \text{ mol m}^{-3} = 1 \text{ mol L}^{-1}$ (the usual reference value), where 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:

$$\mu = \overset{\circ}{\mu} + RT \ln \frac{c}{c^\ominus} = \overset{\circ}{\mu} + RT \ln c_r \quad \text{for } c \ll c^\ominus \quad (\text{mass action equation 1'}).$$

Here, c_r is the *relative concentration*. The $\overset{\circ}{\mu}$, intended as the *basic value* (at fixed concentration c^\ominus) 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 μ is no longer real, but fictive. Note that the basic value μ of a dissolved substance B depends upon pressure p and temperature T , $\overset{\circ}{\mu}_B(p, T)$. This distinguishes it from the *standard value* $\mu_B^\ominus \equiv \overset{\circ}{\mu}_B(p^\ominus, T^\ominus)$ already known to us. The term $RT \ln c_r = \overset{\times}{\mu}$ 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 give these equations a name in order to refer to them more easily. In fact, we will give all relations of this type (there are several more of them) the same name, „*mass action equations*.“ As expected, the tendency of a substance to change 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:



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 μ° of the chemical potential of the dissolved substance coincides with the logarithmic approximation and not with the measured function!

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

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

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

$$\begin{aligned} \mu &= \mu_0 + RT \ln \frac{10c_0}{c_0} \\ \mu_d &= RT \ln 10 = 8.314 \text{ G K}^{-1} \cdot 298 \text{ K} \cdot \ln 10 = 5.708 \text{ kG}. \end{aligned}$$

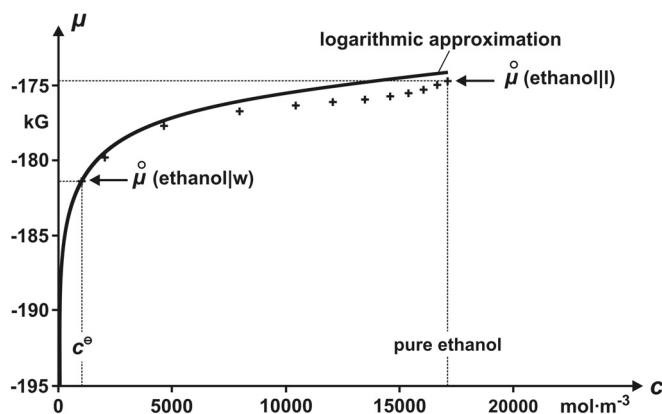
It is helpful to remember the value $\mu_d \approx 5.7 \text{ kG}$ (approximately $\approx 6 \text{ kG}$) in order to quickly estimate the influence of a change of concentration of a substance upon the level of its potential or vice versa.

In summary, when the concentration c of a substance increases to 10 times its initial value at room temperature, its chemical potential μ 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).

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.

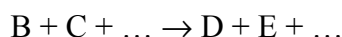
The basic value of the potential of dissolved alcohol (in water) has been added to the graph. This value lies only about 0.1 kG above the actual μ value at standard concentration. The basic value of pure alcohol has also been included.



Using the newly extracted relations, we will again take a closer look at evaporation. When the vapour is diluted by air, say, by a factor of 100 (by two orders of magnitude), its potential goes down by around $2 \cdot 5.7 \text{ kJ} = 11.4 \text{ kJ}$ to about -240.0 kJ . At that point, $\mu(\text{H}_2\text{O}|g)$ actually lies below the value for liquid water and evaporation takes place. At a concentration of $\frac{1}{30}$, the air is already so moist that it cannot absorb any more water. It is said to be saturated. A concentration of $\frac{1}{30}$ means about 1.5 orders of magnitude below the concentration of pure vapour. Therefore, the water vapour potential lies about $1.5 \cdot 5.7 \text{ kJ} = 8.6 \text{ kJ}$ below the value for pure vapour. At -237.2 kJ , 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.

5.3 Concentration dependence of chemical drive

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



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

$$\mathcal{A} = [\mu_B + \mu_C + \dots] - [\mu_D + \mu_E + \dots].$$

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

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

The terms of the equation can be sorted a bit

$$\mathcal{A} = \left[\overset{\circ}{\mu}_B + \overset{\circ}{\mu}_C + \dots - \overset{\circ}{\mu}_D - \overset{\circ}{\mu}_E - \dots \right] + RT \left[\ln c_r(B) + \ln c_r(C) + \dots - \ln c_r(D) - \ln c_r(E) - \dots \right]$$

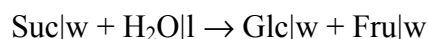
and the final result is

$$\boxed{\mathcal{A} = \overset{\circ}{\mathcal{A}} + RT \ln \frac{c_r(B) \cdot c_r(C) \cdot \dots}{c_r(D) \cdot c_r(E) \cdot \dots}}.$$

We have $\overset{\circ}{\mathcal{A}} = \overset{\circ}{\mu}(B) + \overset{\circ}{\mu}(C) + \dots - \overset{\circ}{\mu}(D) - \overset{\circ}{\mu}(E) - \dots$ for the basic term $\overset{\circ}{\mathcal{A}}$. It expresses the drive when all reaction partners have the standard concentration of 1000 mol m^{-3} .

$RT \ln \frac{c_r(B) \cdot c_r(C) \cdot \dots}{c_r(D) \cdot c_r(E) \cdot \dots} = \overset{\times}{\mathcal{A}}$ in turn, represents the mass action term.

We will explain the influence of concentration shifts upon the drive using the example of decomposing cane sugar



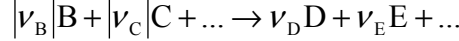
Suc is the abbreviation for cane sugar (sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$), Glc and Fru represent the isomeric monosaccharides grape sugar (glucose, $\text{C}_6\text{H}_{12}\text{O}_6$) and fruit sugar (fructose, $\text{C}_6\text{H}_{12}\text{O}_6$). From the chemical potentials, we obtain the following for the drive \mathcal{A} :

$$\begin{aligned}
\mathcal{A} &= \mu_{\text{Suc}} + \mu_{\text{H}_2\text{O}} - \mu_{\text{Glc}} - \mu_{\text{Fru}} \\
&= \overset{\circ}{\mu}_{\text{Suc}} + RT \ln \left(\frac{c_{\text{Suc}}}{c^{\ominus}} \right) + \overset{\circ}{\mu}_{\text{H}_2\text{O}} - \overset{\circ}{\mu}_{\text{Glc}} - RT \ln \left(\frac{c_{\text{Glc}}}{c^{\ominus}} \right) - \overset{\circ}{\mu}_{\text{Fru}} - RT \ln \left(\frac{c_{\text{Fru}}}{c^{\ominus}} \right) \\
&= \underbrace{\overset{\circ}{\mu}_{\text{Suc}} + \overset{\circ}{\mu}_{\text{H}_2\text{O}} - \overset{\circ}{\mu}_{\text{Glc}} - \overset{\circ}{\mu}_{\text{Fru}}}_{\overset{\circ}{\mathcal{A}}} + RT \ln \frac{c_{\text{Suc}} \cdot c^{\ominus}}{c_{\text{Glc}} \cdot c_{\text{Fru}}}.
\end{aligned}$$

In this mathematical description, we cannot apply the mass action equation to water because its concentration lies far outside the equation's range of validity, $c_{\text{H}_2\text{O}} \approx 50000 \text{ mol m}^{-3}$. 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 possible to replace the actual $\mu_{\text{H}_2\text{O}}$ value with that of pure water. We will indicate the potential for the pure solvent (in this case water) similarly to the basic potentials of dissolved substances $\overset{\circ}{\mu}$: $\overset{\circ}{\mu}_{\text{H}_2\text{O}}$. In general, solvents of dilute solutions can be approximated well by pure substances.

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_2O) 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



we correspondingly obtain

$$\mathcal{A} = [|\nu_{\text{B}}|\mu_{\text{B}} + |\nu_{\text{C}}|\mu_{\text{C}} + \dots] - [\nu_{\text{D}}\mu_{\text{D}} + \nu_{\text{E}}\mu_{\text{E}} + \dots].$$

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

$$\begin{aligned}
\mathcal{A} &= \left[|\nu_{\text{B}}|\overset{\circ}{\mu}_{\text{B}} + |\nu_{\text{B}}|RT \ln c_{\text{r}}(\text{B}) + |\nu_{\text{C}}|\overset{\circ}{\mu}_{\text{C}} + |\nu_{\text{C}}|RT \ln c_{\text{r}}(\text{C}) + \dots \right] \\
&\quad - \left[\nu_{\text{D}}\overset{\circ}{\mu}_{\text{D}} + \nu_{\text{D}}RT \ln c_{\text{r}}(\text{D}) + \nu_{\text{E}}\overset{\circ}{\mu}_{\text{E}} + \nu_{\text{E}}RT \ln c_{\text{r}}(\text{E}) + \dots \right].
\end{aligned}$$

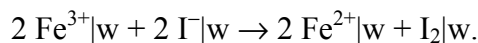
We can rearrange

$$\begin{aligned}
\mathcal{A} &= \left[|\nu_{\text{B}}|\overset{\circ}{\mu}_{\text{B}} + |\nu_{\text{C}}|\overset{\circ}{\mu}_{\text{C}} + \dots - \nu_{\text{D}}\overset{\circ}{\mu}_{\text{D}} - \nu_{\text{E}}\overset{\circ}{\mu}_{\text{E}} - \dots \right] \\
&\quad + RT \left[|\nu_{\text{B}}|\ln c_{\text{r}}(\text{B}) + |\nu_{\text{C}}|\ln c_{\text{r}}(\text{C}) + \dots - \nu_{\text{D}}\ln c_{\text{r}}(\text{D}) - \nu_{\text{E}}\ln c_{\text{r}}(\text{E}) - \dots \right]
\end{aligned}$$

and obtain

$$\boxed{\mathcal{A} = \overset{\circ}{\mathcal{A}} + RT \ln \frac{c_{\text{r}}(\text{B})^{|\nu_{\text{B}}|} \cdot c_{\text{r}}(\text{C})^{|\nu_{\text{C}}|} \cdot \dots}{c_{\text{r}}(\text{D})^{\nu_{\text{D}}} \cdot c_{\text{r}}(\text{E})^{\nu_{\text{E}}} \cdot \dots}}.$$

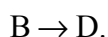
Let us now take another look at a concrete example. For this, we choose the reaction of Fe^{3+} ions with I^- ions:



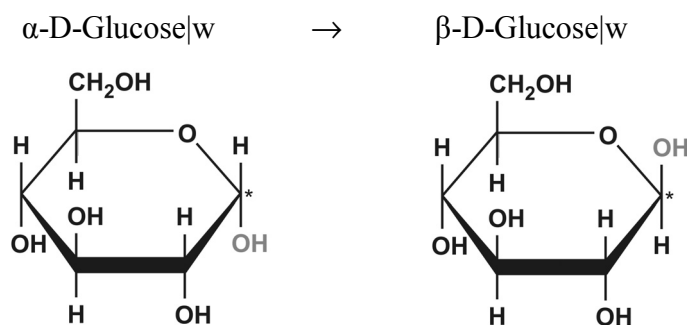
Therefore, the conversion numbers are: $\nu_{\text{Fe}^{3+}} = -2$, $\nu_{\text{I}^-} = -2$, $\nu_{\text{Fe}^{2+}} = +2$ und $\nu_{\text{I}_2} = +1$. Insertion into the formula above results in:

$$\mathcal{A} = \overset{\circ}{\mathcal{A}} + RT \ln \frac{c_r(\text{Fe}^{3+})^2 \cdot c_r(\text{I}^-)^2}{c_r(\text{Fe}^{2+})^2 \cdot c_r(\text{I}_2)}.$$

However, the concentrations do not remain constant during a reaction. They change in the process 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 conversion of a substance B into a substance D:



An example would be the transformation of α -D-glucose into the isomeric β -D-glucose in aqueous solution. These two stereoisomers of glucose $\text{C}_6\text{H}_{12}\text{O}_6$, differ only in the placement of the OH group relative to the chiral center (characterised by *) formed by the ring closure.



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

The two substances are optically active: pure α -D-glucose shows an angle of rotation of $+112^\circ$, pure β -D-glucose, however, one of $+18,7^\circ$. 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 $+112^\circ$ to a value of $+53^\circ$.

In Section 1.6, the extent of reaction ξ was introduced as a measure of the progress of a reaction. It was defined by

$$\xi = \frac{\Delta n_i}{\nu_i} = \frac{n_i(t) - n_i(t_0)}{\nu_i}.$$

The extent of reaction can now be easily converted to the time dependent change of concentration, and respectively, to the concentration at time t :

$$\Delta c_i = c_i(t) - c_i(t_0) = \frac{n_i(t) - n_i(t_0)}{V} = \frac{\nu_i \xi}{V}$$

or rather

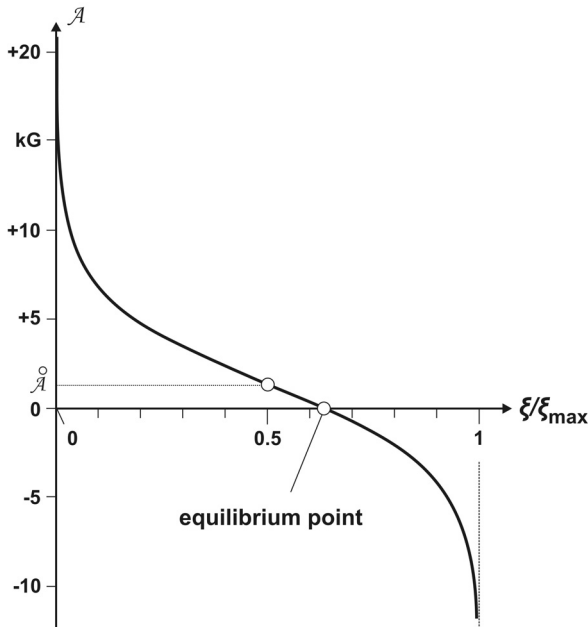
$$c_i(t) = c_i(t_0) + \frac{\nu_i \xi}{V}.$$

The drive of a reaction changes along with the concentrations. If one assumes a concentration of c_0 of the initial substance as well as an absence of the product at the beginning of the reaction at $t_0 = 0$, the following relation for the dependence of the drive upon the extent of reaction is obtained:

$$\mathcal{A} = \overset{\circ}{\mathcal{A}} + RT \ln \frac{(c_0 - \xi/V)/c^\ominus}{(\xi/V)/c^\ominus} = \overset{\circ}{\mathcal{A}} + RT \ln \frac{c_0 - \xi/V}{\xi/V}.$$

For the sake of simplicity, we will now relate the extent of reaction ξ to the maximum possible value ξ_{\max} ($= c_0 \cdot V$, because, in this case, the entire amount of B should have converted to D) resulting in:

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



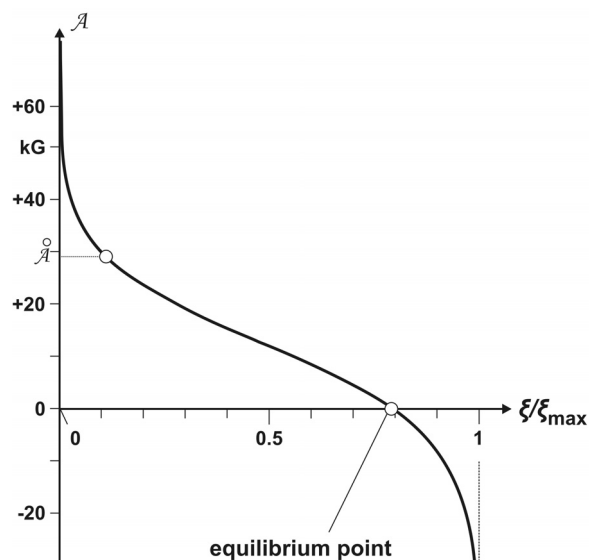
With a standard value of $\overset{\circ}{\mathcal{A}} = 1.25$ kG for the conversion of α -D- into β -D-glucose at room temperature, a characteristic S shaped curve is obtained for the dependence of drive upon extent of reaction ξ . At the beginning of the reaction, meaning for $\xi = 0$, \mathcal{A} equals $+\infty$. \mathcal{A} decreases during the reaction and, at an $\overset{\circ}{\mathcal{A}}$ dependent ξ value, finally reaches a value of zero. When all the initial substance has been used up, meaning at $\xi = \xi_{\max}$, \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:

$$\mathcal{A} = \overset{\circ}{\mathcal{A}} + RT \ln \frac{[(c_0 - 2 \cdot \xi/V)/c^\ominus]^2 \cdot [(c_0 - 2 \cdot \xi/V)/c^\ominus]^2}{[(2 \cdot \xi/V)/c^\ominus]^2 \cdot (\xi/V)/c^\ominus} = \overset{\circ}{\mathcal{A}} + RT \ln \frac{(c_0 - 2 \cdot \xi/V)^4}{4 \cdot (\xi/V)^3 \cdot c^\ominus}$$

For better overview, it would be advisable in this case to create a table. Under the balanced equation for the reaction, the table lists for each substance involved in the first row the standard value of its chemical potential for calculating the drive of the reaction under standard conditions. The initial concentrations of the substances follow in the next row. Finally, the concentrations at an arbitrary time t are listed which can be calculated by using the stoichiometry of the reaction. x is defined as the extent of reaction referred to the volume, i.e. $x = \xi/V$.

	$2 \text{Fe}^{3+} + 2 \text{I}^-$		$\rightarrow 2 \text{Fe}^{2+} + \text{I}_2$		
μ^\ominus :	$2 \cdot (-4.7)$	$2 \cdot (-51.6)$	$2 \cdot (-78.9)$	16.4 kG	$\Rightarrow \overset{\circ}{\mathcal{A}} = +28.8$ kG
$c_{i,0}$:	0.001	0.001	0	0 kmol m ⁻³	
c_i :	$c_0 - 2x$	$c_0 - 2x$	$2x$	x	



Again, we obtain the typical S shaped curve.

Let us remind ourselves about the criteria for a reaction which we were introduced to in Chapter 3: A reaction takes place voluntarily 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.

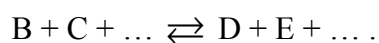
Here are some important consequences for the reaction process:

- Every homogeneous reaction begins voluntarily.
- At a certain extent of reaction, it stops in equilibrium with the environment.
- Equilibrium can be reached from both sides, meaning from the side with the initial substances as well as from the side with the reaction products.

In equilibrium, neither the forward reaction nor the backward reaction take place voluntarily. Macroscopically speaking, there is no more conversion 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 conversions in the two directions compensate for each other. In this case, one speaks of a *dynamic equilibrium*.

5.4 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 homogenous solution



Equilibrium rules when there is no longer any potential drop and the drive \mathcal{A} disappears. Therefore:

$$\mathcal{A} = \overset{\circ}{\mathcal{A}} + RT \ln \frac{c_r(B) \cdot c_r(C) \cdot \dots}{c_r(D) \cdot c_r(E) \cdot \dots} = 0.$$

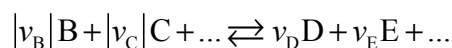
When we divide by RT and take the antilogarithm, we obtain

$$\boxed{\overset{\circ}{K}_c = \left(\frac{c_r(D) \cdot c_r(E) \cdot \dots}{c_r(B) \cdot c_r(C) \cdot \dots} \right)_{\text{eq.}}} \quad \text{with} \quad \boxed{\overset{\circ}{K}_c := \exp \frac{\overset{\circ}{\mathcal{A}}}{RT}}.$$

This equation characterizes the relationship between concentrations in equilibrium which has been referred to by the index eq. and shows a possible form of the mass action law for the

reaction. The quantity $\overset{\circ}{K}_c$ 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 $\overset{\circ}{K}_c$ 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 $\overset{\circ}{K}$ is to be formed from $\overset{\circ}{A}$ (and not from $A!$).

For the more general reaction



we obtain entirely appropriately

$$\overset{\circ}{K}_c = \left(\frac{c_r(D)^{v_D} \cdot c_r(E)^{v_E} \cdot \dots}{c_r(B)^{|v_B|} \cdot c_r(C)^{|v_C|} \cdot \dots} \right)_{\text{eq.}}$$

Commonly, the relative concentrations c_r are replaced by c/c^\ominus and the fixed standard concentration c^\ominus is combined with the equilibrium number $\overset{\circ}{K}_c$ to form the new equilibrium constant $\overset{\circ}{K}_c$ (κ , „dimension factor“):

$$\boxed{\overset{\circ}{K}_c = \kappa \overset{\circ}{K}_c} \quad , \quad \text{where} \quad \kappa = (c^\ominus)^{v_c} \quad \text{with} \quad v_c = v_B + v_C + \dots + v_D + v_E + \dots$$

v_c is the sum of all conversion numbers which, in our example, are -1 for the initial substances B, C, ... and $+1$ for the products D, E, As stated above, $\overset{\circ}{K}_c$ is always a number while the constant $\overset{\circ}{K}_c$ has the unit $(\text{mol m}^{-3})^{v_c}$. Only when v_c happens to be 0, are $\overset{\circ}{K}_c$ and $\overset{\circ}{K}_c$ identical. $\overset{\circ}{K}_c$ is the more convenient quantity for formulating the mass action law,

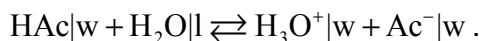
$$\overset{\circ}{K}_c = \left(\frac{c_D \cdot c_E \cdot \dots}{c_B \cdot c_C \cdot \dots} \right)_{\text{eq.}}$$

while, for general considerations, $\overset{\circ}{K}_c$ is preferred since its dimension is the same for all reactions.

Here is an example of what has been said. With the help of a table, we will determine the *acidity constant* of acetic acid (CH_3COOH), abbreviated to HAc, in an aqueous solution, i.e., the equilibrium constant for the *dissociation*



or the equilibrium constant for the *proton exchange* in BRØNSTED's sense (this will be discussed more detailed in the next chapter):



The formulas are two different versions of the same process. In the first case, the mass action law is written as

$$\overset{\circ}{K}_{c,1} = \frac{c_r(\text{H}^+) \cdot c_r(\text{Ac}^-)}{c_r(\text{HAc})}$$

where

$$\begin{aligned}\overset{\circ}{\mathcal{K}}_{c,1} &= \exp \frac{\overset{\circ}{\mathcal{A}}}{RT} = \exp \frac{\overset{\circ}{\mu}(\text{HAc}) - \overset{\circ}{\mu}(\text{H}^+) - \overset{\circ}{\mu}(\text{Ac}^-)}{RT} \\ &= \exp \frac{(-396.46 - 0 + 369.31) \cdot 10^3 \text{ G}}{8.314 \text{ G K}^{-1} \cdot 298 \text{ K}} = 1.74 \cdot 10^{-5}\end{aligned}$$

and in the usual way as

$$\overset{\circ}{K}_{c,1} = \frac{c(\text{H}^+) \cdot c(\text{Ac}^-)}{c(\text{HAc})}$$

where

$$\overset{\circ}{K}_{c,1} = \overset{\circ}{\mathcal{K}}_{c,1} \cdot c^\ominus = 1.74 \cdot 10^{-5} \text{ kmol m}^{-3}$$

with $\nu_c = -1 + 1 + 1 = +1$ and therefore the dimension factor $\kappa = c^\ominus = 1 \text{ kmol m}^{-3}$.

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

$$\overset{\circ}{\mathcal{K}}_{c,2} = \frac{c_r(\text{H}_3\text{O}^+) \cdot c_r(\text{Ac}^-)}{c_r(\text{HAc})}$$

where

$$\begin{aligned}\overset{\circ}{\mathcal{K}}_{c,2} &= \exp \frac{\overset{\circ}{\mu}(\text{HAc}) + \overset{\circ}{\mu}(\text{H}_2\text{O}) - \overset{\circ}{\mu}(\text{H}_3\text{O}^+) - \overset{\circ}{\mu}(\text{Ac}^-)}{RT} \\ &= \exp \frac{(-396.46 - 237.14 + 237.14 + 369.31) \cdot 10^3 \text{ G}}{8.314 \text{ G} \cdot \text{K}^{-1} \cdot 298 \text{ K}} = 1.74 \cdot 10^{-5}\end{aligned}$$

and written in the usual way,

$$\overset{\circ}{K}_{c,2} = \frac{c(\text{H}_3\text{O}^+) \cdot c(\text{Ac}^-)}{c(\text{HAc})}$$

where

$$\overset{\circ}{K}_{c,2} = \overset{\circ}{\mathcal{K}}_{c,2} \cdot c^\ominus = 1.74 \cdot 10^{-5} \text{ kmol m}^{-3}.$$

Also in this case the dimension factor results in $\kappa = c^\ominus = 1 \text{ kmol m}^{-3}$, because the solvent water is treated as pure substance and therefore does not appear in the sum ν_c of conversion numbers.

The equilibrium constants $\overset{\circ}{\mathcal{K}}_{c,1}$ and $\overset{\circ}{\mathcal{K}}_{c,2}$ (or $\overset{\circ}{K}_{c,1}$ and $\overset{\circ}{K}_{c,2}$) have the same value. The same acidity constant $\overset{\circ}{K}_s = \overset{\circ}{\mathcal{K}}_{c,1} = \overset{\circ}{\mathcal{K}}_{c,2}$ is obtained independent of whether the first or second reaction equation is applied, meaning whether the process is considered as dissociation or proton exchange.

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 ionic or molecular interactions.

The magnitude of the equilibrium number determined according to

$$\overset{\circ}{\mathcal{A}} = RT \ln \overset{\circ}{\mathcal{K}}$$

is a good qualitative indication for how a reaction proceeds. The more strongly positive $\overset{\circ}{\mathcal{A}}$ is, the greater $\overset{\circ}{\mathcal{K}}$ ($\overset{\circ}{\mathcal{K}} \gg 1$) is. In this case, the end products dominate in the equilibrium composition. Because of the logarithmic relation, even small changes to $\overset{\circ}{\mathcal{A}}$ lead to noticeable shifts in the equilibrium point. On the other hand, if $\overset{\circ}{\mathcal{A}}$ is strongly negative, $\overset{\circ}{\mathcal{K}}$ approaches zero ($\overset{\circ}{\mathcal{K}} \ll 1$) and the initial substances dominate in the composition of the equilibrium. At the same time, this also means that, even for negative $\overset{\circ}{\mathcal{A}}$, a small amount of the initial substance is still converted to the end products because $\overset{\circ}{\mathcal{K}}$ has a small yet finite value. When $\overset{\circ}{\mathcal{A}} \approx 0$ and therefore $\overset{\circ}{\mathcal{K}} \approx 1$, the initial substances and end products are present in comparable amounts in equilibrium. (Keep in mind, however, that in all three cases discussed, $\mathcal{A} = 0$! 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 voluntary conversion of given amounts of initial substances can be quantitatively determined. If, for example, pure α -D-glucose at the concentration 0.1 mol L^{-1} 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 conversion of α -D-glucose into β -D-glucose (remember the discussion further above). If we indicate the concentration of β -D-glucose in equilibrium by x , we obtain

$$\overset{\circ}{K}_c = \exp \frac{\overset{\circ}{\mathcal{A}}}{RT} = \left(\frac{x}{c_0 - x} \right)_{\text{eq.}}$$

The dimension factor κ equals 1 because of $v_c = 0$. The equilibrium constant at room temperature can be calculated by use of the standard value $\mathcal{A}^\ominus = 1.25 \text{ kJ}$ (see Section 5.3):

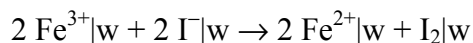
$$\overset{\circ}{K}_c = \exp \frac{1.25 \cdot 10^3 \text{ J}}{8.314 \text{ J K}^{-1} \cdot 298 \text{ K}} \left(\frac{1.25 \cdot 10^3 \text{ J}}{8.314 \text{ J K}^{-1} \cdot 298 \text{ K}} \right) = 1.66 \text{ kmol m}^{-3}$$

From now on, we will not use 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. Solving for x results in:

$$x = \frac{\overset{\circ}{K}_c \cdot c_0}{\overset{\circ}{K}_c + 1} = \frac{1.66 \cdot 0.1 \text{ mol L}^{-1}}{1.66 + 1} = 0.0624 \text{ mol L}^{-1}.$$

According to this, the state of equilibrium shows that 37.6 % of all dissolved molecules are α -D-glucose molecules and 62.4 % are β -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



characterised by the table above, we obtain

$$\overset{\circ}{K}_c = \kappa \cdot \exp \frac{\overset{\circ}{A}}{RT} = \left(\frac{4x^3}{(c_0 - 2x)^4} \right)_{\text{eq.}}$$

with the dimension factor $\kappa = (c^\ominus)^{-1} = 1 \text{ kmol}^{-1} \text{ m}^3$ (because of $\nu_c = -2 - 2 + 2 + 1 = -1$). Because the value of $\overset{\circ}{A}$ is positive and relatively high ($\overset{\circ}{A} = +29 \text{ kG}$), we have $\overset{\circ}{K}_c \gg 1$, i.e. we can expect that the end products dominate in the equilibrium composition. For more detailed data we have to solve for x the equation above. Because a higher degree polynomial is involved a numerical technique using an appropriate mathematical software or a graphical approach are advisable. An equilibrium point of $\xi/\xi_{\text{max}} \approx 0.79$ can be obtained from the figure in Section 5.3. The concentrations of the substances in the equilibrium mixture are therefore $c(\text{Fe}^{3+}) \approx 0.21 \text{ mol m}^{-3}$ and $c(\text{I}^-) \approx 0.21 \text{ mol m}^{-3}$ 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.

The equation above can be reversely used to experimentally determine the basic drive $\overset{\circ}{A}$ of a reaction. In order to do this, it is enough to first calculate the constant $\overset{\circ}{K}$ and then to derive $\overset{\circ}{A}$ 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. As long as the added amount is small the position of equilibrium does not change and we can directly use the equilibrium values obtained in the equation above. When the basic drive is known the drive for any other concentrations can be calculated provided that the c values are small ($c \ll c^\ominus$).

5.5 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^\ominus 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 on 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:

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

 für $p, p_0 \ll 10 \text{ p}^\ominus$ (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):

$$p = p_B + p_C + p_D + \dots \quad (\text{as well as } c = c_B + c_C + c_D + \dots).$$

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 go once more into the problem of the starting or reference values when calculating potentials. Normally, the *standard pressure* $p^\ominus = 101 \text{ kPa}$ is chosen as the initial value for pressure although at this pressure, the chemical potential μ already deviates somewhat from the value the mass action equation yields. In order to have the results remain correct at low pressures, the true μ value 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 valid for standard pressure can be found in tables and then used to calculate the potential. This special value is also called the *basic value* μ° , which should be indicated by the index \circ placed above the symbol:

$$\mu = \mu^\circ + RT \ln \frac{p}{p^\ominus} = \mu^\circ + RT \ln p_r \quad \text{for } p \rightarrow 0 \quad (\text{mass action equation 2'}),$$

where p_r is the relative pressure. In contrast to this, all the μ 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 $c \rightarrow 0$. 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:

$$\mu = \mu_0 + RT \ln \frac{x}{x_0} \quad \begin{array}{l} \text{for } x, x_0 \rightarrow 0 \quad (\text{mass action equation 3}), \\ \text{for } x, x_0 \rightarrow 1 \quad (\text{mass action equation 4}). \end{array}$$

This equation has a remarkable characteristic. It is valid not only in the case of x und x_0 being small, but also for the case of x und x_0 lying near 1, meaning when a mixture is made up almost entirely of the substance being considered. The substance which makes up the major proportion of a mixture is usually called the *solvent* S. It makes no difference whether the

solvent is gaseous, liquid or solid. The effect upon S described by the formula for x , $x_0 \approx 1$ is *indirectly* caused by the mass action of the dissolved substances.

This leads to an important consequence if the standard value $x^\ominus = 1$ is chosen as the initial value. In this case, the initial state of the substance is in its pure form. The corresponding value of the chemical potential is that of the pure substance and is again called the basic value. Moreover, it is real:

$$\boxed{\mu = \overset{\circ}{\mu} + RT \ln x} \quad \text{for } x \rightarrow 1 \quad (\text{mass action equation 4'}).$$

We will deal more fully with this form of the mass action equation in Section 11.2.

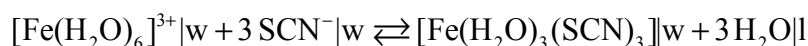
5.6 Applications of the mass action law

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

$$\overset{\circ}{K}_c = \frac{c_r(D)^{v_D} \cdot c_r(E)^{v_E} \cdot \dots}{c_r(B)^{|v_B|} \cdot c_r(C)^{|v_C|} \cdot \dots}$$

remains fulfilled.

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

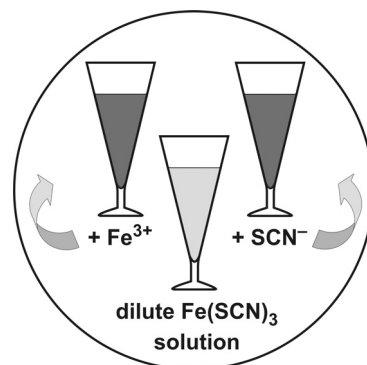


If the mass action law is applied, it results in

$$\overset{\circ}{K}_c = \frac{c_r([\text{Fe}(\text{H}_2\text{O})_3(\text{SCN})_3])}{c_r([\text{Fe}(\text{H}_2\text{O})_6]^{3+}) \cdot c_r(\text{SCN}^-)^3}.$$

Water as solvent is treated as pure substance; therefore, it does not appear in the formula. Dilution with water lowers the concentration of the complex, but also the concentrations of the free ions. Therefore, the denominator will decrease much faster than the numerator. Because the quotient is a constant, the so-called equilibrium number $\overset{\circ}{K}_c$, the numerator has to also decrease: The equilibrium is displaced towards the reactant side, i.e. some iron thiocyanate complex has to decompose again into iron hexaquo complex cations and thiocyanate anions. The pale orange colour of the resulting solution is caused by the iron hexaquo complex.

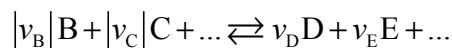
If, for example, Fe^{3+} or SCN^- solutions are added to the pale orange dilute iron thiocyanate solution, it will turn red both times.



Experiment: Iron(III) thiocyanate equilibrium

The addition of excess iron(III) ions results in an increase of the denominator. More iron thiocyanate complex has to be formed in order to use up this extra reactant (along with the other reactant thiocyanate) and re-establish the equilibrium. Similarly, the addition of excess thiocyanate also causes a shift of the equilibrium to the product side.

Homogenous gas equilibria. To obtain homogeneous gas equilibria



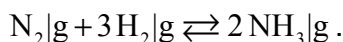
we can derive the equilibrium number analogously to the homogeneous solution equilibria, but instead of the mass action equation 1', we refer to the mass action equation 2':

$$\overset{\circ}{K}_p = \frac{p_r(D)^{v_D} \cdot p_r(E)^{v_E} \cdot \dots}{p_r(B)^{|v_B|} \cdot p_r(C)^{|v_C|} \cdot \dots}.$$

To convert into the conventional equilibrium constant $\overset{\circ}{K}_p$ a dimension factor must again be taken into account:

$$\overset{\circ}{K}_p = \kappa \overset{\circ}{K}_p, \quad \text{where} \quad \kappa = (p^\ominus)^{v_p} \quad \text{with} \quad v_p = v_B + v_C + \dots + v_D + v_E + \dots$$

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



The standard value of the chemical drive is around +33 kJ. The corresponding equilibrium number at room temperature is

$$\overset{\circ}{K}_p = \frac{p_r(NH_3)^2}{p_r(N_2) \cdot p_r(H_2)^3} = \exp \frac{\overset{\circ}{A}}{RT} = \exp \frac{33 \cdot 10^3 \text{ J}}{8.314 \text{ J K}^{-1} \cdot 298 \text{ K}} = 6.1 \cdot 10^5.$$

The conventional equilibrium constant is

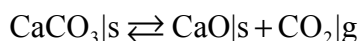
$$\overset{\circ}{K}_p = \frac{p(NH_3)^2}{p(N_2) \cdot p(H_2)^3} = \overset{\circ}{K}_p \cdot (100 \text{ kPa})^{-2} = 61 \text{ kPa}^{-2}$$

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 ($c^\ominus = 1000 \text{ mol m}^{-3}$, $p^\ominus = 100 \text{ kPa} \dots$), the same substance yields different basic values $\overset{\circ}{\mu}_c$, $\overset{\circ}{\mu}_p \dots$ and therefore different equilibrium numbers $\overset{\circ}{K}_c$, $\overset{\circ}{K}_p \dots$ for the same reaction. This is indicated by the varying indexes.

Heterogeneous equilibria. As yet we have only considered homogeneous equilibria, i.e. equilibria in which all substances involved are in the same phase. Next we will discuss heterogeneous equilibria in which the substances are in different phases. First heterogeneous reactions between a gas and a solid reactant exemplified by decomposition equilibria are selected.

Decomposition equilibria. In the case of the decomposition reaction of calcium carbonate described by



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 $RT \ln c_r(B)$ is omitted, i.e., $\mu(B) = \overset{\circ}{\mu}(B)$; 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 5.3).

The equilibrium number $\overset{\circ}{K}_p$ for the decomposition of carbonate is therefore equal

$$\overset{\circ}{K}_p = p_r(\text{CO}_2)$$

with

$$\overset{\circ}{K}_p = \exp \frac{\overset{\circ}{A}}{RT} = \exp \frac{\overset{\circ}{\mu}(\text{CaCO}_3) - \overset{\circ}{\mu}(\text{CaO}) - \overset{\circ}{\mu}(\text{CO}_2)}{RT}.$$

The conventional equilibrium constant results in

$$\overset{\circ}{K}_p = p(\text{CO}_2).$$

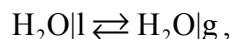
The equilibrium constant is identical with the decomposition pressure, i.e. the pressure of carbon dioxide at equilibrium, and hence not dependent on the amounts of the solid substances. Even though the pure solid substances do not appear in the mass action law they have to be present for establishing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

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

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

The approach can not only be applied on heterogeneous chemical reactions but also on transitions with a change of state of aggregation.

Phase transitions. The evaporation of water represents an example for a phase transition with participation of a gas. The equilibrium number $\overset{\circ}{K}_p$ for the equilibrium between liquid water and water vapour in a closed system,



results in

$$\overset{\circ}{K}_p = p_r(\text{H}_2\text{O}|g).$$

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

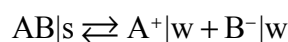
$$\overset{\circ}{K}_p = p(\text{H}_2\text{O}|g).$$

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

But we will discuss phase transitions in more detail in Chapter 9.

Our next topic are heterogeneous *solution equilibria*.

Solubility of (ionic) solids. A substance submerged in a liquid will generally begin to dissolve. The extremely low chemical potential μ of this substance in the pure solvent rises rapidly – for $c \rightarrow 0$, we know that $\mu \rightarrow -\infty$ – 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 rules. 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 on dissolution, like a salt in water



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

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

We obtain for the equilibrium number

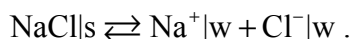
$$\overset{\circ}{K}_{\text{sp}} = c_r(\text{A}^+) \cdot c_r(\text{B}^-)$$

with

$$\overset{\circ}{K}_{\text{sp}} = \exp \frac{\overset{\circ}{A}}{RT} = \exp \frac{\overset{\circ}{\mu}(\text{AB}) - \overset{\circ}{\mu}(\text{A}^+) - \overset{\circ}{\mu}(\text{B}^-)}{RT},$$

as long as some undissolved AB is present, because the mass action term for the solid is omitted. Thus, the product of the relative concentrations of the ions in a saturated solution is constant. The value $\overset{\circ}{K}$ for the process of dissolving receives its own name, *solubility product* (This is indicated by the index sp: $\overset{\circ}{K}_{\text{sp}}$). If a substance dissociates into several ions, then $\overset{\circ}{K}_{\text{sp}}$ consists of the corresponding number of factors.

If the concentration $c(\text{A}^+)$ of one the products of dissociation decreases, the concentration of the second $c(\text{B}^-)$ must rise in order to maintain equilibrium (assuming the concentrations are small enough). If, as the result of some intervention, the product $c_r(\text{A}^+) \cdot c_r(\text{B}^-)$ rises above the value $\overset{\circ}{K}_{\text{sp}}$, the substance AB is separated 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:



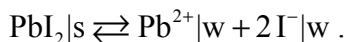
The heterogeneous equilibrium can be described by the solubility product:

$$\overset{\circ}{K}_{\text{sp}} = c_r(\text{Na}^+) \cdot c_r(\text{Cl}^-)$$

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

Experiment: Saturated NaCl solution with Na^+ or Cl^-

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



The following is valid for the solubility product:

$$\overset{\circ}{K}_{\text{sp}} = c_{\text{r}}(\text{Pb}^{2+}) \cdot c_{\text{r}}(\text{I}^-)^2.$$

We can calculate the molar solubility of this salt from the numerical value for the solubility product of $8.6 \cdot 10^{-9}$ at 298 K. Solubility S means the maximum amount of a substance which is soluble under given conditions (temperature, pressure, such as standard conditions) in a certain amount of the solution. In our example, the stoichiometry of equilibrium results in two I^- ions being produced for one Pb^{2+} ion. Therefore, we have

$$c_{\text{pb}^{2+}} = S \quad \text{and} \quad c_{\text{I}^-} = 2S.$$

Insertion results in

$$\overset{\circ}{K}_{\text{sp}} = (S/c^\ominus) \cdot (2S/c^\ominus)^2 = 4S^3/(c^\ominus)^3$$

and the molar solubility is

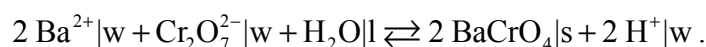
$$S = \sqrt[3]{\overset{\circ}{K}_{\text{sp}}/4c^\ominus} = \sqrt[3]{8.6 \cdot 10^{-9}/4} \text{ mol} \cdot \text{L}^{-1} = 1.3 \cdot 10^{-3} \text{ kmol m}^{-3}.$$

It is now possible to estimate the effect of adding one of the products of dissociation. 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 mol L^{-1} . Now, the solubility S' of lead iodide with the extra iodide ions present can be calculated to be:

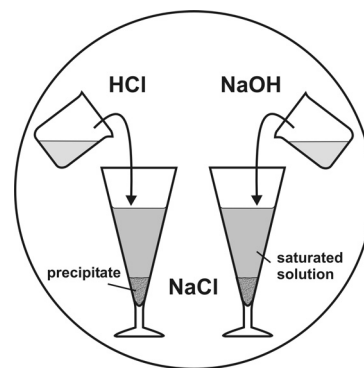
$$S' = \frac{\overset{\circ}{K}_{\text{sp}}}{c_{\text{r}}(\text{I}^-)^2} c^\ominus = \frac{8.6 \cdot 10^{-9}}{0.01} \text{ kmol m}^{-3} = 8.6 \cdot 10^{-7} \text{ kmol m}^{-3}.$$

Adding I^- drastically decreases the solubility of lead iodide as expected.

The solubility of certain slightly soluble compounds can also be otherwise controlled, for example by the pH value. The following interplay between precipitation and dissolution process should terminate this section: When a potassium dichromate solution is added to a barium chloride solution, a yellow precipitate of slightly soluble barium chromate is formed according to



More precisely, the concentrations of the initial substances decrease, i.e. barium chromate precipitates until equilibrium is established according to the mass action law



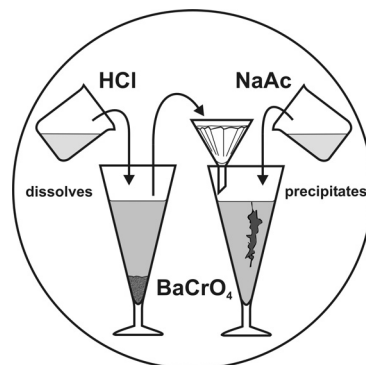
$$\overset{\circ}{K}_c = \frac{c_r(\text{H}^+)^2}{c_r(\text{Ba}^{2+})^2 c_r(\text{Cr}_2\text{O}_7^{2-})}.$$

Pure solids and liquids (the solvent water can be treated approximately as pure substance) are omitted in the expression for the equilibrium number as discussed.

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

Adding H^+ – possibly with diluted hydrochloric acid – the numerator increases so that the denominator must also increase in order for the quotient to remain constant and equal to $\overset{\circ}{K}_c$. 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.

If, on the other hand, the H^+ ions which are released during precipitation are removed in the filtrate by adding sodium acetate ($\text{Ac}^- + \text{H}^+ \rightarrow \text{HAc}$), the numerator decreases. As a result, the value of the denominator must also decrease and BaCrO_4 precipitates.



Solubility of gases. Next we will discuss the solution behaviour 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, by the mass action equation 2'. The equilibrium number which, in this case, is also called the (numerical) *solubility coefficient* $\overset{\circ}{K}_H$, turns out to be

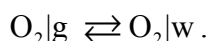
$$\overset{\circ}{K}_H = \frac{c_r(\text{B})}{p_r(\text{B})}.$$

Take into account that in this case, $\overset{\circ}{K}$ corresponds to neither $\overset{\circ}{K}_c$ nor $\overset{\circ}{K}_p$, but represents a so-called „mixed“ constant $\overset{\circ}{K}_{pc}$. 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 solubility coefficient is

$$\overset{\circ}{K}_H = \frac{c(\text{B})}{p(\text{B})}.$$

In 1803, the English chemist William HENRY empirically discovered the relation above which states that the solubility of a gas at constant temperature is proportional to its partial pressure above the solution (*HENRY's law*). $\overset{\circ}{K}_H$ is also known as the HENRY constant.

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



In this case, the standard value of the chemical drive is -16.4 kJ . The (numerical) solubility coefficient at room temperature is equal to

$$\overset{\circ}{K}_H = \frac{c_r(\text{O}_2)}{p_r(\text{O}_2)} = \exp \frac{\overset{\circ}{A}}{RT} = \exp \frac{-16.4 \cdot 10^3 \text{ J}}{8.314 \text{ J K}^{-1} \cdot 298 \text{ K}} = 1.3 \cdot 10^{-3},$$

while the conventional one results in

$$\overset{\circ}{K}_H = \frac{c(\text{O}_2)}{p(\text{O}_2)} = \overset{\circ}{K}_H \cdot \frac{1 \text{ kmol m}^{-3}}{100 \text{ kPa}} = 1.3 \cdot 10^{-5} \text{ mol m}^{-3} \text{ Pa}^{-1}.$$

The partial pressure of O_2 in air is about 20 kPa. For O_2 concentration in air-saturated water at 298 K, we obtain

$$c_r(\text{O}_2) = \overset{\circ}{K}_H \cdot p(\text{O}_2) = 1.3 \cdot 10^{-5} \text{ mol m}^{-3} \text{ Pa}^{-1} \cdot 20 \cdot 10^3 \text{ Pa} = 0.26 \text{ mol m}^{-3}.$$

Concentrations of O_2 in waters which are important to 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 is then:

$$\overset{\circ}{K}_N = \frac{c_r(\text{B})''}{c_r(\text{B})'}$$

where

$$\overset{\circ}{K}_N = \exp \frac{\overset{\circ}{A}}{RT} = \exp \frac{\overset{\circ}{\mu}(\text{B})' - \overset{\circ}{\mu}(\text{B})''}{RT}.$$

Conventionally, we obtain

$$\overset{\circ}{K}_N = \frac{c(\text{B})''}{c(\text{B})'}.$$

The ratio of equilibrium concentrations (or the mole fractions, etc.) of the dissolved substance in two liquid phases is, in the case of small concentrations, a temperature dependent constant (*NERNST's distribution law*). The constant $\overset{\circ}{K}_N$ is also called NERNST's distribution coefficient.

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 circumstances (mostly standard conditions at 298 K and 101 kPa). If the value of \mathcal{K} 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 4.2:

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

Insertion into the equation above yields the following result for the equilibrium number at a temperature T

$$\overset{\circ}{\mathcal{K}}(T) = \exp \frac{\overset{\circ}{\mathcal{A}}(T_0) + \alpha(T - T_0)}{RT}.$$

When the temperature is increased ($\Delta T > 0$), $\overset{\circ}{\mathcal{K}}(T)$ can increase or decrease relative to the initial value $\overset{\circ}{\mathcal{K}}(T_0)$ depending upon the values of $\overset{\circ}{\mathcal{A}}(T_0)$ and α 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 can be of great importance for large-scale technical reactions as well as for environmentally relevant ones.

5.7 Potential diagrams of dissolved substances

Energy must be used in order to transfer matter from a state of low μ value to a state of high μ value. Therefore, the potential μ 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 μ of the substance also increases. While at first, only small changes Δn 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 b if μ is to increase by the same amount. n therefore increases exponentially along with the chemical potential μ .

The example of an electric capacitor can be used to characterize the capacity of a substance. The *chemical capacity* B is defined by the following equation:

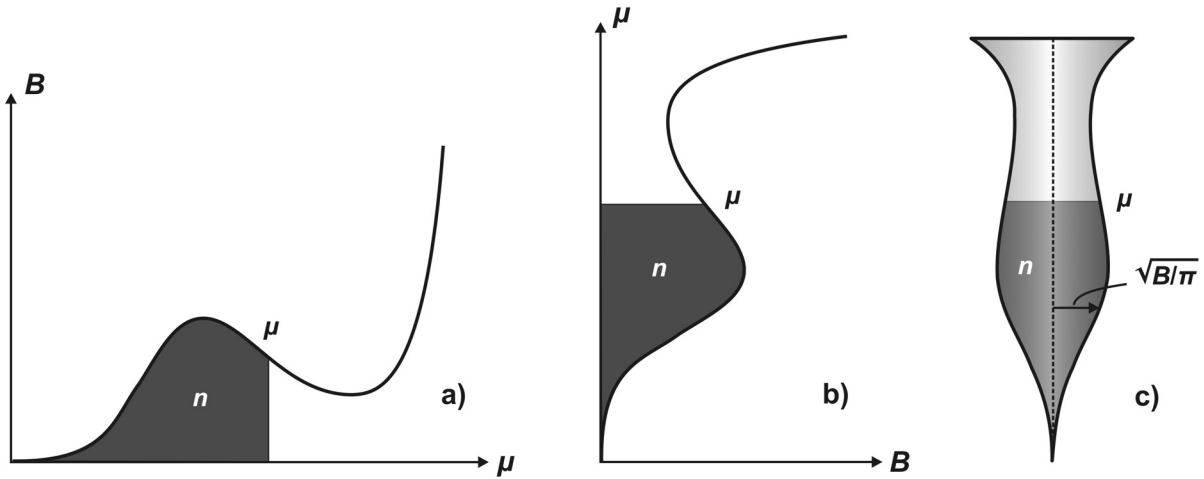
$$B = \frac{dn}{d\mu}.$$

A well known example of the quantity B is the so-called *buffering capacity*, meaning the capacity B_{H^+} of a given amount of a solution for hydrogen ions. This will be gone into in more detail in Section 6.6. 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 *density of chemical capacity*.

If the chemical capacity B of a finite volume V of solution is plotted against the chemical potential μ (compare figure below, part a), the area under the $B(\mu)$ curve from $-\infty$ to the actual potential μ 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 μ with the amount of substance n (figure, 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 (figure, part c). In this case as well, n is the spatial content of the container filled up to the level μ . 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.



As long as the mass action equations are valid, it is easy to express n as a function of μ . To do so, we solve the equation $\mu = \overset{\circ}{\mu} + RT \ln(c / c^{\ominus})$ with $c = n/V$ for n and obtain:

$$\frac{\mu - \overset{\circ}{\mu}}{RT} = \ln \frac{n}{Vc^{\ominus}}$$

or

$$n = Vc^{\ominus} \cdot \exp \frac{\mu - \overset{\circ}{\mu}}{RT}.$$

The chemical capacity is the derivative with respect to μ , for constant Vc^{\ominus} and $\overset{\circ}{\mu}$:

$$B = \frac{Vc^{\ominus}}{RT} \cdot \exp \frac{\mu - \overset{\circ}{\mu}}{RT} = \frac{n}{RT}.$$

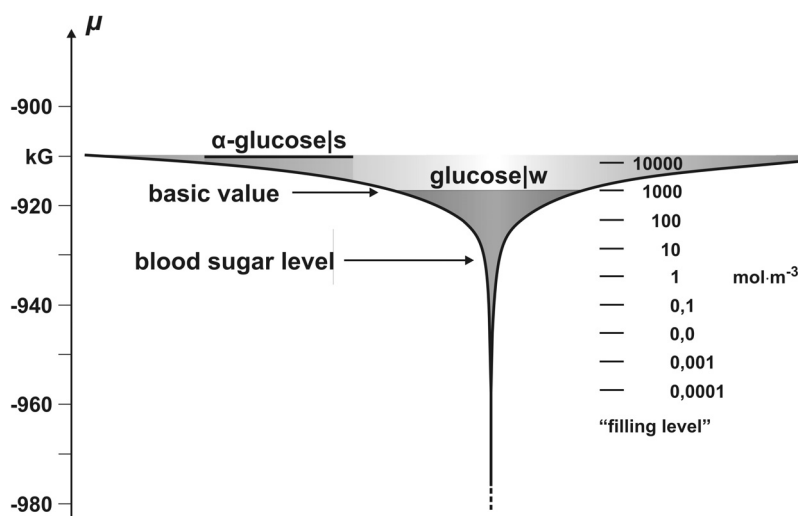
As a consequence, B , like n , depends exponentially upon μ . In this case, the container whose curve we are interested in has the form of an „exponential horn“ which is open at the top.

The chemical capacity density b can be easily calculated from B :

$$b = \frac{B}{V} = \frac{c^\ominus}{RT} \cdot \exp \frac{\mu - \overset{\circ}{\mu}}{RT} = \frac{c}{RT}.$$

Again, it depends exponentially on μ .

We will take a closer look at this approach using the example of glucose. 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, α and β , 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 above 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 contents up to a chosen level equal 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 μ ; for high concentrations, this is only approximate. We do not need to differentiate between the α and the β forms because an equilibrium rather quickly develops between the two isomers. The basic value of the potential applies to this equilibrium mixture. The contents of the chalice have 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.

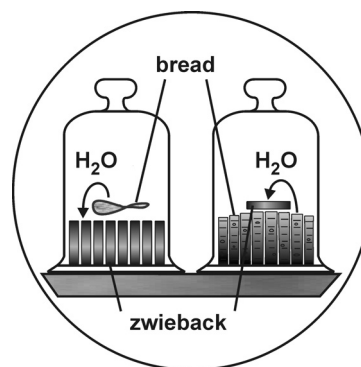
If the amount of dissolved glucose were to be continuously increased, and the fill level of the chalice raised to the level of the solid glucose, the glucose would begin to crystallize. At the same time, the glucose would begin to run over the rim of the chalice. If, on the other hand, solid glucose were present, 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.

11. Flow of Substances

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

11.1 Introduction

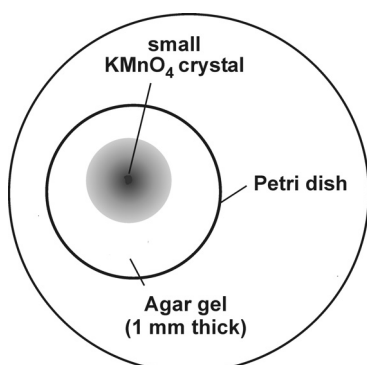
Until now, when we have considered the chemical potential we have primarily concentrated upon chemical reactions and phase changes. However, there is another characteristic of substances that is almost as important. This is the tendency to spread out or disperse in space whether it is empty or filled 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 out 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 after 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.



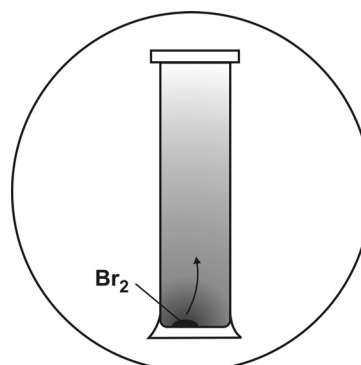
Experiment: A piece of zwieback stored with bread will become soft and bendable. A slice of bread stored with zwieback becomes hard and brittle.

It is easy to follow the spreading of strong smelling or coloured substances. The scent of a bouquet of lilacs, a peeled orange or the pungent odour of potent cheese quickly fill a whole room. The spreading of 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. The vapour from a drop of bromine in a plain cylinder (gas jar) spreads quickly and fills the whole space inside it.

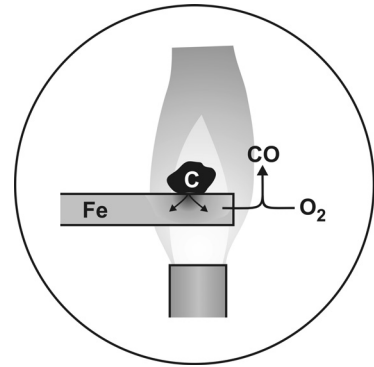
Experiment: Diffusion of KMnO_4 in agar gel (view from above on a thin layer of gel in a Petri dish)



Experiment: Dispersion of Br_2 in air



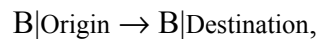
Even crystallized, compact bodies are not impenetrable. Iron can be „carbonized“ by annealing in charcoal powder at approx. 1000 °C. This means that the carbon atoms move into it. The modifications of the grain structure at the border of the sample are visible to the naked eye as a dark area but they 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: „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 reaction

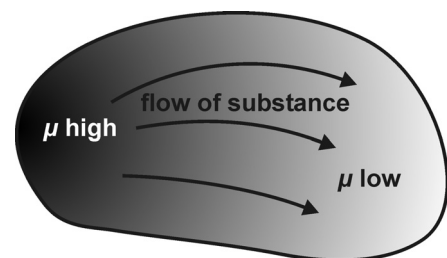


so it is plausible that the chemical potential also controls these processes. The transport of substances always follows the direction of the potential gradient. This means that the substance only moves spontaneously in one direction, the direction where the μ value at the starting point is higher than 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 μ plays a decisive role that we have already been introduced to, namely its concentration dependency (compare Section 5.2): *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 migration of substances and other phenomena related to it. Chapter 12 will deal with the special features that result when the rule mentioned above no longer applies which is the case at higher concentrations.

11.2 Diffusion

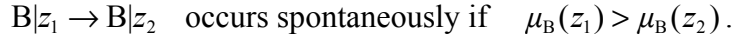
A substance provided that it is mobile enough must distribute in an otherwise homogenous material or space uniformly over the entire area. This is because at locations of lower concentrations, its chemical potential is lower causing the substance to move from regions of higher concentration into areas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



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 neighbouring areas. This characteristic is applied in microscopy in order to colour ar-

eas that would tend to preferentially absorb certain pigments. A pigment more or less evenly applied distributes unevenly even without outside influence.

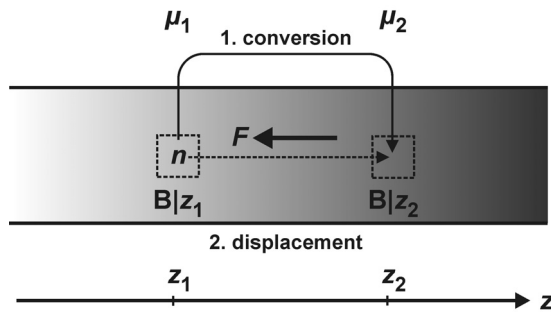
We shall now take a closer look at mass transfer processes. As we have already seen, the determining quantity is the chemical potential. The substance moves spontaneously only in the direction in which the potential falls. If the transfer of a substance B from location z_1 to location z_2 is formulated as a reaction, then



The chemical drive \mathcal{A} of this process is the corresponding potential difference,

$$\mathcal{A} = \mu_B(z_1) - \mu_B(z_2) = -\Delta\mu_B,$$

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 as effort on the one hand for the conversion and on the other hand for the displacement against the force F . For this, let us consider that the potential μ_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 \mathcal{A} is negative. F also counts as negative because it is

oriented opposite to the positive z axis. In general, F depends upon the location z . If the segment $\Delta z = z_2 - z_1$ is made small enough, F can be considered constant. As a consequence, we obtain:

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

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 19, which deals with transport phenomena, we will discuss the velocity of substance transport and the laws pertaining to it (section 19.2).

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 diffusion. Water, alcohol, ether, etc., evaporate into the air (Section 5.1). They convert to a gaseous state although the chemical potential of liquid A is smaller below its boiling point than that of *pure* vapour. What makes this possible is the fact that the vapour 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 μ value of the non-dissolved solute of B, so that B begins to migrate away from it (Section 5.6).

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 vapour pressure formula of pure substances are all examples of this.

11.3 Indirect mass action

When a *small* amount n_F of a foreign substance is dissolved in a liquid A, the chemical potential μ_A of this liquid at constant p and T will decrease. 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*:

$$\mu_A = \dot{\mu}_A - RT \cdot x_F \quad \text{for } x_F \ll 1 \quad \text{„colligative lowering of potential,”}$$

(the term “colligative” is explained at the end of this section). $\dot{\mu}_A$ designates the potential of A in its pure state. 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 change. 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 $\overset{\times}{\mu} = -RT \ln c_r$ 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 $\overset{\times}{\mu}$ do not; they actually increase without limit.

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

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 characteristic, which is valid for all substances, is the direct 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 5).

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 reciprocal relation discussed in Section 8.3 known as *n-n* coupling. When one substance tries to displace (or aid) 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 (fundamental equation: $dW = -pdV + TdS + \mu_A dn_A + \mu_F dn_F$):

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

Taking into account that μ_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:

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

When we started looking at the range of phenomenon related to mass action, we chose the situation where the concentration coefficient γ^\times of the chemical potential at low concentrations c is a universal quantity (Section 5.2). When applied here to substance F, this means:

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

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 space taken up by 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 ,

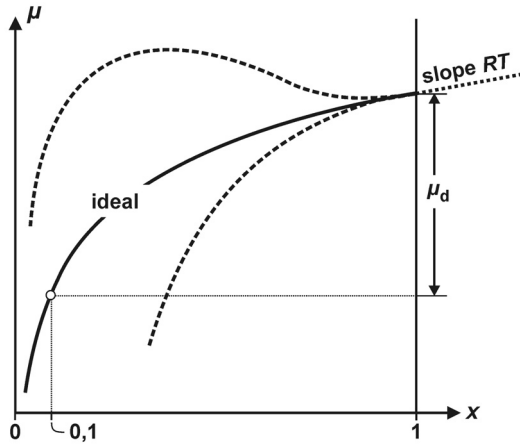
$$\left(\frac{\partial c_F}{\partial n_A} \right)_{p,T,n_F} = -\frac{n_F}{n_A^2 V_A} = -\frac{n_F}{n_A V} = -\frac{c_F}{n_A},$$

and insert the result further above, we obtain:

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

The derivative is not dependent upon n_F , meaning that, with increasing amount n_F , μ_A decreases linearly with constant slope from the initial value $\dot{\mu}_A$:

$$\mu_A = \dot{\mu}_A - \frac{RT}{n_A} \cdot n_F \approx \dot{\mu}_A - RT \cdot x_F.$$

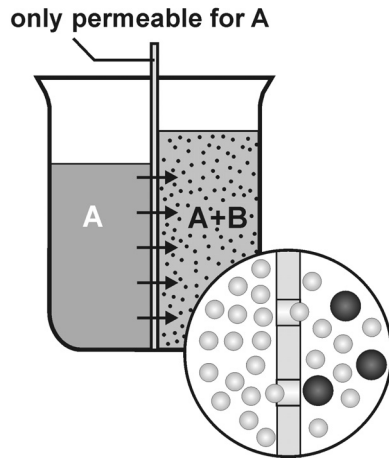


The adjoining figure shows the chemical potential $\mu(x)$ as a function of x within the entire range from $x = 0$ to 1. The solid curve illustrates the ideal logarithmic relation. If the mole fraction is reduced by a power of ten each time, the chemical potential decreases by the same value: the decapotential μ_d of 5.7 kG at room temperature (Section 5.2). As already stated (and derived above), all $\mu(x)$ curves must show the same slope RT for $x \approx 1$ as well as for $x_F \approx 0$. We will go more deeply into this subject in Section 12.2.

“Colligative lowering of potential” leads to several effects: formation of osmotic pressure, lowering of vapour 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 (“assembly 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, vapour 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 $x_{\text{NaCl}} = 0.001$, $x_F = x_{\text{Na}^+} + x_{\text{Cl}^-} = 2 \cdot x_{\text{NaCl}} = 0.002$; this is so because NaCl is fully dissociated into the Na^+ and Cl^- ions. In a calcium chloride solution, we have $x_F = x_{\text{Ca}^{2+}} + x_{\text{Cl}^-} = 3 \cdot x_{\text{CaCl}_2} = 0.003$.

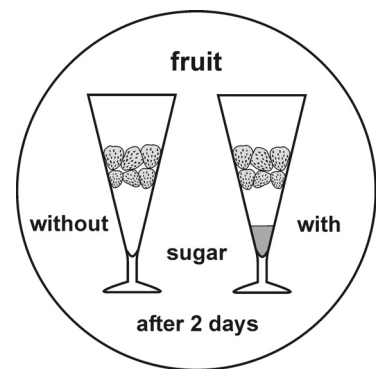
11.4 Osmosis

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), solvent A will migrate through this membrane from the more diluted solution 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 μ_A is also smaller. Thus, the chemical drive for this process of *osmosis* is the difference of potential generated by different concentrations of foreign substances.



The adjoining figure represents the migration of solvent A in the direction opposite to a pressure drop into a solution. The molecules of the dissolved substance B are shown as dots; for clarity, solvent A is shown as a continuum, where the slightly different gray tones indicate the differences of concentrations. The detail shows spheres symbolizing the molecules of the dissolved substance (dark) as well as the solvent (light). In the simple membrane model, selective permeability results from the maximum pore size: Only the smaller solvent molecules manage to move through the membrane. But semipermeability can also occur through other mechanisms.

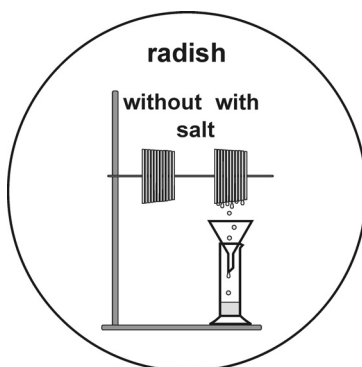
The biological membranes surrounding living cells are also semipermeable. They allow water and molecules of comparable size through while holding back enzymes and proteins inside the cell. In biology, osmotic exchange of water represents a ubiquitous phenomenon. It is responsible for the effect that juice is drawn out from strawberries that are sugared or that cherries swell up and burst after a long rain.



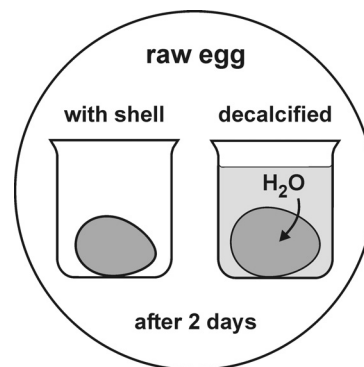
Experiment: Juice “extraction” from sugared fruit

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 radish; the second effect can be demonstrated on a raw decalcified egg in water.

Experiment: Juice “extraction” from slices of salted radish



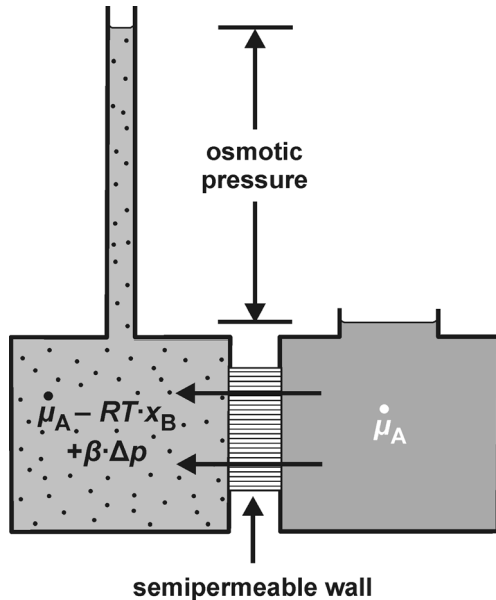
Experiment: Swelling of a decalcified egg in water



A gradual excess pressure results from the inflow of solvent A to the concentrated solution. The chemical potential μ_A also gradually increases so that the potential gradient decreases. The process stops when μ_A on the right and on the left of the wall becomes equal (or when the 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 jar 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 μ_A of the solvent decreases („colligative potential lowering“):

$$\mu_A = \dot{\mu}_A - RT \cdot x_B \quad \text{for } x_B \ll 1.$$



Let us imagine the jar connected to another one by a wall that is permeable only for the solvent (figure on the left). The liquid in the second container is in its pure state. 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 of the solution. The chemical potential grows with increasing pressure (compare Section 4.3):

$$\mu_A = \dot{\mu}_A - RT \cdot x_B + \beta_A \cdot \Delta p.$$

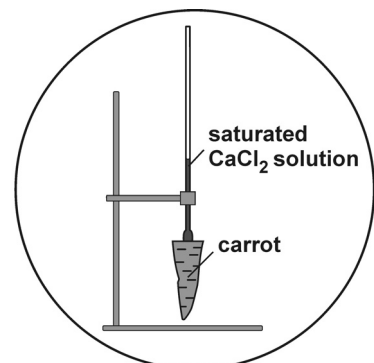
where the pressure coefficient β_A corresponds to the molar volume V_A of the pure solvent (compare Section 8.3). The following is then valid for the osmotic equilibrium:

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

This means that the chemical potential of the solution again corresponds to that of the pure solvent. The excess pressure Δp necessary for establishing equilibrium is the *osmotic pressure* p_{osm} in the solution.

The simple arrangement in the figure above 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 $p_{\text{osm}} = \rho g h$ can be easily calculated from the resulting rise h of the column of liquid, the density ρ 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. For this purpose, the inside of the carrot is hollowed out in a cylindrical form and filled with a coloured 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: 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 $V = n_A \cdot V_{m,A}$ indicates the volume of liquid (ignoring the small amount $n_B \cdot V_{m,B}$ of the foreign substance), then the osmotic pressure p_{osm} results in:

$$\boxed{p_{\text{osm}} = n_B \frac{RT}{V}} \quad \text{VAN'T HOFF's equation.}$$

At room temperature ($T = 298 \text{ K}$), a solution of an arbitrary non-electrolyte with a concentration of 0.01 mol m^{-3} results in an osmotic pressure of 250 kPa ($= 2.5 \text{ bar}$). 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 ideal 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 10.1, 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_{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 μ_A of the liquid for a pressure reduced by p_{osm} and keep in mind that for thin solutions $V \approx n_A \cdot V_A$ and $n_B/n_A \approx x_B$, we again end up with the equation above. This demonstrates that both descriptions are equivalent:

$$\dot{\mu}_A - \beta_A \cdot p_{\text{osm}} = \dot{\mu}_A - V_A \frac{n_B RT}{V} = \dot{\mu}_A - x_B RT.$$

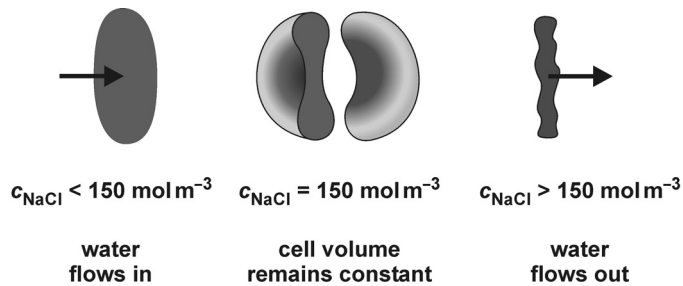
If the diluted solution contains several types of particles which cannot penetrate the membrane, we have

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

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 as high as this concentration. Correspondingly, the osmotic pressure of the solution of this salt is three times that of an equivalent concentration of the solution of a non-electrolyte.

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 biological 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 $p_{\text{osm}} = 300 \text{ mol m}^{-3} \cdot 8,3 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 310 \text{ K} = 770 \text{ kPa}$ can be

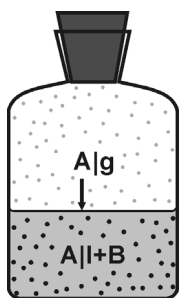


estimated. If red blood cells were to be suspended in pure water, they would have to withstand about 8 times normal atmospheric pressure. In fact, they swell up and burst long before this point (see figure, part a). On the other hand, if red blood cells are put into contact with an aqueous sodium chlo-

ride 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^+ , figure, part 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). Solutions where the water content of the cells remains constant ($\mu(\text{H}_2\text{O})$ inside and outside are equal) are described as *isotonic*. When giving intravenous infusions, it is important to be aware that in order not to damage the blood cells, only an isotonic solution matching the blood may be used. A physiological saline solution has a concentration of 150 mol m^{-3} and therefore an osmolarity of 300 mol m^{-3} . On the other hand, the cell damaging effects of concentrated saline solutions can be put to good use in order to preserve foods. One example is salting (pickling) of meat where the water is removed from possibly unhealthy microorganisms through osmosis. This hinders their cell functions and strongly reduces their reproduction.

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 desalination of sea water as well as wine processing.

11.5 Lowering of vapour pressure



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

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

Also the quantitative treatment is not difficult. The process continues until equality of potentials is regained, $\mu_{\text{A|l}} = \mu_{\text{A|g}}$. For this purpose, reducing the pressure by a small amount Δp is sufficient. The chemical potential $\mu_{\text{A|g}}$ of the vapour 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:

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

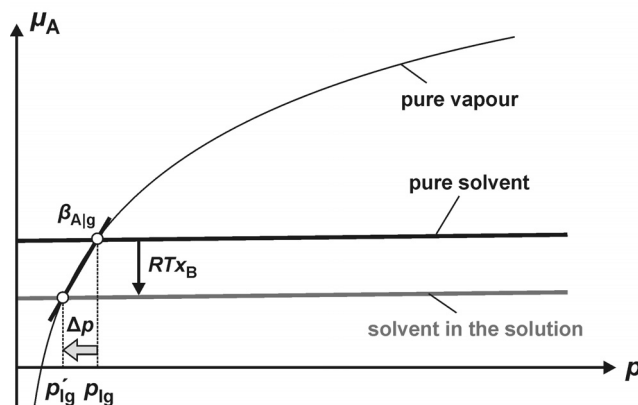
We act on the assumption that $\dot{\mu}_{A|l} = \dot{\mu}_{A|g}$, therefore these contributions cancel each other out. Because moreover we have $\beta_{A|g} = V_{A|g} = RT/p$ (see Section 8.3), the equation can be simplified according to:

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

p corresponds in this context to the vapour pressure p_{lg} of the pure solvent. If it is important for differentiation we add the symbol \bullet and write p_{lg}^\bullet instead of p_{lg} . For the „lowering of vapour pressure” Δp_{lg} we obtain a relation that was discovered empirically in 1890 by François Marie RAOULT:

$$\Delta p_{lg} = -x_B \cdot p_{lg}^\bullet$$

RAOULT’s law.



But let us have a look at the adjoining figure for illustration: At the intersection of the potentials for pure solvent and pure vapour, there is equilibrium between the liquid and its vapour phase at the vapour 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 vapour unchanged.

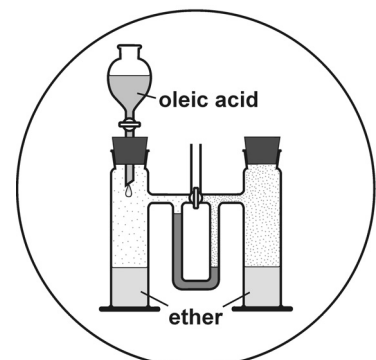
Thus, the intersection of the curves (p'_{lg}) shifts to the left. This means that the vapour pressure is lowered by Δp ($\Delta p < 0!$). With the aid of the “slope triangle” drawn in the figure the slope $\beta_{A|g}$ of the potential curve for pure vapour results in

$$\beta_{A|g} = \frac{-RTx_B}{\Delta p}.$$

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

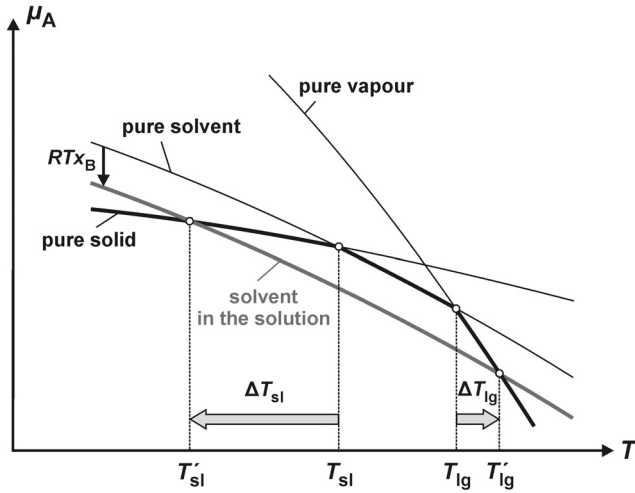
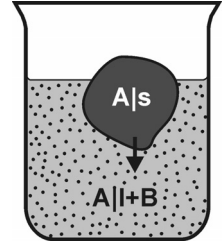
The simple setup shown on the right can serve as a demonstration experiment. The vapour pressure in the wash bottle with added oleic-acid decreases in comparison with the vapour pressure of pure ether. This is shown by the level of liquid in the pressure gauge.

Experiment: Comparison of the vapour pressures of ether and an ether-oleic acid mixture



12.6 Freezing-point depression and boiling-point elevation

A frozen liquid A melts more easily when a substance B that is soluble in the liquid but not in the solid is added. At the normal freezing point T_{sl} of the liquid A, the chemical potentials for the solid and liquid state are equal ($\dot{\mu}_{A|s} = \dot{\mu}_{A|l}$). 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 (adjoining figure) explains this phenomenon: When the chemical potentials 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. 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 ΔT_{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 phase, $\mu_{A|l} = \mu_{A|s}$. Because the changes in temperature T we are interested in are mostly small we can assume a linear dependency 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 coefficient):

$$\mu_{A|l} = \dot{\mu}_{A|l} - RT_{sl} \cdot x_B + \alpha_{A|l} \cdot \Delta T = \dot{\mu}_{A|s} + \alpha_{A|s} \cdot \Delta T = \mu_{A|s}.$$

Again the basic values cancel each other out, $\dot{\mu}_{A|l} = \dot{\mu}_{A|s}$. When the equation is solved for ΔT or more detailed ΔT_{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 8.3). 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 (compare Section 10.5):

$$\Delta T_{sl} = - \frac{RT_{sl} \cdot x_B}{\Delta_{sl}S_A}.$$

The freezing-point depression is like the lowering of vapour pressure directly proportional to the mole fraction x_B of dissolved substance. The additional character \bullet , which symbolizes that the labelled quantity applies to the pure substance can be omitted if misunderstandings are not possible.

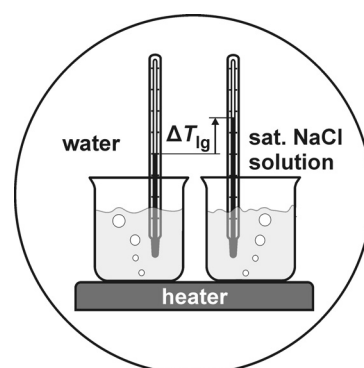


For example, in an aqueous non-electrolyte solution with a mole fraction of $x_B = 0.01$, ΔT_{sl} is about -1 K. A prime example of this effect is the melting effect of road salt. Another example from everyday life is shown in an experiment: When rum, schnaps or whisky is poured over ice, it will become noticeably colder than 0°C .

Experiment: “Whisky on the rocks” as example for the freezing-point depression

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

Experiment: Boiling-point elevation of a saturated solution of table salt



In the diagram above, the position of the equilibrium between liquid and vapour is shifted to a higher temperature. However, this elevation of boiling point is much smaller 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 the freezing-point depression leads to the equation for the boiling-point elevation,

$$\Delta T_{lg} = \frac{RT_{lg}^\bullet \cdot x_B}{\alpha_{A|g} - \alpha_{A|l}},$$

and correspondingly:

$$\Delta T_{lg} = \frac{RT_{lg}^\bullet \cdot x_B}{\Delta_{lg} S_A}.$$

where $\Delta_{lg} S_A$ now represents the molar entropy of vaporization ($S_{A|g} - S_{A|l}$). In an aqueous solution of a non-electrolyte with a molar fraction of $x_B = 0.01$, ΔT_{lg} is only about 0.3 K.

In summary, when a low-volatile foreign substance is dissolved in a liquid, the potential of the pure vapour, which is then higher than that of the solution, can be lowered in two ways. First, by lowering the pressure (section 11.4), and second, by raising the temperature.

11.7 Colligative properties and determining molar mass

The four phenomena just described (osmosis, lowering of vapour pressure, freezing-point depression, and boiling-point elevation) 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 freezing-point depression. $x_B \approx n_B/n_A$ 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 above equation for the freezing-point depression results in

$$\Delta T_{sl} = -k_k \cdot \frac{n_B}{m_A} = -k_k \cdot b_B \quad \text{with} \quad k_k = -\frac{RT_{sl}M_A}{\Delta_{sl}S_A},$$

an only from the pressure and the kind of solvent dependent coefficient with the name “*cryoscopic constant*.” k_k corresponds to the depression of freezing point which is obtained from 1 mol of dissolved substance in 1 kg of solvent. At such high concentrations the equation above is only valid by approximation. For measuring the temperature changes at low concentrations with a sufficient precision, it is advisable to use solvents with k_k values as high as possible. The following table shows the “cryoscopic constants” of some solvents.

Solvent	T_{sl} K	k_k K kg mol ⁻¹	T_{lg} K	k_e K kg mol ⁻¹
Water	273.2	1.86	373.2	0.51
Benzene	278.6	5.07	353.2	2.64
Cyclohexane	279.7	20.8	353.9	2.92
Cyclohexanol	298.1	42.2	434.0	3.5
Campfor	452.0	37.8	-	-

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

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

The coefficient k_e is referred to as “*ebullioscopic constant*.” Because of its higher denominator ($\Delta_{lg}S_A > \Delta_{sl}S_A$), it is smaller than k_k (compare the table above). For this reason, the change of temperature here is smaller than for the depression 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 $M_B = m_B/n_B$.

Formation 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 an elevation of boiling point of 0.005 K and a depression 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.