PHYSICAL CHEMISTRY
IN BRIEF

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Annotation

The *Physical Chemistry In Brief* offers a digest of all major formulas, terms and definitions needed for an understanding of the subject. They are illustrated by schematic figures, simple worked-out examples, and a short accompanying text. The concept of the book makes it different from common university or physical chemistry textbooks. In terms of contents, the *Physical Chemistry In Brief* embraces the fundamental course in physical chemistry as taught at the Institute of Chemical Technology, Prague, i.e. the state behaviour of gases, liquids, solid substances and their mixtures, the fundamentals of chemical thermodynamics, phase equilibrium, chemical equilibrium, the fundamentals of electrochemistry, chemical kinetics and the kinetics of transport processes, colloid chemistry, and partly also the structure of substances and spectra. The reader is assumed to have a reasonable knowledge of mathematics at the level of secondary school, and of the fundamentals of mathematics as taught at the university level.

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Introduction

Dear students,

Physical Chemistry is generally considered to be a difficult subject. We thought long and hard about ways to make its study easier, and this text is the result of our endeavors. The book provides accurate definitions of terms, definitions of major quantities, and a number of relations including specification of the conditions under which they are valid. It also contains a number of schematic figures and examples that clarify the accompanying text. The reader will not find any derivations in this book, although frequent references are made to the initial formulas from which the respective relations are obtained.

In terms of contents, we followed the syllabi of “Physical Chemistry I” and “Physical Chemistry II” as taught at the Institute of Chemical Technology (ICT), Prague up to 2005. However the extent of this work is a little broader as our objective was to cover all the major fields of Physical Chemistry.

This publication is not intended to substitute for any textbooks or books of examples. Yet we believe that it will prove useful during revision lessons leading up to an exam in Physical Chemistry or prior to the final (state) examination, as well as during postgraduate studies. Even experts in Physical Chemistry and related fields may find this work to be useful as a reference.

Physical Chemistry In Brief has two predecessors, “Breviary of Physical Chemistry I” and “Breviary of Physical Chemistry II”. Since the first issue in 1993, the texts have been revised and re-published many times, always selling out. Over the course of time we have thus striven to eliminate both factual and formal errors, as well as to review and rewrite the less accessible passages pointed out to us by both students and colleagues in the Department of Physical Chemistry. Finally, as the number of foreign students coming to study at our institute continues to grow, we decided to give them a proven tool written in the English language. This text is the result of these efforts. A number of changes have been made to the text and the contents have been partially extended. We will be grateful to any reader able to detect and inform us of any errors in our work. Finally, the authors would like to express their thanks to Mrs. Flemrová for her substantial investment in translating this text.

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Chapter 1

Basic terms

A good definition of basic terms is an essential prerequisite for the study of any physicochemical processes. Some of these terms may be also used beyond the field of physical chemistry, but their meaning is often slightly different. In this chapter we will therefore sum up the major basic terms that will be used in the subsequent parts of this book.

1.1 Thermodynamic system

The concept (thermodynamic) **system** as used in this book refers to that part of the world whose thermodynamic properties are the subject of our interest, while the term **surroundings** is used for the remaining part of the universe.

> *Note:* Both a certain part of the real space and a certain part of the imaginary (abstract) space forming a simplified model system, e.g. an ideal gas, may be chosen as a system.

Systems are classified as isolated, closed and open, based on their inter-relations with their surroundings.

1.1.1 Isolated system

A chemical system exchanging neither matter nor energy with its surroundings is an **isolated system.**

1.1.2 Closed system

A chemical system exchanging energy but not matter with its surroundings is a **closed system**.

1.1.3 Open system

A chemical system exchanging both energy and matter with its surroundings is an **open system**.

Example
Differences between individual types of chemical systems may be demonstrated using the example of making coffee. The pot on the heater represents a (practically) closed system until the water is brought to the boil. At the boiling point, when steam is leaking from the pot, it becomes an open system. The ready-made coffee kept in a thermos bottle represents a simple model of an isolated system.

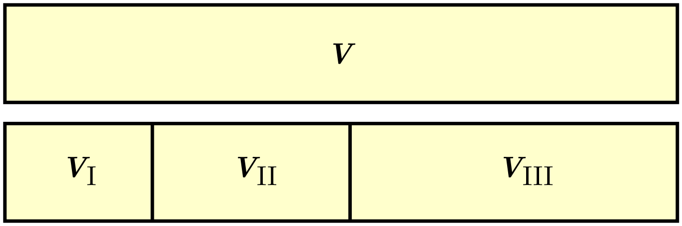
1.1.4 Phase, homogeneous and heterogeneous systems

The term **phase** is used for that portion of the investigated system volume in which its properties are constant or continuously changing in space. If a system behaves in this way throughout all its volume, we call it a **homogeneous system**. If a system contains more phases, we call it a **heterogeneous system**.

Example
Let us imagine a bottle of whisky. How many phases does this system consist of?

Solution

If we are, from the thermodynamic point of view, interested solely in the liquid content of the bottle, the system is homogeneous. It contains one liquid phase (a mixture of water, ethanol and some additives). If, on the other hand, we are interested in the entire content of the bottle but not the bottle itself, the system is heterogeneous. In this case it consists of two phases, liquid and gaseous, with the latter containing air and whisky vapour. If, however, we focus our attention on both the bottle content and the bottle itself, we have a heterogeneous system again, but this time it also contains other phases in addition to the gaseous and liquid ones, i.e. the glass of the bottle, its cap, label, etc.



Obr. 1.1: The volume of a system as an extensive quantity. The volume V is the sum of the volumes of the individual parts (i.e. sub-systems) I, II and III, i.e. $V = V_\mathrm{I} + V_\mathrm{II} + V_\mathrm{III}$.

1.2 Energy

There are two basic forms of energy exchange between a system and its surroundings, **heat** and **work**. A positive value is assigned to such energy exchange during which the system gains energy (work or heat) from its surroundings, i.e. energy is added to the system. A negative value indicates that the system passes energy (work or heat) to its surroundings, i.e. energy is subtracted from the system.

1.2.1 Heat

When the energy of a system changes as a result of a temperature difference between the system and its surroundings (e.g. transfer of kinetic energy of disordered movement of molecules), we speak about exchanged **heat**.

U *Main unit:* J.

1.2.2 Work

Other forms of energy exchange, which are usually driven by some forces acting between the system and its surroundings, are called **work**. Based on the type of interaction between the system and its surroundings, we distinguish volume work [see **3.1.2**], electrical work, surface work, etc.

U *Main unit:* J.

1.3 Thermodynamic quantities

Observation of any system allows us to determine a number of its properties. The properties in which we are interested from the thermodynamic point of view are called **thermodynamic quantities**, or, briefly, quantities. Typical thermodynamic quantities are temperature, pressure, volume, enthalpy and entropy. Neither heat nor work rank among thermodynamic quantities.

> *Note:* Terms such as thermodynamic function, thermodynamic variable, state quantity (i.e. a quantity determining the state of a system, see **1.4**), state function, or state variable are used as synonyms of the term thermodynamic quantity.

1.3.1 Intensive and extensive thermodynamic quantities

Let us consider a homogeneous system without any external force fields present. We distinguish between **extensive** and **intensive** thermodynamic quantities of a system. Intensive quantities are those whose values do not change when the system is divided into smaller sub-systems. Extensive quantities are those whose values are proportional to the amount of substance of the system at a fixed temperature and pressure (see Figure 1.1). Temperature, pressure, and composition expressed by mole fractions are typical intensive quantities. Volume, mass and the number of particles are typical extensive quantities.

> *Note:* Some quantities, e.g. the system surface, are neither extensive nor intensive.

Every extensive quantity may be converted into an intensive one if we relate it to a certain constant mass of the system. We then obtain specific or molar quantities (see **3.2.5**). For every extensive quantity X and the respective **molar and specific** quantities X_{m} and x we may write

$$X = n\,X_{\mathrm{m}}\,, \tag{1.1}$$

$$X = m\,x\,, \tag{1.2}$$

where n is the amount of substance and m is the mass of the system.

S *Symbols:* We will use the subscript $_{\mathrm{m}}$ to denote molar quantities and small letters to denote specific quantities.

1.4 The state of a system and its changes

Any system may be in any moment characterized using a certain number of quantities. These quantities define the **state** of a given system. The degree of generality at which we observe a given system has to be taken into account at the same time. In terms of a microscopic scale, the state of a system is defined by the position and velocity of all its particles. In terms of thermodynamics, however, it is enough to know only a few quantities, e.g. temperature, pressure and composition.

1.4.1 The state of thermodynamic equilibrium

The state of thermodynamic equilibrium (equilibrium state, equilibrium) is a state in which no macroscopic changes occur in the system and all quantities have constant values in time.

Note: In the state of thermodynamic equilibrium, changes take place at the microscopic level. For instance, when the liquid and vapour phases are in equilibrium, some molecules continuously move from the liquid to the vapour phase and others from the vapour to the liquid phase. However, the temperature and pressure of the system do not change.

The state of thermodynamic equilibrium embraces the following partial equilibria:

- mechanical (pressure) equilibrium—the pressure in all parts of the system is the same [1],
- thermal (temperature) equilibrium—the temperature in all parts of the system is equalized,
- concentration equilibrium—the concentration of the system components is the same in all parts of each *phase* of the system, but the composition of individual phases is usually different,
- chemical equilibrium—no changes in composition occur as a result of chemical reactions,
- phase equilibrium—if a system is heterogeneous (see **1.1.4**), the components of its phases are in equilibrium.

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[1] The osmotic equilibrium is an exception.

Note: If a system in the state of thermodynamic equilibrium occurs in an external force field, e.g. the gravitational field, the pressure is not the same in all parts of the system but it changes continuously. The concentration of the system components also changes continuously in each phase, with a discontinual change occurring at the phase boundary.

1.4.2 System's transition to the state of equilibrium

If a system is not in the state of equilibrium, its properties change in time in such a way that it tends toward equilibrium. Thermodynamics postulates that every system under invariable external conditions is bound to attain the state of thermodynamic equilibrium. The time needed for a system to attain equilibrium varies considerably, ranging from fractions of a second needed for pressure equalization up to hundreds of years needed for glass transition to the crystalline state. A measure of the velocity of a system's transition to equilibrium is called the **relaxation time**.

Example

If we immerse several crystals of copper(II) sulphate pentahydrate ($CuSO_4 \cdot {}_5H_2O$) into a closed vessel containing water, the system thus created will be in a non-equilibrium state at the beginning. There will be neither a phase equilibrium between the crystals and the liquid phase nor a concentration equilibrium. After some time the crystals will dissolve (phase equilibrium). If we do not mix the system, the dissolved copper(II) sulphate pentahydrate will slowly diffuse through the solution from the bottom up to the surface, and after many weeks (relaxation time), concentration in all parts of the system will become equal as well (thermodynamic equilibrium).

1.4.3 Thermodynamic process

If the properties of a system change in time, i.e. if at least one thermodynamic quantity changes, we say that a certain **thermodynamic process** takes place in the system. The term process relates to a very broad range of most varied processes, from simple physical changes such as, e.g., heating, various chemical reactions, up to complex multistage processes. Individual kinds of processes may be classified according to several criteria.

1.4.4 Reversible and irreversible processes

The course of any process depends on the conditions under which the given system changes. If we arrange the conditions in such a way that the system is nearly at equilibrium in every moment, and that, consequently, the direction of the process may be reversed by even a very slight change of the initial conditions, the process is called **reversible** or **equilibrium**. A reversible process is thus a sequence of (nearly) equilibrium states of a system.

However, processes in the real world are mostly such that the system is out of equilibrium at least at the beginning. These processes are called **irreversible** or **non-equilibrium** (the direction of the process cannot be reversed by any slight change of external conditions, and the process is a sequence of non-equilibrium states). An equilibrium process is thus actually a limiting case of a non-equilibrium process going on at an infinitesimal velocity.

Example

Infinitely slow heating or infinitely slow compression of a system may serve as an example of equilibrium processes which cannot be carried out in practice. In contrast, water boiling at a temperature of 100°C and pressure of 101 325 Pa is an example of an equilibrium process which may take place in practice. If we lower the temperature slightly, the direction of the process will be reversed and boiling will be replaced by water vapour condensation.

1.4.5 Processes at a constant quantity

In most investigated processes, one or more thermodynamic quantities are maintained constant *during the whole process*. These processes are mostly termed using the prefix **iso-** (is-), and denoted using the symbol $[X]$, with X indicating the given constant quantity. The following processes are encountered most often:

Name of the process	**Constant quantity**	**Symbol**
Isothermal	temperature	$[T]$
Isobaric	pressure	$[p]$
Isochoric	volume	$[V]$
Adiabatic	heat	[ad]
Isentropic	entropy	$[S]$
Isenthalpic	enthalpy	$[H]$
Polytropic	heat capacity	$[C]$

Example

In the initial state, a system of a constant volume has a temperature of 300 K and a pressure of 150 kPa. A certain process takes place in the system, and in the final state the system's temperature is 320 K and its pressure is 150 kPa. Does the process take place under a constant thermodynamic quantity?

Solution

The initial and the final temperatures of the system are different. Consequently, the process cannot be isothermal. Both the initial pressure and the final pressure are identical. In this case it may be, but not necessarily is, an isobaric process. The specification does not allow us to find out whether pressure changes in any way in the course of the process. However, the process is definitely an isochoric one because the system has a constant (i.e. unchanging) volume.

1.4.6 Cyclic process

A cyclic process is such at which the final state of the system is identical with its initial state. In a cyclic process, changes of thermodynamic quantities are zero.

Note: Heat and work are not thermodynamic quantities and therefore they are not zero during a cyclic process.

Example

Let our system be a cube of ice with a mass of 1 g, and the initial state be a temperature of -10 °C and a pressure of 100 kPa. The sequence of processes taking place in the system was as follows: the cube was heated to 0 °C at which it melted. The liquid water was electrolyzed at this temperature. The resulting mixture of hydrogen and oxygen was expanded to 200 Pa and ignited. The water vapour resulting from the reaction had a temperature of 500 °C at the end of the reaction. It was then cooled to -10 °C and compressed to 100 kPa. In the course of compression desublimation (snowing) occurred, and the system returned to its initial thermodynamic state. A cyclic process took place.

1.5 Some basic and derived quantities

1.5.1 Mass m

U *Main unit:* kg.

1.5.2 Amount of substance n

U *Main unit:* mol. 1 mol is $\boldsymbol{N}_\mathbf{A}$ of particles (atoms, molecules, ions. . .), where $\boldsymbol{N}_\mathbf{A} = 6.022025 \times 10^{23}$ is the **Avogadro constant**.

1.5.3 Molar mass M

U *Main unit:* kg mol^{-1}. The molar mass is the mass of one mole of particles. The relation between the amount of substance, mass and molar mass is

$$n = m/M\,. \tag{1.3}$$

This relation applies to both a pure substance and a mixture. The molar mass of a mixture can be calculated using the relation

$$M = \sum_{i=1}^{k} x_i M_i\,, \tag{1.4}$$

where M_i is the molar mass of component i, and x_i is its mole fraction [see **1.6.1**]

1.5.4 Absolute temperature T

U *Main unit:* K.

> *Note:* Temperature given in °C is denoted t (t = T − 273.15)

1.5.5 Pressure p

U *Main unit:* Pa.
Older units: bar (1 bar = 10^5 Pa), atm (1 atm = 101 325 Pa), torr (760 torr = 101 325 Pa).

1.5.6 Volume V

U *Main unit:* m^3.
Older units: litre ($1\,\mathrm{l} = 1\,\mathrm{dm}^3$).

1.6 Pure substance and mixture

We speak about a pure substance (chemical individual) when only one kind of molecules is present in a system. When a system contains more kinds of molecules, we speak about a mixture. The substances of which a mixture is composed are its **components**. According to the number of components we distinguish binary mixtures consisting of only two components, ternary mixtures consisting of three components, quarternary mixtures consisting of four components, etc. In addition to thermodynamic quantities used to describe pure substances (temperature, pressure, volume), the description of a mixtures also requires knowledge of the composition of all its phases, which may be expressed using one of the quantities listed below.

1.6.1 Mole fraction of the i^{th} component x_i

Definition

$$x_i = \frac{n_i}{n}\,, \tag{1.5}$$

where n_i is the amount of substance of component i, n is the total amount of substance of all components

$$n = \sum_{j=1}^{k} n_j, \tag{1.6}$$

and k is the number of components in the mixture.

U *Main unit:* dimensionless quantity.

It follows from the definition (1.5) that the sum of mole fractions equals one

$$\sum_{i=1}^{k} x_i = 1\,. \tag{1.7}$$

Note: Instead of mole fractions, the expression mole percent is often used, meaning 100-times the mole fractions.

Example

A binary mixture contains 4 moles of substance A and 6 moles of substance B. Express the composition of the mixture using mole fraction and mole percent.

Solution

According to (1.6), the amount of substance in the mixture is $n = 4+6 = 10$ mol. From (1.5) we get $x_A = 4/10 = 0.4$, $x_B = 6/10 = 0.6$. The mixture contains 40 mole percent of substance A, and 60 mole percent of substance B.

A mixture in which mole fractions of all components have the same value is called an equimolar mixture.

Example

Calculate the mole fractions of an equimolar mixture of hydrogen and oxygen, and the mole fractions of an equimolar mixture of nitrogen, oxygen and argon.

Solution

It follows from the definition of an equimolar mixture that

$$x_{\mathsf{H_2}} = x_{\mathsf{O_2}} = \frac{1}{2}$$

and

$$x_{\mathsf{N_2}} = x_{\mathsf{O_2}} = x_{\mathsf{Ar}} = \frac{1}{3}\,.$$

1.6.2 Mass fraction w_i

Definition

$$w_i = \frac{m_i}{m}\,, \tag{1.8}$$

where m_i is the mass of component i, and $m = \sum_{i=1}^{k} m_i$ is the mass of the mixture.

U *Main unit:* dimensionless quantity.

The sum of mass fractions of all components equals one

$$\sum_{i=1}^{k} w_i = 1\,. \tag{1.9}$$

We convert mole and mass fractions using the relations:

$$x_i = \frac{w_i/M_i}{\sum\limits_{j=1}^{k} w_j/M_j}\,, \qquad w_i = \frac{x_i M_i}{\sum\limits_{j=1}^{k} x_j M_j}\,. \tag{1.10}$$

Example

A mixture contains 5 g of substance A with a molar mass $M_A = 25\ \mathrm{g\,mol^{-1}}$, and 15 g of substance B with a molar mass $M_B = 75\ \mathrm{g\,mol^{-1}}$. Calculate the mass fractions and the mole fractions.

Solution

Substituting into (1.8) gives

$$w_\mathrm{A} = \frac{5}{5+15} = 0.25\,, \qquad w_\mathrm{B} = \frac{15}{5+15} = 0.75\,.$$

We calculate the mole fractions using the first of equations (1.10)

$$x_\mathrm{A} = \frac{0.25/25}{0.25/25 + 0.75/75} = 0.5\,, \qquad x_\mathrm{B} = \frac{0.75/75}{0.25/25 + 0.75/75} = 0.5\,.$$

1.6.3 Volume fraction ϕ_i

Definition

$$\phi_i = \frac{V_i^\bullet}{\sum\limits_{j=1}^{k} V_j^\bullet} = \frac{x_i V_{m,i}^\bullet}{\sum\limits_{j=1}^{k} x_j V_{m,j}^\bullet}\,, \tag{1.11}$$

where $V_i^\bullet$ and $V_{m,i}^\bullet$ are the volume and the molar volume of a pure substance i in the same state of matter as the mixture.

U *Main unit:* dimensionless quantity.

S *Symbols:* The symbol $X_j^\bullet$ will be used to denote thermodynamic quantity X of a pure substance j at the temperature and pressure of the mixture, with the pure substance being in the same state of matter as the mixture (i.e. if the mixture is liquid, $X_j^\bullet$ will be a thermodynamic quantity of a pure liquid substance). If the mixture is in the solid state, the symbol $^\bullet$ will denote a pure substance in the same crystalline form as the mixture.

The sum of the volume fractions of all components equals one.

$$\sum_{i=1}^{k} \phi_i = 1\,. \tag{1.12}$$

Note: For a mixture of ideal gases, the volume fraction equals the mole fraction

$$\phi_i = x_i\,.$$

Example

Calculate the volume fractions in a solution prepared by mixing 40 cm^3 of ethanol and 160 cm^3 of water. Is it possible to calculate the volume of the solution based on this data?

Solution

From (1.11) we obtain

$$\phi_\text{water} = \frac{160}{160+40} = 0.8\,, \qquad \phi_\text{ethanol} = \frac{40}{160+40} = 0.2.$$

The volume of a solution cannot be calculated using the volumes of pure substances, but it has to be measured. In the considered mixture of ethanol and water it will be smaller than $160 + 40 = 200$ cm^3.

1.6.4 Amount-of-substance concentration c_i

Definition

$$c_i = n_i/V \,, \tag{1.13}$$

where V is the total volume of the mixture.

U *Main unit:* $\mathrm{mol\,m^{-3}}$. In a pure component this quantity is identical with the amount-of-substance density.

> *Note:* The expression amount-of-substance concentration is usually abbreviated to amount concentration or substance concentration. The same applies to the expression amount-of-substance density. When there is no risk of ambiguity, the word concentration may be used alone. In older literature, the term molarity may be found indicating the same quantity (using the unit $\mathrm{mol\,dm^{-3}}$).

Example

A mixture of substances with a volume of $5\,\mathrm{dm^3}$ contains 56 g of nitrogen. Calculate its concentration.

Solution

The amount of substance of nitrogen is

$$n_{\mathrm{N_2}} = \frac{56}{28} = 2\,\mathrm{mol}\,.$$

From equation (1.13) we obtain

$$c_{\mathrm{N_2}} = \frac{2}{5} = 0.4\,\mathrm{mol\,dm^{-3}}\,.$$

1.6.5 Molality $\underline{m}_i$

Definition

$$\underline{m}_i = n_i/m_{\mathrm{solvent}} \tag{1.14}$$

U *Main unit:* mol kg^{-1}. This quantity is used mainly in connection with aqueous solutions of electrolytes.

Example

A total of 58.5 g of NaCl has been mixed with 500 g of water. Calculate the molality of sodium chloride given that you know its molar mass to be $M = 58.5\,\mathrm{g\,mol^{-1}}$.

Solution

By substituting into (1.14) we obtain

$$\underline{m}_{\mathrm{NaCl}} = \frac{58.5/58.5}{0.500} = 2\,\mathrm{mol\,kg^{-1}}.$$

The molality of the obtained solution is 2 mol kg^{-1}.

Chapter 2

State behaviour

The temperature, pressure, volume and amount of a pure substance are not independent. In a homogeneous system, any three of these quantities may be chosen, with the fourth being implicitly given. For instance, we may choose the amount of a given substance, the volume in which it is enclosed, and its temperature. The pressure as the fourth quantity is then implicitly given. The state behaviour of a substance (or, more accurately, the description of its state behaviour) is expressed by the relation between its temperature, pressure, volume and amount of substance. We obtain this relation either experimentally (i.e. we measure the state behaviour) or theoretically (i.e. we calculate the state behaviour).

The state behaviour of a homogeneous mixture is expressed by the relation between the temperature, pressure, volume and the amount of substance of its components. In a k-component mixture, we may choose any $(k + 2)$ of the $(k + 3)$ quantities, with the $(k + 3)^{rd}$ quantity being implicitly given. We may, e.g., choose the amount of a given mixture, its composition (i.e. $k - 1$ data), temperature and pressure. The volume is thus implicitly determined.

2.1 Major terms, quantities and symbols

2.1.1 Molar volume V_m and amount-of-substance (or amount) density c

Definition

$$V_m = V/n\,, \qquad c = 1/V_m\,. \tag{2.1}$$

U *Main unit:* $\mathrm{m^3\,mol^{-1}}$ for molar volume, and $\mathrm{mol\,m^{-3}}$ for amount density.

Example
A system containing 10 moles of nitrogen occupies a volume of 5 $\mathrm{dm^3}$. Calculate the molar volume of nitrogen and its amount density.

Solution
According to (2.1), the molar volume of nitrogen is $5\times10^{-3}/10 = 5\times10^{-4}$ $\mathrm{m^3\,mol^{-1}}$, its amount density is 2×10^3 $\mathrm{mol\,m^{-3}}$.

2.1.2 Specific volume v and density ρ

Definition

$$v = V/m\,, \qquad \rho = 1/v\,, \tag{2.2}$$

where V is the volume of a system and m is its mass.

U *Main unit:* $\mathrm{m^3\,kg^{-1}}$ for specific volume, $\mathrm{kg\,m^{-3}}$ for density.

Example
A system containing 500 g of carbon monoxide occupies a volume of 5 $\mathrm{dm^3}$. Calculate the specific volume and density of carbon monoxide.

Solution
According to formula (2.2), $v = 5\times10^{-3}/0.5 = 10^{-2}$ $\mathrm{m^3\,kg^{-1}}$, and $\rho = 1/v = 100$ $\mathrm{kg\,m^{-3}}$.

Molar and specific volumes and densities may be mutually converted using the relations

$$V_m = Mv\,, \quad c = \rho/M\,, \tag{2.3}$$

where M is the molar mass.

2.1.3 Compressibility factor z

Definition

$$z = \frac{pV}{n\boldsymbol{R}T}\,, \tag{2.4}$$

where $\boldsymbol{R}$ is the universal gas constant, $\boldsymbol{R} = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

U *Main unit:* dimensionless quantity. The compressibility factor of a pure substance is a function of temperature and pressure or temperature and molar volume. In mixtures, the compressibility factor is also a function of composition.

Example

At a temperature of 100 °C and a pressure of 27.6 MPa, two moles of carbon dioxide occupy a volume of 140.06 $\mathrm{cm^3}$. Calculate the compressibility factor.

Solution

From equation (2.4) we get

$$z = \frac{27.6\times10^6 \times 140.06\times10^{-6}}{2 \times 8.314 \times 373.15} = 0.6230\,.$$

2.1.4 Critical point

The term critical point relates to a group of three values $T_\mathrm{c}, p_\mathrm{c}, V_\mathrm{c}$, where

T_c is the **critical temperature**,

p_c is the **critical pressure**,

V_c is the **critical volume**.

At the critical point the properties of liquid and gas (vapour) coincide. The critical temperature is the highest temperature at which a pure substance may exist in the liquid state.

> *Note:* The critical volume is the *molar volume* at the critical point, with the subscript $_m$ usually left out for the sake of greater simplicity.

At the critical point we have

$$\left(\frac{\partial p}{\partial V_\mathrm{m}}\right)_T = 0\,, \qquad \left(\frac{\partial^2 p}{\partial V_\mathrm{m}^2}\right)_T = 0\,, \qquad \text{[critical point]}\,. \tag{2.5}$$

S *Symbols:* Equations (2.5) are to be understood as follows: $p = f(T, V_\mathrm{m})$ is differentiated with respect to V_m at a fixed T. The text in square brackets specifies the conditions under which the equations apply. In the above case, the equations apply at the critical point.

2.1.5 Reduced quantities

Definition

$$\text{reduced temperature} \qquad T_\mathrm{r} = \frac{T}{T_\mathrm{c}}\,, \tag{2.6}$$

$$\text{reduced pressure} \qquad p_\mathrm{r} = \frac{p}{p_\mathrm{c}}\,, \tag{2.7}$$

$$\text{reduced volume} \qquad V_\mathrm{r} = \frac{V_\mathrm{m} p_\mathrm{c}}{\boldsymbol{R} T_\mathrm{c}}\,. \tag{2.8}$$

U *Main unit:* dimensionless quantities.

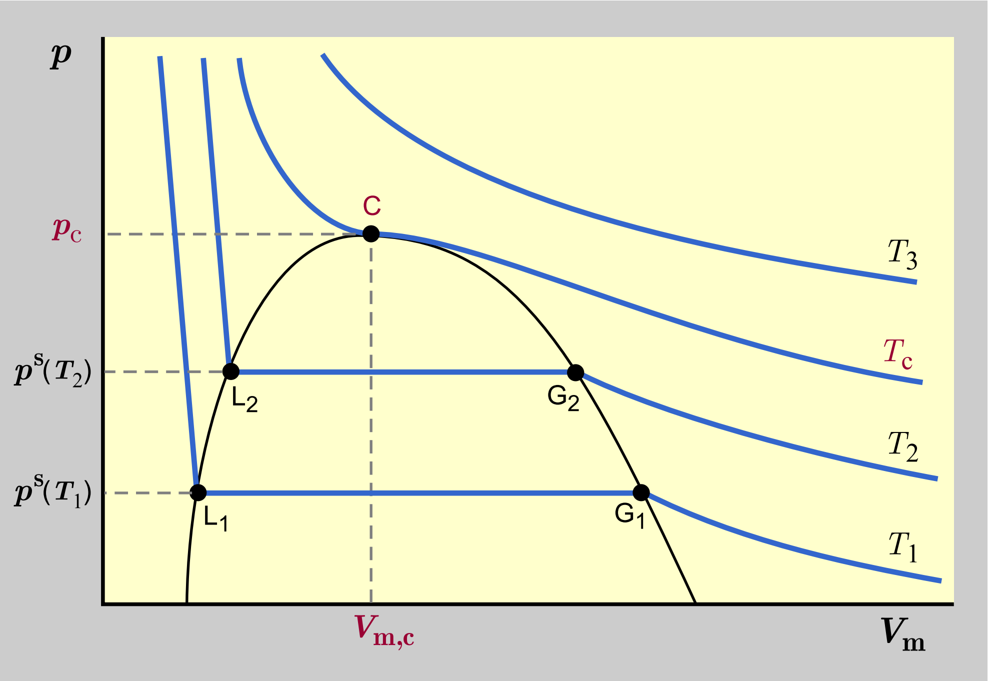
> *Note:* Note the different definition of the reduced volume (the definition (2.8) is used in a generalized diagram of compressibility factors).

2.1.6 Coefficient of thermal expansion α_p

Definition

$$\alpha_p = \frac{1}{V_\mathrm{m}}\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p = \left(\frac{\partial \ln V_\mathrm{m}}{\partial T}\right)_p\,. \tag{2.9}$$

U *Main unit:* K^{-1}.



Obr. 2.1: Dependence of pressure on the molar volume at a fixed temperature. The curves denoted T_1 through T_3 are isotherms. Isotherm T_3 is supercritical, extending over the whole region of gas. Isotherm T_c is critical, point C is the critical point, p_c is the critical pressure, and $V_{m,c} = V_c$ is the molar critical volume. The critical point C is an inflection point of the isotherm T_c. In addition, the tangent to the isotherm going through point C is parallel to the axis V_m. Isotherms T_1 and T_2 are subcritical, each of them consisting of a portion extending in gas and a portion extending in liquid. The curve $L_1L_2CG_2G_1$ separates the gaseous and liquid regions. Points G_1 and G_2 indicate the saturated vapour at temperatures T_1 and T_2 and at corresponding saturated pressures $p^s(T_1)$ and $p^s(T_2)$ Points L_1 and L_2 indicate saturated liquid at the same temperatures and pressures.

Example

Derive the relation for the coefficient of thermal expansion from the equation of state of an ideal gas (2.15).

Solution
From (2.15) it follows that $V_\mathrm{m} = \boldsymbol{R}T/p$ and

$$\alpha_p = \frac{p}{\boldsymbol{R}T}\frac{\boldsymbol{R}}{p} = \frac{1}{T}\,.$$

2.1.7 Coefficient of isothermal compressibility β_T

Definition[1]

$$\beta_T = -\frac{1}{V_\mathrm{m}}\left(\frac{\partial V_\mathrm{m}}{\partial p}\right)_T = -\left(\frac{\partial \ln V_\mathrm{m}}{\partial p}\right)_T\,. \tag{2.10}$$

U *Main unit:* Pa^{-1}.

Example
Derive the relation for the isothermal compressibility coefficient from the equation of state of an ideal gas (2.15).

Solution
From (2.15) we have $V_\mathrm{m} = \boldsymbol{R}T/p$, and

$$\beta_T = -\frac{p}{\boldsymbol{R}T}\left(-\frac{\boldsymbol{R}T}{p^2}\right) = \frac{1}{p}\,.$$

2.1.8 Partial pressure p_i

The partial pressure p_i of component i in a mixture of gases is defined by the relation

$$p_i = x_i p\,, \tag{2.11}$$

where x_i is the mole fraction of component i and p is the pressure of a mixture of gases.

U *Main unit:* Pa.

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[1] Sometimes the symbol κ_T is used.

2.2 Equations of state

2.2.1 Concept of the equation of state

The term equation of state is used for the relation between temperature, pressure, volume and amount of substance in an analytic form, i.e.

$$f(p, V, T, n) = 0\,. \tag{2.12}$$

Given that volume is an extensive quantity (see **1.3.1**), we can write the equation of state as a relation between three variables

$$\phi(p, V_{\mathrm{m}}, T) = 0\,. \tag{2.13}$$

Equations of state are usually written in the form

$$p = f(T, V_{\mathrm{m}}) \quad \text{or} \quad z = f(T, V_{\mathrm{m}}) \quad \text{or} \quad z = f(T, p)\,. \tag{2.14}$$

2.2.2 Equation of state of an ideal gas

$$p = n\boldsymbol{R}T/V \qquad \text{or} \qquad p = \boldsymbol{R}T/V_{\mathrm{m}} \qquad \text{or} \qquad z = 1\,. \tag{2.15}$$

> *Note:* If we use other than base units for p, V, T, n, then the gas constant $\boldsymbol{R}$ may have a value other than $8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

The following laws, historically preceding the equation of state of an ideal gas, led to relation (2.15).

- **Boyle's law**—at constant temperature and constant amount of substance we have

$$pV = \text{const}\ , \qquad [T, n]\,. \tag{2.16}$$

- **Gay-Lussac's law**—at constant pressure and constant amount of substance, the volume of a system is proportional to its absolute temperature

$$V = \text{const}\ T\,, \qquad [p, n]\,. \tag{2.17}$$

- **Avogadro's law**—molar volumes of different gases at the same temperature and pressure have the same values.

$$V_\mathrm{m} = \mathrm{const}\ , \qquad [p, T]\,. \tag{2.18}$$

S *Symbols:* The symbol $[X, Y, \ldots]$ denotes that the equation applies at constant $X, Y, \ldots$

2.2.3 Virial expansion

The virial expansion is an equation of state in which the compressibility factor is expressed in the form of a power series of $1/V_m$, or in the powers of c

$$\begin{aligned} z &= 1 + B(T)/V_\mathrm{m} + C(T)/V_\mathrm{m}^2 + \cdots \\ &= 1 + B(T)\,c + C(T)\,c^2 + \cdots\ . \end{aligned} \tag{2.19}$$

Quantities B, C, ... are called **virial coefficients**; B is the second virial coefficient, C is the third virial coefficient, etc.

S *Symbols:* By writing $B(T)$, $C(T)$ we indicate that in a pure substance, the virial coefficients are functions of temperature only (while in a mixture they also depend on composition).

2.2.4 Boyle temperature

The temperature at which the second virial coefficient is zero, $B = 0$, is called the Boyle temperature, T_B. At this temperature and in its vicinity, the approximation $z = 1$ (the equation of state of an ideal gas) is fulfilled with a high accuracy even at relatively high pressures. At temperatures $T < T_\mathrm{B}$, $B < 0$; at $T > T_\mathrm{B}$, $B > 0$.

Example

Calculate the Boyle temperature if the dependence of the second virial coefficient on temperature is $B = a - b/T$, where a, b are constants.

Solution

Given that $B = 0$, we have $T_\mathrm{B} = b/a$.

2.2.5 Pressure virial expansion

The pressure virial expansion is an equation of state in which the compressibility factor is expressed in the form of a powers series of p

$$z = 1 + \frac{p}{\boldsymbol{R}T}\left[B'(T) + C'(T)p + \cdots\right] . \qquad (2.20)$$

Quantities B', C',... are termed the pressure virial coefficients, and they are functions of temperature. The relation between the virial and pressure virial coefficients is given by

$$\begin{aligned} B' &= B\,, && (2.21)\\ C' &= (C - B^2)/(\boldsymbol{R}T)\,, && (2.22)\\ &\vdots \end{aligned}$$

Example

The second virial coefficient of ammonia at 298.15 K is $-261\,\mathrm{cm^3\,mol^{-1}}$. Calculate the molar volume and the compressibility factor of ammonia at this temperature and a pressure of 0.5 MPa. Assume that at the given temperature and pressure, the terms with higher virial coefficients in equation (2.20) are negligible.

Solution

According to the specification, equation (2.20) rearranges to

$$z = 1 + B'\frac{p}{\boldsymbol{R}T} .$$

Substituting the specified values (according to (2.21), B' equals the second virial coefficient) yields

$$z = 1 + 261\times10^{-6}\,\frac{0.5\times10^6}{8.314\times298.15} = 0.9473 .$$

The molar volume of ammonia is then calculated using equations (2.1) and (2.4)

$$V_\mathrm{m} = \frac{z\boldsymbol{R}T}{p} = \frac{0.9473\times8.314\times298.15}{0.5\times10^6} = 4.6966\times10^{-3}\,\mathrm{m^3\,mol^{-1}} .$$

2.2.6 Van der Waals equation of state

$$\begin{aligned} p &= \frac{n\boldsymbol{R}T}{V-nb} - a\left(\frac{n}{V}\right)^2 = \frac{\boldsymbol{R}T}{V_\mathrm{m}-b} - \frac{a}{V_\mathrm{m}^2}\,, \\ z &= \frac{V_\mathrm{m}}{V_\mathrm{m}-b} - \frac{a}{\boldsymbol{R}TV_\mathrm{m}}\,. \end{aligned} \tag{2.23}$$

Parameters a and b are the constants of the van der Waals equation of state. Their values depend on the kind of gas being described. They can be obtained from experimental data on state behaviour, or they can be estimated from the critical quantities of substances using the relations

$$a = \frac{27}{64}\,\frac{(\boldsymbol{R}T_\mathrm{c})^2}{p_\mathrm{c}}\,, \qquad b = \frac{1}{8}\,\frac{\boldsymbol{R}T_\mathrm{c}}{p_\mathrm{c}}\,, \tag{2.24}$$

which follow from equations (2.5) and (2.23).

For the second virial coefficient, the van der Waals equation yields

$$B = b - \frac{a}{\boldsymbol{R}T} = \frac{1}{8}\,\frac{\boldsymbol{R}T_\mathrm{c}}{p_\mathrm{c}}\left(1 - \frac{27}{8}\,\frac{T_\mathrm{c}}{T}\right)\,. \tag{2.25}$$

For the Boyle temperature, the van der Waals equation of state yields

$$T_\mathrm{B} = \frac{a}{\boldsymbol{R}b} = \frac{27}{8}\,T_\mathrm{c} = 3.375\,T_\mathrm{c}\,. \tag{2.26}$$

Example

Using the van der Waals equation of state calculate the pressure and compressibility factor of a substance whose critical temperature is 800 K and critical pressure is 8.314 MPa, at a temperature of 1000 K and a molar volume of 1100 $\mathrm{cm^3\,mol^{-1}}$.

Solution

We first estimate the constants a and b from the specified critical quantities, using equations (2.24)

$$a = \frac{27}{64}\,\frac{(8.314\times 800)^2}{8.314\times 10^6} = 2.2448\,\mathsf{Pa\,m^6\,mol^{-2}}, \quad b = \frac{8.314\times 800}{8\times 8.314\times 10^6} = 1\times 10^{-4}\,\mathsf{m^3\,mol^{-1}}\,.$$

The pressure is calculated from the first of equations (2.23)

$$p = \frac{8.314\times 800}{1.1\times 10^{-3} - 1\times 10^{-4}} - \frac{2.2448}{(1.1\times 10^{-3})^2} = 6.4588\times 10^6\,\mathsf{Pa}\,.$$

The compressibility factor can be calculated from the second of equations (2.23), or from the definition (2.4). The result is $z = 0.8545$.

2.2.7 Redlich-Kwong equation of state

$$\begin{aligned} p &= \frac{n\boldsymbol{R}T}{V-nb} - \frac{an^2}{T^{1/2}V(V+nb)} = \frac{\boldsymbol{R}T}{V_\mathrm{m}-b} - \frac{a}{T^{1/2}V_\mathrm{m}(V_\mathrm{m}+b)}\,, \\ z &= \frac{V_\mathrm{m}}{V_\mathrm{m}-b} - \frac{a}{\boldsymbol{R}T^{3/2}(V_\mathrm{m}+b)}\,. \end{aligned} \tag{2.27}$$

Parameters a and b are the constants of the Redlich-Kwong equation of state. Their values are different for every substance. They can be obtained from experimental data on state behaviour, or they can be estimated from the critical quantities of substances using the relations

$$a = \frac{1}{9(2^{1/3}-1)}\,\frac{\boldsymbol{R}^2T_\mathrm{c}^{5/2}}{p_\mathrm{c}} = 0.42748\,\frac{\boldsymbol{R}^2T_\mathrm{c}^{5/2}}{p_\mathrm{c}}\,, \tag{2.28}$$

$$b = \frac{2^{1/3}-1}{3}\,\frac{\boldsymbol{R}T_\mathrm{c}}{p_\mathrm{c}} = 0.08664\,\frac{\boldsymbol{R}T_\mathrm{c}}{p_\mathrm{c}}\,, \tag{2.29}$$

which follow from equations (2.5) and (2.27).

Note: The constants of the Redlich-Kwong's equation of state are not identical with the identically denoted constants of the van der Waals equation.

For the second virial coefficient, the Redlich-Kwong equation yields

$$B = 0.08664 \frac{\boldsymbol{R} T_\mathrm{c}}{p_\mathrm{c}} \left[1 - 4.93398 \left(\frac{T_\mathrm{c}}{T} \right)^{3/2} \right] . \tag{2.30}$$

For the Boyle temperature, the Redlich-Kwong equation gives

$$T_\mathrm{B} = 2.898\, T_\mathrm{c} . \tag{2.31}$$

2.2.8 Benedict, Webb and Rubin equation of state

$$\begin{aligned} p &= \frac{\boldsymbol{R}T}{V_\mathrm{m}} + \frac{\boldsymbol{R}TB}{V_\mathrm{m}^2} + \frac{\boldsymbol{R}TC}{V_\mathrm{m}^3} + \frac{a\alpha}{V_\mathrm{m}^6} + \frac{c(1+\gamma/V_\mathrm{m}^2)}{T^2 V_\mathrm{m}^3} \exp(-\gamma/V_\mathrm{m}^2) , \\ z &= 1 + \frac{B}{V_\mathrm{m}} + \frac{C}{V_\mathrm{m}^2} + \frac{a\alpha}{V_\mathrm{m}^5} + \frac{c(1+\gamma/V_\mathrm{m}^2)}{\boldsymbol{R}T^3 V_\mathrm{m}^2} \exp(-\gamma/V_\mathrm{m}^2) , \end{aligned} \tag{2.32}$$

where

$$B = B_0 - A_0/(\boldsymbol{R}T) - C_0/(\boldsymbol{R}T^3) , \; C = b - a/(\boldsymbol{R}T) .$$

The equation contains eight adjustable constants A_0, B_0, C_0, a, b, c, α, γ, which are obtained from experimental data on state behaviour.

2.2.9 Theorem of corresponding states

The theorem of corresponding states says that the compressibility factor is a function of reduced quantities $T_\mathrm{r}, p_\mathrm{r}$ or $T_\mathrm{r}, V_\mathrm{r}$ which is independent of the substance

$$z = f(T_\mathrm{r}, p_\mathrm{r}) \qquad \text{or} \qquad z = f(T_\mathrm{r}, V_\mathrm{r}) . \tag{2.33}$$

Based on experimental data on state behaviour of gases, a diagram of the compressibility factor dependence on reduced variables has been drawn allowing for convenient and generalized (i.e. independent of the substance) estimation of state behaviour. The theorem of corresponding states may be also applied in such a way that the sought for compressibility factor z_A of a substance A is determined using the compressibility factor z_R of a reference substance R whose state behaviour is known

$$z_A(T_r, p_r) = z_R(T_r, p_r)\,.$$

The compressibility factor of a reference substance for a given T_r and p_r is most often calculated using an equation of state. The results of this procedure are the better the more similar is the reference substance to the one under investigation.

Example

The compressibility factor of butane at a temperature of 523.15 K and a pressure of 13.25 MPa is $z = 0.6093$. At which temperature and pressure has butadiene the same compressibility factor? Data: the critical quantities of butane are $T_c = 425.14$ K, $p_c = 3.784$ MPa. The critical quantities of butadiene are $T_c = 425.0$ K, $p_c = 4.33$ MPa.

Solution

We calculate the reduced quantities of butane using equations (2.6) and (2.7)

$$T_r = \frac{523.15}{425.14} = 1.2305\,,\; p_r = \frac{13.25}{3.748} = 3.5016\,.$$

The reduced quantities of butadiene at the same compressibility factor are the same. The temperature and pressure at which the compressibility factor of butadiene equals 0.6093 are

$$T = T_r T_c = 1.2305 \times 425.0 = 522.9\,\mathrm{K}\,,\; p = p_r p_c = 3.5016 \times 4.33 = 15.162\,\mathrm{MPa}\,.$$

2.2.10 Application of equations of state

- The *equation of state of an ideal gas* (2.15)—This equation is commonly applied for gases at low reduced pressures and high reduced temperatures. Its strengths consist in its simplicity and universal character (no constants characterizing the substance are needed). The accuracy of the equation depends on the kind of substance, temperature and pressure. For gases at a normal boiling point (pressure 101 kPa), e.g., the error in volume determination is about 5 percent.

- *Virial expansion* (2.19)—This is a theoretically grounded equation of state, which means that accurate relations between the virial coefficients and intermolecular forces are known. In practice it is applied in such a way that the virial coefficients are substituted by empirical relations (usually polynomials in $1/T$). With a large number of constants this equation allows for a good description of the behaviour or both gases and liquids.
- *Pressure virial expansion* (2.20)—This equation is usually applied only with the second virial coefficient. In this case it is used in the same range as the equation of state of an ideal gas, but it provides more accurate results.
- *Van der Waals equation of state* (2.23)—Its importance is only historical, it is usually not applied in practice. Its simplicity predetermines it for use in teaching.
- *Redlich-Kwong equation of state* (2.27)—One of the most popular equations of state for gases. Some of its modifications are applied in current practice.
- *Benedict, Webb and Rubin equation of state* (2.32)—One of the best equations of state for the gas range. However, it is little accurate in the range of liquid, where it is substituted by its modifications with a larger number of constants (20 and even more).
- *The theorem of corresponding states* (2.33)—The two-parameter theorem presented here (the two parameters are T_c and p_c) allows for estimating state behaviour with an error of about 5 percent.

2.3 State behaviour of liquids and solids

The above equations of state offer little accuracy in describing the state behaviour of liquids. Equations of state with a large number of constants (20 and more) are used to describe the behaviour of fluids in a broad range of temperatures and pressures. When we are interested only in a liquid at not very high pressures, it is easier to use the following procedures.

2.3.1 Description of state behaviour using the coefficients of thermal expansion α_p and isothermal compressibility β_T.

For not very great differences in temperature and pressure, we may consider α_p and β_T for liquids and solids to be constant, and by integrating the definitions (2.9) and (2.10) we obtain

$$\ln \frac{V_{\mathrm{m},2}}{V_{\mathrm{m},1}} = \alpha_p (T_2 - T_1)\,, \tag{2.34}$$

$$\ln \frac{V_{\mathrm{m},1}}{V_{\mathrm{m},2}} = \beta_T (p_2 - p_1)\,. \tag{2.35}$$

Example

The molar volume of liquid heptane at a temperature of 20 °C and a pressure of 101 325 Pa is $V_\mathrm{m} = 146.6\,\mathrm{cm^3\,mol^{-1}}$, and its isothermal compressibility is $\beta_T = 1.4\times10^{-9}\,\mathrm{Pa^{-1}}$. What is the molar volume of heptane at the same temperature and a pressure of 2 MPa?

Solution

Substituting into equation (2.35) gives $V_{\mathrm{m},2} = 146.6\exp[-1.4\times10^{-9}(2\times10^6 - 101325)] = 146.2\,\mathrm{cm^3\,mol^{-1}}$.

2.3.2 Rackett equation of state

$$V_\mathrm{m}^{(\mathrm{l})} = V_\mathrm{c} z_\mathrm{c}^{(1-T/T_\mathrm{c})^{2/7}} \quad \text{[saturated liquid]} \tag{2.36}$$

where z_c is the compressibility factor at the critical point.

S *Symbols:* The superscript (l) denotes the liquid phase.

Note: This equation is suitable for estimating the temperature dependence of the molar volume of a saturated liquid. Saturated liquid is such that at a given temperature is in equilibrium with its vapour (i.e. at boiling, for more information see **7.1.4**). The pressure of a saturated liquid (see **7.1.7**) is the lowest pressure at which a substance may be in the liquid (equilibrium) state at a given temperature. If we want to find the molar volume of a liquid at a pressure higher than that of a saturated liquid, we may use the isothermal compressibility coefficient β_T for the conversion (see (2.35)).

Example

Using the Rackett equation estimate the molar volume and density of liquid methane when boiling at a temperature of 150 K. Data: T_c= 190.55 K, p_c = 4.604 MPa, V_c = 99 cm^3 mol^{-1}.

Solution

Substituting into (2.36) yields

$$V_\mathrm{m}^{(\mathrm{l})} = 99\times10^{-6}\left(\frac{4.604\times10^6\times99\times10^{-6}}{8.314\times190.55}\right)^{(1-150/190.55)^{2/7}} = 44.45\times10^{-6}\ \mathrm{m^3\,mol^{-1}}\,.$$

The density is calculated from (2.3) and (2.1)

$$\rho = \frac{M}{V_\mathrm{m}} = \frac{16\times10^{-3}}{44.45\times10^{-6}} = 360\ \mathrm{kg\,m^{-3}}\,.$$

2.3.3 Solids

The volume of a solid substance is little dependent on temperature and pressure. This dependence is usually ignored, or the volume is calculated using equations (2.34) and (2.35).

2.4 State behaviour of mixtures

We may estimate the state behaviour of gaseous mixtures based on the knowledge of the state behaviour of their pure components using the following methods.

2.4.1 Dalton's law

According to Dalton's law, the pressure of a k-component mixture at temperature T, volume V, and amount of substance $n = \sum_{i=1}^{k} n_i$ equals the sum of the pressures of its individual pure components

$$p(T, V, n) = \sum_{i=1}^{k} p(T, V, n_i) = p(T, V, n_1) + p(T, V, n_2) + \cdots + p(T, V, n_k)\,, \tag{2.37}$$

where $p(T, V, n_i)$ is the pressure of n_i moles of a pure substance i at temperature T and volume V.

Dalton's law applies exactly for an ideal gas. The pressure of a pure substance equals the partial pressure p_i of component i in the mixture.

$$p(T, V, n_i) = p_i \equiv p x_i\,. \tag{2.38}$$

Dalton's law applies only approximately for real gases.

Example

At a certain temperature, the pressure in an autoclave (a system of a fixed volume) containing 2 moles of substance A equals 2.55 MPa. At the same temperature, the pressure in the same autoclave containing 3 moles of substance B equals 4.05 MPa. Using Dalton's law estimate the pressure in the same autoclave containing a mixture consisting of 2 moles of substance A and 3 moles of substance B.

Solution

It follows from the specification that $p(T, V, n_{\mathrm{A}}) = 2.55$ MPa, and $p(T, V, n_{\mathrm{B}}) = 4.05$ MPa, where V is the volume of the autoclave and $T$is the considered temperature. For the pressure of the mixture we have from equation (2.38) $p = 2.55 + 4.05 = 6.60$ MPa

2.4.2 Amagat's law

According to Amagat's law, the volume V, the molar volume V_m and the compressibility factor z of a mixture are given by

$$V = \sum_{j=1}^{k} V_j^\bullet \,, \qquad V_\mathrm{m} = \sum_{j=1}^{k} x_j V_{\mathrm{m},j}^\bullet \,, \qquad z = \sum_{j=1}^{k} x_j z_j^\bullet \,, \tag{2.39}$$

where $V_j^\bullet = V_j^\bullet(T, p, n_j)$ is the volume, $V_{\mathrm{m},j}^\bullet = V_{\mathrm{m},j}^\bullet(T, p)$ is the molar volume, and $z_j^\bullet = z^\bullet(T, p)$ is the compressibility factor of a pure substance j at the temperature and pressure of the mixture and in the same state of matter as the mixture.

If pure gases obey the equation of state of an ideal gas, we must have

$$V_i^\bullet = V x_i \,, \tag{2.40}$$

where V is the volume of the mixture and x_i is the mole fraction of substance i in the mixture.

Example

At a temperature of 25 °C and a pressure of 101 325 Pa, the molar volume of water is 18.07 $\mathrm{cm^3\,mol^{-1}}$, and the molar volume of methanol is 40.73 $\mathrm{cm^3\,mol^{-1}}$. Using Amagat's law, estimate the molar volume of a mixture containing 2 moles of water and 5 moles of methanol at the same temperature and pressure.

Solution

The mole fractions of the components in the mixture are

$$x_{\mathrm{H_2O}} = \frac{2}{2+5} = \frac{2}{7} \,, \quad x_\mathrm{methanol} = \frac{5}{7} \,.$$

We estimate the molar volume of the mixture using the second of equations (2.39).

$$V_\mathrm{m} = \frac{2}{7}\,18.07 + \frac{5}{7}\,40.73 = 34.26\,\mathrm{cm^3\,mol^{-1}} \,.$$

2.4.3 Ideal mixture

A mixture that obeys Amagat's law at all temperatures and pressures is defined as an **ideal mixture**. It often serves as a standard state used to calculate thermodynamic quantities of real mixtures. [see **6.1**].

Note: Amagat's law can be applied to both gaseous and liquid mixtures, and to mixtures in the solid state.

2.4.4 Pseudocritical quantities

The theorem of corresponding states **2.2.9** can be also used for mixtures if we substitute the critical quantities by **pseudocritical** quantities. Pseudocritical quantities of a mixture are calculated from the critical quantities of its components. The simplest relations were suggested by Kay:

$$T'_{\mathrm{c}} = \sum_{j=1}^{k} x_j T_{\mathrm{c},j}\,, \qquad p'_{\mathrm{c}} = \sum_{j=1}^{k} x_j p_{\mathrm{c},j}\,, \qquad V'_{\mathrm{c}} = \sum_{j=1}^{k} x_j \boldsymbol{R} T_{\mathrm{c},j}/p_{\mathrm{c},j}\,. \tag{2.41}$$

Example

The critical temperature and pressure of substance A are given as $T_{\mathrm{c}} = 400\,\mathrm{K}$, $p_{\mathrm{c}} = 4\,\mathrm{MPa}$, and those of substance B as $T_{\mathrm{c}} = 200\,\mathrm{K}$, $p_{\mathrm{c}} = 6\,\mathrm{MPa}$. Calculate the pseudocritical temperature, pseudocritical pressure and pseudocritical volume of a mixture containing 40 moles percent of substance A.

Solution

We substitute into equations (2.41), where the mole fraction of substance A is 0.4, and that of substance B is 0.6.

$$T'_{\mathrm{c}} = 0.4 \times 400 + 0.6 \times 200 = 280\,\mathrm{K}\,,$$

$$p'_{\mathrm{c}} = 0.4 \times 4 + 0.6 \times 6 = 5.2\,\mathrm{MPa}\,,$$

$$V'_{\mathrm{c}} = 0.4\,\frac{8.314 \times 400}{4} + 0.6 \times \frac{8.314 \times 200}{2} = 498.84\,\mathrm{cm^3\,mol^{-1}}\,.$$

2.4.5 Equations of state for mixtures

The state behaviour of mixtures can be described using the same equations of state as those applied when describing the behaviour of pure fluids. In this case, the constants in the equations depend on composition. These constants are usually estimated using the constants of pure substances. This procedure is called the **method of constants combination**.

The following estimates are used for the constants a and b in the Van der Waals (2.23) and the Redlich-Kwong (2.27) equations:

$$a = \left(\sum_{j=1}^{k} x_j a_j^{1/2}\right)^2 , \qquad b = \sum_{j=1}^{k} x_j b_j , \tag{2.42}$$

where $a_j$and b_j are the respective constants of pure substances.

Example
Let the constants in the van der Waals equation for a pure substance A be:
$a_\mathrm{A} = 0.36\,\mathrm{Pa\,m^6\,mol^{-2}}$, $b_\mathrm{A} = 40\times10^{-6}\,\mathrm{m^3\,mol^{-1}}$, and for a pure substance B
$a_\mathrm{B} = 0.64\,\mathrm{Pa\,m^6\,mol^{-2}}$, $b_\mathrm{B} = 70\times10^{-6}\,\mathrm{m^3\,mol^{-1}}$.
Calculate the constants of an equation for an equimolar mixture of substances A and B.

Solution
An equimolar mixture contains the same amount of substance A and B. Hence, the mole fractions of the mixture are $x_A = \frac{1}{2}$, $x_B = \frac{1}{2}$. The constants of the mixture are calculated using equations (2.42)

$$a = \left(\frac{1}{2}\,0.36^{1/2} + \frac{1}{2}\,0.64^{1/2}\right)^2 = 0,49\,\mathrm{Pa\,m^6\,mol^{-2}}$$

$$b = \frac{1}{2}\,40.10\times10^{-6} + \frac{1}{2}\,70.10\times10^{-6} = 55.10\times10^{-6}\,\mathrm{m^3\,mol^{-1}}\,.$$

2.4.6 Liquid and solid mixtures

The volume or density of these mixtures can be estimated relatively easily and with a relatively good accuracy (an error around 1 percent) using Amagat's law (2.39).

Chapter 3

Fundamentals of thermodynamics

3.1 Basic postulates

Thermodynamics is a branch of science based on six postulates which ensued from the generalization of observed and experimental facts. The first postulate relates to the transition of a system to the state of equilibrium [see **1.4.2**]. The second postulate states that the internal energy of a system is an extensive quantity. The remaining four postulates are, for historical reasons, called the laws of thermodynamics.

3.1.1 The zeroth law of thermodynamics

When two systems are in thermal equilibrium, i.e. no heat flows from one system to the other during their thermal contact, then both systems have the same temperature. If system A has the same temperature as system B and system B has the same temperature as system C, then system A also has the same temperature as system C.

Note: The zeroth law of thermodynamics is sometimes called the postulate on the existence of temperature as a thermodynamic quantity. It allows us to find out whether two systems that are not in thermal contact have the same temperature.

Example

Let us consider two students and call one of them system A and the other system C. Find out whether both of them have the same temperature without bringing them to any thermal contact.

Solution

We use a thermometer as system B. We bring student A and student C in thermal contact with the thermometer one by one, and then compare the measured values.

3.1.2 The first law of thermodynamics

There is a function of state called **internal energy** U. For its total differential $\mathrm{d}U$ we write

$$\mathrm{d}U = đQ + đW\,, \tag{3.1}$$

where the symbols $đQ$ and $đW$ are not total differentials but represent infinitesimal values of heat Q and work W supplied to the system.

U *Main unit:* J

Note: Equation (3.1) does not apply to open systems. Extension of the first law to these systems is covered in section **6.4.1**.

The integral form of equation (3.1) is

$$U = Q + W + \text{const} \tag{3.2}$$

Neither the integration constant nor the value of U in a given thermodynamic state can be obtained by any experimental method. Experimentally available are only changes in the internal energy ΔU on the system's transition from one state to another [see **3.2.8**].

$$\Delta U = Q + W\,. \tag{3.3}$$

Example

A closed system performed work of 400 J, with 1000 J of energy in the form of heat supplied to it. How did the system's internal energy change?

Solution

If the system *performed* work, then, according to usage **1.2**, the work $W = -400$ J. Hence the change in the internal energy is

$$\Delta U = Q + W = 1000 + (-400) = 600\,\mathrm{J}\,.$$

If a system exchanges only reversible volume work with its surroundings during a thermodynamic process [see **4.1.1**], then

$$\mathrm{d}U = đQ - p\mathrm{d}V\,. \tag{3.4}$$

If this process is isochoric, $\mathrm{d}V = 0$. The change in the system's internal energy then equals the heat exchanged between the system and its surroundings

$$\Delta U = Q\,, \qquad [V]\,. \tag{3.5}$$

It follows from the first law of thermodynamics that it is impossible to construct any **perpetual motion machine of the first type**—a hypothetical machine doing work cyclically without receiving any energy from the surroundings. There is a simple proof of this fundamental assertion: since the first law of thermodynamics postulates that internal energy is a function of state, we must have for a cyclic process

$$\oint \mathrm{d}U = 0.$$

If a system does not exchange any heat with its surroundings ($đQ = 0$), we obtain from equation (3.1)

$$W = \oint \mathrm{d}W = 0.$$

Hence, the work done is zero.

S *Symbols:* The symbol $\oint$ is used to denote a loop integral (the initial and the end point are identical).

3.1.3 Second law of thermodynamics

There is a function of state called **entropy** S. For its total differential $\mathrm{d}S$ we write

$$\mathrm{d}S = \frac{đQ}{T}\,, \qquad [\text{reversible process}]\,, \tag{3.6}$$

$$\mathrm{d}S \;>\; \frac{đQ}{T}\,, \qquad [\text{irreversible process}]\,. \tag{3.7}$$

U *Main unit:* J K^{-1}

Entropy is defined by equation (3.6) up to the integration constant. The second law of thermodynamics can be used only to calculate entropy changes during reversible processes and not values in a given states.

It follows from the second law of thermodynamics that it is impossible to construct a **perpetual motion mechanism of the second type**—a hypothetical cyclically working machine that receives heat from its surroundings and converts it into work without any losses.

Example

Prove that entropy increases during irreversible processes in an adiabatically isolated system.

Proof

In an adiabatic process $đQ = 0$. By substituting for $đQ$ into the inequality (3.7) we obtain $\mathrm{d}S > 0$. This shows that entropy increases.

Note: Entropy is the degree of disorder in the movement of molecules making up a thermodynamic system. The higher the disorder, the higher is the system's entropy. For example, the entropy of a gas is higher than the entropy of a crystal at the same temperature and pressure.

3.1.4 The third law of thermodynamics

At a temperature of 0 K, the entropy of a pure substance in its most stable crystalline form is zero

$$\lim_{T\to 0} S = 0\,. \tag{3.8}$$

This postulate supplements the second law of thermodynamics by defining the natural referential value of entropy. Equation (3.8) allows for the calculation of entropy in a given thermodynamic state of a system [see **3.2.8** and **3.5.5**].

3.1.4.1 Impossibility to attain a temperature of 0 K

The third law of thermodynamics implies that a temperature of 0 K cannot be attained by any process with a finite number of steps.

3.2 Definition of fundamental thermodynamic quantities

T, p, V, n, U, S as defined in the preceding sections represent basic thermodynamic functions. In this section we will define further basic thermodynamic functions: enthalpy, Helmholtz energy, Gibbs energy, heat capacities and fugacity.

3.2.1 Enthalpy

Enthalpy H is a function of state defined by the relation

$$H = U + pV\,. \tag{3.9}$$

U *Main unit:* J.

> *Note:* Similarly as internal energy, enthalpy is defined up to the additive constant.

If a system exchanges only heat and reversible volume work with its surroundings during a thermodynamic process [see **4.1.1**], we have

$$\mathrm{d}H = \text{đ}Q + V\,\mathrm{d}p\,. \tag{3.10}$$

If this process is isobaric ($\mathrm{d}p = 0$), the change in the enthalpy of a system is equal to the heat supplied to the system

$$\Delta H = Q\,, \qquad\qquad [p]\,. \tag{3.11}$$

Example

A system containing 5 moles of an ideal gas was heated from temperature $T_1 = 300$ K to temperature $T_2 = 400$ K. The internal energy of the gas increased by $\Delta U = 800$ J. How did the enthalpy of the system change?

Solution

It follows from the definition (3.9) that

$$\Delta H = \Delta U + \Delta(pV)\,,$$

where $\Delta(pV) = p_2V_2 - p_1V_1$. For an ideal gas $pV = n\boldsymbol{R}T$. Then

$$\Delta H = \Delta U + n\boldsymbol{R}\Delta T = 800 + 5 \times 8.314 \times (400 - 300) = 4957\ \mathrm{J}\,.$$

3.2.2 Helmholtz energy

The Helmholtz energy F is a function of state defined by the relation

$$F = U - TS\,. \tag{3.12}$$

U *Main unit:* J.

Note: The Helmholtz energy is defined up to the additive constant, just like internal energy.

The change in the Helmholtz energy ΔF during a reversible isothermal process is equal to the work supplied to the system

$$\Delta F = W\,, \qquad [T,\ \text{reversible process}]\,. \tag{3.13}$$

Example

During a certain isothermal process, internal energy changed by ΔU and entropy by ΔS. Derive the relation for the change in the Helmholtz energy. Is it possible to calculate the change in the Helmholtz energy during a non-isothermal process if in addition to ΔU and ΔS we also know the initial and final temperatures?

Solution

For an isothermal process we obtain from (3.12)

$$\Delta F = \Delta U - \Delta(TS) = \Delta U - T\Delta S, \quad [T]\,.$$

For a non-isothermal process we have

$$\Delta F = \Delta U - \Delta(TS) = \Delta U - T_2 S_2 + T_1 S_1\,.$$

Since the values of entropy in the initial and final states, $S_1\,, S_2$, are not specified and we only know that $\Delta S = S_2 - S_1$, the change in the Helmholtz energy cannot be calculated.

3.2.3 Gibbs energy

The Gibbs energy (or the Gibbs function) G is a function of state defined by the relation

$$G = H - TS\,. \tag{3.14}$$

U *Main unit:* J.

Note: The Gibbs energy is defined up to the additive constant, just like internal energy.

Example

During a certain thermodynamic process, a system passed from its initial state defined by the values of volume V_1 and pressure p_1 to its final state defined by the values p_2 and V_2. The change in the Helmholtz energy was ΔF. Calculate the change in the Gibbs energy.

Solution

From the definitions (3.9), (3.12) and (3.14) for H, F, and G we obtain

$$G = H - TS = U + pV - TS = F + pV\,,$$

from which it follows:

$$\Delta G = \Delta F + \Delta(pV) = \Delta F + p_2 V_2 - p_1 V_1\,.$$

The change in the Gibbs energy ΔG during a reversible isothermal and isobaric process is equal to other than volume work, W_{other}, supplied to the system

$$\Delta G = W_{\mathrm{other}} \equiv W - W_{\mathrm{vol}} = W + p\Delta V\,, \qquad [T,\ p,\ \text{reversible process}]\,. \tag{3.15}$$

Example

The change in the Gibbs energy during the oxidation of one mole of glucose, according to the reaction

$$\mathrm{C_6H_{12}O_6} + 6\,\mathrm{O_2} = 6\,\mathrm{CO_2} + 6\,\mathrm{H_2O}$$

is $\Delta G = -2870$ kJ mol^{-1}. How high can a person weighing 75 kg climb if he or she has eaten one mole (186 g) of glucose? The biological efficiency is 25%.

Solution

In our example, W_{other} is equal to mechanical work needed for lifting a load to a height h

$$W_{\mathrm{other}} = -mgh\,,$$

where m is the mass of the load and g is the gravitational acceleration. If we project a human body as an isothermal and isobaric system in which reversible processes occur and which does not perform any volume work, then equation (3.15) leads us to

$$\Delta G = -mgh \quad \longrightarrow \quad h = -\frac{\Delta G}{mg} = \frac{-2\,870\,000}{75 \times 9.8} = 3905\,\mathrm{m}\,.$$

We obtain the real height by multiplying the result by the biological efficiency,

$$3905 \times 0.25 = 976\,\mathrm{m}\,.$$

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3.2.4 Heat capacities

The heat capacity C for a given process is defined by the following relation

$$C = \left(\frac{đ\,Q}{\mathrm{d}\,T}\right)_{\text{process}} . \tag{3.16}$$

U *Main unit:* J K^{-1}.

The isochoric heat capacity, C_V, and the isobaric heat capacity, C_p, are defined by the relations

$$C_V = \left(\frac{đQ}{\mathrm{d}T}\right)_{\text{izochoric}} = \left(\frac{\partial U}{\partial T}\right)_V , \tag{3.17}$$

$$C_p = \left(\frac{đQ}{\mathrm{d}T}\right)_{\text{izobaric}} = \left(\frac{\partial H}{\partial T}\right)_p . \tag{3.18}$$

For C_V and C_p we have

$$C_V > 0\,, \qquad \lim_{T\to 0} C_V = 0\,, \tag{3.19}$$

$$C_p > 0\,, \qquad \lim_{T\to 0} C_p = 0\,. \tag{3.20}$$

The relations between C_V and C_p are given in section **3.5.1**.

Example

The enthalpy of argon at room temperature and pressure obeys the relation

$$H = \frac{5}{2} n\boldsymbol{R}T + \text{const} ,$$

where n is the amount of substance. What is the heat capacity of argon at constant pressure?

Solution

From the definition (3.18) we obtain

$$C_p = \frac{5}{2} n\boldsymbol{R}\,.$$

Example

A heat of $Q = 100$ J was supplied to a system for isochoric heating of a substance from $T_1 = 300$ K to $T_2 = 305$ K. Estimate the value of C_V. Do the given data also allow us to estimate C_p if we know that the substance is an ideal gas?

Solution

We can approximate the derivative of the function by the ratio of differences. From the definition (3.17) we thus obtain

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \approx \frac{\Delta U}{\Delta T}\,.$$

It follows from the specification and from equation (3.5) that the supplied heat equals the change in internal energy ΔU. Hence

$$C_V \approx \frac{100}{305-300} = 20\ \mathrm{J\ K^{-1}}\,.$$

For an ideal gas

$$H \equiv U + pV = U + n\boldsymbol{R}T \quad \longrightarrow \quad \Delta H = \Delta U + n\boldsymbol{R}\Delta T\,.$$

From the definition of C_p we have

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \approx \frac{\Delta U + n\boldsymbol{R}\Delta T}{\Delta T} = \frac{100 + n \times 8.314 \times (305-300)}{305-300} = 20 + 8.314 \times n\,.$$

In this case it does not matter that C_p is a derivative with respect to temperature at constant pressure, or that the studied process is not isobaric (in an ideal gas, the heat capacities depend on temperature only [see **3.5.1**]). However, we cannot calculate the value of C_p because we do not know the amount of substance n.

3.2.5 Molar thermodynamic functions

All the thermodynamic functions defined above are extensive quantities [**see 1.3.1**]. In chemistry we work most often with intensive, molar quantities, which are denoted using the subscript $_\mathrm{m}$. It holds, e.g., that

$$U_\mathrm{m} \equiv U/n, \quad S_\mathrm{m} \equiv S/n, \quad C_{p\mathrm{m}} \equiv C_p/n\,.$$

Example

A thermodynamic process took place in a system containing 5 mol of nitrogen during which the Gibbs energy increased by 100 J. What was the change in the Gibbs molar energy?

Solution

$$\Delta G_\mathrm{m} = \frac{\Delta G}{n} = \frac{100}{5} = 20 \text{ J mol}^{-1}.$$

3.2.6 Fugacity

Fugacity is defined by the relation

$$f = p^\mathrm{st} \exp\left(\frac{G_\mathrm{m}(T,p) - G^\circ_\mathrm{m}(T,p^\mathrm{st})}{\boldsymbol{R}T}\right)\,, \tag{3.21}$$

where p^st is the standard pressure (usually $p^\mathrm{st} = 101\ 325$ Pa), and $G_\mathrm{m}(T,p)$ is the molar Gibbs energy at temperature T and pressure p, and $G^\circ(T,p^\mathrm{st})$ is the molar Gibbs energy of a system in an ideal gaseous state at temperature T and pressure p^st.

U *Main unit:* Pa.

S *Symbols:* Symbol X° denotes thermodynamic quantities of an ideal gas at the chosen standard pressure [see also **6.1.2**].

Fugacity is a thermodynamic quantity which is useful when solving phase and chemical equilibria.

Note: For an ideal gas, fugacity equals pressure [see **3.5.8**].

3.2.7 Fugacity coefficient

The fugacity/pressure ratio is called the **fugacity coefficient** ϕ

$$\phi = \frac{f}{p}\,. \tag{3.22}$$

U *Main unit:* dimensionless quantity.

> *Note:* For an ideal gas $\phi = 1$.

Example

Knowing the values of the molar Gibbs energy of carbon dioxide $G_\mathrm{m}(T,p) = -53\,183$ J/mol at T = 350 K and p = 10 MPa, and $G^\circ_\mathrm{m}(T,p^\mathrm{st}) = -65\,675.14$ J/mol, where p^st = 101.325 kPa, calculate its fugacity and the fugacity coefficient at 350 K and 10 MPa.

Solution

By substituting into the definition (3.21) we obtain

$$f = 0.101325 \times \exp\left(\frac{-53183 - (-65675.14)}{8.314 \times 350}\right) = 7.415\ \mathrm{MPa}\,, \quad \phi = \frac{7.415}{10} = 0.7415.$$

3.2.8 Absolute and relative thermodynamic quantities

If a numerical value can be unambiguously assigned to a thermodynamic quantity of a system in a given state, we say that the quantity is absolute. If a numerical value can be assigned only to a change in a thermodynamic quantity during the system's transition from one thermodynamic state to another, we say that the quantity is relative.

Temperature, pressure, volume, amount of substance, fugacity, and heat capacities represent typical absolute quantities. For these quantities there exist natural and universal (independent of the substance) referential states. Such referential states are temperature 0 K, volume 0 m^3, pressure or fugacity 0 Pa. Internal energy, enthalpy, the Helmholtz energy and the Gibbs energy represent typical relative quantities. There do not exist any universal referential states for these quantities.

Entropy represents an interesting case. The second law of thermodynamics defines entropy as a relative quantity, but the third law transfers it to the group of absolute quantities. In order to accentuate this fact, the expression *absolute entropy* is sometimes used instead of the word entropy.

3.3 Some properties of the total differential

3.3.1 Total differential

Let us consider functions $M(x, y)$ and $N(x, y)$ continuous and differentiable (to the second order) on a simply connected region (for details, see a basic course of differential calculus). The necessary and sufficient condition for the differential form

$$\mathrm{d}z = M(x, y)\mathrm{d}x + N(x, y)\mathrm{d}y \tag{3.23}$$

to be the total differential of the function $z = z(x, y)$ is the equality of the derivatives

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y , \tag{3.24}$$

at all points of the region, where

$$M = \left(\frac{\partial z}{\partial x}\right)_y , \quad N = \left(\frac{\partial z}{\partial y}\right)_x .$$

Hence for the total differential of the function $z = z(x, y)$ it holds

$$\mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y . \tag{3.25}$$

Note: Equation (3.24) requires that the mixed second partial derivatives should be independent of the order of differentiation, i.e. that

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} . \tag{3.26}$$

Example

Is the differential form

$$\mathrm{d}z = (10xy^3 + 7)\mathrm{d}x + 15x^2y^2\mathrm{d}y$$

the total differential of function z?

Solution

By comparing with (3.23) we obtain

$$M = \left(\frac{\partial z}{\partial x}\right)_y = 10xy^3 + 7 \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y}\right)_x = 15x^2y^2 \,.$$

It holds that

$$\left(\frac{\partial M}{\partial y}\right) = \frac{\partial^2 z}{\partial x \partial y} = 30xy^2 \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right) = \frac{\partial^2 z}{\partial y \partial x} = 30xy^2 \,.$$

The mixed second derivatives are identical and consequently function z has a total differential.

Sometimes we need to know the derivative of x with respect to y at a fixed z. Equation (3.25) rearranges to

$$0 = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y \,, \qquad [z] \tag{3.27}$$

and from this relation we obtain

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y} \,. \tag{3.28}$$

This formula is identical with that for the differentiation of an implicitly defined function $z(x, y) = 0$ (see a course of differential calculus).

Example

Using the van der Waals equation of state

$$p = \frac{\boldsymbol{R}T}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2}$$

calculate the derivative of molar volume with respect to temperature at constant pressure.

Solution

It is rather difficult to express explicitly molar volume using the van der Waals equation (it is an algebraic equation of the third order, see the basic course on algebra). We therefore use relation (3.28)

$$\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p = -\frac{\left(\dfrac{\partial p}{\partial T}\right)_V}{\left(\dfrac{\partial p}{\partial V}\right)_T} = -\frac{\dfrac{\boldsymbol{R}}{V_\mathrm{m}-b}}{-\dfrac{\boldsymbol{R}T}{(V_\mathrm{m}-b)^2}+\dfrac{2a}{V_\mathrm{m}^3}}\,.$$

3.3.2 Total differential and state functions

All state functions (p, V, T, n, U, H, S, F, G, C_p, C_V, f, $\ldots$) have total differentials. Heat and work are not state functions and they do not have any total differential.

Example

Prove that condition (3.26) holds for the pressure of an ideal gas as a function of temperature and volume at a constant amount of substance.

Proof

According to the equation of state for an ideal gas (2.15), pressure is

$$p = \frac{n\boldsymbol{R}T}{V}\,.$$

For the total differential of pressure it holds [see (3.25)]

$$\mathrm{d}p = \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial p}{\partial V}\right)_T \mathrm{d}V = \frac{n\boldsymbol{R}}{V}\mathrm{d}T - \frac{n\boldsymbol{R}T}{V^2}\mathrm{d}V\,.$$

The condition (3.26) is fulfilled here:

$$n\boldsymbol{R}\left(\frac{\partial(1/V)}{\partial V}\right)_T = -\frac{n\boldsymbol{R}}{V^2}\left(\frac{\partial T}{\partial T}\right)_V\,.$$

$\mathrm{d}p$ is thus a total differential and pressure is a function of state. A similar proof can be established for pressure calculated using any equation of state.

Example

By substituting the expression $T\mathrm{d}S$ following from (3.6) for $đQ$ into equation (3.1) we obtain

$$đW = \mathrm{d}U - T\mathrm{d}S\,.$$

Prove that work W is not a state function.

Proof

Comparison with (3.23) shows that $M = 1$, $N = -T$, $x = U$, and $y = S$. Hence

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial 1}{\partial S}\right)_U \neq \left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial(-T)}{\partial U}\right)_S$$

because $\left(\frac{\partial T}{\partial U}\right)_S$ is generally different from zero. This shows that $đW$ is not a total differential and therefore work is not a state function.

3.3.3 Total differential of the product and ratio of two functions

Similar rules as those governing differentiation hold for the total differential of the product and the ratio of functions x and y.

$$\mathrm{d}(xy) = x\mathrm{d}y + y\mathrm{d}x\,, \qquad \mathrm{d}\left(\frac{x}{y}\right) = \frac{1}{y}\mathrm{d}x - \frac{x}{y^2}\mathrm{d}y\,. \tag{3.29}$$

For example, according to (3.29) we have for the total differential of the product of volume and pressure

$$\mathrm{d}(pV) = p\mathrm{d}V + V\mathrm{d}p\,.$$

3.3.4 Integration of the total differential

The integral of the total differential from point (x_1,y_1) to point (x_2,y_2) does not depend on the path between these points. We can, e.g., first integrate with respect to x at a fixed y_1, and then with respect to y at a fixed x_2

$$z(x_2, y_2) = z(x_1, y_1) + \int_{x_1}^{x_2} \left(\frac{\partial z}{\partial x}\right)_{y=y_1} \mathrm{d}x + \int_{y_1}^{y_2} \left(\frac{\partial z}{\partial y}\right)_{x=x_2} \mathrm{d}y\,, \tag{3.30}$$

or we can first integrate with respect to y at a fixed x_1 and then with respect to x at a fixed y_2

$$z(x_2, y_2) = z(x_1, y_1) + \int_{y_1}^{y_2} \left(\frac{\partial z}{\partial y}\right)_{x=x_1} \mathrm{d}y + \int_{x_1}^{x_2} \left(\frac{\partial z}{\partial x}\right)_{y=y_2} \mathrm{d}x\,, \tag{3.31}$$

or we can choose any other path linking points (x_1,y_1) and (x_2,y_2) in the plane x, y.

S *Symbols:* The expression $\left(\frac{\partial z}{\partial x}\right)_{y=y_1}$ denotes the partial derivative of the function $z = f\,(x, y)$ with respect to x at constant y at the value $y = y_1$.

It is often necessary to integrate $\mathrm{d}z$ with one fixed independent variable. For the integration from x_1 to x_2 at constant y it applies that

$$z(x_2, y) = z(x_1, y) + \int_{x_1}^{x_2} \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x\,, \qquad [y]\,. \tag{3.32}$$

3.4 Combined formulations of the first and second laws of thermodynamics

In this section we will assume (if not otherwise stated) that every system referred to is closed and homogeneous, that it exchanges only volume work with its surroundings, and that all the occurring processes are reversible. For the sake of simplicity, we will not explicitly indicate these assumptions.

3.4.1 Gibbs equations

By combining equations (3.4) and (3.6), and the definitions (3.9), (3.12) and (3.14) of the thermodynamic functions H, F, G we obtain relations which are called the combined formulations of the first and second laws of thermodynamics, or the Gibbs equations:

$$\begin{aligned} \mathrm{d}U &= T\mathrm{d}S - p\mathrm{d}V\,, && (3.33)\\ \mathrm{d}H &= T\mathrm{d}S + V\mathrm{d}p\,, && (3.34)\\ \mathrm{d}F &= -S\mathrm{d}T - p\mathrm{d}V\,, && (3.35)\\ \mathrm{d}G &= -S\mathrm{d}T + V\mathrm{d}p\,. && (3.36) \end{aligned}$$

In equation (3.33), internal energy is a function of variables S and V. Variables S and V will be called the **natural variables** of function U. The natural variables of enthalpy are S and p, those of the Helmholtz energy are T and V, and those of the Gibbs energy are T and p.

Note: Extension of the Gibbs equations to open systems is dealt with in section **6.4.1**.

3.4.2 Derivatives of U, H, F, and G with respect to natural variables

If we consider the internal energy U as a function of S and V, its total differential according to (3.25) equals

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V\,. \qquad (3.37)$$

By comparing (3.33) and (3.37) we obtain

$$\left(\frac{\partial U}{\partial S}\right)_V = T\,, \qquad \left(\frac{\partial U}{\partial V}\right)_S = -p\,. \tag{3.38}$$

In a similar way we obtain for $H = f(S,p)$, $F = f(T,V)$, $G = f(T,p)$

$$\left(\frac{\partial H}{\partial S}\right)_p = T\,, \qquad \left(\frac{\partial H}{\partial p}\right)_S = V\,, \tag{3.39}$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S\,, \qquad \left(\frac{\partial F}{\partial V}\right)_T = -p\,, \tag{3.40}$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S\,, \qquad \left(\frac{\partial G}{\partial p}\right)_T = V\,. \tag{3.41}$$

3.4.3 Maxwell relations

By applying the equalities of mixed derivatives (3.26) to the Gibbs equations (3.33) through (3.36), i.e. to the total differentials of the functions U, H, F, G, we obtain the so-called Maxwell relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V\,, \tag{3.42}$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p\,, \tag{3.43}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T\,, \tag{3.44}$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T\,. \tag{3.45}$$

Maxwell relations, in particular (3.44) and (3.45), rank among the major thermodynamic relations. They are used to derive many other equations.

3.4.4 Total differential of entropy as a function of T, V and T, p

The total differential of entropy as a function of temperature and volume, $S = f(T, V)$, is

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V\,. \tag{3.46}$$

At a fixed volume it follows from (3.6) and (3.17)

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{đQ}{\mathrm{d}T}\right)_{\text{isochoric}} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V = \frac{C_V}{T}\,. \tag{3.47}$$

For the differentiation of entropy with respect to volume, Maxwell relation (3.44) applies. Equation (3.46) can be rearranged to

$$\mathrm{d}S = \frac{C_V}{T}\,\mathrm{d}T + \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V\,. \tag{3.48}$$

In the same way we obtain for entropy as a function of temperature and pressure

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}\left(\frac{đQ}{dT}\right)_{\text{isobaric}} = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p = \frac{C_p}{T} \tag{3.49}$$

and using Maxwell relation (3.45) we get

$$\mathrm{d}S = \frac{C_p}{T}\,\mathrm{d}T - \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p\,. \tag{3.50}$$

3.4.5 Conversion from natural variables to variables T, V or T, p

Internal energy may be converted from the function of natural variables to the function of variables T, V using equation (3.33), into which we substitute relation (3.48) for $\mathrm{d}S$. Hence we have

$$\mathrm{d}U = C_V\,\mathrm{d}T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\mathrm{d}V\,. \tag{3.51}$$

In the same way, $H = f(S, p)$ may be converted to $H = f(T, p)$. By combining equations (3.34) and (3.50) we arrive at

$$\mathrm{d}H = C_p\,\mathrm{d}T + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}p\,. \tag{3.52}$$

According to (3.25), the total differential of the function $U = f(T, V)$ is equal to the expression

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V\,. \tag{3.53}$$

By comparing (3.51) and (3.53) we get

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V\,, \tag{3.54}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p\,. \tag{3.55}$$

Note: The derivative of internal energy with respect to volume is called cohesive pressure.

Similarly we obtain the respective partial derivatives of the dependence $H = f(T, p)$

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p\,, \tag{3.56}$$

$$\left(\frac{\partial H}{\partial p}\right)_T = -\; T + V\left(\frac{\partial V}{\partial T}\right)_p\,. \tag{3.57}$$

Example

Prove that the internal energy of an ideal gas is only a function of temperature, i.e. that at a fixed temperature it depends neither on volume nor on pressure.

Proof

For an ideal gas we have

$$T\left(\frac{\partial p}{\partial T}\right)_V - p = T\frac{n\boldsymbol{R}}{V} - p = 0\,.$$

It follows from equation (3.55) that $\left(\dfrac{\partial U}{\partial V}\right)_T = 0$. Hence the internal energy of an ideal gas does not depend on volume. In order to prove the independence of the internal energy of an ideal gas on pressure, we first write its total differential as a function of T and p. By combining the equation

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p$$

with equation (3.51) we get

$$\mathrm{d}U = \left\{C_V + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\left(\frac{\partial V}{\partial T}\right)_p\right\}\mathrm{d}T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}V\,.$$

From this expression it follows that

$$\left(\frac{\partial U}{\partial p}\right)_T = \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\left(\frac{\partial V}{\partial p}\right)_T\,.$$

As was shown above, the expression in brackets for an ideal gas is zero. Hence the internal energy of an ideal gas is independent of pressure.

3.4.6 Conditions of thermodynamic equilibrium

The state of thermodynamic equilibrium is defined in **1.4.1**. From the second law of thermodynamics [see equations (3.6) and (3.7)] it follows that during irreversible processes the entropy of an isolated system increases

$$\mathrm{d}S > 0\,, \qquad \text{[isolated system, irreversible process]} \tag{3.58}$$

and that it has its maximum in the state of thermodynamic equilibrium

$$\mathrm{d}S = 0\,, \qquad \text{[isolated system, reversible process]} \tag{3.59}$$

From this we arrive at the following conditions of thermodynamic equilibrium for the thermodynamic functions S, U, H, F, and G

function	condition of extreme	kind of extreme
entropy	$\mathrm{d}S = 0 \quad [U, V]$	maximum
entropy	$\mathrm{d}S = 0 \quad [H, p]$	maximum
internal energy	$\mathrm{d}U = 0 \quad [S, V]$	minimum
enthalpy	$\mathrm{d}H = 0 \quad [S, p]$	minimum
Helmholtz energy	$\mathrm{d}F = 0 \quad [T, V]$	minimum
Gibbs energy	$\mathrm{d}G = 0 \quad [T, p]$	minimum

The conditions of the functions extremes given in the table above are called the **extensive criteria of equilibrium**, and they may be used to derive the so-called **intensive criteria** [see **7.2.0.1**].

Note: Note the connection between the equations in the above table and the Gibbs equations (3.33) through (3.36). It follows from equation (3.33), e.g., that at $[S, V]$, $\mathrm{d}U = 0$, and at $[U, V]$, $\mathrm{d}S = 0$.

Example

Ascertain the change in the Helmholtz energy during reversible and irreversible processes at constant volume and temperature.

Solution

From the condition $\mathrm{d}F = 0$ at $[T, V]$ we obtain by integration

$$\Delta F = 0, \qquad [\text{reversible process, } T, V]$$

Since at $[T, V]$ the Helmholtz energy has its minimum at equilibrium, it holds that during all irreversible processes occurring at constant temperature and volume, the Helmhotz energy of the system decreases

$$\Delta F < 0, \qquad [\text{irreversible process, } T, V]\,.$$

Analogous relations can be obtained for other thermodynamic functions.

The criteria of thermodynamic equilibrium are applied in calculating phase and chemical equilibria. The choice of criterion depends on the conditions of equilibrium. Equilibria at constant temperature and pressure are studied most often, in which case the criterion $\mathrm{d}G = 0$, $[T, p]$ is applied [see (7.1)].

3.5 Changes of thermodynamic quantities

Only two of the three state variables p, V, T are independent at a constant amount of substance n, while the third is determined by an equation of state [see equations (2.12)]. The thermodynamic quantities C_V, U, F are usually considered to be functions of temperature and volume, while the quantities C_p, H, G are considered to be functions of temperature and pressure. Entropy is considered to be the function of T, V or T, p. When deriving the function dependence of thermodynamic quantities, we proceed from the knowledge of the equation of state and of the dependence of heat capacity (C_p or C_V) on temperature.

If a phase transition occurs during a change of state variables [see **7.1.3**], the corresponding changes of thermodynamic functions have to be considered. During phase transitions, changes of enthalpies and volumes are usually known experimentally while the changes of other thermodynamic functions are calculated from them.

3.5.1 Heat capacities

3.5.1.1 Temperature dependence

A number of empirical relations are applied in calculating the temperature dependence of the heat capacities of gases, liquids and solids, e.g.

$$C_{p\mathrm{m}}(T,p) = a + bT + cT^2\,, \qquad [p]\,, \tag{3.60}$$

$$C_{V\mathrm{m}}(T,V) = a' + b'T + c'T^2\,, \qquad [V]\,, \tag{3.61}$$

where the constants a, b, c, a', b', c' are determined using the measured data.

> *Note:* This and other similar empirical relations can be used reliably only in the temperature interval for which the constants were determined.

For crystalline substances in the vicinity of absolute zero, $T \in (0, T_1)$, where $T_1 \approx 15\,\mathrm{K}$, the **Debye relation** applies

$$C_{V\mathrm{m}} = C_{p\mathrm{m}} = \mathrm{const}\, T^3\,. \tag{3.62}$$

3.5.1.2 C_p dependence on pressure

$$C_p(T,p_2) = C_p(T,p_1) - \int_{p_1}^{p_2} T \left(\frac{\partial^2 V}{\partial T^2}\right)_p \mathrm{d}p\,, \qquad [T]\,. \tag{3.63}$$

3.5.1.3 C_V dependence on volume

$$C_V(T,V_2) = C_V(T,V_1) + \int_{V_1}^{V_2} T \left(\frac{\partial^2 p}{\partial T^2}\right)_V \mathrm{d}V\,, \qquad [T]\,. \tag{3.64}$$

3.5.1.4 Relations between heat capacities

$$\begin{aligned} C_p &= C_V + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p = C_V + T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p \\ &= C_V - T\frac{\left(\frac{\partial V}{\partial T}\right)_p^2}{\left(\frac{\partial V}{\partial p}\right)_T} = C_V - T\frac{\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V_\mathrm{m}}\right)_T}\,. \end{aligned} \tag{3.65}$$

The following relation applies between heat capacities and the coefficients of isothermal compressibility β [see **2.1.7**] and thermal expansion α [see **2.1.6**]

$$C_p = C_V + TV\frac{\alpha^2}{\beta}\,. \tag{3.66}$$

3.5.1.5 Ideal gas

The heat capacities of an ideal gas are functions of temperature only. Relations (3.65) rearrange to the **Mayer relation**

$$C^\circ_{pm}(T) = C^\circ_{Vm}(T) + \boldsymbol{R}\,. \tag{3.67}$$

Example

Derive the relation for the calculation of the $C_{p\mathrm{m}}(T,p)$ pressure dependence in a gas that obeys the equation of state

$$V_\mathrm{m} = \frac{\boldsymbol{R}T}{p} + b - \frac{a}{\boldsymbol{R}T^2}\,,$$

where a, b are constants independent of temperature and pressure.

Solution

We calculate $\left(\frac{\partial^2 V_\mathrm{m}}{\partial T^2}\right)_p$ from the given equation of state

$$\left(\frac{\partial^2 V_\mathrm{m}}{\partial T^2}\right)_p = -\frac{6a}{\boldsymbol{R}T^4}\,.$$

We divide equation (3.63) by the amount of substance n in order to obtain the relation between molar quantities, and we choose $p_1 = 0$. Thus we obtain

$$C_{p\mathrm{m}}(T,p) = C^\circ_{p\mathrm{m}}(T) - \int_0^p T\left(\frac{\partial^2 V_\mathrm{m}}{\partial T^2}\right)_p \mathrm{d}p\,,$$

where $C^\circ_{p\mathrm{m}}(T) = C_{p\mathrm{m}}(T,0)$, because a substance at zero pressure behaves as an ideal gas. We substitute for the second derivative of volume with respect to temperature, and integrate

$$C_{p\mathrm{m}}(T,p) = C^\circ_{p\mathrm{m}}(T) - T\int_0^p \left(-\frac{6a}{\boldsymbol{R}T^4}\right)\mathrm{d}p = C^\circ_{p\mathrm{m}}(T) + \frac{6a}{\boldsymbol{R}T^3}p\,.$$

3.5.2 Internal energy

3.5.2.1 Temperature and volume dependence for a homogeneous system

By integrating the total differential (3.51) with respect to the general prescription (3.30) we obtain

$$U(T,V) = U(T_1,V_1) + \int_{T_1}^{T} C_V(T,V_1)\,\mathrm{d}T + \int_{V_1}^{V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\mathrm{d}V\,. \qquad (3.68)$$

The volume V_1 is often chosen as large as would allow for a system in its initial state to behave as an ideal gas. In the limit $V_1 \to \infty$ at a constant amount of substance, equation (3.68) rearranges to

$$U(T,V) = U^\circ(T_1) + \int_{T_1}^{T} C_V^\circ(T)\,\mathrm{d}T + \int_{\infty}^{V} \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] \mathrm{d}V\,. \tag{3.69}$$

If the volume is constant, equation (3.68) simplifies to

$$U(T,V) = U(T_1,V) + \int_{T_1}^{T} C_V(T,V)\,\mathrm{d}T\,, \qquad [V]\,. \tag{3.70}$$

For an isothermal process, equation (3.68) becomes

$$U(T,V) = U(T,V_1) + \int_{V_1}^{V} \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] \mathrm{d}V\,, \qquad [T]\,. \tag{3.71}$$

3.5.2.2 Ideal gas

For an ideal gas, the partial derivative of internal energy with respect to volume is zero, as follows from (3.55) [see also the example in section **3.4.5**]. The internal energy of an ideal gas is thus a function of temperature only (isothermal processes in an ideal gas are processes at constant internal energy). Equation (3.70) for an ideal gas is

$$U^\circ(T) = U^\circ(T_1) + \int_{T_1}^{T} C_V^\circ(T)\mathrm{d}T\,. \tag{3.72}$$

3.5.2.3 Changes at phase transitions

The changes of internal energy during a crystalline transformation, melting and boiling ($\Delta_{\mathrm{cryst}}U$, $\Delta_{\mathrm{fus}}U$ and $\Delta_{\mathrm{vap}}U$) are calculated as follows

$$\Delta U \ = \Delta H - p\Delta V\,, \qquad [T,p]\,, \tag{3.73}$$

where ΔH and ΔV are changes of enthalpy and volume at the respective phase transition.

Example

Derive the relation for the dependence of the internal energy of an ideal gas on temperature and amount of substance if

$$C^\circ_{p\mathrm{m}} = a + bT + cT^2\,.$$

Solution

In equation (3.72) we take into account that $C^\circ_V(T) = nC^\circ_{V\mathrm{m}}$, where n is the amount of substance, and that for an ideal gas the Mayer relation (3.67) applies. We obtain

$$\begin{aligned} U(T) &= U(T_1) + n\int_{T_1}^{T} (C^\circ_{p\mathrm{m}} - \boldsymbol{R})\,\mathrm{d}T \\ &= U(T_1) + n\left[(a-\boldsymbol{R})(T-T_1) + \frac{b}{2}(T^2-T_1^2) + \frac{c}{3}(T^3-T_1^3)\right]. \end{aligned}$$

3.5.3 Enthalpy

3.5.3.1 Temperature and pressure dependence for a homogeneous system

By integrating the total differential (3.52) with respect to the general prescription (3.30) we obtain

$$H(T,p) = H(T_1,p_1) + \int_{T_1}^{T} C_p(T,p_1)\,\mathrm{d}T + \int_{p_1}^{p}\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}p\,. \qquad (3.74)$$

If $p_1 = 0$, the system in its initial state behaves as an ideal gas, and equation (3.74) rearranges to

$$H(T,p) = H^\circ(T_1) + \int_{T_1}^{T} C^\circ_p(T)\,\mathrm{d}T + \int_{0}^{p}\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}p\,. \qquad (3.75)$$

If pressure stays unchanged during a thermodynamic process, equation (3.74) simplifies to

$$H(T,p) = H(T_1,p) + \int_{T_1}^{T} C_p(T,p)\,\mathrm{d}T\,, \qquad [p]\,. \qquad (3.76)$$

For an isothermal process, equation (3.74) becomes

$$H(T,p) = H(T,p_1) + \int_{p_1}^{p} \left[V - T \left(\frac{\partial V}{\partial T} \right)_p \right] \mathrm{d}p \,, \qquad [T] \,. \tag{3.77}$$

3.5.3.2 Ideal gas

For an ideal gas, the partial derivative of enthalpy with respect to pressure is zero, as follows from (3.57). The enthalpy of an ideal gas is thus a function of temperature only (isothermal processes in an ideal gas are identical with processes at constant enthalpy). Equation (3.76) for an ideal gas is

$$H^\circ(T) = H^\circ(T_1) + \int_{T_1}^{T} C_p^\circ(T)\, \mathrm{d}T \,. \tag{3.78}$$

3.5.3.3 Changes at phase transitions

Enthalpy changes at phase transitions are usually known experimentally.

Example

Derive the pressure dependence of enthalpy at constant temperature for a gas obeying the pressure virial expansion with the second virial coefficient [see equation (2.20)], i.e. the equation of state

$$z = 1 + \frac{B}{\boldsymbol{R}T} p \,,$$

where $B = f(T)$ is the second virial coefficient.

Solution

We use equation (3.75) which at constant temperature simplifies to

$$H(T,p) = H^\circ(T) + \int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] \mathrm{d}p\,.$$

From the given equation of state we express the volume

$$V = \frac{n\boldsymbol{R}T}{p} + nB\,,$$

its derivative with respect to temperature

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{n\boldsymbol{R}}{p} + n\frac{\mathrm{d}B}{\mathrm{d}T}$$

and the expression

$$V - T\left(\frac{\partial V}{\partial T}\right)_p = n\left(B - T\frac{\mathrm{d}B}{\mathrm{d}T}\right)\,,$$

which we substitute into the relation for the pressure dependence of enthalpy, and integrate

$$H(T,p) = H^\circ(T) + \int_0^p n\left(B - T\frac{\mathrm{d}B}{\mathrm{d}T}\right)\mathrm{d}p = H^\circ(T) + n\left(B - T\frac{\mathrm{d}B}{\mathrm{d}T}\right)p\,.$$

3.5.4 Entropy

3.5.4.1 Temperature and volume dependence for a homogeneous system

By integrating the total differential (3.48) with respect to the general prescription (3.30) we obtain

$$S(T,V) = S(T_1,V_1) + \int_{T_1}^{T} \frac{C_V(T,V_1)}{T}\,\mathrm{d}T + \int_{V_1}^{V}\left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V\,. \tag{3.79}$$

Volume V_1 is often chosen as large as to allow for a system in its initial state to behave as an ideal gas. In the limit $V_1 \to \infty$ at constant amount of substance, equation (3.79) rearranges to

$$S(T,V) = S^\circ(T_1,V^{\mathrm{st}}) + \int_{T_1}^{T} \frac{C_V^\circ(T)}{T}\,\mathrm{d}T + n\boldsymbol{R}\ln\frac{V}{V^{\mathrm{st}}} + \int_{\infty}^{V}\left[\left(\frac{\partial p}{\partial T}\right)_V - \frac{n\boldsymbol{R}}{V}\right]\mathrm{d}V\,, \tag{3.80}$$

where $V^{\mathrm{st}} = n\boldsymbol{R}T/p^{\mathrm{st}}$, and p^{st} is a standard pressure.

If the volume stays unchanged during a thermodynamic process, equation (3.68) simplifies to

$$S(T,V) = S(T_1,V) + \int_{T_1}^{T} \frac{C_V(T,V)}{T}\,\mathrm{d}T\,, \qquad [V]\,. \tag{3.81}$$

For an isothermal process, equation (3.79) becomes

$$S(T,V) = S(T,V_1) + \int_{V_1}^{V}\left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V\,, \qquad [T]\,. \tag{3.82}$$

3.5.4.2 Temperature and pressure dependence for a homogeneous system

By integrating the total differential (3.50) with respect to the general prescription (3.30) we obtain

$$S(T,p) = S(T_1,p_1) + \int_{T_1}^{T} \frac{C_p(T,p_1)}{T}\,\mathrm{d}T - \int_{p_1}^{p}\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p\,. \tag{3.83}$$

If $p_1 = 0$, the system in its initial state behaves as an ideal gas and equation (3.83) becomes

$$S(T,p) = S^\circ(T_1,p^{\mathrm{st}}) + \int_{T_1}^{T} \frac{C_p^\circ(T)}{T}\,\mathrm{d}T - n\boldsymbol{R}\ln\frac{p}{p^{\mathrm{st}}} + \int_{0}^{p}\left[\frac{n\boldsymbol{R}}{p} - \left(\frac{\partial V}{\partial T}\right)_p\right]\mathrm{d}p\,, \tag{3.84}$$

where p^{st} is a chosen standard pressure.

If the pressure stays unchanged during a thermodynamic process, equation (3.83) simplifies to

$$S(T,p) = S(T_1,p) + \int_{T_1}^{T} \frac{C_p(T,p)}{T}\,\mathrm{d}T\,, \qquad [p]\,. \tag{3.85}$$

For an isothermal process, equation (3.83) becomes

$$S(T,p) = S(T,p_1) - \int_{p_1}^{p}\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p\,, \qquad [T]\,. \tag{3.86}$$

3.5.4.3 Ideal gas

For an ideal gas equation (3.79) simplifies to

$$S(T,V) = S(T_1,V_1) + \int_{T_1}^{T} \frac{C_V^\circ(T)}{T}\,\mathrm{d}T + n\boldsymbol{R}\ln\frac{V}{V_1}\,. \tag{3.87}$$

Equation (3.83) becomes

$$S(T,p) = S(T_1,p_1) + \int_{T_1}^{T} \frac{C_p^\circ(T)}{T}\,\mathrm{d}T - n\boldsymbol{R}\ln\frac{p}{p_1}\,. \tag{3.88}$$

3.5.4.4 Changes at phase transitions

Entropy changes at a crystalline transformation, melting and boiling, $\Delta_{\mathrm{cryst}}S$, $\Delta_{\mathrm{fus}}S$ and $\Delta_{\mathrm{vap}}S$ at reversible phase transitions are calculated using the relation

$$\Delta S = \frac{\Delta H}{T}\,, \qquad [T,\ p,\ \text{reversible phase transition}] \tag{3.89}$$

where ΔH is the enthalpy change at the given phase transition. For irreversible phase transitions, we have the inequality

$$\Delta S > \frac{\Delta H}{T}\,, \qquad [T,\ p,\ \text{irreversible phase transition}] \tag{3.90}$$

In this case the entropy change is calculated using the procedure described in **3.5.9**.

Example

Derive the relation for the dependence of entropy of a gas on temperature, volume and amount of substance. Assume that the gas obeys the van der Waals equation of state [see **2.2.6**]

$$\left(p + \frac{a}{V_{\mathrm{m}}^2}\right)(V_{\mathrm{m}} - b) = \boldsymbol{R}T\,,$$

and that the temperature dependence of the molar isochoric heat capacity of an ideal gas can be approximated using the relation

$$C_{V\mathrm{m}}^\circ = A + BT\,.$$

Solution

We use equation (3.80) and rewrite it to the relation between molar quantities. Thus we get

$$S_\mathrm{m}(T, V_\mathrm{m}) = S^\circ_\mathrm{m}(T_1, V^\mathrm{st}_\mathrm{m}) + \int_{T_1}^{T} \frac{C^\circ_{V\mathrm{m}}(T)}{T}\,\mathrm{d}T + \boldsymbol{R}\ln\frac{V_\mathrm{m}}{V^\mathrm{st}_\mathrm{m}} + \int_{\infty}^{V}\left[\left(\frac{\partial p}{\partial T}\right)_{V_\mathrm{m}} - \frac{\boldsymbol{R}}{V_\mathrm{m}}\right]\mathrm{d}V_\mathrm{m}\,.$$

From the van der Waals equation we have

$$\left(\frac{\partial p}{\partial T}\right)_{V_\mathrm{m}} = \frac{\boldsymbol{R}}{V_\mathrm{m} - b}\,.$$

We substitute for the derivative and for $C^\circ_{V\mathrm{m}}$, and integrate:

$$\begin{aligned} S_\mathrm{m}(T, V_\mathrm{m}) &= S^\circ_\mathrm{m}(T_1, V^\mathrm{st}_\mathrm{m}) + \int_{T_1}^{T}\frac{A + BT}{T}\mathrm{d}T + \boldsymbol{R}\ln\frac{V_\mathrm{m}}{V^\mathrm{st}_\mathrm{m}} + \boldsymbol{R}\int_{\infty}^{V_\mathrm{m}}\left(\frac{1}{V_\mathrm{m} - b} - \frac{1}{V_\mathrm{m}}\right)\mathrm{d}V_\mathrm{m} \\ &= S^\circ_\mathrm{m}(T_1, V^\mathrm{st}_\mathrm{m}) + A\ln\frac{T}{T_1} + B(T - T_1) + \boldsymbol{R}\ln\frac{V_\mathrm{m}}{V^\mathrm{st}_\mathrm{m}} + \boldsymbol{R}\ln\frac{V_\mathrm{m} - b}{V_\mathrm{m}}\,. \end{aligned}$$

Finally, the dependence on the amount of substance is, according to **3.2.5**,

$$S(T, V_\mathrm{m}, n) = nS_\mathrm{m}(T, V_\mathrm{m})\,.$$

3.5.5 Absolute entropy

This term is understood as the value of entropy in a given state (T, p) [see **3.2.8**]. To calculate it we proceed from the state ($T = 0$, $p^\mathrm{st} = 101.325$ kPa), and by way of a sequence of thermodynamic processes we arrive at the state (T,p) while summing the entropy changes during the individual processes

$$S(T, p) = S(T_1, p^\mathrm{st}) + \Delta S^{(\mathrm{s})} + \Delta_\mathrm{fus}S + \Delta S^{(\mathrm{l})} + \Delta_\mathrm{vap}S + \Delta S^{(\mathrm{g})}\,, \tag{3.91}$$

where $S(T_1, p^{\text{st}})$ is the entropy of a substance at a sufficiently low temperature T_1, such that the Debye relation (3.62) holds for $T \le T_1$

$$S(T_1, p^{\text{st}}) = n \int_0^{T_1} \frac{\text{const } T^3}{T}\, \mathrm{d}T = n \frac{\text{const } T_1^3}{3}\,.$$

$\Delta S^{(\text{s})}$ is the entropy change on heating the substance from T_1 to the normal melting temperature T_{fus},

$$\Delta S^{(\text{s})} = \int_{T_1}^{T_{\text{fus}}} \frac{C_p^{(\text{s})}(T, p^{\text{st}})}{T} \mathrm{d}T\,.$$

$\Delta_{\text{fus}} S$ is the entropy change on melting

$$\Delta_{\text{fus}} S = \frac{\Delta_{\text{fus}} H}{T_{\text{fus}}}\,.$$

$\Delta S^{(\text{l})}$ is the entropy change on heating a liquid substance from the normal melting temperature to the normal boiling temperature,

$$\Delta S^{(\text{l})} = \int_{T_{\text{fus}}}^{T_{\text{vap}}} \frac{C_p^{(\text{l})}(T, p^{\text{st}})}{T} \mathrm{d}T\,.$$

$\Delta_{\text{vap}} S$ is the entropy change on boiling

$$\Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H}{T_{\text{vap}}}\,.$$

$\Delta S^{(\text{g})}$ is the entropy change of a gaseous substance on its transition from the point $(T_{\text{vap}},\ p^{\text{st}})$ to (T, p)

$$\Delta S^{(\text{g})} = \int_{T_{\text{vap}}}^{T} \frac{C_p(T, p^{\text{st}})}{T} \mathrm{d}T - \int_{p^{\text{st}}}^{p} \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p\,.$$

S *Symbols:* The superscripts $^{(\text{s})}$, $^{(\text{l})}$, $^{(\text{g})}$ are used to denote quantities in a solid, liquid and gaseous phase.

> *Note:* If a substance in the solid state transforms from one crystalline form to another (e.g. rhombic sulphur→ monoclinic sulphur), the entropy change at this phase transition has to be included in the formula.

Example

Calculate the absolute molar entropy of liquid sulphur dioxide at $T = 200$ K and at the standard pressure 101.325 kPa. Data: $T_1 = 15$ K, $C_{pm}^{(\mathrm{s})} = 3.77\,\mathrm{J\,mol^{-1}\,K^{-1}}$ at T_1, $\Delta S^{(\mathrm{s})} = 84.2\,\mathrm{J\,mol^{-1}\,K^{-1}}$, $T_{\mathrm{fus}} = 197.64$ K, $\Delta_{\mathrm{fus}}H = 7403\,\mathrm{J\,mol^{-1}}$, $C_{pm}^{(\mathrm{l})} = 87.2\,\mathrm{J\,mol^{-1}\,K^{-1}}$. Sulphur dioxide exists in only one crystalline form.

Solution

We determine the constant in the Debye relation (3.62) from the condition

$$\mathrm{const}\,T^3 = C_{pm}^{(\mathrm{s})} \quad \text{at} \quad T = T_1 .$$

Individual entropy contributions have the following values:

$$S(T_1) = \int_0^{T_1} \frac{\mathrm{const}\ T^3}{T}\mathrm{d}T = \frac{\mathrm{const}\,T_1^3}{3} = \frac{3.77}{3} = 1.257\ \mathrm{Jmol^{-1}K^{-1}}\,.$$

$$\Delta_{\mathrm{fus}}S = \frac{\Delta_{\mathrm{fus}}H}{T_{\mathrm{fus}}} = \frac{7403}{197.64} = 37.457\ \mathrm{Jmol^{-1}K^{-1}}\,.$$

$$\Delta S^{(\mathrm{l})} = \int_{T_{\mathrm{fus}}}^{T} \frac{C_{pm}^{(\mathrm{l})}}{T}\mathrm{d}T = 87.2\ln\frac{200}{197.64} = 1.035\ \mathrm{Jmol^{-1}\ K^{-1}}\,.$$

The absolute molar entropy of liquid sulphur dioxide is $S_{\mathrm{m}}(T, p^{\mathrm{st}}) = 1.257 + 84.200 + 37.457 + 1.035 = 123.949$ J mol$^{-1}K^{-1}$.

3.5.6 Helmholtz energy

3.5.6.1 Dependence on temperature and volume

The Helmholtz energy is calculated from the definition (3.12), and from the dependence of internal energy (3.68) and entropy (3.79) on T and V

$$F(T,V) = F(T_1,V_1) + [U(T,V) - TS(T,V)] - [U(T_1,V_1) - T_1S(T_1,V_1)]\,. \tag{3.92}$$

The change in the Helmhotz energy with volume at constant temperature can be calculated by integrating equation (3.35) with respect to the general prescription (3.31)

$$F(T,V_2) = F(T,V_1) - \int_{V_1}^{V_2} p\,\mathrm{d}V\,, \qquad [T]\,. \tag{3.93}$$

3.5.6.2 Changes at phase transitions

The changes of the Helmholtz energy at crystalline transformations, melting and boiling, $\Delta_{\text{cryst}}F$, $\Delta_{\text{fus}}F$ and $\Delta_{\text{vap}}F$ during reversible phase transitions are calculated from the relation

$$\Delta F = -p\Delta V\,, \qquad [T,\ p,\ \text{reversible phase transition}]\,, \tag{3.94}$$

where ΔV is the respective change in volume.

For irreversible phase transitions, we have the inequality

$$\Delta F < -p\Delta V\,, \qquad [T,\ p,\ \text{irreversible phase transition}]\,. \tag{3.95}$$

In this case the change in the Helmhotz energy is calculated using the procedure described in **3.5.9**.

Example

Calculate the change in the Helmholtz energy during reversible evaporation of 1.8 kg of liquid water at $T = 373.15$ K and $p = 101.325$ kPa. Assume that in the given state the equation of state of an ideal gas holds for water vapour, and that the volume of liquid water is negligible as compared with that of vapour.

Solution

The assigned values T and p correspond to the normal boiling point [see **7.1.5**] of water, i.e. to a reversible phase transition. Hence we use relation (3.94). The change in volume on evaporation, based on the specification, is:

$$\Delta V = V^{(\mathrm{g})} - V^{(\mathrm{l})} \doteq V^{(\mathrm{g})} = \frac{n\boldsymbol{R}T}{p}\,,$$

where the amount of substance of water is $n = \frac{1800}{18} = 100$ mol. Then

$$\Delta F = -\Delta V = -100 \times 8.314 \times 373.15 = -310.24\ \mathrm{kJ}.$$

3.5.7 Gibbs energy

3.5.7.1 Temperature and pressure dependence

The Gibbs energy is calculated from the definition (3.14), and from the dependence of enthalpy (3.74) and entropy (3.83) on T and p

$$G(T,p) = G(T_1,p_1) + [H(T,p) - TS(T,p)] - [H(T_1,p_1) - T_1S(T_1,p_1)]\ . \tag{3.96}$$

The change in the Gibbs energy with pressure at constant temperature can be calculated by integrating equation (3.36) with respect to the general prescription (3.31)

$$G(T,p_2) = G(T,p_1) + \int_{p_1}^{p_2} V\,\mathrm{d}p\,, \qquad [T]\,. \tag{3.97}$$

3.5.7.2 Changes at phase transitions

The Gibbs energy does not change during reversible phase transitions

$$\Delta G = 0\,, \qquad [T,\ p,\ \text{reversible phase transition}]\,. \tag{3.98}$$

For irreversible phase transitions, we have the inequality

$$\Delta G < 0\,, \qquad [T,\ p,\ \text{irreversible phase transition}]\,. \tag{3.99}$$

and the change in the Gibbs energy is calculated using the procedure described in **3.5.9**.

3.5.8 Fugacity

Dependence on state variables for a homogeneous system

The following equations follow from the definition (3.21)

$$f = p \exp\left[\int_0^p \frac{z-1}{p}\mathrm{d}p\right]\,, \tag{3.100}$$

and

$$f = \frac{\boldsymbol{R}T}{V_\mathrm{m}} \exp\left[z - 1 - \int_\infty^{V_\mathrm{m}} \frac{z-1}{V_\mathrm{m}}\mathrm{d}V_\mathrm{m}\right]\,, \tag{3.101}$$

where z is the compressibility factor. Relation (3.100) and (3.101) in particular are used to calculate fugacity from equations of state.

3.5.8.1 Ideal gas

For an ideal gas, fugacity is equal to pressure

$$f = p\,, \qquad [\text{ideal gas}]\,. \tag{3.102}$$

3.5.8.2 Changes at phase transitions

At reversible phase transitions, fugacity does not change. If, e.g., the liquid phase is in equilibrium with the gaseous phase, we have

$$f^{(\mathrm{l})} = f^{(\mathrm{g})}\,, \qquad [T, p]\,. \tag{3.103}$$

> *Note:* According to the theorem of corresponding states [see **2.2.9**], the fugacity coefficient $\phi = f/p$ is the function of reduced temperature T_r and reduced pressure p_r. To estimate fugacity, we use generalized diagrams of the fugacity coefficient as a function of T_r and p_r.

Example

Calculate the fugacity of ethane at temperature 270 K and pressure 1000 kPa. For ethane at this temperature and pressure under 1200 kPa, the equation of state $z = 1 - 1.1359 \cdot 10^{-4} p$ applies, with pressure given in kPa.

Solution

We substitute for the compressibility factor z from equation (3.100) and integrate

$$f = p\exp(-1.1359 \times 10^{-4} \times p) = 1000 \times \exp(-0.11359) = 892.7\ \mathrm{kPa}\,.$$

3.5.9 Changes of thermodynamic quantities during irreversible processes

Some formulas presented in this chapter cannot be directly applied to irreversible processes as they apply only for reversible processes. On the other hand, a change in a thermodynamic quantity depends solely on the initial and final state of the system, but it does not depend on the path from the initial to the final state. In calculations, the irreversible path from the initial to the final state is therefore substituted by an appropriately chosen reversible path. We present two examples of this procedure.

Example

Determine the entropy change during an irreversible adiabatic transition of a system from the state (T_1,p_1) to the state (T_2,p_2).

Solution

If the adiabatic process were reversible, we would have $\Delta S = 0$ because equation (3.6) would apply and $đQ$ would be equal to 0. We substitute the irreversible adiabatic process by a reversible isobaric and a reversible isothermal process. Then

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p(T,p_1)}{T}\mathrm{d}T - \int_{p_1}^{p_2} \left(\frac{\partial V}{\partial T}\right)_{p,T=T_2} \mathrm{d}p\,.$$

Note: Note that when calculating ΔS in the above example we did not use the information that the process was adiabatic. To determine changes of thermodynamic quantities, it is enough to know the initial and final state of the system (T_1,p_1) and (T_2,p_2), respectively.

Example

Calculate the changes ΔH, ΔS, and ΔG during the solidification of a supercooled one-component liquid at $T < T_{\mathrm{fus}}$ and $p = p_{\mathrm{fus}}$, where T_{fus} is the temperature of solidification and p_{fus} is the pressure of solidification. (Note that the temperature of melting and solidification are the same for pure substances. However, enthalpy of solidification is minus enthalpy of melting).

Solution

For an irreversible phase transition, we have the inequalities (3.90) and (3.99) from which the changes of S and G cannot be calculated. Hence we substitute the irreversible process with a sequence of three reversible processes: the heating of the liquid from T to T_{fus}, the equilibrium (i.e. reversible) change of the state of matter, and the cooling of the solid from the temperature of solidification to temperature T. We thus obtain:

$$\begin{aligned}
\Delta H &= \int_{T}^{T_{\mathrm{fus}}} C_p^{(\mathrm{l})}\,\mathrm{d}T - \Delta_{\mathrm{fus}}H + \int_{T_{\mathrm{fus}}}^{T} C_p^{(\mathrm{s})}\,\mathrm{d}T\,,\\
\Delta S &= \int_{T}^{T_{\mathrm{fus}}} \frac{C_p^{(\mathrm{l})}}{T}\,\mathrm{d}T - \frac{\Delta_{\mathrm{fus}}H}{T_{\mathrm{fus}}} + \int_{T_{\mathrm{fus}}}^{T} \frac{C_p^{(\mathrm{s})}}{T}\,\mathrm{d}T\,,\\
\Delta G &= \Delta H - T\Delta S\\
&= -\Delta_{\mathrm{fus}}H\left[1-\frac{T}{T_{\mathrm{fus}}}\right] + \int_{T_{\mathrm{fus}}}^{T} (C_p^{(\mathrm{s})} - C_p^{(\mathrm{l})})\,\mathrm{d}T\\
&\quad - T\int_{T_{\mathrm{fus}}}^{T} \frac{C_p^{(\mathrm{s})} - C_p^{(\mathrm{l})}}{T}\,\mathrm{d}T\,.
\end{aligned}$$

Chapter 4

Application of thermodynamics

4.1 Work

4.1.1 Reversible volume work

The reversible volume work, W_{vol} is connected with a change of the system volume from the initial value V_1 to the final value V_2. We have

$$W_{\text{vol}} = -\int_{V_1}^{V_2} p \, \mathrm{d}V \,, \tag{4.1}$$

where p is the pressure of the system.

U *Main unit:* J

> *Note:* It follows from the equation that during compression $p > 0\,, V_2 < V_1\,, W_{\text{vol}} > 0$ (work is supplied to the system), during expansion $p > 0\,, V_2 > V_1\,, W_{\text{vol}} < 0$ (work is done by the system), which is in compliance with the usage **1.2**.

Work is not a state function [see **3.3.2**] and its value does not depend on the initial (p_1, V_1) and final (p_2, V_2) state only, but also on the path. In terms of mathematical expression it means that in (4.1) we need to know the dependence of the integrand on the integration variable, $p = f(V)$. Several examples of the specification of $p = f(V)$ and calculation of W_{vol} are given below.

- Isobaric process

$$p = \text{const} \qquad \Longrightarrow \qquad W_{\text{vol}} = -p(V_2 - V_1)\,. \tag{4.2}$$

- Isochoric process

$$\mathrm{d}V = 0 \qquad \Longrightarrow \qquad W_{\text{vol}} = 0\,. \tag{4.3}$$

- Isothermal process, the equation of state of an ideal gas

$$p = n\boldsymbol{R}T/V \qquad \Longrightarrow \qquad W_{\text{vol}} = -n\boldsymbol{R}T\ln(V_2/V_1)\,. \tag{4.4}$$

- Isothermal process, the van der Waals equation of state

$$p = \frac{n\boldsymbol{R}T}{V - nb} - \frac{n^2 a}{V^2} \qquad \Longrightarrow \qquad W_{\text{vol}} = -n\boldsymbol{R}T\ln\frac{V_2 - nb}{V_1 - nb} + n^2 a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)\,. \tag{4.5}$$

- Adiabatic process for which Poisson's equations [see **4.2.1**] apply

$$p = \text{const}\,V^{-\kappa} \qquad \Longrightarrow \qquad W_{\text{vol}} = -\frac{\text{const}}{1-\kappa}\left(V_2^{1-\kappa} - V_1^{1-\kappa}\right) = C_V(T_2 - T_1)\,. \tag{4.6}$$

4.1.2 Irreversible volume work

In this case the external pressure p_{ex} is different from the system pressure p. During expansion it is lower and during compression higher than the system pressure. We have

$$W_{\text{vol}} = -\int_{V_1}^{V_2} p_{\text{ex}}\,\mathrm{d}V \tag{4.7}$$

To calculate work we need to know $p_{\text{ex}} = f(V)$. The simplest case is a constant external pressure. Then

$$p_{\text{ex}} = \text{const} \qquad \Longrightarrow \qquad W_{\text{vol}} = -p_{\text{ex}}(V_2 - V_1) \tag{4.8}$$

Note: Irreversible volume work is always higher than reversible volume work. Two cases may occur:

- During irreversible compression, we have to supply more work to the system for compression from the initial volume V_1 to the final volume V_2 than in the case of reversible compression,
- During irreversible expansion, the work done ($W_{\text{done}} = -W_{\text{vol}}$) is smaller than during reversible expansion, and consequently the supplied work is greater.

Example
Determine work during expansion into vacuum.

Solution
In this case $p_{\rm ex} = 0$. According to relation (4.8), $W_{\rm vol} = 0$.

4.1.3 Other kinds of work

- Surface work—work connected with a change of the system surface from the initial value A_1 to the final value A_2. We have

$$W_{\rm surf} = \int_{A_1}^{A_2} \gamma \, {\rm d}A \,, \tag{4.9}$$

  where γ is the surface tension.
- Electrical work—work connected with the transfer of electric charge Q across the potential difference E. We have

$$W_{\rm el} = -\int_0^Q E \, {\rm d}Q \,. \tag{4.10}$$

4.1.4 Shaft work

Shaft work $W_{\rm sh}$ is defined by the relation

$$W_{\rm sh} = \int_{p_1}^{p_2} V \, {\rm d}p \,. \tag{4.11}$$

Using the relation for the total differential of the product of two functions (3.29) we obtain

$$V \, {\rm d}p = {\rm d}(pV) - p{\rm d}V$$

and after integration we arrive at the relation between shaft work and volume work

$$W_{\rm sh} = p_2V_2 - p_1V_1 - \int_{V_1}^{V_2} p{\rm d}V = p_2V_2 - p_1V_1 + W_{\rm vol} \,. \tag{4.12}$$

Shaft work is applied for machines with a steady flow of the substance [see **4.3.3**].

> *Note:* Do not let yourself be mistaken by the name of the quantity W_{sh}. In contrast to volume, surface or electrical work, shaft work is not a kind of work W embraced by the first law of thermodynamics.

Example

If a system exchanges only volume work with its surroundings during an adiabatic process, shaft work is equal to the enthalpy change. Prove this assertion.

Proof

It follows from the specification and from the first law of thermodynamics (3.3) that

$$\Delta U = W_{\mathrm{vol}}, \quad [Q = 0] \,.$$

From the definition of enthalpy (3.9) and relation (4.12) we then obtain

$$\Delta H = \Delta U + \Delta(pV) = W_{\mathrm{vol}} + p_2V_2 - p_1V_1 = W_{\mathrm{sh}} \,.$$

4.2 Heat

That portion of internal energy which can be exchanged between a system and its surroundings only when there is a difference in temperature (while passing from a warmer to a cooler place) is called heat. Heat is not a state function [see **3.3.2**], and consequently its value does not depend on the initial (p_1, V_1) and final (p_2, V_2) state only, but also on the path. It is usually calculated from the change of internal energy and work using the first law of thermodynamics (3.3).

$$Q = \Delta U - W\,. \tag{4.13}$$

In the case of reversible processes, the Second Law of thermodynamics [see equations (3.6)] may be also used to calculate heat, provided that we know the dependence between temperature and entropy

$$Q = \int_{S_1}^{S_2} T\,\mathrm{d}S = T_2S_2 - T_1S_1 - \int_{T_1}^{T_2} S\,\mathrm{d}T\,. \tag{4.14}$$

Several typical examples of heat calculation are given below.

- Adiabatic process

$$Q = 0\,. \tag{4.15}$$

- Isochoric process, no work done

$$Q = \Delta U = U(T_2, V) - U(T_1, V)\,. \tag{4.16}$$

- Isobaric process, only volume work done

$$Q = \Delta H = H(T_2, p) - H(T_1, p)\,. \tag{4.17}$$

- Isothermal reversible process, ideal gas

$$Q = -W = n\boldsymbol{R}T\ln\frac{V_2}{V_1} = -n\boldsymbol{R}T\ln\frac{p_2}{p_1}\,. \tag{4.18}$$

- Isothermal reversible process, the van der Waals equation of state

$$Q = n\boldsymbol{R}T\ln\frac{V_2 - nb}{V_1 - nb}\,. \tag{4.19}$$

- General reversible isothermal process

$$Q = T\int_{S_1}^{S_2}\mathrm{d}S = T\,(S_2 - S_1) = T\Delta S\,. \tag{4.20}$$

4.2.1 Adiabatic process—Poisson's equations

During an adiabatic process [see **1.4.5**], the system does not exchange heat with its surroundings, i.e. $Q = 0$. Work during an adiabatic process (both reversible and irreversible) is equal to the change of internal energy

$$W = \Delta U\,. \tag{4.21}$$

Provided that the following conditions are fulfilled during an adiabatic process, i.e. that

- the process is reversible,
- the system exchanges only volume work with its surroundings,
- the system is an ideal gas,
- the heat capacities C_V and C_p do not depend on temperature,

the following relations, called **Poisson's equations**, apply between T, p and V:

$$pV^{\kappa} = \text{const}\,, \qquad p^{1/\kappa}V = \text{const}\,, \tag{4.22}$$

$$TV^{\kappa-1} = \text{const}\,, \qquad VT^{1/(\kappa-1)} = \text{const}\,, \tag{4.23}$$

$$Tp^{(1-\kappa)/\kappa} = \text{const}\,, \qquad pT^{\kappa/(1-\kappa)} = \text{const}\,, \tag{4.24}$$

where

$$\kappa = \frac{C_p}{C_V} = \frac{C_{p\mathrm{m}}}{C_{V\mathrm{m}}}\,. \tag{4.25}$$

Note: The curves defined by relations (4.22) through (4.24) are called reversible adiabatic lines or isentropic lines.

Example

An ideal gas expanded adiabatically from temperature $T_1 = 300$ K and pressure $p_1 = 1$ MPa to pressure $p_2 = 100$ kPa. Provided that Poisson's equations hold and that $C_{p\mathrm{m}} = \frac{5}{2}\boldsymbol{R}$, find temperature T_2 after the expansion.

Solution

It follows from equation (4.24) that

$$T_2 = T_1 \left(\frac{P_1}{p_2}\right)^{(1-\kappa)/\kappa} .$$

We calculate κ from the Mayer relation (3.67) and from relation (4.25)

$$\kappa = \frac{C_{pm}}{C_{pm} - \boldsymbol{R}} = \frac{5}{3}$$

and after substituting into the relation for T_2 we calculate

$$T_2 = 300 \left(\frac{10^6}{10^5}\right)^{(1-5/3)/(5/3)} = 119.3\,\mathrm{K} .$$

Example

Prove that a reversible adiabatic process is identical with an isentropic process.

Solution

During an adiabatic process, $đQ = 0$, and relation (3.6) holds for reversible processes. Hence $\mathrm{d}S = 0$, and consequently entropy does not change during this process, ($\Delta S = 0$). The process is thus isentropic.

4.2.2 Irreversible adiabatic process

A typical example is an irreversible adiabatic expansion against a constant external pressure p_{ex} completed at pressure equalization ($p = p_{\mathrm{ex}}$). For the volume work, relation (4.8) applies

$$W_{\mathrm{vol}} = -p_{\mathrm{ex}}(V_2 - V_1) . \tag{4.26}$$

If the heat capacity C_V is constant, we also have [see (4.6)]

$$W_{\mathrm{vol}} = C_V(T_2 - T_1) . \tag{4.27}$$

If a system behaves as an ideal gas, we may write (4.26) in the form

$$W_{\mathrm{vol}} = -p_{\mathrm{ex}} \left(\frac{n\boldsymbol{R}T_2}{p_{\mathrm{ex}}} - \frac{n\boldsymbol{R}T_1}{p_1} \right) . \tag{4.28}$$

Note: Equations (4.26) − (4.28) do not serve only for the calculation of work. If we know the initial state of a system, i.e. T_1, p_1 ($V_1 = n\boldsymbol{R}T_1/p_1$), and p_{ex}, we can ascertain the final state, i.e. T_2, V_2 by solving the equations.

Example

An ideal gas expanded adiabatically from temperature $T_1 = 300$ K and pressure $p_1 = 1$ MPa to pressure $p_2 = 100$ kPa. Provided that the external pressure was constant for the whole time of expansion and equal to pressure p_2, and that $C_{pm} = \frac{5}{2}\boldsymbol{R}$, find the temperature after expansion, T_2. Is it possible to calculate volumes V_1 and V_2 at the beginning and end of the expansion?

Solution

We rewrite equation (4.27) to the form

$$W_{\mathrm{vol}} = n(C_{pm} - \boldsymbol{R})(T_2 - T_1) \,,$$

compare it with (4.28)

$$n(C_{pm} - \boldsymbol{R})(T_2 - T_1) = -p_2 \left(\frac{n\boldsymbol{R}T_2}{p_2} - \frac{n\boldsymbol{R}T_1}{p_1} \right)$$

and after rearrangement we obtain

$$T_2 = T_1 \left(1 + \frac{\boldsymbol{R}}{C_{pm}} \, \frac{p_2 - p_1}{p_1} \right) = 192\,\mathrm{K} \,.$$

The volumes cannot be determined from the specification because we do not know the amount of substance of the expanding gas.

4.3 Heat engines

A **heat engine** is a device that cyclically converts heat into work. According to the Second Law of thermodynamics, this conversion cannot be complete [see **3.1.3**]. In the strict sense of the word, a heat engine means a device that cyclically receives heat Q_2 ($Q_2 > 0$) from the warmer reservoir of temperature T_2. It converts part of it into work $W_{\text{done}} = -W$, which it supplies to the surroundings. At the same time it supplies heat $Q_{\text{supplied}} = -Q_1$ ($Q_1 < 0$) to the cooler reservoir of temperature T_1, and returns to the initial state. During this cyclic process, the change of internal energy is zero, and consequently we have

$$Q_1 + W + Q_2 = 0\,.$$

Example

A heat engine received 600 J of heat from the warmer reservoir, supplied 500 J of heat to the cooler reservoir, and returned to the initial state. Ascertain the work performed by the engine.

Solution

It follows from the specification that $Q_1 = 600$ J, $Q_2 = -500$ J, $Q = Q_1 + Q_2 = 100$ J. Since the system returned to its original state, $\Delta U = 0$. From equation (4.13) we thus have

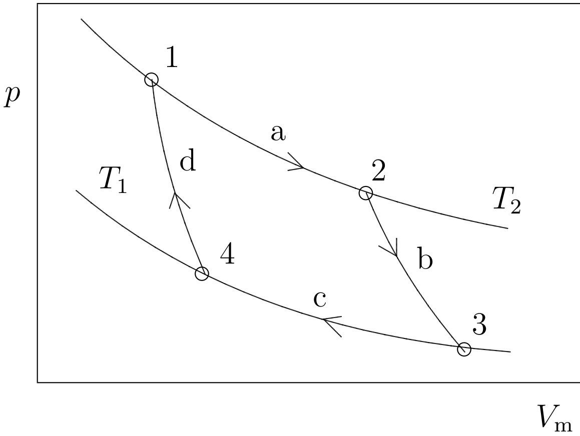
$$W = -Q = -100\,\mathrm{J}\,.$$

The work *performed by the engine* is $W_{\text{done}} = -W = -(-100\,\mathrm{J}) = +100\,\mathrm{J}\,.$

4.3.1 The Carnot heat engine

Let the temperature of the warmer reservoir be T_2 and that of the cooler reservoir be T_1. One cycle is comprised of four partial reversible processes:

(a) isothermal expansion at temperature T_2
(b) adiabatic expansion from temperature T_2 to temperature T_1
(c) isothermal compression at temperature T_1
(d) adiabatic compression from temperature T_1 to the initial point.



Obr. 4.1: The Carnot cycle in variables $p - V_{\mathrm{m}}$. The curves a and c are the isotherms $[T_2]$ and $[\,T_1]$, curves b and d are adiabats.

Figure 4.1 shows a diagram of the Carnot cycle in the pressure—molar volume coordinates, Figure 4.2 shows it in the temperature—molar entropy coordinates. The **Carnot engine efficiency** η is defined by the relation

$$\eta = \frac{\text{work done}}{\text{heat supplied from the warmer container}} = \frac{-W}{Q_2}\,. \tag{4.29}$$

It also holds that

$$\eta = \frac{T_2 - T_1}{T_2}\,. \tag{4.30}$$

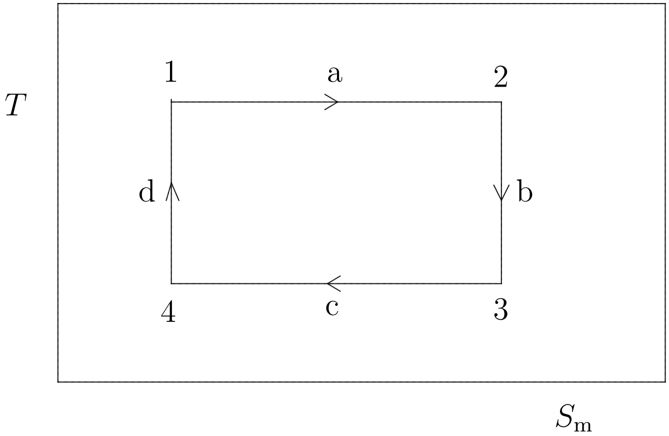
This equation is called the Carnot formulation of the Second Law of thermodynamics.

> *Note:* A reversibly operating heat engine cannot exist in practice because, among other reasons, the processes in such an engine would progress at an infinitesimal rate.

The following inequality holds for the efficiency of two engines operating reversibly and irreversibly between the same reservoirs:

$$\eta_{\text{reversible engine}} > \eta_{\text{irreversible engine}}\,. \tag{4.31}$$

This inequality is called the Clausius formulation of the Second Law of thermodynamics.



Obr. 4.2: The Carnot cycle in variables $T - S_{\mathrm{m}}$. The line segments a and c running parallel to the axis S_{m} are the isotherms $[T_2]$ and $[T_1]$. The line segments b and d running parallel to the axis T are adiabats (all processes in the Carnot cycle are reversible, the reversible adiabats are isentropic lines).

Note: The inequality (4.31) has nothing to do with mechanical losses (e.g. by friction). It is based on the fact that irreversible work is smaller than reversible work.

Example

The Carnot heat engine received heat $Q_2 = 100$ J from a heat reservoir of temperature $T_2 = 600$ K, performed work, delivered heat $-Q_1$ to the cooler reservoir of temperature $T_1 = 300$ K, and returned to the initial state. Calculate the engine's efficiency, the performed work and the supplied heat.

Solution

From relation (4.30) we have

$$\eta = \frac{T_2 - T_1}{T_2} = \frac{600 - 300}{600} = \frac{1}{2}\,.$$

Using relation (4.29) we calculate the work performed by the engine

$$W_{\text{done}} = -W = Q_2\eta = 100 \times \frac{1}{2} = 50\,\mathsf{J}\,.$$

Since the initial and final state are identical, the internal energy change is

$$\Delta U = 0\,.$$

We substitute this result into (3.3)

$$0 = Q + W = Q_2 + Q_1 + W$$

and calculate the supplied heat

$$Q_1 = -Q_2 - W = -100 - (-50) = -50\,\mathsf{J}\,.$$

The Carnot engine supplied $-Q_1 = +50$ J of heat to the cooler reservoir.

Example

Prove that the Carnot engine efficiency can never equal one.

Proof

It follows from relation (4.30) that $\eta = 1$ only when $T_1 = 0$ K or $T_2 \to \infty$. According to the Third Law of thermodynamics (**3.1.4**), however, temperature 0 K cannot be attained. An infinitely high temperature T_2 cannot be attained, either.

4.3.2 Cooling engine

A cooling engine is a device that cyclically absorbs heat Q_1 from the cooler reservoir of temperature T_1 and transfers it to the warmer reservoir of temperature T_2. The work W is needed for this transfer.

The **cooling engine efficiency** (economy) is defined by the relation

$$\beta = \frac{\text{heat taken from the cooler reservoir}}{\text{work needed for this heat transfer}} = \frac{Q_1}{W}\,. \tag{4.32}$$

The efficiency of a reversible cooling engine operating between the temperatures T_1 and T_2 is always higher than that of an irreversible engine [compare with (4.31)], and it is

$$\beta = \frac{T_1}{T_2 - T_1}\,. \tag{4.33}$$

Example

A refrigerator is a device consisting of a cooling engine and a cooler reservoir (i.e. the space in which foods are kept) of temperature T_1. The room in which the fridge is placed represents the warmer reservoir of temperature T_2. If we neglect the losses, the work W needed for the transfer of heat from the space of the fridge to the room equals the amount of electric energy consumed from the electric network. If $T_1 = 275$ K, and $T_2 = 300$ K, assess the amount of electric energy needed for the transfer of 1100 J of heat from the cooled space to the room.

Solution

According to (4.33), the cooling engine efficiency is:

$$\beta = \frac{275}{300 - 275} = 11\,.$$

We calculate the work needed for the heat transfer from (4.32)

$$W = \frac{Q_1}{\beta} = \frac{1100}{11} = 100\,\mathrm{J}\,.$$

A total of 100 J of electric energy is needed to transfer 1100 J of heat.

A **Heat pump** is a device consisting of a cooling engine and a warmer reservoir of temperature T_2. The surroundings represent the cooler reservoir of temperature T_1. A heat pump serves for the heating of a room using heat absorbed from, e.g. a cooler stream. Both in the case of a refrigerator and in the case of a heat pump, work is consumed on heat transfer from the cooler to the warmer place. The difference between the two devices rests only in the purpose to which they serve.

Example

Let us imagine a cottage whose temperature inside is $T_2 = 290$ K, and a nearby stream of temperature $T_1 = 277$ K. The cottage is not adiabatically insulated from its surroundings, and consequently the heat Q has to be supplied per a time unit in order to maintain constant temperature in the rooms. Prove that it is cheaper to heat the cottage using a heat pump than using an electric storage heater.

Proof

When using a heat pump, the heat Q supplied to the cottage equals the sum of work W and heat Q_1 supplied to the pump, $Q = W + Q_1$. From this and from (4.32) and (4.33) it follows that

$$W = Q\,\frac{T_2 - T_1}{T_2} = \frac{Q}{22.3}\,.$$

When a heat pump is used, the electric energy needed for heating equals W. In the case of an electric storage heater converting electric energy into heat, it equals Q. In terms of electric energy consumption, a heat pump comes 22.3× cheaper under the given conditions.

4.3.3 Heat engine with steady flow of substance

A heat engine with a steady flow of substance is a device that exchanges shaft work $W_{\rm sh}$ with its surroundings at the cost of the energy of the working medium flow.

From the energy balance applied to a steady state (while neglecting the potential and kinetic energy of the current) we have

$$U_1 + p_1V_1 + W_{\rm sh} + Q = U_2 + p_2V_2\,. \tag{4.34}$$

This relation may be written in the form

$$H_2 - H_1 = Q + W_{\mathrm{sh}}\,, \tag{4.35}$$

which may be considered the formulation of the first law of thermodynamics for heat engines with a steady flow of the working medium [compare with relation (3.3)].

In the event that no heat is exchanged with the surroundings (the engine works adiabatically), the shaft work equals the loss of enthalpy in the medium passing through the engine.

The shaft work W_{sh} [see **4.1.4**] may be understood as volume work corrected for work needed to drive the working medium in and out of the engine.

Note: It is important to realize the difference between the Carnot heat engine [see **4.3.1**] and a heat engine with a steady flow of substance. In the Carnot engine, the working medium is part of the engine, and this engine exchanges only heat and work with its surroundings. In a heat engine with a steady flow of substance, the working medium passes through the engine. A steam turbine or a petrol engine are typical examples of the latter.

Example

Water steam of temperature $t_1 = 500°\mathrm{C}$ and pressure $p_1 = 10$ MPa flows into a steam turbine converting shaft work into electric energy. For this temperature and pressure, the following values of molar enthalpy and molar volume can be found in tables: $H_{\mathrm{m1}} = 60705$ J/mol, $V_{\mathrm{m1}} = 0.6039$ dm^3/mol. After leaving the steam turbine, the steam has a temperature $t_2 = 160°\mathrm{C}$ and pressure $p_2 = 0.5$ MPa ($H_{\mathrm{m2}} = 49800$ J/mol, $V_{\mathrm{m2}} = 7.056$ dm^3/mol). What amount of electric energy can be obtained from one mole of steam provided that the turbine operates adiabatically? How much is accounted for by volume work? Why cannot volume work be fully converted into electric energy?

Solution

From equation (4.35) and from the assumption that the process is adiabatic it follows that

$$W_{\rm sh} = \Delta H = 49800 - 60705 = -10905 \text{ J}.$$

The obtained electric energy is $-W_{\rm sh}$= 10905 J.
We calculate the volume work from (4.12)

$$W_{\rm vol} = W_{\rm sh} + p_1V_1 - p_2V_2 = -10905 + 7.056 \times 500 - 0.6039 \times 10000 = -13416 \text{ J}.$$

The volume work $W_{\rm vol} = -13416$ J cannot be used to the full to generate electric energy. Part of this work, 13416 − 10905 = 2511 J, is consumed on pushing water steam through the turbine.

4.3.4 The Joule-Thomson effect

When a fluid passes through a barrier that offers resistance to it (e.g. porous glass or a throttle), a change in temperature and pressure occurs in the fluid. This fact is called the Joule-Thomson effect. If the fluid passing through the barrier does not exchange heat with the surroundings, the transfer through the barrier is an isenthalpic process

$$H(T_1, p_1) = H(T_2, p_2)\,, \tag{4.36}$$

where the subscripts $_1$ and $_2$ indicate the state of the system before and after the barrier. The ratio of the temperature and pressure difference, $\dfrac{T_2 - T_1}{p_2 - p_1}$, is called the **integral Joule-Thomson coefficient**.

Note: There is a connection between an engine with a steady flow of substance and the Joule-Thomson phenomenon. If an engine with a steady flow operates adiabatically and does not exchange any shaft work with its surroundings, equation (4.35) rearranges to (4.36), i.e. the Joule-Thomson effect occurs.

4.3.5 The Joule-Thomson coefficient

The **differential Joule-Thomson coefficient**, μ_{JT}, is defined by the relation

$$\mu_{\mathrm{JT}} = \lim_{p_2 \to p_1} \frac{T_2 - T_1}{p_2 - p_1} = \left(\frac{\partial T}{\partial p}\right)_H , \tag{4.37}$$

U *Main unit:* K Pa^{-1}.

It follows from relation (4.36) that $H = H(T, p) = \text{const}$. From this and from equations (3.27) and (3.28) we get

$$\mu_{\mathrm{JT}} = -\frac{\left(\dfrac{\partial H}{\partial p}\right)_T}{\left(\dfrac{\partial H}{\partial T}\right)_p} . \tag{4.38}$$

Substituting for the partial derivatives from (3.56) and (3.57) leads us to the relations which are used for the calculation of the Joule-Thomson coefficient from the equations of state

$$\mu_{\mathrm{JT}} = \frac{T\left(\dfrac{\partial V}{\partial T}\right)_p - V}{C_p} . \tag{4.39}$$

Example

Derive the relation for the Joule-Thomson coefficient as a function of temperature and molar volume for an ideal gas and for a gas obeying the van der Waals equation of state (2.23).

Solution

From the equation of state of an ideal gas we obtain

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{n\boldsymbol{R}}{p} = \frac{V}{T}$$

By substituting into (4.39) we can see that $\mu_{\mathrm{JT}} = 0$.

From the van der Waals equation we obtain (see the example in **3.3.1**)

$$\left(\frac{\partial V}{\partial T}\right)_p = -n\,\frac{\frac{\boldsymbol{R}}{V_{\mathrm{m}}-b}}{-\frac{\boldsymbol{R}T}{(V_{\mathrm{m}}-b)^2} + 2\frac{a}{V_{\mathrm{m}}^3}}$$

and substitute into (4.39)

$$\mu_{\mathrm{JT}} = \frac{\frac{\boldsymbol{R}T(V_{\mathrm{m}}-b)V_{\mathrm{m}}^3}{\boldsymbol{R}TV_{\mathrm{m}}^3-2a(V_{\mathrm{m}}-b)^2} - V_{\mathrm{m}}}{C_{p\mathrm{m}}} = \frac{V_{\mathrm{m}}}{C_{p\mathrm{m}}}\,\frac{2a(V_{\mathrm{m}}-b)^2 - \boldsymbol{R}TbV_{\mathrm{m}}^2}{\boldsymbol{R}TV_{\mathrm{m}}^3 - 2a(V_{\mathrm{m}}-b)^2}\,.$$

4.3.6 Inversion temperature

From the definition of the Joule-Thomson coefficient (4.37) it follows that a fluid passing through a barrier cools on expansion when $\mu_{\mathrm{JT}} > 0$, and heats up when $\mu_{\mathrm{JT}} < 0$.

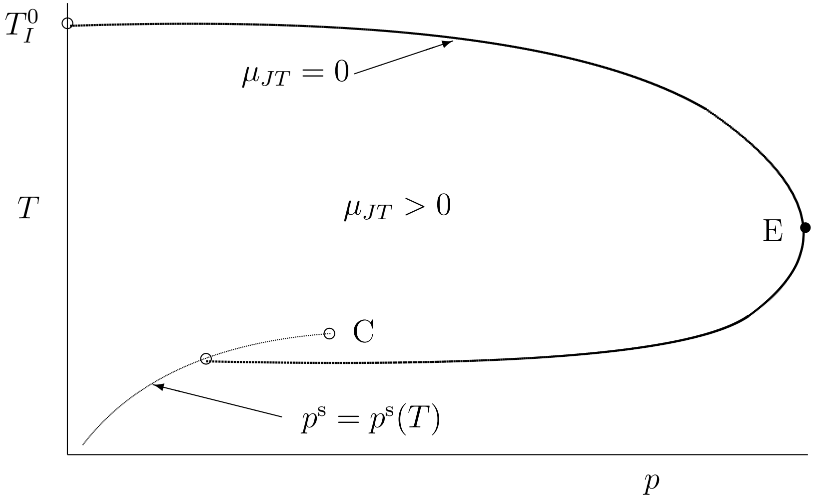
$$p_2 < p_1 \quad \text{and} \quad \mu_{\mathrm{JT}} > 0 \quad \longrightarrow \quad T_2 < T_1 \quad [H]\,, \tag{4.40}$$

$$p_2 < p_1 \quad \text{and} \quad \mu_{\mathrm{JT}} < 0 \quad \longrightarrow \quad T_2 > T_1 \quad [H]\,. \tag{4.41}$$

The temperature at which $\mu_{\mathrm{JT}} = 0$ at a given pressure is called the **inversion temperature**, T_{inv}. The dependence of the inversion temperature on pressure is schematically drawn in Figure 4.3.

Example

From the van der Waals equation derive the relation for the inversion temperature at zero pressure.



Obr. 4.3: Dependence of the inversion temperature on pressure. The Joule-Thomson coefficient is positive inside the curve delimiting this dependence and negative outside this boundary. T_I^0 is the inversion temperature at zero pressure. C is the critical point. The weak line ending in the critical point is the dependence of the saturated vapour pressure on temperature. The pressure corresponding to the point E is the highest pressure at which the Joule-Thomson coefficient can be positive

Solution

We proceed from the formula used in the preceding example for μ_{JT} of a van der Waals gas. For $\mu_{\mathrm{JT}} = 0$, the numerator in the formula is zero

$$\boldsymbol{R}T\, b\, V_{\mathrm{m}}^2 - 2a(V_{\mathrm{m}} - b)^2 = 0$$

and

$$T_{\mathrm{inv}} = \frac{2a}{\boldsymbol{R}b}\left(\frac{V_{\mathrm{m}} - b}{V_{\mathrm{m}}}\right)^2 .$$

At zero pressure is $V_{\mathrm{m}} = \infty$, and hence

$$\lim_{p\to 0} T_{\mathrm{inv}} = \lim_{V_{\mathrm{m}}\to\infty} T_{\mathrm{inv}} = \lim_{V_{\mathrm{m}}\to\infty} \frac{2a}{\boldsymbol{R}b}\left(\frac{V_{\mathrm{m}} - b}{V_{\mathrm{m}}}\right)^2 = \frac{2a}{\boldsymbol{R}b}\,, \qquad [p = 0]\,.$$

Example

Using the relation following from the van der Waals equation, estimate the inversion temperature at zero pressure for several common gases given that you know the critical temperatures of the gases. Which gases cool and which heat up during isenthalpic expansion at room temperatures and low pressures?

Data: helium, $T_c = 5.3$ K; hydrogen, $T_c = 33.2$ K; nitrogen, $T_c = 126.3$ K; oxygen, $T_c = 154.6$ K; carbon dioxide, $T_c = 304.2$ K.

Solution

The constants a, b of the van der Waals equation can be estimated using the critical temperature and pressure from relations (2.24). By substituting these relations into the equation for the inversion temperature from the preceding example, we get

$$T_{\text{inv}} = \frac{2a}{\boldsymbol{R}b} = \frac{27}{4} T_c \,, \qquad [p = 0] \,.$$

The estimated inversion temperatures are as follows (experimental values are given in brackets): helium, 35.8 K (40 K); hydrogen, 176 K (202 K); nitrogen, 852 K (621 K); oxygen, 1043 K (764 K); carbon dioxide, 2053 K (1500 K).

It follows from Figure 4.4 that at low pressures and temperatures lower than the inversion temperature, $\mu_{\text{JT}} > 0$ and gases cool on expansion. At room temperatures, $T \sim 300$ K, nitrogen, oxygen and carbon dioxide cool on expansion at constant enthalpy while hydrogen and helium heat up.

Chapter 5

Thermochemistry

Thermochemistry in a strict sense of the word means that part of thermodynamics which deals with heat released during chemical reactions, or heat that has to be supplied in order for a reaction to take place. In a broader sense of the word, thermochemistry deals with the changes in thermodynamic quantities of chemically reacting systems.

We will write the general chemical reaction either in the form

$$a\,\mathrm{A} + b\,\mathrm{B} + \cdots = r\,\mathrm{R} + s\,\mathrm{S} + \cdots\,, \tag{5.1}$$

where a, b, ..., r, s, ... represent the stoichiometric coefficients while the capital letters indicate the reactants, or in a more compact form

$$0 = \sum_{i=1}^{n} \nu_i\,\mathrm{R}_i\,, \tag{5.2}$$

where ν_i is the stoichiometric coefficient of substance R_i and n is the number of substances participating in the reaction. Note that when we use the form (5.2), the ν_i values are positive for the products and negative for the reactants (initial substances).

Example

Write the neutralization of sulphuric acid by sodium hydroxide in the form of equation (5.1), and in that of equation (5.2).

Solution

$$2\,\mathsf{NaOH} + \mathsf{H_2SO_4} = \mathsf{Na_2SO_4} + 2\,\mathsf{H_2O}$$

and

$$0 = \mathsf{Na_2SO_4} + 2\,\mathsf{H_2O} - 2\,\mathsf{NaOH} - \mathsf{H_2SO_4}$$

5.1 Heat of reaction and thermodynamic quantities of reaction

D *Definition*

The heat of reaction Q_r of the reaction (5.1) is the heat exchanged between a system and its surroundings and needed for the reaction of a units of a pure substance A, b units of a pure substance B, ... to form r units of a pure substance R, s units of a pure substance S, ... at constant temperature. The unit can be a molecule, mol or kmol. When a moles of substance A react with b moles of substance B..., the heat of reaction is related to one mole.

> *Note:* Sometimes we may encounter the terms *heat of neutralization*, *heat of combustion*, *heat of hydrogenation*, etc. All these heats represent special cases of the heat of reaction, and their names only specify the type of chemical reaction taking place.

An **exothermic reaction** is such during which $Q_r < 0$ (heat is evolved).
An **endothermic reaction** is such during which $Q_r > 0$ (heat is absorbed).

If a reaction proceeds at constant pressure and no other but volume work is performed, the heat of reaction is equal to the **reaction enthalpy**, i.e. to the difference between the enthalpies of the products and reactants

$$\begin{aligned} Q_r &= \Delta_{\mathrm{r}} H = \sum_{i=R,S,\cdots} H_i - \sum_{i=A,B,\cdots} H_i \\ &= rH_{\mathrm{m,R}} + sH_{\mathrm{m,S}} + \cdots - aH_{\mathrm{m,A}} - bH_{\mathrm{m,B}} - \cdots = \sum_{i=1}^{n} \nu_i H_{\mathrm{m}i}\,, \quad [T,p]\,, \end{aligned} \tag{5.3}$$

where $H_{\mathrm{m}i}$ is the molar enthalpy of a pure substance i. If a reaction proceeds at constant volume and no work is performed, the heat of reaction is equal to the **internal energy of reaction**, i.e. to the difference between the internal energies of the products and reactants

$$\begin{aligned} Q_r &= \Delta_{\mathrm{r}} U = \sum_{i=R,S,\cdots} U_i - \sum_{i=A,B,\cdots} U_i \\ &= r U_{\mathrm{m,R}} + s U_{\mathrm{m,S}} + \cdots - a U_{\mathrm{m,A}} - b U_{\mathrm{m,B}} - \cdots = \sum_{i=1}^{n} \nu_i U_{\mathrm{m}i}\,, \quad [T, V]\,. \end{aligned} \tag{5.4}$$

Other thermodynamic quantities of reaction, e.g. the **reaction entropy** $\Delta_{\mathrm{r}} S$ or the **reaction Gibbs energy** $\Delta_{\mathrm{r}} G$, are defined similarly as the reaction enthalpy and the reaction internal energy.

Note: Note that the heat of reaction and thermodynamic quantities of reaction are defined for an idealized process with both reactants and products in their respective standard states (as pure substances). The changes in thermodynamic quantities caused by the mixing of substances are not considered here.

5.1.1 Linear combination of chemical reactions

If we multiply all stoichiometric coefficients of the general reaction

$$a_1\,\mathrm{A} + b_1\,\mathrm{B} + \cdots = r_1\,\mathrm{R} + s_1\,\mathrm{S} + \cdots \tag{5.5}$$

by an arbitrary number α, and the stoichiometric coefficients of the reaction

$$a_2\,\mathrm{A} + b_2\,\mathrm{B} + \cdots = r_2\,\mathrm{R} + s_2\,\mathrm{S} + \cdots \tag{5.6}$$

by an arbitrary number β, and add these two reactions, we obtain the reaction

$$(\alpha a_1 + \beta a_2)\,\mathrm{A} + (\alpha b_1 + \beta b_2)\,\mathrm{B} + \cdots = (\alpha r_1 + \beta r_2)\,\mathrm{R} + (\alpha s_1 + \beta s_2)\,\mathrm{S}\,, \tag{5.7}$$

which is called the **linear combination of reactions** (5.5) and (5.6). The linear combination of a greater number of chemical reactions is defined in a similar way.

Example

The chemical reaction

$$\mathsf{CH_4 + CO_2 = 2\,CO + 2\,H_2} \tag{5.8}$$

is the linear combination of the reactions

$$\begin{aligned} \mathsf{C + 2\,H_2} &= \mathsf{CH_4}\,, \qquad (5.9)\\ \mathsf{C} + \frac{1}{2}\mathsf{O_2} &= \mathsf{CO}\,, \qquad (5.10)\\ \mathsf{C + O_2} &= \mathsf{CO_2}\,. \qquad (5.11) \end{aligned}$$

We obtain equation (5.8) by subtracting equations (5.9) and (5.11) from twice equation (5.10).

5.1.2 Hess's law

If a chemical reaction R is a linear combination of reactions R_1, R_2, ..., its reaction enthalpy is the same linear combination of the reaction enthalpies of the reactions R_1, R_2, ...

> *Note:* Hess's law is a consequence of the fact that enthalpy is a state function. An analogy of Hess's law also holds for other thermodynamic quantities of reaction, e.g. the reaction entropy or the Gibbs energy.

Example

At temperature T = 298 K and pressure p = 101.325 kPa, the reaction enthalpy of the reaction (5.9) equals −74.852 kJ/mol, that of the reaction (5.10) equals −110.529 kJ/mol, and that of the reaction (5.11) equals −393.522 kJ/mol. Calculate the reaction enthalpy of the reaction (5.8).

Solution

Based on the result of the preceding example, the reaction enthalpy is

$$2 \times (-110.529) + (-1) \times (-74.852) + (-1) \times (-393.522) = 247.316\,\mathsf{kJ\,mol^{-1}}\,.$$

5.2 Standard reaction enthalpy $\Delta_{\rm r} H^\circ$

D *Definition*

The standard reaction enthalpy is the reaction heat of a chemical reaction that proceeds at constant temperature T (it must be stated) and standard pressure $p^{\rm st} = 101.325\,\text{kPa}$.

> *Note:* A less accurate term standard heat of reaction is often used for the standard reaction enthalpy in the same meaning.

5.2.1 Standard enthalpy of formation $\Delta_{\rm f} H^\circ$

Definition: The standard enthalpy of formation is the standard reaction enthalpy of a reaction during which one mole of a given substance is formed from elements. The elements are assumed to enter the reaction in those phases which are the most stable at a given temperature and standard pressure; if the elements are gaseous, they are considered in their most stable molecular forms in the state of an ideal gas.

> *Note:* At common temperatures, carbon exists in the crystalline modification of graphite and not diamond; hydrogen, nitrogen and oxygen exist in the form of two-atom molecules H_2, N_2, O_2.

Example

The standard reaction enthalpy of the reaction (5.9) is the standard enthalpy of formation of methane, the standard reaction enthalpy of the reaction (5.10) is the standard enthalpy of formation of carbon monoxide.

In consequence of Hess's law, the standard reaction enthalpy of every chemical reaction equals the difference between the standard enthalpies of formation of its products and reactants multiplied by the respective stoichiometric coefficients. For the general reaction (5.1) we thus have

$$\begin{aligned}\Delta_{\rm r} H^\circ &= r\,\Delta_{\rm f} H^\circ_{\rm R} + s\,\Delta_{\rm f} H^\circ_{\rm S} + \cdots - a\,\Delta_{\rm f} H^\circ_{\rm A} - b\,\Delta_{\rm f} H^\circ_{\rm B} - \cdots \\ &= \sum_{i=1}^{n} \nu_i\,\Delta_{\rm f} H^\circ_i \qquad (5.12)\end{aligned}$$

Note: It follows from the definition that the standard enthalpy of formation of elements in their most stable phases and molecular forms are zero.

5.2.2 Standard enthalpy of combustion $\Delta_{\mathrm{c}}H^\circ$

Definition: The standard enthalpy of combustion is the standard reaction enthalpy of a reaction during which one mole of a substance reacts with oxygen while producing defined waste products of the reaction.

Note: If a substance contains elements C, H, N, Cl, S, the defined waste products are gaseous CO_2, N_2, HCl, SO_2, and water in their most stable state at a given temperature, i.e. either gaseous or liquid.

If we know the enthalpies of combustion of all substances present in the general reaction (5.1), then for the reaction enthalpy of this reaction we write

$$\begin{aligned}\Delta_{\mathrm{r}}H^\circ &= a\,\Delta_{\mathrm{c}}H^\circ_{\mathrm{A}} + b\,\Delta_{\mathrm{c}}H^\circ_{\mathrm{B}} + \;\cdots\; - r\,\Delta_{\mathrm{c}}H^\circ_{\mathrm{R}} - s\,\Delta_{\mathrm{c}}H^\circ_{\mathrm{S}} - \;\cdots \\ &= -\sum_{i=1}^{n} \nu_i\,\Delta_{\mathrm{c}}H^\circ_i\,. \end{aligned} \tag{5.13}$$

This equation is the consequence of Hess's law [compare with equation (5.12)].

Example

The reaction enthalpy of the reaction (5.11) is the standard enthalpy of combustion of carbon, the reaction enthalpy of the reaction (5.10) is not.

Note: The term **heating value** is often used in practice, indicating the change in enthalpy during the combustion of a defined amount of fuel to gaseous (water, carbon dioxide, . . .) and solid products (ash).

Example

Calculate the standard reaction enthalpy of combustion of methane using the equation

$$\mathsf{CH_4} + 2\,\mathsf{O_2} = \mathsf{CO_2} + 2\,\mathsf{H_2O}(g).$$

at temperature 298.15 K and $p^{\mathrm{st}} = 101.325$ kPa. Is this reaction enthalpy the standard enthalpy of combustion of methane? Data: At T = 298.15 K and p = 101.325 kPa, $\Delta_{\mathrm{f}} H^{\circ}(\mathsf{H_2O}(g))$ = −241.827 kJ/mol, $\Delta_{\mathrm{f}} H^{\circ}(\mathsf{CO_2})$ = −393.522 kJ/mol, $\Delta_{\mathrm{f}} H^{\circ}(\mathsf{CH_4})$ = −74.852 kJ/mol. The enthalpy of formation of molecular oxygen is zero.

Solution

Based on equation (5.12) we have

$$\begin{aligned}\Delta_{\mathrm{r}} H^{\circ} &= \Delta_{\mathrm{f}} H^{\circ}(\mathsf{CO_2}) + 2\Delta_{\mathrm{f}} H^{\circ}(\mathsf{H_{20}}(g)) - \Delta_{\mathrm{f}} H^{\circ}(\mathsf{CH_4}) - 2\Delta_{\mathrm{f}} H^{\circ}(\mathsf{O_2}) \\ &= -393.522 + 2 \times (-242.827) - (-74.852) - 2 \times 0 = -802.324 \text{ kJ/mol}\end{aligned}$$

In this case the reaction enthalpy is not the standard enthalpy of combustion. In the above chemical reaction water is in the gaseous state, but the most stable state of water at the given temperature and pressure is liquid.

5.3 Kirchhoff's law—dependence of the reaction enthalpy on temperature

For the derivative of the reaction enthalpy with respect to the temperature of the general reaction (5.1) we have

$$\left(\frac{\partial \Delta_\mathrm{r} H}{\partial T}\right)_p = \Delta C_p\,, \tag{5.14}$$

where

$$\Delta C_p = r\,C_{pm}(\mathrm{R}) + s\,C_{p\mathrm{m}}(\mathrm{S}) + \ \cdots\ - a\,C_{p\mathrm{m}}(\mathrm{A}) - b\,C_{p\mathrm{m}}(\mathrm{B}) - \ \cdots = \sum_{i=1}^{n} \nu_i C_{p\mathrm{m}i}\,. \tag{5.15}$$

Equation (5.14) follows from the definition of the reaction enthalpy (5.3) and from the definition of the isobaric heat capacity (3.18). By integrating (5.14) from temperature T_1 to T_2 we obtain

$$\Delta_\mathrm{r} H(T_2) = \Delta_\mathrm{r} H(T_1) + \int_{T_1}^{T_2} \Delta C_p\, dT\,, \qquad [p]\,. \tag{5.16}$$

This relation is called Kirchhoff's law. It allows us to convert reaction enthalpies from one temperature to another if we know the dependence of the heat capacities of substances on temperature.

Note: $\Delta_\mathrm{r} H(T_2)$ is the reaction enthalpy of a reaction that took place at temperature T_2, i.e. both the reactants and products have the same temperature T_2.

Example

Based on the result of the preceding example and the data on the molar isobaric heat capacities of substances, calculate the enthalpy of combustion of methane at temperature 1500 K. How will the enthalpy of combustion change if we use air (approximately 20 mole percent O_2, 80 mole percent N_2) instead of oxygen for methane combustion? Data: $C_{pm}(\mathrm{CO_2}) = 51.0$ J/mol, $C_{pm}(\mathrm{H_2O}(g)) = 39.8$ J/mol, $C_{pm}(\mathrm{CH_4}) = 66.9$ J/mol, $C_{pm}(\mathrm{O_2}) = 33.7$ J/mol, $C_{pm}(\mathrm{N_2}) = 34.8$ J/mol.

Solution

From the result of the preceding example we know that the enthalpy of combustion of methane (while gaseous water originates) at $T = 298.15$ K is -802.324 kJ/mol. We use equation (5.16) for conversion to temperature 1500 K:

$$\Delta_{\rm c}H^\circ(T = 1500\,\mathsf{K}) = \Delta_{\rm c}H^\circ(T = 298.15\,\mathsf{K}) + \int_{298.15}^{1500} \Delta C_p \mathrm{d}T\,,$$

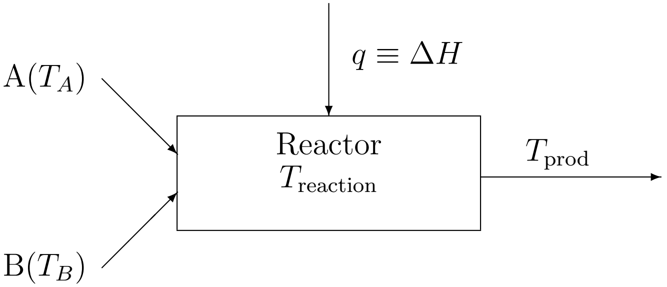
where

$$\begin{aligned} \Delta C_p &= C_{p\rm m}(\mathsf{CO_2}) + 2C_{p\rm m}(\mathsf{H_2O}) - C_{p\rm m}(\mathsf{CH_4}) - 2C_{p\rm m}(\mathsf{O_2}) \\ &= 51.0 + 2 \times 39.8 - 66.9 - 2 \times 33.7 = -3.7\ \mathsf{J/mol}\,. \end{aligned}$$

By substituting into the preceding equation and integrating we obtain

$$\Delta_{\rm c}H^\circ(T = 1500\,\mathsf{K}) = -802\,324 - 3.7 \times (1500 - 298.15) = -806\,771\,\mathsf{J\,mol^{-1}}\,.$$

It follows from the reaction enthalpy definition that the enthalpy of combustion does not depend on whether the burning is driven by oxygen or air.



Obr. 5.1: The enthalpy balance of a system in which the chemical reaction A + B = products takes place. Substances A and B enter the reactor at temperatures T_A and T_B, the products leave the reactor at temperature T_{prod}. The temperature in the reactor is T_{reaction}. ΔH is the enthalpy (heat) exchanged between the reactor and its surroundings.

5.4 Enthalpy balances

Let the reaction (5.1) take place in a reactor. Substance A enters the reactor at temperature T_A, substance B at temperature T_B … and the products exit the reactor at temperature T_{prod}; the reaction itself proceeds at temperature T_{reaction}, see Figure 5.1.

The change in enthalpy ΔH needed for this process to take place is

$$\begin{aligned}
\Delta H &= \int_{T_A}^{T_{\text{reaction}}} a\, C_{pm}(\mathrm{A})\,\mathrm{d}T + \int_{T_B}^{T_{\text{reaction}}} b\, C_{pm}(\mathrm{B})\,\mathrm{d}T + \cdots \\
&\quad + \Delta_{\mathrm{r}} H(T_{\text{reaction}}) \\
&\quad + \int_{T_{\text{reaction}}}^{T_{\text{prod}}} r\, C_{pm}(\mathrm{R})\,\mathrm{d}T + \int_{T_{\text{reaction}}}^{T_{\text{prod}}} s\, C_{pm}(\mathrm{S})\,\mathrm{d}T + \cdots \\
&= \Delta_{\mathrm{r}} H(T_1) + \int_{T_1}^{T_{\text{prod}}} r\, C_{pm}(\mathrm{R})\,\mathrm{d}T + \int_{T_1}^{T_{\text{prod}}} s\, C_{pm}(\mathrm{S})\,\mathrm{d}T \cdots \\
&\quad - \int_{T_1}^{T_A} a\, C_{pm}(\mathrm{A})\,\mathrm{d}T - \int_{T_1}^{T_B} b\, C_{pm}(\mathrm{B})\,\mathrm{d}T - \cdots , \qquad [p] , \qquad (5.17)
\end{aligned}$$

where T_1 is the temperature (most often 298.15 K) at which we know the reaction enthalpy of the given reaction. The first equation can be verbally interpreted as follows: the first member on the right side is the enthalpy needed for the heating of the initial substance A from temperature

T_A to the temperature of the reaction T_{reaction}, the second member is the enthalpy needed for the heating of substance B, the third member is the enthalpy supplied to the system by the reaction at temperature T_{reaction}, and the other members are the enthalpies needed for the heating of the products from temperature T_{reaction} to temperature T_{prod} at the exit from the reaction.

> *Note:* Equation (5.17) does not represent the most general enthalpy balance of a system in which a chemical reaction occurs. We might consider cases in which the products exit the reactor at different temperatures, when the reaction does not proceed quantitatively, when the reactants are not in a stoichiometric ratio, or when an inert substance is present in the reacting mixture. Generalization of equation (5.17) to these cases is quite easy.

If the reaction proceeds at constant volume of the system, we balance the internal energy instead of enthalpy. In the balance equation (5.17) we substitute $\Delta_{\mathrm{r}}H$ with the reaction internal energy $\Delta_{\mathrm{r}}U$, and the isobaric heat capacities C_p with the isochoric capacities C_V.

5.4.1 Adiabatic temperature of reaction

If we prevent a system in which a chemical reaction occurs from exchanging heat with its surroundings, we speak about an adiabatic course of the reaction. In such a case we write [compare with (5.17)]

$$\begin{aligned} 0 \;\; = \;\; & \Delta_{\mathrm{r}}H(T_1) + \int_{T_1}^{T_{\mathrm{prod}}} r\,C_{pm}(\mathrm{R})\,\mathrm{d}T + \int_{T_1}^{T_{\mathrm{prod}}} s\,C_{pm}(\mathrm{S})\,\mathrm{d}T \;\cdots \\ & - \int_{T_1}^{T_A} a\,C_{pm}(\mathrm{A})\,\mathrm{d}T - \int_{T_1}^{T_B} b\,C_{pm}(\mathrm{B})\,\mathrm{d}T - \;\cdots\;, \quad [p]\,, \end{aligned} \tag{5.18}$$

with the unknown temperature T_{prod} termed the **adiabatic temperature of reaction**. The term adiabatic temperature of reaction is usually applied to exothermic reactions. Equation (5.18) may then be interpreted as follows: the amount of heat contained in the reactants and the reaction heat of the reaction are used to heat the products to the adiabatic temperature of reaction.

Note: In the enthalpy balance (5.18) it is assumed that the chemical reaction proceeds quantitatively, and that no inert substances (i.e. substances which do not participate in the reaction) are present in the system. If it is not so, members corresponding to the heating of those reactants that do not react during the reaction and of inert substances have to be added to the equation.

The **theoretical flame temperature** is the adiabatic temperature of reaction during burning. The real mean flame temperature is lower than the theoretical temperature due to losses.

Example

Calculate the theoretical flame temperature of methane burnt by air when the air is in a 50 percent surplus. For convenience, suppose that the air is composed of oxygen ($x_{\mathrm{O}_2} = 0.2$) and nitrogen ($x_{\mathrm{N}_2} = 0.8$). Gases enter the reaction at temperature 298.15 K. The reaction proceeds at constant pressure 101.325 kPa. Use data from the examples in **5.3** and **5.2.2** for the calculation.

Solution

We need 2 mol O_2 to burn 1 mol CH_4. Since the air is in a 50 percent surplus, it enters the reaction with three moles of oxygen. Given that the amount of nitrogen in air is four-times higher ($x_{\mathrm{N}_2}/x_{\mathrm{O}_2} = 0.8/0.2 = 4$), a total of $4 \times 3 = 12$ mol N_2 is present in the system during combustion. The whole process can be formally described using an equation in the form

$$\mathrm{CH_4} + 3\,\mathrm{O_2} + 12\,\mathrm{N_2} = \mathrm{CO_2} + 2\,\mathrm{H_2O} + \mathrm{O_2} + 12\,\mathrm{N_2}\,,$$

whose right side lists not only the products of the chemical reaction, water and carbon dioxide, but also excess oxygen and (theoretically inert) nitrogen contained in the air. We use the result from the example in **5.2.2**, $\Delta_{\mathrm{r}} H(T = 298.15\,\mathrm{K}) = -802\,324\,\mathrm{J}$, and apply equation (5.18) to obtain

$$\begin{aligned} 0 &= -802\,324 + \int_{298.15}^{T_{\mathrm{prod}}} \left[C_{pm}(\mathrm{CO_2}) + 2C_{pm}(\mathrm{H_2O}) + C_{pm}(\mathrm{O_2}) + 12C_{pm}(\mathrm{N_2})\right] \mathrm{d}T \\ &= -802\,324 + 581.9 \times (T_{\mathrm{prod}} - 298.15) \quad \Longrightarrow \quad T_{\mathrm{prod}} = 1676.9\,\mathrm{K}\,. \end{aligned}$$

Chapter 6

Thermodynamics of homogeneous mixtures

While Chapter **3** presented basic thermodynamic definitions and relations concerning pure substances and mixtures with fixed composition, this chapter presents relations specific for mixtures of variable composition.

6.1 Ideal mixtures

The simplest model used for the description of thermodynamic properties of mixtures is an **ideal mixture** which is defined in the following section.

6.1.1 General ideal mixture

The mixtures which obey Amagat's law [see **2.4.2**] at all temperatures and pressures, i.e. the mixtures for which we have

$$V = \sum_{i=1}^{k} n_i V^{\bullet}_{\mathrm{m},i} \ , \qquad (6.1)$$

are called ideal mixtures. $V^{\bullet}_{\mathrm{m},i}$ in this relation represent the volumes of pure components in the same phase as the mixture at the temperature and pressure of the system, and the sum extends over all components of the system.

Note: We will use the terms ideal mixture and ideal solution as synonymous.

The molar thermodynamic quantities of an ideal mixture are given by the following relations:

$$V_{\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i V^{\bullet}_{\mathrm{m},i}\,, \tag{6.2}$$

$$H_{\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i H^{\bullet}_{\mathrm{m},i}\,, \tag{6.3}$$

$$U_{\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i U^{\bullet}_{\mathrm{m},i}\,, \tag{6.4}$$

$$C_{V\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i C^{\bullet}_{V\mathrm{m},i}\,, \tag{6.5}$$

$$C_{p\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i C^{\bullet}_{p\mathrm{m},i}\,, \tag{6.6}$$

$$S_{\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i S^{\bullet}_{\mathrm{m},i} - \boldsymbol{R}\sum_{i=1}^{k} x_i \ln x_i\,, \tag{6.7}$$

$$G_{\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i G^{\bullet}_{\mathrm{m},i} + \boldsymbol{R}T\sum_{i=1}^{k} x_i \ln x_i\,, \tag{6.8}$$

$$F_{\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i F^{\bullet}_{\mathrm{m},i} + \boldsymbol{R}T\sum_{i=1}^{k} x_i \ln x_i\,. \tag{6.9}$$

6.1.2 Ideal mixture of ideal gases

A special case of an ideal mixture is an ideal mixture of gases with all its components obeying the equation of state of an ideal gas. Equation (6.2) then rearranges to

$$V_m = \frac{\boldsymbol{R}T}{p}\,. \tag{6.10}$$

When calculating the molar thermodynamic quantities of an ideal mixture of ideal gases, we proceed either from the properties of the gas at the temperature and pressure of the system, in which case equations (6.3) to (6.9) apply, or, more often, from the properties of the gas at the temperature of the system and standard pressure, in which case we have

$$H_{\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i H^{\circ}_{\mathrm{m},i}\,, \tag{6.11}$$

$$U_{\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i U^{\circ}_{\mathrm{m},i}\,, \tag{6.12}$$

$$C_{V\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i C^{\circ}_{V\mathrm{m},i}\,, \tag{6.13}$$

$$C_{p\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i C^{\circ}_{p\mathrm{m},i}\,, \tag{6.14}$$

$$S_{\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i S^{\circ}_{\mathrm{m},i} - \boldsymbol{R}\ln\frac{p}{p^{\mathrm{st}}} - \boldsymbol{R}\sum_{i=1}^{k} x_i \ln x_i\,, \tag{6.15}$$

$$G_{\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i G^{\circ}_{\mathrm{m},i} + \boldsymbol{R}T\ln\frac{p}{p^{\mathrm{st}}} + \boldsymbol{R}T\sum_{i=1}^{k} x_i \ln x_i\,, \tag{6.16}$$

$$F_{\mathrm{m,id.\,mix}} = \sum_{i=1}^{k} x_i F^{\circ}_{\mathrm{m},i} + \boldsymbol{R}T\ln\frac{p}{p^{\mathrm{st}}} + \boldsymbol{R}T\sum_{i=1}^{k} x_i \ln x_i\,. \tag{6.17}$$

Example

If the molar quantities in equations (6.3) to (6.9) and (6.11) to (6.17) are the molar quantities of an ideal mixture of ideal gases for a given temperature, pressure and composition, then both sets of equations must lead to the same result. Prove that the difference in their form is caused by conversion from different standard states.

Solution

Since the enthalpy and internal energy of an ideal gas are functions of temperature only [see **3.5.3**, **3.5.2**], we have

$$\begin{aligned} H^{\bullet}_{\mathrm{m},i}(T,p) &= H^{\circ}_{\mathrm{m},i}(T,p^{\mathrm{st}})\,, \\ U^{\bullet}_{\mathrm{m},i}(T,p) &= U^{\circ}_{\mathrm{m},i}(T,p^{\mathrm{st}}),. \end{aligned}$$

The entropy of an ideal gas depends on pressure and for its conversion we write [see **3.5.4**]

$$S^{\bullet}_{\mathrm{m},i}(T,p) = S^{\circ}_{\mathrm{m},i}(T,p^{\mathrm{st}}) - \boldsymbol{R}\ln\frac{p}{p^{\mathrm{st}}}\,.$$

From the definitions (3.12) and (3.14) we obtain conversion for F and G.

6.2 Integral quantities

The assumption of an ideal mixture (6.1) does not apply to most common mixtures. Consequently, we use mixing, excess or solution (differential or integral) quantities to describe changes in thermodynamic quantities during mixing.

6.2.1 Mixing quantities

A change in the molar thermodynamic quantity Y_m, which accompanies the formation of a mixture from pure substances in the same phase at constant temperature and pressure, is termed the **molar mixing quantity**

$$\Delta Y^\mathrm{M} = Y_\mathrm{m} - \sum_{i=1}^{k} x_i Y^\bullet_{\mathrm{m},i}\,. \tag{6.18}$$

For an ideal mixture [see **6.1**] we get

$$\Delta V^\mathrm{M} = 0\,, \tag{6.19}$$

$$\Delta H^\mathrm{M} = 0\,, \tag{6.20}$$

$$\Delta U^\mathrm{M} = 0\,, \tag{6.21}$$

$$\Delta C_\mathrm{V}^\mathrm{M} = 0\,, \tag{6.22}$$

$$\Delta C_p^\mathrm{M} = 0\,, \tag{6.23}$$

$$\Delta S^\mathrm{M} = -\boldsymbol{R} \sum_{i=1}^{k} x_i \ln x_i\,, \tag{6.24}$$

$$\Delta G^\mathrm{M} = \boldsymbol{R}T \sum_{i=1}^{k} x_i \ln x_i\,, \tag{6.25}$$

$$\Delta F^\mathrm{M} = \boldsymbol{R}T \sum_{i=1}^{k} x_i \ln x_i\,. \tag{6.26}$$

Example
A mixture containing 40 mole percent acetone(1) and 60 mole percent benzene(2) has a molar volume $V_{\rm m} = 83.179\,{\rm cm^3\,mol^{-1}}$ at temperature 25 °C and normal pressure. Calculate the mixing volume of this mixture if the molar volumes of the pure substances are $V_{\rm m,1} = 73.936\,{\rm cm^3\,mol^{-1}}$ and $V_{\rm m,2} = 89.412\,{\rm cm^3\,mol^{-1}}$.

Solution
Substituting for volume into (6.18) gives
$\Delta V^M = 83.179 - 0.4 \times 73.936 - 0.6 \times 89.412 = -0.0426\,{\rm cm^3\,mol^{-1}}$.

Note: Note that although the values of the enthalpy, internal energy, Helmholtz energy and Gibbs energy of a mixture cannot be determined absolutely, it is possible to determine absolutely their mixing quantities.

6.2.2 Excess quantities

In addition to mixing quantities, **excess quantities** are also used. In this case the properties a mixture are related to the properties of an ideal mixture [see **6.1**]. The molar excess quantities are defined by the relation

$$\Delta Y^{\rm E} = Y_m - Y_{\rm m,id.\,mix}\,, \tag{6.27}$$

where $Y_{\rm m,id.\,mix}$ is the corresponding molar thermodynamic quantity determined based on the relation valid for an ideal mixture, (6.2) to (6.9).

The following relations apply between mixing and excess quantities:

$$\Delta V^{\rm E} = \Delta V^{\rm M}\,, \tag{6.28}$$

$$\Delta H^{\rm E} = \Delta H^{\rm M}\,, \tag{6.29}$$

$$\Delta U^{\rm E} = \Delta U^{\rm M}\,, \tag{6.30}$$

$$\Delta C_{\rm V}^{\rm E} = \Delta C_{\rm V}^{\rm M}\,, \tag{6.31}$$

$$\Delta C_p^{\rm E} = \Delta C_p^{\rm M}\,, \tag{6.32}$$

$$\Delta S^{\rm E} = \Delta S^{\rm M} + \boldsymbol{R}\sum_{i=1}^{k} x_i \ln x_i\,, \tag{6.33}$$

$$\Delta G^{\mathrm{E}} = \Delta G^{\mathrm{M}} - \boldsymbol{R}T \sum_{i=1}^{k} x_i \ln x_i \,, \tag{6.34}$$

$$\Delta F^{\mathrm{E}} = \Delta F^{\mathrm{M}} - \boldsymbol{R}T \sum_{i=1}^{k} x_i \ln x_i \,. \tag{6.35}$$

6.2.3 Heat of solution (integral)

The heat of solution is defined by the relation

$$\Delta_{\mathrm{sol}} H_i = \frac{Q}{n_i} \,, \qquad [T, p] \,, \tag{6.36}$$

where Q is the heat exchanged with the surroundings, which accompanies the solution of n_i moles of a substance i in n_{solv} moles of a solvent at specified temperature and pressure.

> *Note:* The heat of solution defined in this way is sometimes termed the integral heat of solution in order to prevent confusion with the differential heat of solution of a component [see **6.3.5**].

$\Delta_{\mathrm{sol}} H_i$ depends on temperature T, pressure p, and on the composition of the resulting mixture.

Dependence of the integral heat of solution on composition can be expressed in two ways:

a) using a relative amount of solvent

$$n_{\mathrm{rel}} = \frac{n_{\mathrm{solv}}}{n_i} \tag{6.37}$$

in which case the heat of solution $\Delta_{\mathrm{sol}} H_i$ is defined as the amount of heat accompanying solution of 1 mole of a substance in n_{rel} moles of a solvent;

b) using molality $\underline{m}_i$ of the dissolved substance in the resulting mixture.

Example

During the dissolution of 0.2 mol NH_3(g) in 54.045 g $H_2O(\ell)$ at 25 °C and pressure 101.325 kPa, it was found out that a heat of 6870 J passed to the surroundings. Calculate the heat of solution of ammonia and n_{rel}.

Solution

It follows from the specification that $Q = -6870$ J. Substituting into (6.36) gives

$$\Delta_{\text{sol}} H_i = \frac{-6870}{0.2} = -34530\,\text{J}\,\text{mol}^{-1}.$$

The relative amount of solvent according to (6.37) is

$$n_{\text{rel}} = \frac{54.045/18.015}{0.2} = 15\,.$$

Calculation of the enthalpy of a binary mixture using the heat of solution. If we denote the solvent with the subscript 1 and the solute with the subscript 2, we get

$$H = n_{\text{rel}} H^{\bullet}_{\text{m},1} + H^{\otimes}_{\text{m},2} + \Delta_{\text{sol}} H_2\,, \tag{6.38}$$

where H is the enthalpy of the mixture and $H^{\otimes}_{\text{m},2}$ is the molar enthalpy of a pure substance 2.
S *Symbols:* The superscript $^{\otimes}$ indicates a pure substance which may be in a different phase than that of the mixture before solution at a given temperature and pressure.

6.2.3.1 Relations between the heat of solution and the enthalpy of mixing for a binary mixture

Given that a pure substance 2 is in the same phase as the mixture, i.e. $H^{\otimes}_{\text{m},2} = H^{\bullet}_{\text{m},2}$, it holds

$$\Delta H^{\text{M}} = \Delta H^{\text{E}} = \frac{\Delta_{\text{sol}} H_2}{n_{\text{rel}} + 1}\,, \tag{6.39}$$

$$\Delta_{\text{sol}} H_2 = \frac{\Delta H^{\text{M}}}{x_2}\,. \tag{6.40}$$

Example

If we mix 4.607 g (≡ 0.1 mol) of ethanol with 88.273 g (≡ 4.9 mol) of water at temperature 25 °C and pressure 101.325 kPa, a heat of 980 J will pass to the surroundings. Calculate the heat of solution of ethanol and the enthalpy of mixing.

Solution

Substituting into (6.36) and (6.39) gives

$$\begin{aligned}\Delta_{\mathrm{sol}} H_{\mathrm{ethanol}} &= \frac{-980}{0.1} = -9800\,\mathsf{J\,mol^{-1}}\,. \\ \Delta H^{\mathrm{M}} &= \frac{-9800}{4.9/0.1+1} = -196\,\mathsf{J\,mol^{-1}}.\end{aligned}$$

Note: Itis important to point out that the enthalpy of mixing ΔH^{M} relates to one mole of a mixture while the heat of solution relates to one mole of a solute.

6.3 Differential quantities

Instead of integral quantities describing a mixture as a whole, we may also use differential quantities which describe its individual components.

6.3.1 Partial molar quantities

Partial molar quantities are most often used for a general description of the behaviour of individual components of a mixture. For any extensive thermodynamic quantity Y, the partial molar quantity is defined using the relation

$$\overline{Y}_i = \left(\frac{\partial Y}{\partial n_i}\right)_{T,p,n_{j\neq i}} . \tag{6.41}$$

> *Note:* According to this definition, partial molar quantities are related to one mole of i^{th} component, but we leave out the subscript $_{\mathrm{m}}$ for the sake of simplicity.

6.3.2 Properties of partial molar quantities

6.3.2.1 Relations between system and partial molar quantities

For a $k-$component mixture we have:

$$Y_{\mathrm{m}} = \sum_{i=1}^{k} x_i \overline{Y}_i \qquad \text{resp.} \qquad Y = \sum_{i=1}^{k} n_i \overline{Y}_i \, . \tag{6.42}$$

The **Gibbs-Duhem equation**

$$\sum_{i=1}^{k} x_i \left(\frac{\partial \overline{Y}_i}{\partial x_j}\right)_{T,p,x_{\ell\neq j}} = 0 \qquad j = 1.2, \ldots, k-1 \, . \tag{6.43}$$

> *Note:* This relation represents a thermodynamic link between partial molar quantities; it may be used to test the consistency of the measured partial molar data or to calculate one partial molar quantity provided that we know the others.

6.3.2.2 Relations between partial molar quantities

The relations between partial molar quantities are analogous to those applying between system quantities, e.g.

$$\overline{H}_i = \overline{U}_i + p\,\overline{V}_i\,, \tag{6.44}$$

$$\overline{G}_i = \overline{H}_i - T\overline{S}_i\,. \tag{6.45}$$

Example

For a certain substance at temperature 400 K and pressure 10 MPa we have $\overline{V}_i = 280\,\mathrm{cm^3\,mol^{-1}}$, $\overline{H}_i = -1000\,\mathrm{J\,mol^{-1}}$, $\overline{S}_i = 250\,\mathrm{J\,mol^{-1}\,K^{-1}}$. Using this data calculate the partial molar internal energy and the partial molar Gibbs energy.

Solution

Substituting into (6.44) and (6.45) gives

$$\begin{aligned}\overline{U}_i &= \overline{H}_i - p\overline{V}_i = -1000 - 10\times 280 = -3800\,\mathrm{J\,mol^{-1}}\,,\\ \overline{G}_i &= \overline{H}_i - T\overline{S}_i = -1000 - 400\times 250 = -101000\,\mathrm{J\,mol^{-1}}\,.\end{aligned}$$

6.3.2.3 Partial molar quantities of an ideal mixture

From relations (6.2) to (6.9) we obtain

$$\overline{V}_{i,\mathrm{id.\,mix}} = V^{\bullet}_{\mathrm{m},i}\,, \tag{6.46}$$

$$\overline{H}_{i,\mathrm{id.\,mix}} = H^{\bullet}_{\mathrm{m},i}\,, \tag{6.47}$$

$$\overline{U}_{i,\mathrm{id.\,mix}} = U^{\bullet}_{\mathrm{m},i}\,, \tag{6.48}$$

$$\overline{S}_{i,\mathrm{id.\,mix}} = S^{\bullet}_{\mathrm{m},i} - \boldsymbol{R}\ln x_i\,, \tag{6.49}$$

$$\overline{G}_{i,\mathrm{id.\,mix}} = G^{\bullet}_{\mathrm{m},i} + \boldsymbol{R}T\ln x_i\,, \tag{6.50}$$

$$\overline{F}_{i,\mathrm{id.\,mix}} = F^{\bullet}_{\mathrm{m},i} + \boldsymbol{R}T\ln x_i\,. \tag{6.51}$$

6.3.3 Determination of partial molar quantities

While determining the partial molar quantities of a real mixture we proceed from

- Respective system quantities by applying the **definition relation** (6.41).
- Dependence of **molar quantities** Y_m on the mole fraction.
  In this case we have the following relations for the partial molar quantities $\overline{Y}_1$ and $\overline{Y}_2$ in a binary system

$$\overline{Y}_1 = Y_\mathrm{m} + x_2 \left(\frac{\partial Y_\mathrm{m}}{\partial x_1}\right)_{T,p}, \qquad \overline{Y}_2 = Y_\mathrm{m} - x_1 \left(\frac{\partial Y_\mathrm{m}}{\partial x_1}\right)_{T,p}. \tag{6.52}$$

Note: Figure 6.1 shows why the graphical version of this method is called the method of intercepts.

- Dependence of **excess quantities** on the mole fraction
  In this case we have for a binary mixture

$$\overline{Y}_1 = \overline{Y}_{1,\mathrm{id.\,mix}} + \Delta Y^\mathrm{E} + x_2 \left(\frac{\partial \Delta Y^\mathrm{E}}{\partial x_1}\right)_{T,p}, \tag{6.53}$$

$$\overline{Y}_2 = \overline{Y}_{2,\mathrm{id.\,mix}} + \Delta Y^\mathrm{E} - x_1 \left(\frac{\partial \Delta Y^\mathrm{E}}{\partial x_1}\right)_{T,p} \tag{6.54}$$

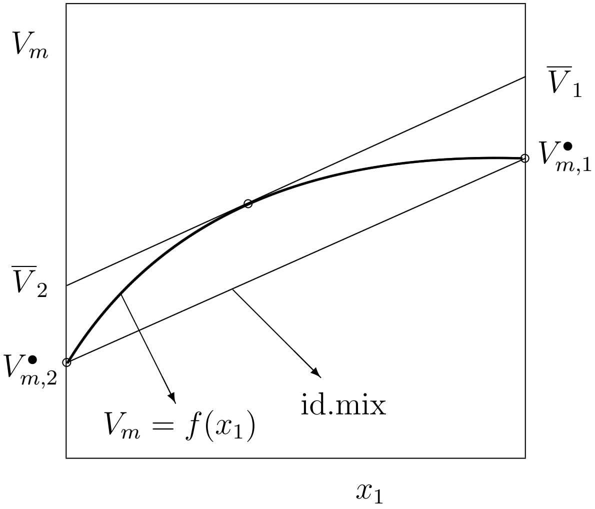
and $\overline{Y}_{i,\mathrm{id.\,mix}}$ are defined by relations (6.46) to (6.51).

Example

Dependence of the molar volume of a mixture of acetone and benzene on composition at temperature 25 °C is expressed by the equation

$$V_\mathrm{m} = 73.936\, x_1 + 89.412(1 - x_1) - 0.272\, x_1\,(1 - x_1)\ \mathrm{cm^3\,mol^{-1}},$$

where x_1 is the mole fraction of acetone. Calculate the partial molar volumes of both components at this temperature and $x_1 = 0.4$.



Obr. 6.1: Graphical determination of the partial molar volume using the method of intercepts. The thick curve describes the dependence of the molar volume V_m on the mole fraction x_1 of component 1. The intercepts cut out by the tangent to this curve on the vertical lines for $x_1 = 0$ and $x_1 = 1$ determine the partial molar volumes of components $\overline{V}_2$ and $\overline{V}_1$. $V^\bullet_{\mathrm{m},1}$ and $V^\bullet_{\mathrm{m},2}$ are the volumes of pure substances 1 and 2. The line segment connecting them describes the dependence of the molar volume of an ideal mixture on the mole fraction.

Solution

For $x_1 = 0.4$ we have

$$\begin{aligned} V_\mathrm{m} &= 0.4 \times 73.936 + 0.6 \times 89.412 - 0.4 \times 0.6 \times 0.272 = 83.156\,\mathrm{cm^3\,mol^{-1}}\,, \\ \left(\frac{\partial V_\mathrm{m}}{\partial x_1}\right) &= 73.936 - 89.412 - 0.272 \times (1 - 2 \times 0.4) = -15.530\,\mathrm{cm^3\,mol^{-1}} \end{aligned}$$

We substitute into (6.52) $\overline{V}_1 = 83.156 + 0.6 \times (-15.530) = 73.838\,\mathrm{cm^3\,mol^{-1}}$, $\overline{V}_2 = 89.368\,\mathrm{cm^3\,mol^{-1}}$.

6.3.4 Excess partial molar quantities

For real mixtures we sometimes use excess partial molar quantities:

$$\overline{Y}_i^{\mathrm{E}} = \overline{Y}_i - \overline{Y}_{i,\mathrm{id.\,mix}}\,. \tag{6.55}$$

In an ideal mixture, all quantities $\overline{Y}_i^{\mathrm{E}}$ thus equal zero while in real mixtures their value expresses the degree of non-ideal behaviour of the mixture. We obtain relations for $\overline{Y}_i^{\mathrm{E}}$ from those for partial molar quantities using equation (6.41) by substituting relations (6.46) to (6.51).

Example

Prove that the excess partial molar Gibbs energy $\overline{G}_i^{\mathrm{E}}$ is a partial molar quantity derived from the excess Gibbs energy ΔG^E.

Solution

We proceed from the definition relation (6.27)

$$\begin{aligned}
\Delta G^E &= G_{\mathrm{m}} - G_{\mathrm{m,id.\,mix}} = \\
&= \sum_{i=1}^{k} x_i \overline{G}_i - \sum_{i=1}^{k} x_i G^{\bullet}_{\mathrm{m},i} - \boldsymbol{R}T \sum_{i=1}^{k} x_i \ln x_i = \\
&= \sum_{i=1}^{k} x_i (\overline{G}_i - G^{\bullet}_{\mathrm{m},i} - \boldsymbol{R}T \ln x_i) = \\
&= \sum_{i=1}^{k} x_i \overline{G}_i^{\mathrm{E}}\,.
\end{aligned}$$

By multiplying n on both sides and subsequent differentiation we obtain

$$\overline{G}_i^{\mathrm{E}} = \left(\frac{\partial n \Delta G^{\mathrm{E}}}{\partial n_i}\right)_{T,p,n_{j\neq i}}\,,$$

which is the definition relation for partial molar quantities [see (6.41)].

6.3.5 Differential heat of solution and dilution

If we denote the solvent in a $k-$component mixture as component 1, we can define

- the **differential heat of solution** of solute i ($i >$1) using the relation

$$\overline{H}_i^{\otimes} = \overline{H}_i - H_{\mathrm{m},i}^{\otimes}\,. \tag{6.56}$$

> *Note:* If a pure solute is in the same phase as the mixture, i.e. $H_{\mathrm{m},i}^{\otimes} = H_{\mathrm{m},i}^{\bullet}$, the differential heat of solution of the substance equals its excess partial molar enthalpy $\overline{H}_i^{\otimes} = \overline{H}_i^{\mathrm{E}}$

- the **differential heat of dilution**, which is a term used for the excess partial molar enthalpy of a solvent, using the relation

$$\overline{H}_1^{\mathrm{E}} = \overline{H}_1 - H_{\mathrm{m},1}^{\bullet}\,. \tag{6.57}$$

> *Note:* The differential heats of solution depend on the concentration of the solution. During dissolving a first portion of the substance in a pure solvent, this heat is usually termed the **first differential heat of solution**; during dissolving a last portion of the substance in an almost saturated solution the corresponding heat is termed the **last differential heat of solution**.

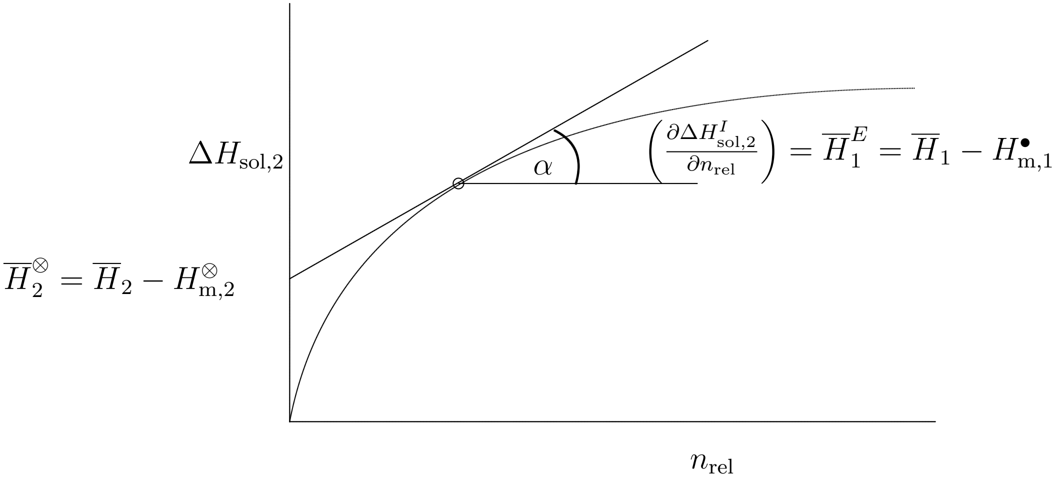
- Conversions between integral and differential heats:
  If we know $\Delta H^M(x_1)$ or $\Delta_{\mathrm{sol}} H_2(n_{\mathrm{rel}})$, we can derive the following relations for a binary mixture from relations (6.36) to (6.40):

$$\overline{H}_1^{\mathrm{E}} = \Delta H^{\mathrm{M}} + x_2 \left(\frac{\partial \Delta H^{\mathrm{M}}}{\partial x_1}\right)_{T,p} = \left(\frac{\partial \Delta_{\mathrm{sol}} H_2}{\partial n_{\mathrm{rel}}}\right)_{T,p}\,, \tag{6.58}$$

$$\overline{H}_2^{\otimes} = \Delta H^{\mathrm{M}} - x_1 \left(\frac{\partial \Delta H^{\mathrm{M}}}{\partial x_1}\right)_{T,p} = \tag{6.59}$$

$$= \Delta_{\mathrm{sol}} H_2 - n_{\mathrm{rel}} \left(\frac{\partial \Delta_{\mathrm{sol}} H_2}{\partial n_{\mathrm{rel}}}\right)_{T,p}\,. \tag{6.60}$$

> *Note:* $\overline{H}_i^{\mathrm{E}}$ is (see the preceding example) a partial molar quantity relating to ΔH^E. However, for quantities defined by the first law of thermodynamics, $\Delta Y^E = \Delta Y^M$ [see **6.2.2**].



Obr. 6.2: Dependence of the integral heat of solution on the relative amount of a solvent. The slope of the tangent shows the differential heat of dilution. The intercept on the vertical axis equals the differential heat of solution.

Relations between the integral heat of solution and the differential heats of solution are illustrated in Figure **6.2**.

Example

Dependence of the enthalpy of mixing of ethanol(1) and water(2) on composition at temperature 298 K has the minimal value $-783\,\mathrm{J\,mol^{-1}}$ at $x_1 = 0.17$ (mole fraction of ethanol). Calculate the differential heat of solution of ethanol given this composition.

Solution

Since in the minimum $(\partial \Delta H^M/\partial x_1) = 0$, we obtain from relation (6.58) $\overline{H}^{\mathrm{E}}_1 = -783 + (1 - 0.17) \times (0) = -783\,\mathrm{J\,mol^{-1}}$.

6.4 Thermodynamics of an open system and the chemical potential

6.4.1 Thermodynamic quantities in an open system

In an open system [see **1.1.3**], the first law of thermodynamics does not apply. The Gibbs equations do not apply in the form defined in **3.4.1** but in the extended form

$$\begin{aligned}
\mathrm{d}U &= T\mathrm{d}S - p\mathrm{d}V + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i\,, && (6.61)\\
\mathrm{d}H &= T\mathrm{d}S + V\mathrm{d}p + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i\,, && (6.62)\\
\mathrm{d}F &= -S\mathrm{d}T - p\mathrm{d}V + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i\,, && (6.63)\\
\mathrm{d}G &= -S\mathrm{d}T + V\mathrm{d}p + \sum_{i=1}^{k} \mu_i \mathrm{d}n_i\,, && (6.64)
\end{aligned}$$

where μ_i are the **chemical potentials** of the system components.

6.4.2 Chemical potential

It follows from equations (6.64) and (6.41) that the chemical potential is identical with the partial molar Gibbs energy of the component

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} = \overline{G}_i\,. \tag{6.65}$$

However, it also follows from equations (6.61) to (6.64) that we must have

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j\neq i}} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_{j\neq i}}\,. \tag{6.66}$$

> *Note:* Since these relations are derivatives at constant natural variables and not at constant temperature and pressure, they are not partial molar quantities.

- The dependence of the chemical potential on temperature is expressed by the equation

$$\mu_i(T_2) = \mu_i(T_1) + \int_{T_1}^{T_2} \left(\frac{\partial \mu_i}{\partial T}\right)_{p,n} \mathrm{d}T\,, \tag{6.67}$$

with $(\partial\mu_i/\partial T)_{p,n}$ obtained by differentiating equation (3.41) with respect to n_i.

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,n} = \left(\frac{\partial \overline{G}_i}{\partial T}\right)_{p,n} = -\,\overline{S}_i\,. \tag{6.68}$$

- The dependence of the chemical potential on pressure is expressed by the equation

$$\mu_i(p_2) = \mu_i(p_1) + \int_{p_1}^{p_2} \left(\frac{\partial \mu_i}{\partial p}\right)_{T,n} \mathrm{d}p\,, \tag{6.69}$$

where

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{p,n} = \left(\frac{\partial \overline{G}_i}{\partial p}\right)_{T,n} = \overline{V}_i\,. \tag{6.70}$$

S *Symbols:* The subscript $_n$ emphasizes that this is a change at constant amounts of substance of all components, i.e. also at constant composition.

- Dependence of the chemical potential on composition
  The chemical potential is written as a sum of two terms

$$\mu_i = \mu_i^{\mathrm{st}} + \boldsymbol{R}T\,\ln a_i\,, \tag{6.71}$$

of which the first, μ_i^{st}, the standard chemical potential[1] of a component [see **6.5.4**] does not depend on composition. Dependent on composition is the activity of the i^{th} component in the mixture, a_i [see **6.5.4**] in the second term of the equation.

---

[1] According to the new IUPAC recommendations, a general (unspecified) standard state is denoted as $\mu_i^{\ominus}$.

For the choice of the standard state [see **6.5.3**] of a pure component at the temperature and pressure of the system $\mu_i^{\mathrm{st}} = \mu_i^{\bullet}$, and we have

$$\begin{aligned}
\mu_i(T, p, x_1, \ldots, x_{k-1}) &= \mu_i^{\bullet}(T, p) + \boldsymbol{R}T \ln a_i && (6.72)\\
&= \mu_i^{\bullet}(T, p) + \boldsymbol{R}T \ln \frac{f_i(T, p, x_1, \ldots, x_{k-1})}{f_i^{\bullet}(T, p)}\\
&= \mu_i^{\bullet}(T, p) + \boldsymbol{R}T \ln x_i \gamma_i(T, p, x_1, \ldots, x_{k-1})\,, && (6.73)
\end{aligned}$$

where γ_i is the activity coefficient of the i^{th} component in a $k-$component mixture [see **6.5.5**], and f_i indicates the fugacity of the same component in the mixture. [see **6.5.2**]

6.5 Fugacity and activity

6.5.1 Fugacity

The fugacity of a pure substance was defined in section **3.2.6**. For mixtures, the fugacity of a component is defined by the relation

$$f_i = p^{\mathrm{st}} \exp\left(\frac{\overline{G}_i - G^{\circ}_{\mathrm{m},i}}{\boldsymbol{R}T}\right) = p^{\mathrm{st}} \exp\left(\frac{\mu_i - G^{\circ}_{\mathrm{m},i}}{\boldsymbol{R}T}\right) . \tag{6.74}$$

U *Main unit:* Pa.

- The dependence of fugacity on temperature is expressed by the relation

$$\ln f_i(T_2) = \ln f_i(T_1) + \int_{T_1}^{T_2} \left(\frac{\partial \ln f_i}{\partial T}\right)_{p,n} \mathrm{d}T , \tag{6.75}$$

  where

$$\left(\frac{\partial \ln f_i}{\partial T}\right)_{p,n} = -\frac{\overline{H}_i - H^{\circ}_{\mathrm{m},i}}{\boldsymbol{R}T^2} . \tag{6.76}$$

- The dependence of fugacity on pressure is expressed by the relation

$$\ln f_i(p_2) = \ln f_i(p_1) + \int_{p_1}^{p_2} \left(\frac{\partial \ln f_i}{\partial p}\right)_{T,n} dp , \tag{6.77}$$

  where

$$\left(\frac{\partial \ln f_i}{\partial p}\right)_{T,n} = \frac{\overline{V}_i}{\boldsymbol{R}T} . \tag{6.78}$$

- For an ideal mixture of ideal gases [see **6.1.2**] we have

$$f_i = p_i = x_i p . \tag{6.79}$$

  In this case the fugacity of the i^{th} component in a mixture equals its partial pressure.

- For an ideal mixture of real fluids [see **6.1**] we write

$$f_i = x_i f_i^{\bullet} . \tag{6.80}$$

  The fugacity of the i^{th} component in a mixture can be calculated from the fugacity of the pure i^{th} component. Relation (6.80) is termed the **Lewis-Randall rule**.

- For a real mixture we have

$$f_i = \phi_i x_i p\,, \tag{6.81}$$

  where ϕ_i is the fugacity coefficient [see **6.5.2**]

6.5.2 Fugacity coefficient

The **fugacity coefficient** [see **3.2.7**] of the i^{th} component in a mixture is defined by the relation

$$\phi_i = \frac{f_i}{p\,x_i}\,. \tag{6.82}$$

U *Main unit:* dimensionless quantity.

- The **dependence of the fugacity coefficient on temperature** is expressed by the relation

$$\ln\phi_i(T_2) = \ln\phi_i(T_1) + \int_{T_1}^{T_2}\left(\frac{\partial\ln\phi_i}{\partial T}\right)_{p,n}\mathrm{d}T\,, \tag{6.83}$$

  where

$$\left(\frac{\partial\ln\phi_i}{\partial T}\right)_{p,n} = -\frac{\overline{H}_i - H^\circ_{\mathrm{m},i}}{\boldsymbol{R}T^2}\,. \tag{6.84}$$

- The **dependence of the fugacity coefficient on pressure** is expressed by the relation

$$\ln\phi_i(p_2) = \ln\phi_i(p_1) + \int_{p_1}^{p_2}\left(\frac{\partial\ln\phi_i}{\partial p}\right)_{T,n}\mathrm{d}p\,, \tag{6.85}$$

  where

$$\left(\frac{\partial\ln\phi_i}{\partial p}\right)_{T,n} = \frac{\overline{V}_i}{\boldsymbol{R}T} - \frac{1}{p}\,. \tag{6.86}$$

- In the case of an **ideal mixture** [see **6.1**], the **Lewis-Randall rule** applies

$$\phi_i = \phi_i^\bullet\,, \tag{6.87}$$

  i.e. the fugacity coefficient does not depend on composition but only on temperature and pressure. For an ideal mixture of ideal gases [see **6.1.2**] we than have

$$\phi_i = 1\,. \tag{6.88}$$

Example

Calculate the fugacity coefficient and fugacity of carbon dioxide in an equimolar mixture with hydrogen at temperature 30 °C and pressure 1 MPa given that the following equation of state applies to this mixture

$$V_\mathrm{m} = \frac{\boldsymbol{R}T}{p} + B_{11}x_1^2 + B_{22}x_2^2 + 2B_{12}x_1x_2$$

where x_1 is the mole fraction of carbon dioxide and x_2 is the mole fraction of hydrogen. The second virial coefficients have the following values: $B_{11} = -119\,\mathrm{cm^3\,mol^{-1}}$, $B_{22} = 14\,\mathrm{cm^3\,mol^{-1}}$ and $B_{12} = -1\,\mathrm{cm^3\,mol^{-1}}$.

Solution

We calculate the fugacity coefficient using equation (6.85), and obtain the needed partial molar volume of carbon dioxide from the equation of state and relation (6.52).

$$\overline{V}_1 = \frac{\boldsymbol{R}T}{p} + (2\,B_{12} - B_{11} - B_{22})x_2^2 + B_{11}\,.$$

We integrate (6.85) to obtain

$$\begin{aligned}
\ln\phi_1 &= \int_0^p \left[\frac{\overline{V}_i}{\boldsymbol{R}T} - \frac{1}{p}\right] \mathrm{d}p = \\
&= [(2B_{12} - B_{11} - B_{22})x_2^2 + B_{11}]\frac{p}{\boldsymbol{R}T} = \\
&= [(-2 \times 1 + 119 - 14) \times 0.5^2 - 119] \times \frac{1}{8.314 \times 303.15} = \\
&= -0.026\,.
\end{aligned}$$

Hence $\phi_1 = 0.974$, and for the fugacity of carbon dioxide we have

$$f_1 = \phi_1 p x_1 = 0.974 \times 1 \times 0.5 = 0.487\,\mathrm{MPa}.$$

6.5.3 Standard states

To determine μ_i^{st} in relation (6.71), we need to choose the **standard** or **reference state** of a given component of a given mixture. This choice is in principle arbitrary, but the following standard states are usually chosen for practical reasons:

- **Mixtures of gases**
  For components in the gaseous phase, the *standard state of an ideal gas at standard pressure* is used. In the case of this choice, μ_i^{st} is the chemical potential of a pure substance i in the state of an ideal gas at the temperature of the mixture and standard pressure, usually $p^{\mathrm{st}} = 101\,325$ Pa.
- **Mixtures of liquids and solid substances**
  For components in a liquid or solid phase, the *standard state of a pure substance at the temperature and pressure of the system* is used. μ_i^{st} is the chemical potential of a pure substance i, which at the temperature and pressure of the mixture is in the same phase as the mixture.
- **Diluted solutions**
  For components present in mixtures in only a small amount (e.g. ions of salts in aqueous solutions or gases dissolved in liquids), one of the three following standard states may be chosen:
  - *Standard state of a hypothetical pure substance at infinite dilution.*
    μ_i^{st} is the chemical potential of component i obtained by linear extrapolation of the dependence $\mu_i = f(\ln x_i)$ from the region of very low concentrations to the value at $x_i = 1$ (i.e. hypothetically pure substance)
  - *Standard state of a unit molar concentration*.
    μ_i^{st} is the chemical potential of component i obtained by linear extrapolation of the dependence $\mu_i = f(\ln c_i)$ from the region of very low concentrations to the value at $c_i = c^{\mathrm{st}} = 1\,\mathrm{mol\,dm^{-3}}$.
  - *Standard state of unit molality*. μ_i^{st} is the chemical potential of component i obtained by linear extrapolation of the dependence $\mu_i = f(\ln \underline{m}_i)$ from the region of very low concentrations to the value at $\underline{m}_i = \underline{m}^{\mathrm{st}} = 1\,\mathrm{mol\,kg^{-1}}$.

The same standard states as those used for the chemical potential are used for its derivatives with respect to temperature and pressure, i.e. entropy and volume [see (6.68) and (6.70)], and for other thermodynamic quantities, e.g. enthalpy or fugacity.

S *Symbols:* The values of thermodynamic quantities in the standard state of an ideal gas at the standard pressure are denoted using the superscript $^\circ$, e.g. $H^\circ_{\mathrm{m},i}$, $S^\circ_{\mathrm{m},i}$, $\cdots$.

The values of thermodynamic quantities in the standard state of a pure component at the temperature and pressure of the system are denoted using the superscript $^\bullet$, e.g. $H^\bullet_{\mathrm{m},i}$, $S^\bullet_{\mathrm{m},i}$, $\cdots$.

The values of thermodynamic quantities in the standard state of a hypothetical pure substance at infinite dilution will be denoted using the superscript $^{[x]}$, e.g. $H^{[x]}_{\mathrm{m},i}$, $S^{[x]}_{\mathrm{m},i}$, $\cdots$.

The values of thermodynamic quantities in the standard state of a unit molar concentration will be denoted using the superscript $^{[c]}$, e.g. $H^{[c]}_{\mathrm{m},i}$, $S^{[c]}_{\mathrm{m},i}$, $\cdots$.

The values of thermodynamic quantities in the standard state of unit molality will be denoted using the superscript $^{[m]}$, e.g. $H^{[m]}_{\mathrm{m},i}$, $S^{[m]}_{\mathrm{m},i}$, $\cdots$.

> *Note:* For the activity and the activity coefficients, however, symbols $a_i^{[x]}$, $a_i^{[c]}$, $a_i^{[m]}$, $\gamma_1^{[x]}$, $\gamma_i^{[c]}$, $\gamma_i^{[m]}$ are used in a different meaning [see **6.5.4**, **6.5.5**].

Figure **6.3** illustrates the standard values of enthalpy of component 1 in a binary mixture.

6.5.4 Activity

The activity of the i^{th} component in a mixture is defined by the relation

$$a_i = \frac{f_i}{f_i^{\mathrm{st}}}\,, \tag{6.89}$$

where f_i^{st} is the fugacity in the chosen standard state [see **6.1.2**].

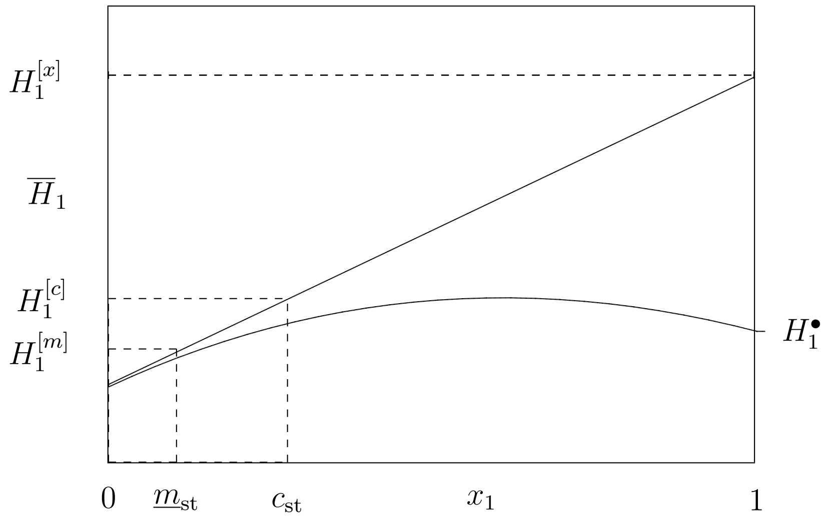
U *Main unit:* dimensionless quantity.

An alternative definition of activity follows from the relation for fugacity (6.74)

$$a_i = \exp\left(\frac{\mu_i - \mu_i^{\mathrm{st}}}{\boldsymbol{R}T}\right) = \exp\left(\frac{\overline{G}_i - G^{\mathrm{st}}_{\mathrm{m},i}}{\boldsymbol{R}T}\right)\,. \tag{6.90}$$

- The dependence of activity on temperature is expressed by the relation

$$\ln a_i(T_2) = \ln a_i(T_1) + \int_{T_1}^{T_2} \left(\frac{\partial \ln a_i}{\partial T}\right)_{p,n} \mathrm{d}T\,, \tag{6.91}$$



Obr. 6.3: Definition of the standard states for component 1 in a binary mixture. The curve ending at point $H_1^\bullet$ represents the dependence of partial molar enthalpy on composition, and the straight line is its tangent at point $x_1 = 0$. $H_1^\bullet$ is the standard enthalpy of a pure component. $H_1^{[x]}$ is the standard enthalpy in the standard state of a hypothetical pure component at infinite dilution, $H_1^{[c]}$ is the standard enthalpy in the state of unit molar concentration, and $H_1^{[m]}$ is the standard enthalpy in the state of unit molality.

where

$$\left(\frac{\partial \ln a_i}{\partial T}\right)_{p,n} = -\frac{\overline{H}_i - H_i^{\rm st}}{\boldsymbol{R}T^2}\,. \tag{6.92}$$

- The dependence of activity on pressure is expressed by the relation

$$\ln a_i(p_2) = \ln a_i(p_1) + \int_{p_1}^{p_2} \left(\frac{\partial \ln a_i}{\partial p}\right)_{T,n} {\rm d}p\,, \tag{6.93}$$

where

$$\left(\frac{\partial \ln a_i}{\partial p}\right)_{T,n} = \frac{\overline{V}_i - V_i^{\rm st}}{\boldsymbol{R}T}\,. \tag{6.94}$$

- Dependence of activity on composition
  Activity can be written as a product of dimensionless concentration ($x_i,\ c_i/c^{\rm st}, \underline{m}_i/\underline{m}^{\rm st}$) and the activity coefficient [see **6.5.5**], which is the function of temperature, pressure and composition.
- For the standard state of a pure component at the temperature and pressure of the system we have
  $$\lim_{x_i\to 1} a_i/x_i = 1\,. \qquad (6.95)$$
  It follows from this relation that when choosing the given standard state, we can replace activity with a mole fraction in the component prevailing in the mixture.
- For the standard states of infinite dilution we have
  $$\lim_{x_i\to 0} \frac{a_i^{[x]}}{x_i} = 1\,, \qquad (6.96)$$
  $$\lim_{c_i\to 0} \frac{a_i^{[c]}c^{\rm st}}{c_i} = 1\,, \qquad (6.97)$$
  $$\lim_{\underline{m}_i\to 0} \frac{a_i^{[m]}\underline{m}^{\rm st}}{\underline{m}_i} = 1\,. \qquad (6.98)$$
  It follows from these limits that when choosing the standard states of infinite dilution, we can replace activity with the respective concentration quantity in the component which is enough diluted in the solution.
- For an ideal mixture, activity equals dimensionless concentration ($x_i,\ c_i/c^{\rm st}$ or $\underline{m}_i/\underline{m}^{\rm st}$) for an arbitrary composition.

Example

A mixture of benzene and toluene in the liquid phase behaves as an ideal mixture. Calculate the activity of benzene in a mixture that results from the mixing of one mole of benzene with nine moles of toluene at 25 °C.

Solution

The mole fraction of benzene and its activity are
$x_{\rm benzene} = n_{\rm benzene}/(n_{\rm benzene} + n_{\rm toluene}) = 1/(1+9) = 0.1$, $a_{\rm benzene} = 0.1$.

Example

A mixture of light and heavy water in the liquid phase behaves ideally. Calculate the activities of heavy water $a_{\mathrm{D_2O}}$, $a^{[x]}_{\mathrm{D_2O}}$, and $a^{[\underline{m}]}_{\mathrm{D_2O}}$ in a mixture resulting from the addition of 1 g D_2O to 500 g H_2O.

Solution

We first calculate the mole fraction and molality of heavy water

$$\begin{aligned} x_{\mathrm{D_2O}} &= \frac{1/20.027}{500/18.015 + 1/20.027} = 0.001796 \\ \underline{m}_{\mathrm{D_2O}} &= \frac{1/20.027}{0.5} = 0.09987\,\mathrm{mol\,kg^{-1}}\,. \end{aligned}$$

The activities of heavy water in the given mixture are

$$\begin{aligned} a_{\mathrm{D_2O}} &= a^{[x]}_{\mathrm{D_2O}} = x_{\mathrm{D_2O}} = 0.001796\,, \\ a^{[\underline{m}]}_{\mathrm{D_2O}} &= \frac{\underline{m}_{\mathrm{D_2O}}}{\underline{m}^{\mathrm{st}}} = 0.09987\,. \end{aligned}$$

6.5.5 Activity coefficient

The value of the **activity coefficient** depends on the chosen standard state. The following activity coefficients are used most often

$$\gamma_i = \frac{a_i}{x_i}\,, \tag{6.99}$$

$$\gamma_i^{[x]} = \frac{a_i^{[x]}}{x_i}\,, \tag{6.100}$$

$$\gamma_i^{[c]} = \frac{a_i^{[c]}}{c_i/c^{\mathrm{st}}}\,, \tag{6.101}$$

$$\gamma_i^{[\underline{m}]} = \frac{a_i^{[\underline{m}]}}{\underline{m}_i/\underline{m}^{\mathrm{st}}}\,. \tag{6.102}$$

U *Main unit:* dimensionless quantity.

Example
For a solution of sucrose (2) in water (1), which at 100 °C contains one mole percent sucrose, we have $\gamma_2 = 0.0064,\ \gamma_2^{[x]} = 1.108$ and $\gamma_2^{[m]} = 1.097$. Calculate the respective activities.

Solution
The molality of sucrose in the given solution is
$\mathrm{m}_2 = (1000 \times 0.01)/(18.015 \times 0.99) = 0.5607\,\mathrm{mol\,kg^{-1}}$, and the activities are obtained from relations (6.99), (6.100) and (6.102).

$$\begin{aligned} a_2 &= 0.01 \times 0.0064 = 0.000064\,, \\ a_2^{[x]} &= 0.01 \times 1.108 = 0.01108\,, \\ a_2^{[m]} &= (0.5607/1) \times 1.097 = 0.6151\,. \end{aligned}$$

Relation to the partial mole excess Gibbs energy

The activity coefficient γ_i is related to the partial molar excess Gibbs energy by

$$\boldsymbol{R}T \ln \gamma_i = \overline{G}_i^{\mathrm{E}}\,. \tag{6.103}$$

Given that $\boldsymbol{R}T \ln \gamma_i$ is the partial molar quantity to ΔG^E, we have

$$\Delta G^{\mathrm{E}} = \boldsymbol{R}T \sum_{i=1}^{k} x_i \ln \gamma_i\,. \tag{6.104}$$

Example
Derive relation (6.103).

Solution

According to (6.55) we have

$$\overline{G}_i^{\rm E} = \overline{G}_i - \overline{G}_{i,\rm id.\,mix}\,,$$

where, according to (6.50)

$$\overline{G}_{i,\rm id.\,mix} = G^{\bullet}_{{\rm m},i} + \boldsymbol{R}T \ln x_i\,.$$

From (6.90) we get the relation for the partial molar Gibbs energy (chemical potential) in the form

$$\overline{G}_i = G^{\bullet}_{{\rm m},i} + \boldsymbol{R}T \ln a_i = G^{\bullet}_{{\rm m},i} + \boldsymbol{R}T \ln x_i\gamma_i\,.$$

By subtracting we obtain the required relation $\overline{G}_i^{\rm E} = \boldsymbol{R}T \ln \gamma_i$.

Example

The activity coefficients $\gamma_1 = 2.27$ and $\gamma_2 = 1.041$ were found for a methanol (1) — ethyl acetate (2) system at 313.15 K and $x_1 = 0.2$. Calculate the excess Gibbs energy in this mixture.

Solution

From relation (6.104) we obtain
$\Delta G^E = 8.314 \times 313.15 \times [0.2 \times \ln 2.27 + 0.8 \times \ln 1.041\,] = 510.6\,{\rm J\,mol^{-1}}$.

The **dependence of the activity coefficient on temperature** is expressed by the relation

$$\ln \gamma_i(T_2) = \ln \gamma_i(T_1) + \int_{T_1}^{T_2} \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{p,n} {\rm d}T\,, \tag{6.105}$$

where

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{p,n} = -\frac{\overline{H}_i - H^{\rm st}_{{\rm m},i}}{\boldsymbol{R}T^2}\,. \tag{6.106}$$

Example

The activity coefficient of ethanol in an ethanol (1)—water (2) mixture containing 17 mole percent ethanol at temperature 298.15 K is $\gamma_1 = 2.485$. The differential heat of solution of ethanol in this mixture is $-783\,\mathrm{J\,mol}^{/1}$. Estimate the activity coefficient of ethanol at the given composition and temperature 303.15 K. Assume independence of $\overline{H}_i^{\mathrm{E}}$ on temperature.

Solution

We integrate (6.106) to obtain

$$\begin{aligned}\ln\frac{\gamma_1(T_2)}{\gamma_1(T_1)} &= -\frac{\overline{H}_1^{\mathrm{E}}}{\boldsymbol{R}}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \\ &= -\frac{-783}{8.314}\left(\frac{1}{298.15}-\frac{1}{303.15}\right) = 0.00521\,.\end{aligned}$$

Hence $\ln\gamma_1 = \ln 2.485 + 0.00521 = 0.9155$ and $\gamma_1 = 2.498$.

The **dependence of the activity coefficient on pressure** is expressed by the relation

$$\ln\gamma_i(p_2) = \ln\gamma_i(p_1) + \int_{p_1}^{p_2}\left(\frac{\partial\ln\gamma_i}{\partial p}\right)_{T,n}\mathrm{d}p\,, \tag{6.107}$$

where

$$\left(\frac{\partial\ln\gamma_i}{\partial p}\right)_{T,n} = \frac{\overline{V}_i - V_i^{\mathrm{st}}}{\boldsymbol{R}T}\,. \tag{6.108}$$

Note: The dependence of the activity coefficient on composition is dealt with in section **6.5.6**.

6.5.5.1 Relation between $\gamma_i^{[x]}$ and γ_i

The relation between the activity coefficients $\gamma_i^{[x]}$ and γ_i is

$$\ln\gamma_i^{[x]} = \ln\gamma_i - \ln\gamma_i^{\infty}\,, \tag{6.109}$$

where γ_i^∞ is the limiting activity coefficient γ_i in a mixture in which component i is infinitely diluted.

6.5.5.2 Relation between the activity coefficient and the osmotic coefficient

For mixtures with one prevailing component (e.g. aqueous solutions of salts), **osmotic coefficients** are also used in addition to activity coefficients. The osmotic coefficient of a solvent $\phi_1^{[c]}$ is defined as

$$\phi_1^{[c]} = 1 + \frac{\ln \gamma_1^{[c]}}{\ln(c_1/c^{\mathrm{st}})} \tag{6.110}$$

The coefficients $\phi_1^{[x]}$ and $\phi_1^{[m]}$ are defined in a similar way.

6.5.6 Dependence of the excess Gibbs energy and of the activity coefficients on composition

Various empirical and semi-empirical relations are used for the dependence of ΔG^E on composition and possibly also on temperature. Two of them are presented here.

6.5.6.1 Wilson equation

The Wilson equation is used in practice most often. Its form for a k-component system is

$$\begin{aligned} \frac{\Delta G^{\mathrm{E}}}{\boldsymbol{R}T} &= -\sum_{i=1}^{k} x_i \ln\left(\sum_{j=1}^{k} x_j A_{ij}\right), \qquad (6.111) \\ A_{ij} &= \frac{V^\bullet_{m,j}}{V^\bullet_{m,i}} \exp(-\frac{a_{ij}}{T}), \quad a_{ij} \neq a_{ji}, \quad a_{ii} = a_{jj} = 0, \end{aligned}$$

where $V^\bullet_{\mathrm{m},1}$, $V^\bullet_{\mathrm{m},2}$ are the molar volumes of components in the liquid state, and a_{ij} are the adjustable constants.

For the activity coefficients we have

$$\ln \gamma_i = 1 - \ln\left(\sum_{j=1}^{k} x_j A_{ij}\right) - \sum_{j=1}^{k} x_j \frac{A_{ji}}{\sum_{\ell=1}^{k} x_\ell A_{j\ell}}. \tag{6.112}$$

6.5.6.2 Regular solution

For a binary system, the model of a strictly regular solution is the simplest.

$$\frac{\Delta G^{\mathrm{E}}}{\boldsymbol{R}T} = b\,x_1 x_2\,. \tag{6.113}$$

For the activity coefficients we have

$$\ln\gamma_1 = b\,x_2^2\,, \quad \ln\gamma_2 = b\,x_1^2\,. \tag{6.114}$$

Chapter 7

Phase equilibria

7.1 Basic terms

7.1.1 Phase equilibrium

When a system composed of two or more phases [see **1.1.4**] is in the state of thermodynamic equilibrium [see **1.4.1**], we say that the system has attained **phase equilibrium.**

Example
Liquid water and water vapour are in phase equilibrium at temperature 100 °C and pressure 101 325 Pa. Liquid water at 40 °C and ice at -10 °C are not in phase equilibrium. An irreversible process occurs during which ice heats and melts, and liquid water cools. In the state of thermodynamic equilibrium, which the system attains after some time, there may be either a one-phase system (all ice melts or all liquid water freezes), or a two-phase system (with phase equilibrium existing between ice and liquid water at 0 °C).

7.1.2 Coexisting phases

When a system is in the state of phase equilibrium, we call its phases **coexisting phases**. Coexisting phases always have the same temperature and pressure. In the case of multicomponent equilibria, the compositions of individual phases are identical only exceptionally [see **7.6.6**].

7.1.3 Phase transition

The term phase transition applies to a process during which a certain amount of substance changes from one phase to another. Phase transitions may be reversible or irreversible. (For the classification of phase transitions into first-order and second-order transitions see **7.2.1**).

Example

Give an example of an irreversible and reversible phase transitions.

Solution

Ice melting in water at 40 °C and 101.325 kPa represents an irreversible phase transition. It is typical of irreversible phase transitions that a slight change of conditions does not change the direction of the process in any way. In our case a slight change of the initial temperature of water (e.g. from 40 °C to 39.9 °C) or pressure (e.g. from 101.325 kPa to 101 k Pa) would not initiate the freezing of water.

Ice melting at 0 °C and 101.325 kPa may serve as an example of a reversible phase transition. In this case the slightest lowering of temperature or pressure would replace melting with freezing.

Typical phase transitions in one-component systems are shown in the following table:

Type of phase transition			Name of the process
Liquid	→	gas (vapour)	vaporization, boiling
Gas (vapour)	→	liquid	condensation
Solid	→	liquid	melting, fusion
Liquid	→	solid	freezing
Solid	→	gas	sublimation
Gas	→	solid	(vapour) deposition
Crystalline form	→	another crystalline form	transformation of the crystalline form

All these types of phase transition exist in multicomponent systems as well. In these systems, however, such processes may occur which would be impossible in pure substances. For example, the gas → liquid phase transition also involves, besides condensation, the dissolution of the gas in the liquid, the solid → liquid phase transition also involves, besides melting, the dissolution of the solid in the liquid. In multicomponent systems, transition from one liquid phase to another—extraction—may also occur.

7.1.4 Boiling point

In pure substances, the **boiling point** is determined by the boiling temperature and the boiling pressure. The **boiling temperature** is a temperature at which a liquid of a given composition is in phase equilibrium with its vapour at a chosen pressure p. The **boiling pressure** is a pressure at which a liquid of a given composition is in equilibrium with its vapour at a chosen temperature. The boiling pressure of pure substances is called the **saturated vapour pressure**, see 7.1.7. In mixtures, the boiling point is determined by the boiling temperature, the boiling pressure and the composition of the liquid phase.

Example
The boiling temperature of water at $p = 8.59$ MPa is 300 °C. The boiling temperature of an equimolar mixture of ethanol and water at 13.3 kPa is 35.9 °C.

7.1.5 Normal boiling point

The normal boiling point is determined by the normal boiling temperature, normal pressure $p = 101.325\,\text{kPa}$ and the composition of the liquid. The **normal boiling temperature** is a temperature at which a liquid of a given composition is in phase equilibrium with its vapour at the normal pressure.

Example
The normal boiling temperature of ethanol is 351.44 K.

7.1.6 Dew point

The dew point is determined by the temperature, pressure and composition of the vapour phase. In a pure substance it is identical with the boiling point. The **dew temperature** is a temperature at which a vapour of a given composition is in equilibrium with its liquid at a chosen pressure p. The **dew pressure** is a pressure at which a vapour of a given composition is in equilibrium with its liquid at a given temperature.

7.1.7 Saturated vapour pressure

The saturated vapour pressure is a pressure in a one-component system at which the gaseous phase is in equilibrium with the liquid or solid phase at a given temperature. The saturated vapour pressure is the highest pressure at which a substance can be in the equilibrium gaseous state at a given temperature. It is also the lowest pressure at which a substance can exist in the liquid or solid equilibrium state at a given temperature.

S *Symbols:* The saturated vapour pressure of component i will be denoted p_i^{s}.

Note: The term saturated vapour pressure is used for pure substances only. The substances which have a higher pressure of saturated vapour at a given temperature are called **more volatile**.

Example

In all substances, the saturated vapour pressure at the normal boiling point equals 101 325 Pa.

Note: It often happens that there is a gas (usually air) of pressure p over a liquid. If at a given temperature $p_i^{\mathrm{s}} < p$, we say that the liquid **vaporizes**, if $p_i^{\mathrm{s}} = p$, we say that the liquid **boils**.

7.1.8 Melting point

The **melting point** is determined by the melting temperature, melting pressure and the composition of the solid phase. The **melting temperature** is a temperature at which the solid phase of a given composition is in phase equilibrium with its liquid at a chosen pressure p. The **melting pressure** is a pressure at which the solid phase of a given composition is in phase equilibrium with its liquid at a chosen temperature.

7.1.9 Normal melting point

The **normal melting point** is determined by the normal melting temperature, normal pressure p=101 325 Pa and the composition of the solid phase. The **normal melting temperature** is a temperature at which the solid phase of a given composition is in phase equilibrium with its liquid at the normal pressure.

Example
The normal melting temperature of water is 273.15 K.

7.1.10 Freezing point

The **freezing point** is determined by the freezing temperature, freezing pressure and the composition of the liquid phase. In a pure substance, the freezing point is identical with the melting point. The **freezing temperature** is a temperature at which a liquid of a given composition is in phase equilibrium with its solid phase at a chosen pressure p. The **freezing pressure** is a pressure at which a liquid of a given composition is in phase equilibrium with its solid phase at a chosen temperature.

7.1.11 Triple point

The triple point is a particular temperature and pressure in a one-component system at which three different phases can coexist in equilibrium. These three phases are normally solid, liquid and gaseous. However, there are also triple points at which two solid and one liquid, or two solid and one gaseous, or three solid phases are in equilibrium.

Note: The term triple point is used only for pure substances. The system at the triple point has no degree of freedom [see **7.3.4**].

Example
Water has one of its triple points at 0.01 °C and 611 Pa, the temperature and pressure at which ice, liquid water and water vapour are in equilibrium. Besides this one, water has at least six more triple points.

Note: In a one-component system, there cannot be four or more phases in equilibrium. The maximum number of phases equals the number of components +2, as follows from the Gibbs phase rule [see **7.3.4**].

7.2 Thermodynamic conditions of equilibrium in multiphase systems

7.2.0.1 Extensive and intensive criteria of phase equilibrium

In the state of phase equilibrium, the coexisting phases have the same temperature and pressure. Hence, the following criterion is applied in the study of phase equilibria [see **3.4.6**]

$$\mathrm{d}G = 0\,, \qquad [T, p]\,. \tag{7.1}$$

From this equation and from the definition of the chemical potential of a component in a mixture (6.65) we have

$$\mu_i^{(1)} = \mu_i^{(2)} = \cdots = \mu_i^{(f)}\,, \quad i = 1, 2, \ldots, k\,, \quad [T, p]\,, \tag{7.2}$$

where $\mu_i^{(j)}$ is the chemical potential of component i in phase j, f is the number of phases, and k is the number of components in the system.

From (7.2) and from the definition of the fugacity of a component in a mixture (6.74) we have

$$f_i^{(1)} = f_i^{(2)} = \cdots = f_i^{(f)}\,, \quad i = 1.2, \ldots, k\,, \quad [T, p]\,, \tag{7.3}$$

where $f_i^{(j)}$ is the fugacity of component i in phase j.

If we choose the same standard state in all phases, we can rearrange equation (7.3) using (6.89) to obtain

$$a_i^{(1)} = a_i^{(2)} = \ \cdots \ = a_i^{(f)}\,, \qquad i = 1.2, \ldots, k\,, \qquad [T, p]\,, \tag{7.4}$$

where $a_i^{(j)}$ is the activity of component i in phase j.

Equation (7.1) is called the **extensive criterion of phase equilibrium** (it is written for the extensive thermodynamic function G). Equations (7.2), (7.3), and (7.4) are called the **intensive criteria of phase equilibria** (they are written for the intensive thermodynamic functions μ_i, f_i, a_i).

> *Note:* When studying the phase equilibria of pure substances, it is totally unimportant which of the criteria (7.1) through (7.4) we use. When studying the equilibria of mixtures, we choose intensive criteria which state the conditions of equilibrium for each component. If one of the phases is gaseous, it is practicable to choose criterion (7.3), while criterion (7.2) is chosen for the solid-liquid equilibria, and criterion (7.4) for the liquid-liquid equilibria.

7.2.1 Phase transitions of the first and second order

It follows from the condition of phase equilibrium (7.1) that during phase transitions the Gibbs energy is a continuous function of temperature and pressure. If the first derivatives of the Gibbs energy, i.e. entropy and volume [see 3.41] are discontinuous at a phase transition,

$$S^{(1)} \neq S^{(2)} \quad \text{a} \quad V^{(1)} \neq V^{(2)}\,, \tag{7.5}$$

the process is classified as a **first-order phase transition**.

If the first derivatives of the Gibbs energy are continuous while its second derivatives, i.e. the isobaric heat capacity [see (3.18)] and the isothermal compressibility coefficient [see (2.10)] are discontinuous,

$$S^{(1)} = S^{(2)}\,,\ C_p^{(1)} \neq C_p^{(2)} \quad \text{a} \quad V^{(1)} = V^{(2)}\,,\ \beta^{(1)} \neq \beta^{(2)}\,, \tag{7.6}$$

the process is classified as a **second-order phase transition**.

> *Note:* Melting, sublimation, boiling and (in most cases) transformation of crystalline modifications represent first-order phase transitions. Glass transitions, some transformations of crystalline modifications, or the transition from the ferromagnetic to the diamagnetic state represent second-order phase transitions.

7.3 Gibbs phase rule

7.3.1 Independent and dependent variables

The thermodynamic state of a $k-$component one-phase system is fully characterized by the temperature, pressure and amount of substance of all its components. We will call these quantities **independent variables**. Other thermodynamic quantities, e.g. the volume, Gibbs energy or enthalpy, are the **dependent variables** of a system and they are the functions of $T,\ p,\ n_1,\ n_2, \dots n_k$.

Note: The above classification of thermodynamic quantities into independent and dependent variables is most usual but it is not unambiguous. We may, e.g., choose enthalpy, pressure and amount of substance as independent variables, in which case the system's temperature becomes a dependent variable.

7.3.2 Intensive independent variables

We are often interested solely in relations between the intensive variables of a system [see **1.3.1**] and not in the system's size, i.e. its total amount of substance. In this case the number of independent variables drops by one. $T,\ p,\ x_1, \dots, x_{k-1}$ (the molar fraction of the k^{th} component is calculated from relation (1.7)), $x_k = 1 - \sum_{i=1}^{k-1} x_i$) are usually chosen as independent variables, and we will call them **intensive independent variables**. Other *intensive* thermodynamic quantities, e.g. the molar volume, molar Gibbs energy or molar enthalpy, are the functions of intensive independent variables.

In a $k-$component system formed by f *separate* phases, i.e. phases which do not coexist, the intensive independent variables are the temperatures, pressures and compositions of all phases. The other intensive thermodynamic quantities in a given phase are the functions of the temperature, pressure and composition (i.e. the molar fractions) of that particular phase.

When studying a system under certain fixed conditions, the number of intensive independent variables drops by the number of these conditions.

Example

Give the number of intensive independent variables in a system formed by gaseous nitrogen, oxygen and argon, and in an isobaric system formed by the same gases.

Solution

The number of intensive independent variables is 4: pressure, temperature, the molar fraction of nitrogen and the molar fraction of oxygen. The number of intensive independent variables in an isobaric system is 3. Pressure is constant and it is not understood as an intensive variable (the system is studied under a fixed condition $[p]$).

Example

Give the number of intensive independent variables in gaseous air while assuming that air is a mixture of nitrogen, oxygen and argon of the composition $x_{\mathrm{N}_2} = 0.78,\ x_{\mathrm{O}_2} = 0.21$.

Solution

The composition of air is invariable (the system is studied under two fixed conditions). The number of intensive independent variables is 2: pressure and temperature.

7.3.3 Degrees of freedom

Every intensive independent variable in a $k-$component system formed by f coexisting phases for which there exists an interval in which it may be changed without changing the number and type of components and phases is referred to as the **degree of freedom**.

The **number of degrees of freedom** is the number of intensive independent variables which unambiguously specify a system in the state of thermodynamic equilibrium. The number of degrees of freedom is always lower than or equal to the number of intensive independent variables. Equality occurs in homogeneous systems.

7.3.4 Gibbs phase rule

In a $k-$component, $f-$phase system, the number of degrees of freedom v is

$$v = k - f + 2 - C\,, \tag{7.7}$$

where C is the number of the other fixed conditions.

Note: The word *other* is used here to emphasize that the conditions of phase equilibrium (e.g. (7.2)) are already comprised in the formula.

Example

Give the number of degrees of freedom at boiling: a) for a pure substance, b) for a mixture.

Solution

We find the number of degrees of freedom using equation (7.7).
Ad a) In a pure substance there are two phases at boiling and $C = 0$:

$$v = 1 - 2 + 2 - 0 = 1.$$

The system has one degree of freedom, its state being unambiguously determined either by the boiling temperature or by the saturated vapour pressure.
Ad b) A binary mixture has two degrees of freedom at boiling

$$v = 2 - 2 + 2 - 0 = 2.$$

and the state of the system is unambiguously determined by either of the following pairs of data: $T,\ p$, or $T,\ x_1$, or $T,\ y_1$, or $p,\ x_1$, or $p,\ y_1$, or $x_1,\ y_1$, where x_1 is the molar fraction of component 1 in liquid, and y_1 is the molar fraction of component 1 in vapour.

7.4 Phase diagrams

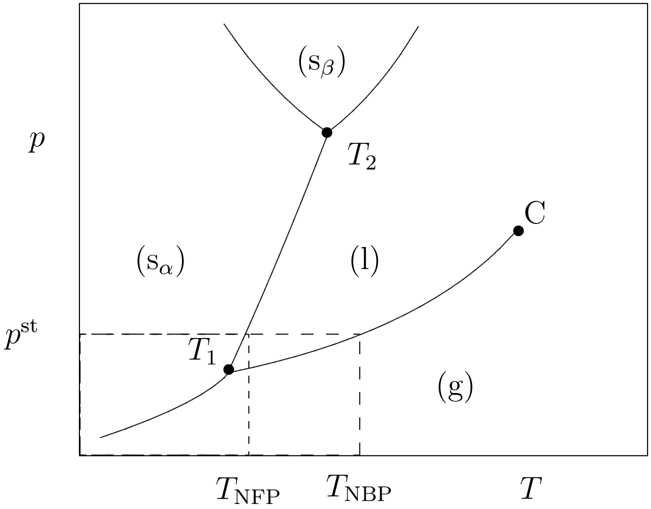
7.4.1 General terms

- **Phase diagram** is a diagram allowing us to determine in which phase or phases a system exists under a given temperature, pressure, and the global (also total) composition of the system.
- **Phase diagram of a pure substance** shows the dependence of equilibrium pressure on equilibrium temperature. The lines in the diagram represent the curves of the boiling, melting, sublimation and crystalline transformation points.
- **Phase diagrams of two-component systems** usually show the dependence of equilibrium pressures on composition at a fixed temperature (isothermal diagrams), or the dependence of equilibrium temperatures on composition at a fixed pressure (isobaric diagrams).
- **Phase diagrams of three-component systems** delimit the homogeneous and heterogeneous regions in dependence on the mixture composition at constant temperature and pressure. They are drawn as triangular diagrams.
- **Binodal** line is a set of points (a curve) separating the homogeneous and heterogeneous regions from one another.
- **Conode** or the tie-line is a straight line connecting two points on the binodal line of a phase diagram which represent the composition of the coexisting (conjugated) phases.

7.4.2 Phase diagram of a one-component system

The phase diagram of a one-component system delimits the regions in which its individual phases exist at various temperatures and pressures (Figure **7.1**).

- The areas denoted (g), (l), (s_α), (s_β) are one-phase regions.
- The lines in the diagram indicate the regions in which two phases coexist; the number of degrees of freedom [see (7.7)] drops to 1.
- The curves intersections indicate **triple points** (in Figure **7.1** there are two triple points denoted T_1 and T_2). They are points with zero degrees of freedom.



Obr. 7.1: Phase diagram $p-T$ of a one-component system. p^{st} is the normal pressure, T_{NFP} is the normal melting (freezing, fusion) temperature, and T_{NBP} is the normal boiling temperature. Point C is the critical point, T_1 and T_2 are the triple points.

Example

Describe what is going on in a system whose phase diagram is shown in Figure 7.1 during heating at constant pressure $p = p^{st}$.

Solution

If the system shown in Figure 7.1 is kept under constant pressure p^{st}, then for temperatures $T < T_{\mathrm{NFP}}$ it is in the solid phase (s_α). T_{NFP} denotes the melting temperature (if $p^{\mathrm{st}} = 101\,325$ Pa, it is the normal melting temperature). Although there is one degree of freedom on the curves in Figure 7.1, this number drops to zero when the pressure is chosen (another fixed condition) [see 7.3]. If heat is supplied to the system from its surroundings, the temperature does not change until all of the solid phase has melted. In the temperature region $T_{\mathrm{NFP}} < T < T_{\mathrm{NBP}}$, only the liquid phase exists in the system. At the boiling temperature T_{NBP}, the second phase, gas, occurs. At the given temperature both phases are in equilibrium, with neither their temperature nor their pressure changing while heat is being supplied to the system, and with only the amount of the gaseous phase increasing. After all of the liquid has evaporated, isobaric heating of the gas occurs.

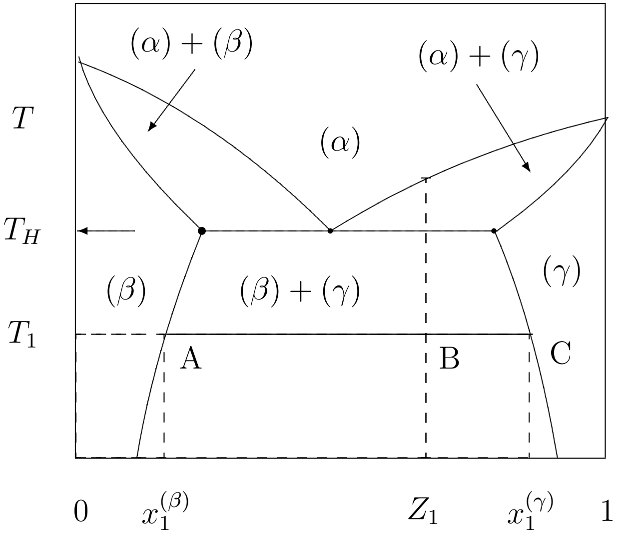
7.4.3 Phase diagrams of two-component (binary) mixtures

The phase diagram of a two-component mixture [see Figure 7.2] delimits the homogeneous and heterogeneous [see 1.1.4] regions at different compositions of the mixture for different temperatures (isobaric diagram) or pressures (isothermal diagram).

- In the regions denoted (α), (β) and (γ) in Figure 7.2, the system is homogeneous (one-phase)
- In the regions denoted $(\alpha) + (\beta)$, $(\alpha) + (\gamma)$ and $(\beta) + (\gamma)$ in Figure 7.2, the system is heterogeneous, i.e. it is formed by two phases whose composition can be found on the binodal lines [see 7.4.1]. The conodes (tie lines) are identical with the isotherms or isobars and they are usually not drawn.

Example

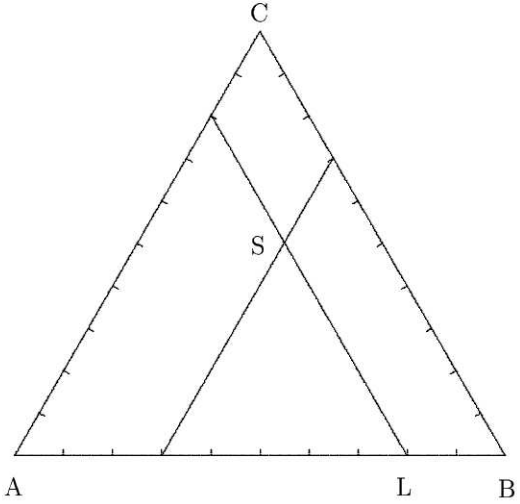
Describe what is going on in the system shown in Figure 7.2 during isobaric heating of a mixture of global composition Z_1 from the initial temperature T_1.



Obr. 7.2: Isobaric phase diagram of a two-component system. The meaning of the symbols is explained in the text.

Solution

At the initial temperature T_1, the system of global composition Z_1 is in the heterogeneous region. It splits into two phases whose composition is given by the intersections of the isotherm T_1 with the binodal lines ($x_1^{(\beta)}$ and $x_1^{(\gamma)}$ in the diagram). The relative amount of both phases is given by the lever rule (i.e. the material balance, see **7.4.5**). With increasing temperature the system continues to be composed of two phases, with only the composition of both phases changing. At temperature T_H, three phases are in equilibrium in the system, with phase (α) added to phases (β) and (γ); their composition is again given by the intersections of the given isotherm with the respective binodal lines. The number of degrees of freedom drops to zero (three coexisting phases in a two-component system at constant pressure), and the system stays at temperature T_H until one of the phases disappears. When a mixture of global composition Z_1 is heated, it is phase (β) that ceases to exist.



Obr. 7.3: Triangular diagram.

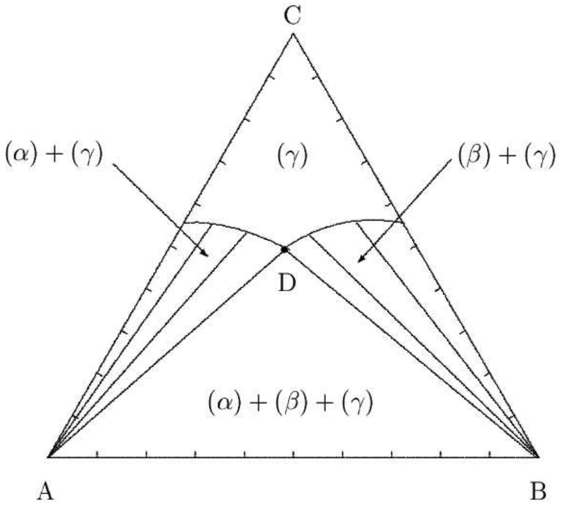
7.4.4 Phase diagrams of three-component (ternary) mixtures

Phase diagrams of three-component mixtures delimit the homogeneous and heterogeneous regions at a different composition of the mixture at a constant pressure and temperature.

- For three-component systems, **triangular diagrams** [see Figure **7.3**] are used to illustrate phase equilibria. The vertices represent pure substances A, B, C. The sides of the triangle represent the composition of two-component mixtures (point L indicates a mixture of substances A + B in a 2/8 ratio). On the line segments parallel to any of the sides there is a constant relative amount of that substance which is indicated by the opposite vertex.

- The region denoted (γ) in Figure **7.4** is a homogeneous region with two degrees of freedom [see **7.3**].

- The regions $(\alpha) + (\gamma)$ and $(\beta) + (\gamma)$ are heterogeneous. In these regions the system splits into two phases: a pure substance and a mixture of the composition given by the intersection of the conode (tie line) with the binodal line [see **7.4.1**].



Obr. 7.4: Example of an isobaric-isothermal diagram of a three-component. system.

- The region $(\alpha) + (\beta) + (\gamma)$ is also heterogeneous. Here the system is formed by three phases: pure substance A, pure substance B, and a mixture of the composition given by point D.

Example

What composition is represented by point S in Figure 7.3?

Solution

Point S is the intersection of the line segment on which all mixtures containing 20 % of substance A can be found with the line segment on which there is 30 % of substance B. This point thus represents a system composed of 20 % of substance A and 30% of substance B. If we draw a line in point S parallel to side AB, we can see that the given three-component mixture contains 50 % of substance C.

7.4.5 Material balance

Let us have a system composed of k components and f coexisting phases. Each component of this system must satisfy the balance equation

$$n_i = \sum_{j=1}^{f} x_i^{(j)} n^{(j)}\,, \qquad i = 1, 2, \ldots, k\,, \tag{7.8}$$

where n_i is the amount of substance of component i in the system, $x_i^{(j)}$ is the molar fraction of the i^{th} component in the j^{th} phase, and $n^{(j)}$ is the total amount of substance in the j^{th} phase,

$$n^{(j)} = \sum_{i=1}^{k} n_i^{(j)}\,, \qquad j = 1, 2, \ldots, k\,. \tag{7.9}$$

Here $n_i^{(j)}$ is the amount of substance of the i^{th} component in the j^{th} phase.

Example

If we mix 4 moles of methanol (1) and 6 moles of n-hexane (2) at 25 °C and a standard pressure, two liquid phases will be formed of the composition $x_1^{(\ell_1)} = 0.10$ and $x_1^{(\ell_2)} = 0.86$. Calculate the amount of substance of the resulting phases.

Solution

Substituting into (7.8) gives

$$\begin{aligned} 4 &= 0.1\, n^{(\ell_1)} + 0.86\, n^{(\ell_2)}\,, \\ 6 &= 0.9\, n^{(\ell_1)} + 0.14\, n^{(\ell_2)}\,, \end{aligned}$$

From this we calculate $n^{(\ell_1)} = 6.05$ mol and $n^{(\ell_2)} = 3.95$ mol.

7.4.5.1 Lever rule

In a two-phase system, the material balance can be interpreted using the so-called lever rule. From Figure **7.2** it is evident that a two-component mixture of global composition Z_1 at temperature T_1 splits into two phases of the composition $x_1^{(\gamma)}$ and $x_1^{(\beta)}$. The amounts of substance of phases (γ) and (β) are in the ratio of the lengths of the line segments $\overline{AB}$ and $\overline{BC}$.

$$\frac{n^{(\gamma)}}{n^{(\beta)}} = \frac{Z_1 - x_1^{(\beta)}}{x_1^{(\gamma)} - Z_1} = \frac{\overline{AB}}{\overline{BC}}\,. \tag{7.10}$$

7.5 Phase equilibria of pure substances

For a pure component the intensive criterion of phase equilibrium (7.2) simplifies to

$$G_m^{(1)} = G_m^{(2)}\,, \tag{7.11}$$

where $G_{\mathrm{m}}^{(j)}$ is the molar Gibbs energy in the j^{th} phase, which in a pure component is identical with the chemical potential. Similarly, equation (7.3) simplifies to

$$f^{(1)} = f^{(2)}\,. \tag{7.12}$$

7.5.1 Clapeyron equation

From the extensive criterion of equilibrium (7.1) and from the Gibbs equation (3.36) we have

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S^{(2)} - S^{(1)}}{V^{(2)} - V^{(1)}} = \frac{H^{(2)} - H^{(1)}}{T[V^{(2)} - V^{(1)}]} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H_{\mathrm{m}}}{T\Delta V_{\mathrm{m}}}\,, \quad \text{[phase equilibrium]}\,, \tag{7.13}$$

where $S^{(j)}$, $H^{(j)}$, $V^{(j)}$ are the entropy, enthalpy and volume of phase j, and ΔH_{m}, ΔV_{m} are the molar changes in enthalpy and volume during the phase transition. This relation is called the **Clapeyron equation**. It expresses the relation between a change in temperature and a change in pressure under the conditions of equilibrium between two phases.

> *Note:* The Clapeyron equation applies exactly to all first-order phase transitions [see **7.2.1**].

7.5.2 Clausius-Clapeyron equation

If one of the phases undergoing a phase transition is a gas at not very high pressures, the Clapeyron equation (7.13) may be simplified to

$$\frac{\mathrm{d}\ln p^{\mathrm{s}}}{\mathrm{d}T} = \frac{\Delta H_{\mathrm{m}}}{\boldsymbol{R}T^2}\,, \tag{7.14}$$

which is called the **Clausius-Clapeyron equation**. It can be derived from (7.13) on condition that the gaseous phase is formed by an ideal gas, and that the volume of the liquid or solid phase is negligible compared to the volume of the gas. The equation is a good approximation when describing the temperature-pressure dependence at boiling (condensation), and at sublimation (vapour deposition), provided that the system pressure is not very high.

Note: In equation (7.14) we denote the saturated vapour pressure using the agreed symbol p^{s}, while in equation (7.13) we do not use any special symbol for equilibrium pressure because p can denote the saturated vapour pressure as well as the melting pressure or the pressure of a crystalline transformation.

7.5.3 Liquid-vapour equilibrium

This subsection deals with the temperature-pressure dependence at boiling, i.e. the relation between the boiling temperature and the saturated vapour pressure in the region of temperatures at which the liquid exists (i.e. from the triple point to the critical point).

In the vicinity of the normal boiling point and at temperatures lower than T_{NBP}, the Clausius-Clapeyron equation (7.14) is an excellent approximation. Its integral form is

$$\ln \frac{p^{\mathrm{s}}(T_2)}{p^{\mathrm{s}}(T_1)} = \frac{1}{\boldsymbol{R}} \int_{T_1}^{T_2} \frac{\Delta H_{\mathrm{m}}}{T^2}\, \mathrm{d}T\,, \tag{7.15}$$

where $\Delta H_{\mathrm{m}} = \Delta_{\mathrm{vap}} H \equiv H_{\mathrm{m}}^{(\mathrm{g})} - H_{\mathrm{m}}^{(\mathrm{l})}$ is the **enthalpy of vaporization** (older term heat of vaporization), and $p^{\mathrm{s}}(T_2)$, $p^{\mathrm{s}}(T_1)$ are the saturated vapour pressures at temperatures T_2, T_1. To calculate the integral we need to know the temperature dependence of the enthalpy of vaporization. In a small temperature range, the enthalpy of vaporization can be considered constant, and equation (7.15) turns into

$$\ln \frac{p^{\mathrm{s}}(T_2)}{p^{\mathrm{s}}(T_1)} = \frac{\Delta_{\mathrm{vap}} H}{\boldsymbol{R}} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)\,. \tag{7.16}$$

Example

The normal boiling temperature of butane is $T = 272.7$ K, its enthalpy of vaporization at this temperature is $\Delta_{\mathrm{vap}} H = 22.4\,\mathrm{kJ\,mol^{-1}}$. Find out whether butane would boil at Mount Everest at $-30\,^{\circ}\mathrm{C}$, where the atmospheric pressure is 32 kPa. Assume that the enthalpy of vaporization does not depend on temperature.

Solution

We use equation (7.16) into which we substitute the following values: $T_1 = 272.7\,\mathrm{K}$, $p^{\mathrm{s}}(T_1) = 101325\,\mathrm{Pa}$, $p^{\mathrm{s}}(T_2) = 32000$ Pa.

$$\ln\frac{32000}{101325} = \frac{22400}{8.314}\left(\frac{1}{272.7} - \frac{1}{T_2}\right) \quad \to \quad T_2 = 244.2\,\mathrm{K} \quad \to \quad t = -28.9\,^{\circ}\mathrm{C}\,.$$

Butane would not boil at Mount Everest at $-30\,^{\circ}\mathrm{C}$, it would be in the liquid state of matter.

For the dependence of the saturated vapour pressure on the temperature, a number of empirical relations have been suggested, e.g. the **Antoine equation**

$$\ln p^{\mathrm{s}} = A - \frac{B}{T + C}\,, \tag{7.17}$$

where A, B, C represent adjustable constants.

Example

The Antoine equation constants for toluene are $A = 14.01415$, $B = 3106.4$, $C = -53.15$ (for pressure given in kPa). Calculate the normal boiling temperature and the enthalpy of vaporization at this temperature.

Solution

According to **7.1.5**, the normal boiling temperature is the temperature at a saturated vapour pressure of 101 325 Pa. By substituting in (7.17) we get

$$T = \frac{B}{A - \ln p^{\mathrm{s}}} - C = \frac{3106.46}{14.01415 - \ln 101.325} + 53.15 = 384.77\,\mathrm{K}$$

We then calculate the enthalpy of vaporization from equation (7.14)

$$\begin{aligned}\Delta_{\mathrm{vap}}H &= \boldsymbol{R}T^2\frac{\mathrm{d}\ln p^{\mathrm{s}}}{\mathrm{d}T} = \boldsymbol{R}T^2\frac{B}{(T+C)^2}\\ &= 8.314 \times 384.77^2\frac{3106.46}{(384.77 - 53.15)^2} = 34770\,\mathrm{J\,mol^{-1}}\,.\end{aligned}$$

7.5.4 Solid-vapour equilibrium

This subsection deals with the temperature-pressure dependence at sublimation (vapour deposition) in the temperature region from 0 K to the triple point temperature. The Clausius-Clapeyron equation (7.14) and its integrated forms (7.15) and (7.16), in which the **enthalpy of sublimation** $\Delta_{\mathrm{sub}}H$ acts in place of $\Delta_{\mathrm{vap}}H$, usually provide an excellent approximation all over this region. The Antoine equation (7.17) is also commonly used.

7.5.5 Solid-liquid equilibrium

This subsection deals with the temperature-pressure dependence at melting (freezing). The Clapeyron equation (7.13) is used in this case. Its integral form is

$$p_2 = p_1 + \int_{T_1}^{T_2} \frac{\Delta H_{\mathrm{m}}}{T\Delta V_{\mathrm{m}}}\,\mathrm{d}T\,, \tag{7.18}$$

where $\Delta H_{\mathrm{m}} = \Delta_{\mathrm{fus}}H \equiv H_{\mathrm{m}}^{(\mathrm{l})} - H_{\mathrm{m}}^{(\mathrm{s})}$ is the **enthalpy of melting (fusion)**, $\Delta V_{\mathrm{m}} = \Delta_{\mathrm{fus}}V \equiv V_{\mathrm{m}}^{(\mathrm{l})} - V_{\mathrm{m}}^{(\mathrm{s})}$ is the change in volume at melting, and $p_1,\ p_2$ are pressures at melting temperatures $T_1,\ T_2$. $\Delta_{\mathrm{fus}}H,\ \Delta_{\mathrm{fus}}V$ can be mostly considered constants. Equation (7.18) may then be simplified to

$$p_2 = p_1 + \frac{\Delta_{\mathrm{fus}}H}{\Delta_{\mathrm{fus}}V}\ln\frac{T_2}{T_1}\,. \tag{7.19}$$

Example

The normal melting temperature of water is 0 °C. At this temperature the enthalpy of melting $\Delta_{\mathrm{fus}}H = 6008\,\mathrm{J\,mol^{-1}}$, the molar volumes of liquid water and ice are $V_{\mathrm{m}}^{(\mathrm{l})} = 18\,\mathrm{cm^3\,mol^{-1}}$, and $V_{\mathrm{m}}^{(\mathrm{s})} = 19.8\,\mathrm{cm^3\,mol^{-1}}$. Assuming that neither the enthalpy of melting nor the molar volumes change with temperature, calculate the pressure at which the melting temperature of water is $-1\,^{\circ}\mathrm{C}$.

Solution

We use equation (7.19) in which

$\Delta_{\text{fus}} V = 18 \times 10^{-6} - 19.8 \times 10^{-6} = -1.8 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1}$.

Given the definition of the normal melting point [see **7.1.9**], $p_1 = 101\ 325$ Pa. We obtain

$$p_2 = 101325 + \frac{6008}{-1.8 \times 10^{-6}} \ln \frac{272.15}{273.15} = 12.2 \times 10^6\,\text{Pa} = 12.2\,\text{MPa}\,.$$

7.5.6 Solid-solid equilibrium

This section deals with the temperature-pressure dependence during transformations of one crystalline form into another. When the process is a first-order phase transition, we use the Clapeyron equation (7.13) and its integral forms (7.18), (7.19), where ΔH_{m} and ΔV_{m} represent changes in molar enthalpy and volume during transition from one solid phase into another.

7.5.7 Equilibrium between three phases

This equilibrium occurs at triple points [see **7.1.11**]. The criterion of phase equilibrium applies

$$G_m^{(1)} = G_m^{(2)} = G_m^{(3)}\,, \tag{7.20}$$

where $G_{\text{m}}^{(j)}$ is the molar Gibbs energy in the j^{th} phase. The criterion written using the fugacities is

$$f^{(1)} = f^{(2)} = f^{(3)}\,. \tag{7.21}$$

At the triple point, at which the solid, liquid and gaseous phases are in equilibrium, the following relation applies between the enthalpy of sublimation, melting and vaporization:

$$\Delta_{\text{sub}} H = \Delta_{\text{fus}} H + \Delta_{\text{vap}} H\,. \tag{7.22}$$

7.6 Liquid-vapour equilibrium in mixtures

This section deals with the relations between temperature, pressure, liquid composition and vapour composition during the boiling and condensation of mixtures. These relations are needed for the description of one of the major separation methods, distillation.

7.6.1 The concept of liquid-vapour equilibrium

Let us consider a multicomponent system formed by two coexisting phases (liquid and gaseous), in the state of thermodynamic equilibrium. We usually speak about liquid-vapour equilibrium (in contrast to liquid-gas equilibrium [see **7.7**]) when all components of the system are below their critical temperatures at a given temperature.

7.6.2 Raoult's law

When a $k-$component mixture in the vapour phase behaves as an ideal gas and in the liquid phase forms an ideal solution [see **6.1.1**], we can write for each component of the system

$$p\,y_i = x_i p_i^{\mathrm{s}}\,, \qquad i = 1.2, \ldots, k\,, \tag{7.23}$$

where y_i is the molar fraction of the i^{th} component in the vapour phase, which is at pressure p and temperature T ($p_i^{\mathrm{s}} = p_i^{\mathrm{s}}(T)$, see **7.5.3**) in equilibrium with the liquid phase in which the molar fraction of the i^{th} component x_i. The condition for equilibrium between the liquid and vapour phase written in this way is called **Raoult's law**. In order to find out at which temperatures, pressures and compositions of both the vapour and liquid phase a system may be in equilibrium, it is sufficient to know the temperature dependence of the saturated vapour pressure for all components present in the system.

In order to determine the state of a $k-$component two-phase system, we need to determine $2k$ [see **7.3**] values, i.e. T, p, $x_1, \ldots, x_{k-1}$, $y_1, \ldots, y_{k-1}$. Since it is possible to write k equilibrium conditions of the type (7.23), it is always necessary to specify k arbitrary quantities. For a binary system obeying Raoult's law, this situation is analyzed in the following table.

Specified	Calculated	From equation	How
T, x_1	p	$p = x_1 p_1^{\mathrm{s}} + x_2 p_2^{\mathrm{s}}$	analytically
	y_1	$y_1 = x_1 p_1^{\mathrm{s}}/p$	analytically
T, y_1	p	$p = (y_1/p_1^{\mathrm{s}} + y_2/p_2^{\mathrm{s}})^{-1}$	analytically
	x_1	$x_1 = p\, y_1/p_1^{\mathrm{s}}$	analytically
T, p	x_1	$x_1 = (p - p_2^{\mathrm{s}})/(p_1^{\mathrm{s}} - p_2^{\mathrm{s}})$	analytically
	y_1	$y_1 = x_1 p_1^{\mathrm{s}}/p$	analytically
p, x_1	T	$p = x_1 p_1^{\mathrm{s}}(T) + x_2 p_2^{\mathrm{s}}(T)$	numerically
	y_1	$y_1 = x_1 p_1^{\mathrm{s}}/p$	analytically
p, y_1	T	$p = (y_1/p_1^{\mathrm{s}}(T) + y_2/p_2^{\mathrm{s}}(T))^{-1}$	numerically
	x_1	$x_1 = p\, y_1/p_1^{\mathrm{s}}$	analytically
x_1, y_1	T	$y_1/y_2 = p_1^{\mathrm{s}}(T) x_1/\left(p_2^{\mathrm{s}}(T) x_2\right)$	numerically
	p	$p = x_1 p_1^{\mathrm{s}} + x_2 p_2^{\mathrm{s}}$	analytically

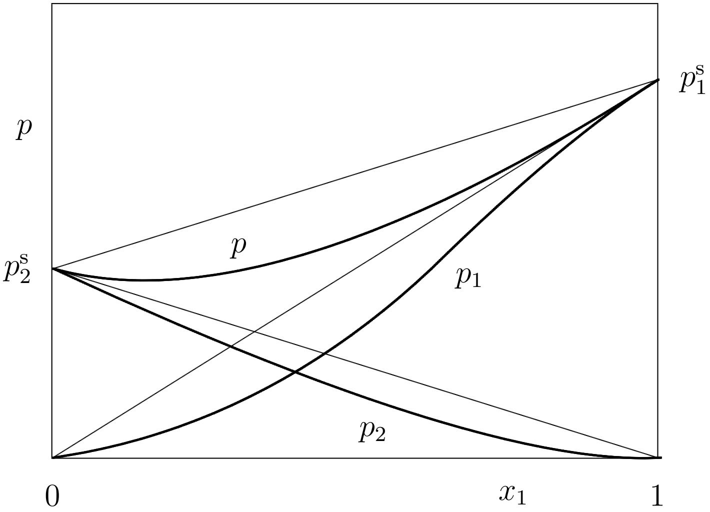
Figure 7.5 shows the dependence of the total and partial pressures of individual components on the composition of the liquid phase in a binary system. If Raoult's law applies, the relations $p = f(x_1)$ and $p_1 = p y_i = f(x_1)$ are linear ($p = p_2^{\mathrm{s}} + (p_1^{\mathrm{s}} - p_2^{\mathrm{s}})x_1$). The values given by Raoult's law are represented by line segments in the diagram.

Note: For most liquid mixtures, the approximation using an ideal solution is rather rough. In practice, therefore, more accurate relations presented in the following section are usually used in place of Raoult's law.

7.6.3 Liquid-vapour equilibrium with an ideal vapour and a real liquid phase

If the vapour phase behaves as an ideal gas but the liquid phase is not an ideal mixture, we can write

$$p\, y_i = \gamma_i x_i p_i^{\mathrm{s}}\,, \qquad i = 1.2, \ldots, k\,, \tag{7.24}$$



Obr. 7.5: Dependence of the total pressure p and partial pressures p_1 and p_2 on the composition of the liquid phase in a two-component system. The line segments represent the relations for an ideal mixture. p_1^{s} and p_2^{s} are the saturated vapour pressures of the individual components.

where γ_i is the activity coefficient of component i in a liquid mixture, which is defined by relation (6.99).

Note: Equation (7.24) is a very good approximation for equilibria at not very high pressures.

Example

Calculate the activity coefficients of water and ethanol in the system ethanol (1)—water (2) at 70 °C using the following data: $x_1 = 0.252$; $y_1 = 0.552$; $p = 62.39\,\mathrm{kPa}$; $p_1^{\mathrm{s}} = 72.3\,\mathrm{kPa}$; $p_2^{\mathrm{s}} = 31.09\,\mathrm{kPa}$.

Obr. 7.6: Isothermal diagram of a two-component system. The curves illustrate the dependence of the dew and boiling pressures on the molar fraction of component 1 in the liquid and vapour phases.

Solution

Substituting into (7.24) gives

$$\gamma_1 = \frac{y_1\,p}{x_1 p_1^{\mathrm{s}}} = \frac{0.552 \times 62.39}{0.252 \times 72.3} = 1.890\,,$$
$$\gamma_2 = \frac{y_2\,p}{x_2 p_2^{\mathrm{s}}} = \frac{0.448 \times 62.39}{0.748 \times 31.09} = 1.202\,.$$

7.6.4 General solution of liquid-vapour equilibrium

From the intensive criterion of equilibrium (7.3) it follows for each component $i,\ i = 1, 2, \ldots k$

$$p\,y_i\phi_i(T, p, y_1, y_2, \ldots, y_{k-1}) = \gamma_i(x_1, x_2, \ldots, x_{k-1}, T, p) x_i \phi_i^{\mathrm{s}}(T, p_i^{\mathrm{s}}(T)) p_i^{\mathrm{s}}(T)\,, \qquad (7.25)$$

where ϕ_i is the fugacity coefficient of component i in a gaseous mixture of composition $(y_1,\ y_2, \ldots y_{k-1})$ at the temperature and pressure of the system [see(6.82)] and $\phi_i^{\mathrm{s}}(T, p_i^{\mathrm{s}}(T))$ is its fugacity coefficient at a state of pure saturated vapour at the system temperature.

Equation (7.25) can be written for each component of the mixture; however, numerical methods always have to be used for the calculation.

> *Note:* If the experimental pressure is higher than that calculated from Raoult's law, we say that the system exhibits **positive deviations** from Raoult's law. If the experimental pressure is lower than that following from Raoult's law, we say that the system exhibits **negative deviations** from Raoult's law, which is the case shown in Figure **7.5**.

7.6.5 Phase diagrams of two-component systems

- **Isothermal diagram**

Figure **7.6** presents a system with positive deviations from Raoult's law. The lower curve is the **curve of dew points** [see **7.1.6**], the upper curve is the **curve of boiling points** [see **7.1.4**]. In the region between these two curves, the system is heterogeneous. In the two-phase region, the composition of both phases is unambiguously given for a fixed temperature and a chosen pressure, as can be seen in the diagram and as follows from the Gibbs phase rule [see **7.3**]. Similarly, for a chosen temperature and composition of one phase, the composition of the second phase and the pressure are fixed.

- **Isobaric diagram**
  Figure **7.7**. shows the curve of dew temperatures (the upper curve) and the curve of boiling temperatures (the lower curve). In the two-phase region there is one degree of freedom at constant pressure, at point A there are zero degrees of freedom (another fixed condition, $y_1 = x_1$, occurs—see (7.7)).
- ***y–x* diagram**
  For every isobaric or isothermal diagram, we may draw a corresponding diagram of the vapour phase—liquid phase composition, the so-called y–x diagram [see Figure **7.8**].

7.6.6 Azeotropic point

- If for coexisting phases in a $k-$component system

$$y_i = x_i\,, \qquad i = 1.2, \dots, k\,, \tag{7.26}$$

  [see point A in Figure **7.7**], we speak about an **azeotropic point** or, shortly, an azeotrope.
- At the azeotropic point it also applies that

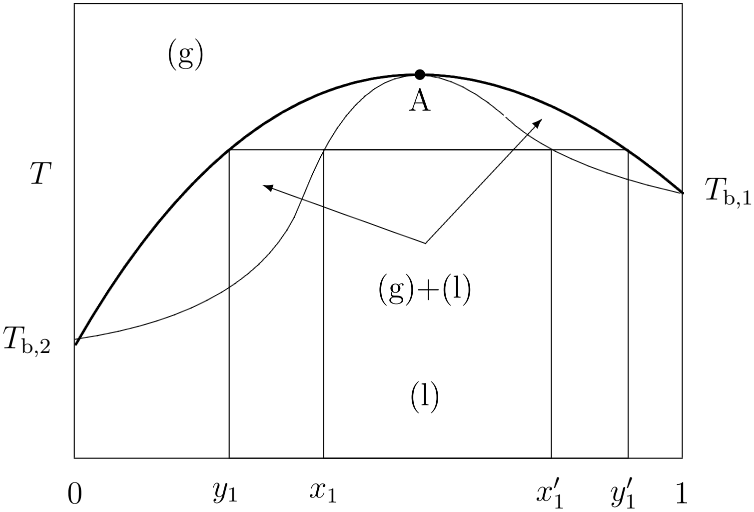
$$\left(\frac{\partial p}{\partial x_i}\right)_{\rm az} = 0\,, \qquad \left(\frac{\partial p}{\partial y_i}\right)_{\rm az} = 0\,, \qquad [T]\,, \qquad i = 1.2, \dots, k\ , \tag{7.27}$$

  or

$$\left(\frac{\partial T}{\partial x_i}\right)_{\rm az} = 0\,, \qquad \left(\frac{\partial T}{\partial y_i}\right)_{\rm az} = 0\,, \qquad [p]\,, \qquad i = 1.2, \dots, k\ . \tag{7.28}$$

- For an ideally behaving vapour phase, combining (7.24) and (7.26) gives

$$\frac{\gamma_i}{\gamma_j} = \frac{p_j^{\rm s}}{p_i^{\rm s}}\,. \tag{7.29}$$

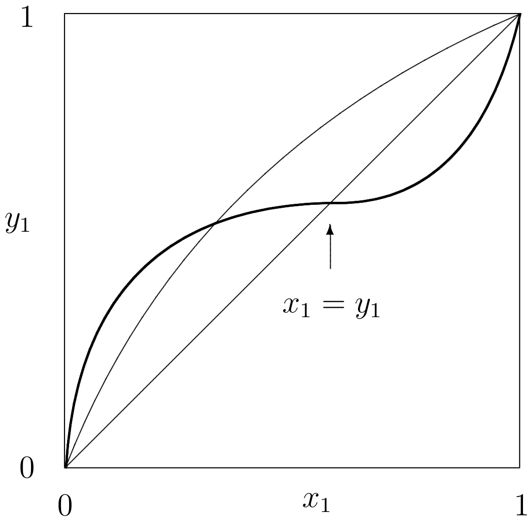


Obr. 7.7: Isobaric diagram of a two-component system with an azeotropic point. The upper curve shows the dependence of dew temperatures on the molar fraction of component 1 while the lower curve represents the dependence of boiling temperatures. $T_{\mathrm{b},1}$ and $T_{\mathrm{b},2}$ are the boiling temperatures of the pure components.

Note: An azeotrope cannot occur in ideal solutions.

Example

In the binary system tetrachlormethane(1)—ethanol(2), an azeotropic point was measured at 65.08 °C and a total pressure of 101 kPa. Under these conditions the vapour phase behaves as an ideal gas. What are the values of the activity coefficients at this point if at the given temperature the saturated vapour pressures of the individual components are $p_1^{\mathrm{s}} = 70.78$ kPa and $p_2^{\mathrm{s}} = 59.84$ kPa?



Obr. 7.8: $y - x$ diagrams of two two-component systems. The bold line shows the dependence of the vapour phase composition on the liquid phase composition for a system with a positive azeotrope; the azeotropic point is indicated by the arrow. The thinner line shows the same dependence for a system without an azeotropic point.

Solution

From relations (7.24) and (7.26) it follows that at the azeotropic point

$$\gamma_i = p/p_i^{\mathrm{s}}$$

and thus $\gamma_1 = 1.43$ and $\gamma_2 = 1.69$.

Note: In order to compare mutual volatility of two components in a mixture, **relative volatility** is defined as

$$\alpha_{ij} = \frac{y_i\, x_j}{x_i\, y_j}\,. \tag{7.30}$$

From (7.26) we can see that at the azeotropic point, relative volatilities equal 1.

Azeotropic point in a two-component system

- When there is a minimum on the curve of boiling temperatures in an isobaric diagram for a binary system, we speak about an azeotrope with a **boiling point minimum**. It exists in systems with positive deviations from Raoult's law, and consequently it is called **positive azeotrope**.
  On the y–x diagram [see Figure **7.8**], the system with a positive azeotrope is represented by the thick line. For the derivative of the y_i dependence on x_i in the vicinity of the positive azeotrope we can write
  $$0 < \left(\frac{\partial y_i}{\partial x_i}\right) < 1\,. \tag{7.31}$$

- In systems with negative deviations from Raoult's law, an azeotrope with a **boiling point maximum**, or a **negative azeotrope,** may occur [see Figure **7.7**].
  For the derivative of the y_i dependence on x_i in the vicinity of the negative azeotrope we write
  $$\left(\frac{\partial y_i}{\partial x_i}\right) > 1\,. \tag{7.32}$$

7.6.7 Effect of the non-volatile substance content on the boiling pressure and temperature

If we add a small amount of a non-volatile substance 2 ($p_2^{\mathrm{s}} \approx 0$) to a pure liquid substance 1 at constant temperature, the initial boiling pressure, which is equal to the saturated vapour pressure p_1^{s}, always drops. After adding a non-volatile substance, the boiling pressure p becomes to a good approximation

$$p = x_1 p_1^{\mathrm{s}}\,. \tag{7.33}$$

- **The decrease in the boiling pressure at constant temperature** is given by the relation
  $$\Delta p = p_1^{\mathrm{s}} - p = x_2 p_1^{\mathrm{s}} \doteq \frac{m_2 M_1}{M_2 m_1} p_1^{\mathrm{s}}\,, \tag{7.34}$$
  where p is th e boiling pressure of a liquid solution of composition x_2; m_1 and m_2 are the masses of the components.

- **The increase in the boiling temperature at constant pressure** is given by the relation

$$\Delta T = T - T_{\mathrm{b},1} \doteq K_{\mathrm{E}} \underline{m}_2 = K_{\mathrm{E}} \frac{m_2}{M_2 m_1}\,, \tag{7.35}$$

where T is the boiling temperature of the dilute solution and $T_{\mathrm{b},1}$ is the boiling temperature of the pure solvent, $\underline{m}_2$ is the molality of the solute[1] K_{E} denotes the ebullioscopic constant which may be determined from the properties of the pure solvent

$$K_{\mathrm{E}} = \frac{\boldsymbol{R} T_{\mathrm{b},1}^2 M_1}{\Delta_{\mathrm{vap}} H_1}\,, \tag{7.36}$$

where $\Delta_{\mathrm{vap}} H_1$ is the enthalpy of vaporization of the pure solvent at the boiling temperature $T_{\mathrm{b},1}$.

Example

After the dissolution of 1 g of a certain substance in 100 g water(1), an increase in the normal boiling temperature by 0.05 °C was measured. What was the molar mass of this substance?
Data: The enthalpy of vaporization of water $\Delta_{\mathrm{vap}} H_1 = 40.650\,\mathrm{kJ\,mol^{-1}}$.

Solution

We first calculate the ebullioscopic constant of water

$$K_{\mathrm{E}} = \frac{\boldsymbol{R} T_{\mathrm{NBP},1}^2 M_1}{\Delta_{\mathrm{vap}} H_1} = \frac{8.314 \times 373.15^2 \times 0.018}{40650} = 0.513\,\mathrm{kg\,K\,mol^{-1}}.$$

From equation (7.35) we calculate the molar mass of the unknown substance

$$M = \frac{0.513 \times 0.001}{0.05 \times 0.1} = 0.103\,\mathrm{kg\,mol^{-1}} = 103\,\mathrm{g\,mol^{-1}}.$$

---

[1] If the solute dissociates, $\underline{m}_2$ has to be replaced by $\nu\alpha\underline{m}_2$, where ν is the number of particles formed by the dissociation of the molecule, and α is the degree of dissociation.

7.6.8 High-pressure liquid-vapour equilibrium

The calculation of liquid-vapour equilibrium at high pressures is based on the equilibrium conditions

$$f_i^{(\mathrm{l})} = f_i^{(\mathrm{g})}\,, \quad i = 1.2\ldots, k\,, \tag{7.37}$$

$$T^{(\mathrm{l})} = T^{(\mathrm{g})}\,, \tag{7.38}$$

$$p^{(\mathrm{l})} = p^{(\mathrm{g})} \tag{7.39}$$

with pressure and fugacities calculated using the equations of state capable of expressing the state behaviour of both phases.

7.7 Liquid-gas equilibrium in mixtures

This problem concerns the solubility of gases in liquids in dependence of temperature, pressure, and the liquid composition.

7.7.1 Basic concepts

- **Liquid-gas equilibrium**
  Let us have a multicomponent system formed by two coexisting phases, liquid and gaseous. If the system temperature is higher than the critical temperature of any of its components, we have to use the standard state of a pure hypothetical substance at an infinite dilution for this component [see **6.5.3**]. In such cases we speak about **liquid-gas** equilibrium.

  Note: If the system temperature is lower than the critical temperatures of all its components, we may calculate phase equilibrium either as liquid-vapour equilibrium or as liquid-gas equilibrium.

- **Gas solubility**
  Gas solubility is understood as an equilibrium concentration of the gaseous component in the liquid phase of a given composition at a given temperature and pressure.

7.7.2 Henry's law for a binary system

The relation

$$f_2 = K_\mathrm{H} x_2\,, \tag{7.40}$$

where f_2 is the fugacity of component 2 in the gaseous phase and x_2 is its molar fraction in the liquid, is called Henry's law, and the constant $K_\mathrm{H} = f(T, p)$ is called **Henry's constant**. Component 2 is that which prevails in the gas, component 1 is that which prevails in the liquid.

- At larger deviations from Henry's law, relation (7.40) is made more accurate by way of introducing the activity coefficient

  $$f_2 = K_\mathrm{H} x_2 \gamma_2^{[x]}\,, \tag{7.41}$$

  where $\gamma_2^{[x]}$ defined by relation (6.100) is a function of composition.

- At low pressures, the gaseous phase may be approximated by an ideal gas, and the fugacity of the component may be replaced by its partial pressure. Equation (7.40) thus becomes
$$p_2 = p\,y_2 = K_{\mathrm{H}} x_2\,, \tag{7.42}$$
where y_2 is the molar fraction of component 2 in the gas. Equation (7.42) is sometimes also called Henry's law.
- If the liquid phase is an ideal solution, the gaseous phase is an ideal gas, and $x_1 \to 1$, the following relation between the partial pressure of component 2 and the total pressure applies
$$p_2 = p\,y_2 = p - p_1^{\mathrm{s}}\,, \tag{7.43}$$
where p_1^{s} is the saturated vapour pressure of component 1.

Example

0.05 mol CO_2 dissolves in 100 g of water ($n = 5.551$ mol) at 4 °C and the normal pressure. Calculate Henry's constant if $p_1^{\mathrm{s}}(4\,^\circ\mathrm{C}) = 813$ Pa.

Solution

The molar fraction of CO_2 in liquid is
$$x_{\mathrm{CO_2}} = \frac{0.05}{5.551 + 0.05} = 0.00893\,.$$

From relations (7.42) and (7.43) we obtain
$$K_{\mathrm{H}} = \frac{p_{\mathrm{CO_2}}}{x_{\mathrm{CO_2}}} = \frac{p - p^{\mathrm{s}}_{\mathrm{H_2O}}}{x_{\mathrm{CO_2}}} = \frac{101325 - 813}{0.00893} = 11.26\,\mathrm{MPa}\,.$$

Henry's law is approximate because it assumes independence of K_{H} on composition. It is based on the assumption that $x_2 \ll 1$, i.e. that the solubility of gas in liquid is low.

7.7.3 Estimates of Henry's constant

Henry's constant is usually determined experimentally from gas solubility measurements. If the temperature of the system is below the critical temperature of the gaseous component, we may estimate Henry's constant using the following formulas.

By comparing (7.40) with (7.25) we obtain the relation

$$K_{\mathrm{H}} = \gamma_2^{\infty} f_2^{\bullet}\,, \tag{7.44}$$

where $f_2^{\bullet}(T,p)$ is the fugacity of pure liquid component 2 and γ_2^{∞} is the limiting activity coefficient of component 2 in a liquid mixture in which this component is infinitely diluted. If the gaseous phase behaves ideally, equation (7.44) becomes

$$K_{\mathrm{H}} = \gamma_2^{\infty} p_2^{\mathrm{s}}\,. \tag{7.45}$$

If, in addition, the liquid phase is an ideal solution (7.23), then

$$K_{\mathrm{H}} = p_2^{\mathrm{s}}\,. \tag{7.46}$$

Example

1. Estimate the solubility of propane(2) in liquid heptane at 25 °C and a partial pressure of propane $p_2 = 101$ kPa. At this temperature, the saturated vapour pressure of propane is 969 kPa.
2. Estimate γ_2^{∞} if you know that the experimental value of solubility expressed by the molar fraction of propane is 0.117.

Solution

1. From relations (7.42) and (7.46) we get

$$x_2 = \frac{p_2}{K_{\mathrm{H}}} = \frac{p_2}{p_2^{\mathrm{s}}} = \frac{0.101}{0.969} = 0.104\,.$$

Agreement with the experimental value 0.117 is very good.

2. To estimate the limiting activity coefficient, we use relation (7.45) and the experimental value of solubility

$$\gamma_2^{\infty} = \frac{p_2}{p_2^{\mathrm{s}} \cdot (x_2)_{\mathrm{exp}}} = \frac{0.104}{0.117} = 0.889\,.$$

7.7.4 Effect of temperature and pressure on gas solubility

Effect of temperature

Temperature affects gas solubility through of Henry's constant in (7.40). Conversion of K_H from one temperature to another is performed using the formula

$$\ln K_\mathrm{H}(T_2) = \ln K_\mathrm{H}(T_1) - \int_{T_1}^{T_2} \frac{\overline{H}_2^{\otimes}}{\boldsymbol{R}T^2}\,\mathrm{d}T\,, \tag{7.47}$$

where $\overline{H}_2^{\otimes} = \overline{H}_2 - H_{\mathrm{m},2}^{\otimes}$ is the differential heat of solution of the gaseous component in a given solvent [see equation (6.56)].

7.7.4.1 Effect of pressure

Pressure affects gas solubility both directly and through of Henry's constant.

- The direct effect is evident from relation (7.42), according to which solubility increases linearly with a growing partial pressure.
- The effect of pressure on Henry's constant is given by the relation

$$K_\mathrm{H}(p_2) = K_\mathrm{H}(p_1) + \int_{p_1}^{p_2} \frac{\overline{V}_2^{\infty}}{\boldsymbol{R}T}\,\mathrm{d}p\,, \tag{7.48}$$

  where $\overline{V}_2^{\infty}$ is the partial molar volume of gas dissolved in the liquid phase at infinite dilution. Given the small value of $\overline{V}_2^{\infty}/(\boldsymbol{R}T)$, this effect is rather weak.

7.7.5 Other ways to express gas solubility

Gas solubility may be also expressed by the volume of gas dissolved in a unit volume of the solvent. Based on the way in which the volume of the dissolved gas is defined, we distinguish two different cases (in both of them we assume the validity of the equation of state of an ideal gas).

- **Bunsen's absorption coefficient**—the volume of the dissolved gas is calculated at the standard temperature $T^\mathrm{st} = 273.15$ K and a given partial pressure p_2. Then

$$\alpha = \frac{V_{T^\mathrm{st}}^{(\mathrm{g})}}{V_1^{(\ell)}}\,. \tag{7.49}$$

In relation (7.49), $V_{T^{\mathrm{st}}}^{(\mathrm{g})} = n_2 \boldsymbol{R} T^{\mathrm{st}}/p_2$. More often we may encounter the form

$$\alpha = \frac{V^{\mathrm{st}} p^{\mathrm{st}}}{V_1^{(\ell)} p_2} = \frac{n_2 \boldsymbol{R} T^{\mathrm{st}}}{n_1 V_{\mathrm{m},1}^{(\ell)} p_2}\,, \tag{7.50}$$

where $V^{\mathrm{st}} = n_2 \boldsymbol{R} T^{\mathrm{st}}/p^{\mathrm{st}}$ is the volume of the dissolved gas calculated from the equation of state of an ideal gas at $T^{\mathrm{st}} = 273.15$ K and $p^{\mathrm{st}} = 101.325\,\mathrm{kPa}$. $V_1^{(\ell)} = n_1 V_{\mathrm{m},1}^{(\ell)}$ is the volume of n_1 moles of the solvent at a given temperature and pressure.

- **Ostwald's absorption coefficient**—the volume of the dissolved gas is calculated at a given temperature and a given partial pressure.

$$\beta = \frac{V_2^{(\mathrm{g})}}{V_1^{(\ell)}}\,, \tag{7.51}$$

where $V_2^{(\mathrm{g})} = n_2 \boldsymbol{R} T/p_2$ is the volume of the dissolved gas calculated from the equation of state of an ideal gas at the temperature of the system and a partial pressure p_2.

U *Main unit:* dimensionless quantity.

- **Conversions between coefficients**

$$\alpha = \beta \frac{T^{\mathrm{st}}}{T}\,. \tag{7.52}$$

The molar fraction of gas in the liquid phase, x_2, may be calculated from the absorption coefficients using the equation

$$x_2 = \left(1 + \frac{\boldsymbol{R} T}{V_{\mathrm{m},1}^{(\ell)}\, p_2\, \beta}\right)^{-1} = \left(1 + \frac{\boldsymbol{R} T^{\mathrm{st}}}{V_{\mathrm{m},1}^{(\ell)}\, p_2\, \alpha}\right)^{-1} \tag{7.53}$$

Example

1 dm^3 of gaseous CO_2 dissolves in 1 dm^3 of water at 17 °C and a partial pressure of carbon dioxide $p_{\mathrm{CO}_2} = 101.32\,\mathrm{kPa}$. Calculate Bunsen's and Ostwald's absorption coefficients.

Solution

It follows from the specification that $V_2^{(\mathrm{g})} = 1\,\mathrm{dm}^3$ and $V_1^{(\ell)} = 1\,\mathrm{dm}^3$. Substituting into (7.51) gives $\beta = 1$. We obtain Bunsen's absorption coefficient from (7.52)

$$\alpha = 1 \times \frac{273.15}{273.15 + 17} = 0.941 .$$

7.7.6 Liquid-gas equilibrium in more complex systems

This subsection deals with the solubility of gaseous mixtures in liquid, gas solubility in a mixture of liquids, and gas solubility in aqueous solutions of salts.

- **Solubility of gaseous mixtures in liquid**

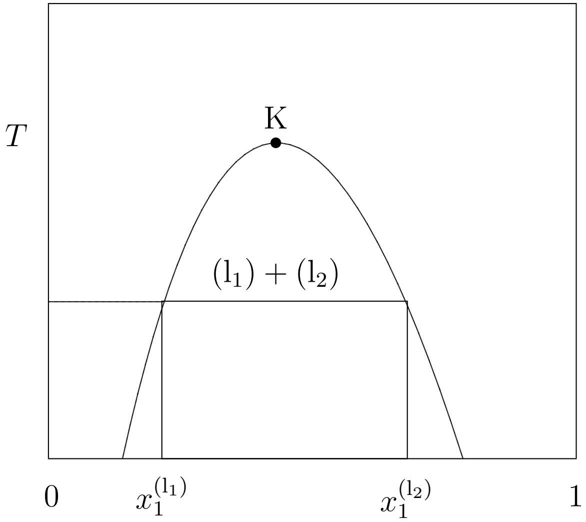
  Henry's law (7.40) can be directly extended to a (k -1)-component gaseous mixture

  $$f_i = K_{\mathrm{H,1i}}\, x_i\,, \qquad i = 2.3, \dots k\,, \tag{7.54}$$

  where $K_{\mathrm{H,1i}}$ is Henry's constant of component i in a liquid component 1. If the solubility of gases is not too high, $K_{\mathrm{H,1i}}$ may be identified with Henry's constant in a binary system containing a liquid component 1 and a gaseous component i.
- **Gas solubility in a mixture of liquids**

  In this case equation (7.40) applies, with Henry's constant being the function not only of temperature and pressure, but also of the liquid solvent composition.
- **Gas solubility in aqueous solutions of salts**

  Just like in a mixture of liquids, also in this case Henry's constant depends on solvent composition, i.e. the concentration of the aqueous solution. The presence of a salt may increase gas solubility as compared with its solubility in pure water (this phenomenon is known as the **salting-in effect**), or (more often) it may decrease its solubility (the **salting-out effect**).



Obr. 7.9: Isobaric diagram of a two-component system with two liquid phases. The curve describes the dependence of equilibrium temperature on the composition of the partially miscible liquid phases ℓ_1 and ℓ_2. Point C is the upper critical point of solution.

7.8 Liquid-liquid equilibrium

Some liquids are only partially mutually miscible (e.g. water and phenol), and their mixture can split into two liquid phases. The dependence between the composition of the coexisting liquid phases and temperature is studied in this connection. The pressure dependence is small and usually it is not studied.

> *Note:* Equilibrium between liquid phases is typical for mixtures; it does not exist in one-component systems.

7.8.1 Conditions of equilibrium at constant temperature and pressure

The intensive criterion of equilibrium (7.4) between f liquid phases in a $k-$component system may be written in the form

$$x_i^{(1)}\gamma_i^{(1)} = x_i^{(2)}\gamma_i^{(2)} = \ldots = x_i^{(f)}\gamma_i^{(f)}\,, \qquad i = 1, 2, \ldots, k\,. \tag{7.55}$$

If we know the composition of one liquid phase and the activity coefficients, we may use equations (7.55) to calculate the composition of the other liquid phases.

> *Note:* Given that activity coefficients are non-linear functions of composition [see e.g. (6.114)], it is necessary to solve a set of non-linear equations when calculating the composition of the coexisting phases.

7.8.2 Two-component system containing two liquid phases

The course of the binodal line for these systems is usually illustrated in isobaric diagrams $T-x_1$ [see Figure 7.9]. The composition of the coexisting phases varies with temperature, and the tie lines run parallel to the axis x. Point C represents the **upper critical temperature**, which is the highest temperature at which a system may split into two phases. There are also systems with a **lower critical temperature**, or those with both upper and lower critical temperatures.

7.8.3 Two-component system containing two liquid phases and one gaseous phase

At constant pressure, this system does not have any degree of freedom [see **7.3**]. Temperature does not change until one of the phases disappears.

- **Heterogeneous azeotrope**
  If two liquid phases are in equilibrium with a gaseous phase the composition of which is $y_1 \in (x_1^{(\ell_1)}, x_1^{(\ell_2)})$, we speak about a heterogeneous azeotrope [see Figure **7.2**, where $(\alpha) = (g)$, $(\beta) = (\ell_1)$, and $(\gamma) = (\ell_2)$].

Note: In the case of a heterogeneous azeotrope, the composition of the vapour phase is not identical with the composition of the equilibrium liquid phases.

- **Ideal vapour phase, both components totally immiscible in the liquid phase**
  The overall pressure above a heterogeneous mixture is

$$p = p_1^{\mathrm{s}} + p_2^{\mathrm{s}} \tag{7.56}$$

and the composition of the vapour phase is

$$y_1 = \frac{p_1^{\mathrm{s}}}{p_1^{\mathrm{s}} + p_2^{\mathrm{s}}}\,. \tag{7.57}$$

Note: The consequence of relation (7.56) is that a heterogeneous mixture of two very little miscible substances boils at a temperature which is lower than the boiling point of any of its components.

7.8.4 Three-component system containing two liquid phases

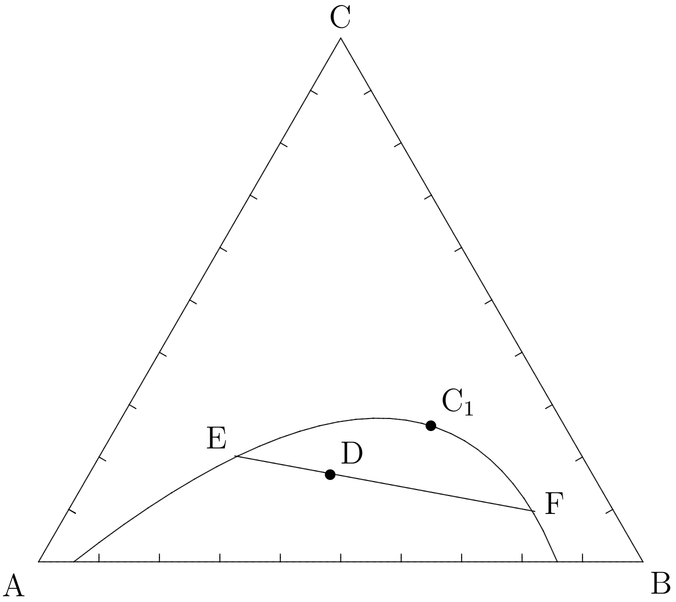
Figure **7.10** shows a binodal line $\mathrm{EC_1F}$ and a tie line EDF. The system of a global composition given by point D split into two liquid phases whose composition is given [see **7.4.4**] by points E and F on the binodal line. The amount of substance ratio of both liquid phases is given by the lever rule [see **7.4.5**]. The compositions of both coexisting phases merge at point $\mathrm{C_1}$ (the critical point).

- The **distribution coefficient** is defined as the ratio of the molar fractions or concentrations of the i^{th} component in one and the other liquid phases.

$$K_{x,i} = \frac{x_i^{(\ell_2)}}{x_i^{(\ell_1)}} \qquad \text{or} \qquad K_{c,i} = \frac{c_i^{(\ell_2)}}{c_i^{(\ell_1)}}\,, \qquad i = 1,2,3\,. \tag{7.58}$$

From (7.55) we also have

$$K_{x,i} = \frac{\gamma_i^{(\ell_1)}}{\gamma_i^{(\ell_2)}}\,. \tag{7.59}$$



Obr. 7.10: Isobaric-isothermal diagram of three component system.

This relation makes it clear that the distribution coefficient generally depends on temperature, pressure and composition; at the critical point (point C$_1$ in Figure **7.10**), the distribution coefficients are equal to 1.

- **Extraction, Nernst's distribution law**

  Let us have two immiscible liquids, components 1 and 2. In liquid 1, another substance, component 3, is dissolved. If we add substance 2 to a mixture of substances 1 and 3, then the transfer of part of the dissolved substance from liquid 1 to liquid 2 is called extraction. If we choose n_0 to denote the initial amount of the extracted substance, which is contained in volume V_1 of solvent 1, and n_p to denote the amount of substance which during extraction passes to solvent 2, whose volume is V_2, we write

$$n_\mathrm{p} = n_0 \frac{K_{c,3} V_2}{V_1 + K_{c,3} V_2} \,. \tag{7.60}$$

If the extraction is performed $k-$times with the same volume V_2 of pure solvent 2, we can write the following formula for the residual amount n_r

$$n_\mathrm{r} = n_0 - n_\mathrm{p} = n_0 \left(\frac{V_1}{V_1 + K_{c,3} V_2}\right)^k . \tag{7.61}$$

Note: **Nernst's distribution law (7.58)** assumes a constant value of the distribution coefficient. This assumption is justified if the solubility of component 3 in both immiscible liquids is low. At infinite dilution of the component in both liquid phases, the distribution coefficient acquires the limiting value which is given by the ratio of the limiting activity coefficients [compare with (7.59)].

Example

1000 cm^3 of water contains $n_0 = 0.0001$ moles of iodine. What amount of iodine remains in the aqueous solution after extraction by carbon disulphide if we use: a) 50 cm^3 in a one-off extraction, b) 10 cm^3 in an extraction repeated five-times. Nernst's distribution coefficient is $K_{c,\mathrm{I}_2} = c_{\mathrm{I}_2}^{\mathrm{CS}_2} / c_{\mathrm{I}_2}^{\mathrm{H_2O}} = 600.$

Solution

a) from (7.61) we obtain

$$n_\mathrm{r} = 0.0001 \frac{1000}{1000 + 600 \times 50} = 3.33 \times 10^{-6} .$$

b)

$$n_\mathrm{r} = 0.0001 \left(\frac{1000}{1000 + 600 \times 10}\right)^5 = 5.94 \times 10^{-9} .$$

In case b), i.e. after repeating the extraction five-times, about 500-times less iodine remains in water than in the case of the one-off extraction.

7.9 Liquid-solid equilibrium in mixtures

This section deals with relations between the temperature and composition of phases during the freezing and melting of mixtures. The effect of pressure on melting and freezing is small and usually it is not studied.

7.9.1 Basic terms

Note: Since most experimental data on liquid-solid phase equilibrium relate to atmospheric pressure, the value of equilibrium pressure in these cases is often not stated.

- A set of equilibrium freezing temperatures [see **7.1.10**] changing in a given system with the composition of the liquid phase (the upper line in the binary system in Figure **7.12**) is known as the **liquidus**.
- A set of equilibrium melting temperatures [see **7.1.8**] changing in a given system with the composition of the solid phase (the lower line in the binary system in Figure **7.12**) is known as the **solidus**.
- The **eutectic point** (denoted E in Figures **7.11**, **7.13**, **7.14a**, **7.15**) in a two-component system is defined as the point of intersection of both curves of the liquidus whose slopes have opposite signs in the vicinity of this point. At this point there are three phases in equilibrium, and according to the Gibbs phase law [see **7.3**], the system has no degree of freedom at this point at constant pressure.
- The **peritectic point** (denoted P in Figures **7.14b**, **7.15b**) is the point in the vicinity of which the slopes of both curves of freezing have the same sign. At this point there are three phases in equilibrium, and according to the Gibbs phase law [see **7.3**], the system has no degree of freedom at this point at constant pressure

7.9.2 General condition of equilibrium

From the intensive criterion of equilibrium (7.2) $\mu_i^{(\mathrm{l})} = \mu_i^{(\mathrm{s})}$ we may derive

$$\ln \frac{\gamma_i^{(\mathrm{l})} x_i^{(\mathrm{l})}}{\gamma_i^{(\mathrm{s})} x_i^{(\mathrm{s})}} = \int_{T_{\mathrm{f}i}}^{T} \frac{\Delta_{\mathrm{fus}} H_i}{\boldsymbol{R} T^2}\, \mathrm{d}T \,. \tag{7.62}$$

For integration we need to know the temperature dependence of the enthalpy of melting of a pure $i^{\rm th}$ component, $\Delta_{\rm fus}H_i$. $T_{{\rm f}i}$ is the melting (fusion) temperature of a pure $i^{\rm th}$ component.

7.9.3 Two-component systems with totally immiscible components in the solid phase

The coexistence curve of a liquid mixture with crystals of component 2 (line $T_{\rm f,2}$E in Figure **7.11**) is given by the equation

$$\ln \gamma_2^{(\rm l)} x_2^{(\rm l)} = \int_{T_{\rm f,2}}^{T} \frac{\Delta_{\rm fus}H_2}{\boldsymbol{R}T^2}\, dT\,. \tag{7.63}$$

and the coexistence curve of a liquid mixture with crystals of component 1 (line E$T_{\rm f,1}$) by the equation

$$\ln \gamma_1^{(\rm l)} x_1^{(\rm l)} = \int_{T_{\rm f,1}}^{T} \frac{\Delta_{\rm fus}H_1}{\boldsymbol{R}T^2}\, dT\,. \tag{7.64}$$

The common solution of both equations gives the temperature and composition of the eutectic point E [see **7.9.1**].

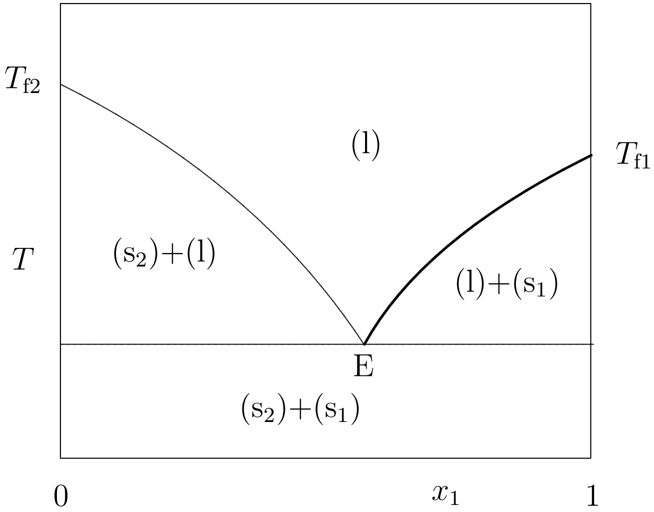
Note: Most organic substances do not mix in the solid phase.

- **Ideal solubility**
  If the liquid phase forms an ideal solution and the enthalpy of melting is independent on temperature, we have

$$-\ln x_1^{(\rm l)} = \frac{\Delta_{\rm fus}H_1}{\boldsymbol{R}}\left(\frac{1}{T} - \frac{1}{T_{\rm f,1}}\right) \tag{7.65}$$

  and similarly for the second part of the liquidus curve. From this it follows that:

  1. The slope of the dependence T–x_1 does not depend on substance 2.
  2. Solubility increases with increasing temperature.
  3. Of the two substances with roughly the same enthalpies of melting, the one with a lower temperature of melting will dissolve more.



Obr. 7.11: Dependence of the freezing temperature on composition in a two-component system whose components are immiscible in the solid phase. $T_{f,1}$ and $T_{f,2}$ are the freezing temperatures of pure components 1 and 2, E is the eutectic point.

4. Of the two substances with a comparable temperature of melting, the one with a lower enthalpy of melting will dissolve more.

- For the temperature dependence of the solubility of salts we can write for low values of molality

$$\ln \frac{\underline{m}_2^{(l)}(T)}{\underline{m}_2^{(l)}(T')} = \frac{\overline{H}_2^{\otimes}}{\nu \boldsymbol{R}} \left(\frac{1}{T'} - \frac{1}{T} \right) , \tag{7.66}$$

where ν is the total number of ions to which a salt of the molality $\underline{m}_2^{(l)}$ dissociates in a given solvent, and $\overline{H}_2^{\otimes}$ is its last differential heat of solution.

- For **lowering of the melting temperature** by dissolving a component 2 in a pure liquid substance 1 it holds in the ideal solution approximation

$$\Delta T = T_{f,1} - T \doteq K_C \underline{m}_2 = K_C \frac{m_2}{M_2 m_1} , \tag{7.67}$$

where T is the melting temperature of a dilute solution, $T_{\mathrm{f},1}$ is the melting temperature of a pure solvent, $\underline{m}_2$ denotes the molality of solute[2], m_1 or m_2 denote the mass of the respective component, and K_C denotes the cryoscopic constant which may be determined from the properties of a pure solvent

$$K_\mathrm{C} = \frac{\boldsymbol{R} T_{\mathrm{f},1}^2 M_1}{\Delta_\mathrm{fus} H_1}\,. \tag{7.68}$$

7.9.4 Two-component systems with completely miscible components in both the liquid and solid phases

In Figure **7.12**, the liquidus is indicated by the thicker line and the solidus by the thinner line. Both curves may be calculated by solving two equations (7.62) for $i = 1$ and 2, provided that we know the dependence of all activity coefficients on composition. Sometimes we may encounter the type shown in Figure **7.12b**, where the liquidus and solidus meet. It is an analogy to the azeotropic point in the liquid-vapour equilibrium [see **7.6.6**].

7.9.5 Two-component systems with partially miscible components in either the liquid or the solid phase

- Components partially miscible in the liquid phase and totally immiscible in the solid phase. Figure **7.13** is an extension of Figure **7.11** with the region of two liquids added. Points C, D, E represent the coexistence of three phases, with the number of degrees of freedom decreasing, according to the Gibbs phase law [see **7.3**], to zero.
- Components completely miscible in the liquid phase and partially miscible in the solid phase. In the event of large differences in the melting points, the case shown in Figure **7.14a** transfers to that shown in Figure **7.14b**. Point E is the eutectic point and point P is the peritectic point [see **7.9.1**].

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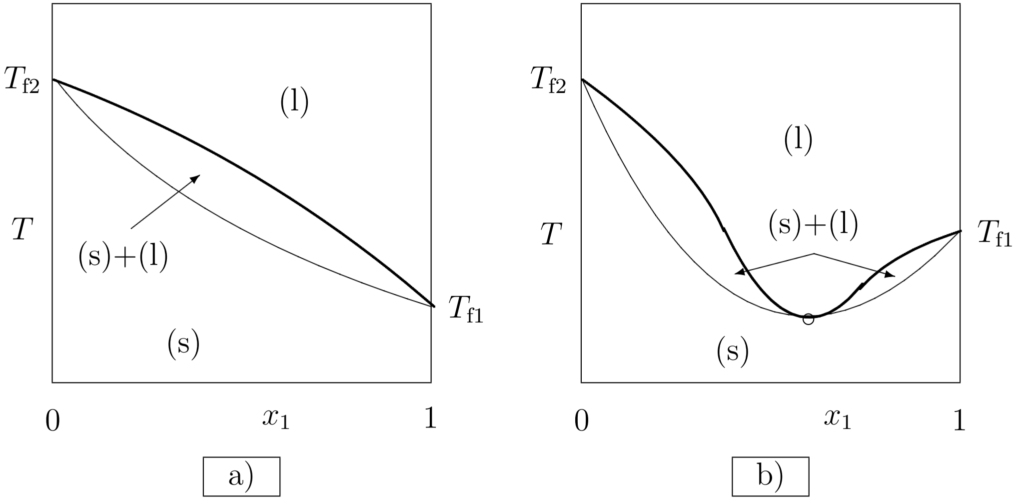
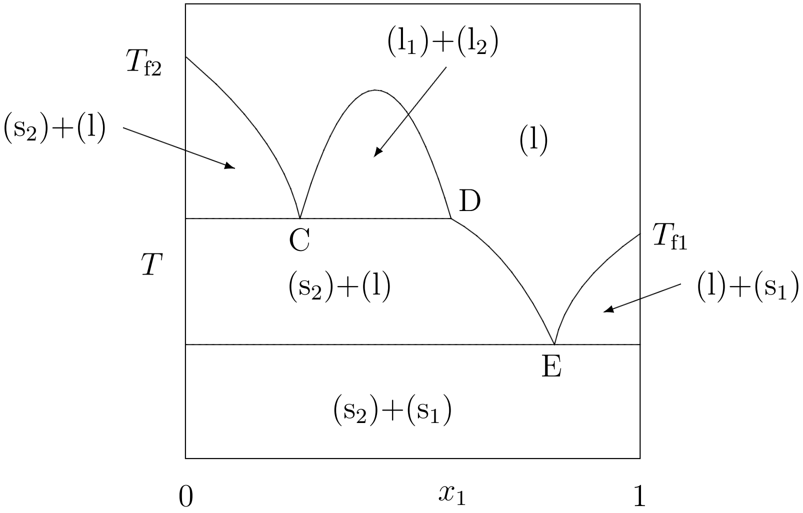
[2] If the solute dissociates, $\underline{m}_2$ has to be replaced by $\nu\alpha\underline{m}_2$, where ν is the number of particles formed by the dissociation of the molecule, and α is the degree of dissociation.



Obr. 7.12: Two cases of the dependence of the freezing temperature (the upper curves) and the melting temperature (the lower curves) on composition in a two-component system with components completely miscible in both the liquid and solid phases. Case b) is an analogy to the azeotropic behaviour.



Obr. 7.13: Dependence of the freezing temperature on composition for a two-component system; the liquid phases are partially miscible, the solid phases are immiscible.

Obr. 7.14: Dependence of the freezing temperature (the upper curves) and the melting temperature (the lower curves) on composition for a two-component system; the components are completely miscible in the liquid phase, the solid phases are partially miscible. Case a) is typical of mixtures with small differences in the melting temperatures of pure components; case b) is typical of mixtures with great differences in the melting temperatures of pure components.

7.9.6 Formation of a compound in the solid phase

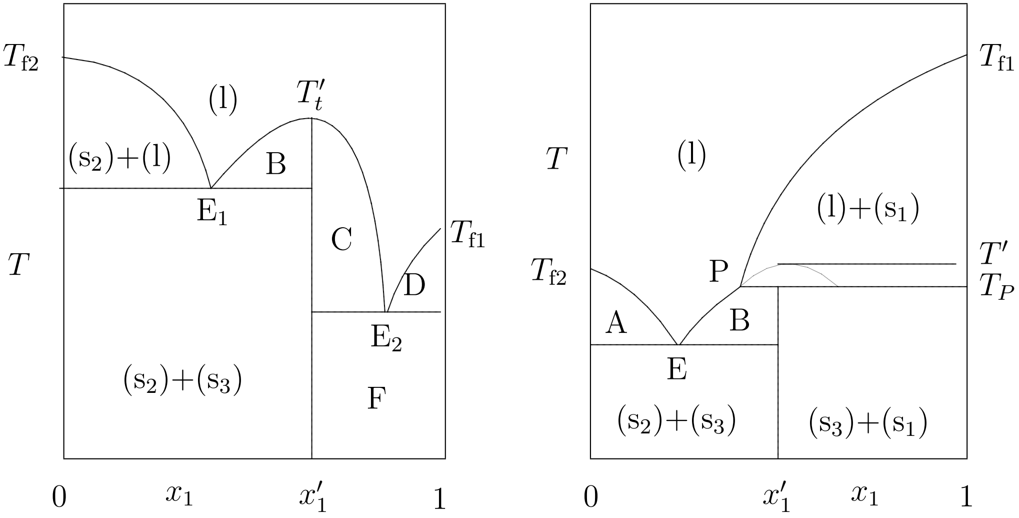
In Figure **7.15a**, substances 1 and 2 form a compound of composition x'_1. This compound is stable at its melting temperature T'_f, which is known as the **congruent melting point**. In Figure **7.15b** the compound of composition x'_1 is not stable at its melting temperature and T'_f is known as the **incongruent melting point** in view of the fact that, in contrast to the congruent melting point, there is a different composition of the liquid and solid phases in this case.

7.9.7 Three-component systems

A three-component diagram delimits the homogeneous and heterogeneous regions in a three-component system at constant temperature and pressure (usually atmospheric).

Figure 7.4 shows the solubility of two salts A and B in water (component C). The liquid phase is denoted (γ) and the solid phases are denoted (α) and (β).

When we want to observe changes in equilibrium composition at different temperatures, we have to use three-dimensional diagrams.



a) b)

Obr. 7.15: Dependence of the temperatures of freezing and melting on composition for two-component systems whose components form a compound in the solid phase. In case a) the compound is stable at the melting temperature, in case b) it is unstable at the melting temperature. Individual letters denote the following regions and points, A: (s$_2$) + (l); B, C: (s$_3$) + (l); D: (s$_1$) + (l); E, E$_1$, E$_2$: eutectic points; P: peritectic point, F: (s$_1$) + (s$_3$).

7.10 Gas-solid equilibrium in mixtures

This section deals with the relations between temperature, pressure, and the composition of phases during sublimation and vapour deposition of mixtures.

7.10.1 General condition of equilibrium

From the intensive criterion of equilibrium (7.2) $\mu_i^{(\mathrm{g})} = \mu_i^{(\mathrm{s})}$ we may derive

$$\ln \frac{f_i^{(\mathrm{g})} / f_i^{\bullet,(g)}}{\gamma_i^{(\mathrm{s})} x_i^{(\mathrm{s})}} = \int_{T_{\mathrm{s,i}}}^{T} \frac{\Delta_{\mathrm{sub}} H_i}{\boldsymbol{R} T^2}\,\mathrm{d}T - \int_{p_i^{\mathrm{s}}}^{p} \frac{\Delta_{\mathrm{sub}} V_i}{\boldsymbol{R} T}\,\mathrm{d}p\,. \tag{7.69}$$

For integration we need to know the dependence of the volume change during sublimation on pressure, and the dependence of the enthalpy of sublimation of a pure i^{th} component $\Delta_{\mathrm{sub}} H_i$ on temperature. $T_{\mathrm{s,i}}$ is the temperature of sublimation of a pure i^{th} component, p_i^{s} is the respective saturated vapour pressure.

7.10.2 Isobaric equilibrium in a two-component system

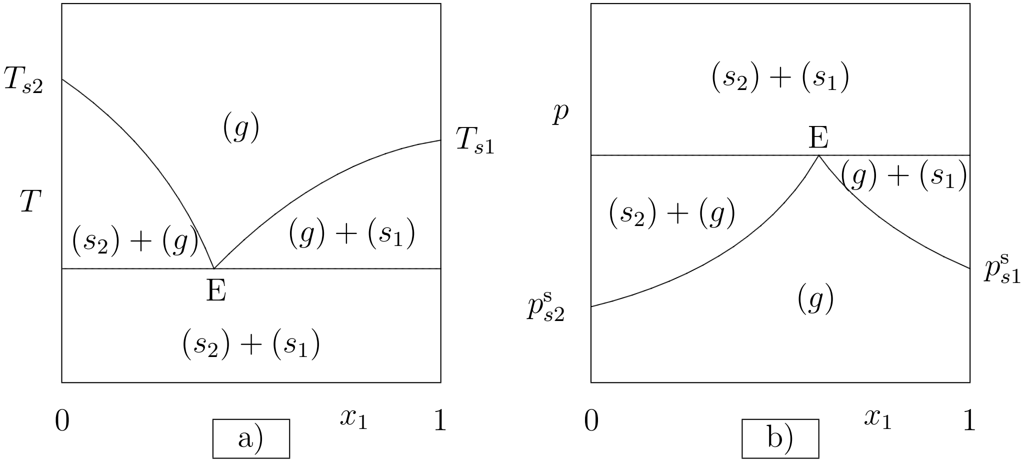
For a binary mixture whose components form an ideal gaseous mixture over the solid phase of pure crystals of component 1, we have (provided that $\Delta_{\mathrm{sub}} H_i$ is independent of temperature)

$$-\ln y_1^{(\mathrm{g})} = \frac{\Delta_{\mathrm{sub}} H_1}{\boldsymbol{R}} \left(\frac{1}{T} - \frac{1}{T_{\mathrm{f},1}} \right), \tag{7.70}$$

where $T_{\mathrm{f},1}$ is the melting temperature of a pure substance 1. The same relation applies to the second component. The common solution of the equations for both components gives the temperature and composition at point E, which is called the **eutectic point of vapour**. Figure **7.16a** shows the dependence of the vapour phase composition on temperature for this case.

7.10.3 Isothermal equilibrium in a two-component system

Let us consider a mixture whose components form an ideal gaseous mixture and are immiscible in the solid phase. Given that the volume of the solid phase is usually much smaller than that



Obr. 7.16: Solid-gas phase equilibrium in two-component systems whose components are immiscible in the solid phase: a) Dependence of the temperature of sublimation on composition (isobaric diagram); b) dependence of the pressure of sublimation on composition (isothermal diagram).

of the gaseous phase, we may replace the sublimation volume with the volume of an ideal gas $\Delta_{\mathrm{sub}} V_i \doteq \boldsymbol{R}T/p$. Then for the molar fractions of the components in the gaseous phase it applies that

$$y_i^{(\mathrm{g})} = \frac{p_i^{\mathrm{s}}}{p}\,. \tag{7.71}$$

The pressure dependence of the vapour phase composition is shown in Figure **7.16b**.

7.11 Osmotic equilibrium

Let us have a solution (this phase will be denoted $'$) separated from a pure solvent (this phase will be denoted $''$) by a semipermeable membrane, i.e. a membrane through which only the molecules of the solvent can permeate. In order for the equilibrium condition (7.2) for solvent to be satisfied, both phases separated by the membrane must be under different pressures. Their difference is called **osmotic pressure**

$$\pi = p' - p'' . \tag{7.72}$$

For osmotic pressure we can write

$$\pi = -\frac{\phi_1 \boldsymbol{R} T \ln x_1}{V_1^\bullet} , \tag{7.73}$$

where ϕ_1 is the osmotic coefficient [see (6.110)], x_1 is the molar fraction of the solvent, and $V_1^\bullet$ is the molar volume of a pure solvent at mean pressure $(p' + p'')/2$.

For very diluted, ideal and incompressible solutions, relation (7.73) simplifies to

$$\pi = \boldsymbol{R} T \sum_{i=2}^{n} c_i , \tag{7.74}$$

where c_i stands for the amount-of-substance concentrations of the particles (molecules or ions) of the dissolved substances. This equation is called the **van't Hoff equation**. According to this equation, osmotic pressure does not depend on the kind of solvent used.

Reverse osmosis allows for obtaining a pure liquid from a solution by way of increasing pressure over the membrane.

Example

Calculate the osmotic pressure over the solution of sucrose in water, separated from pure water by a semipermeable membrane, below which neither dilution nor reverse osmosis occurs at 60 °C. The amount-of-substance concentration of the solution is $0.1923\,\mathrm{mol\,dm^{-3}}$.

Solution

From the specification it follows that $c = 192.3\,\mathrm{mol\,m^{-3}}$. According to (7.74) it applies that

$$\pi = \boldsymbol{R} T c_2 = 8.314 \times 333.15 \times 192.3 = 532.6\,\mathrm{kPa}.$$

Chapter 8

Chemical equilibrium

This chapter deals with systems in which chemical reactions take place. In the course of a chemical reaction, the composition of the reacting system approaches its equilibrium composition. The rate at which this equilibrium can be attained is dealt with by another field of physical chemistry, chemical kinetics [see 9]. Calculations of the equilibrium composition and the effect of temperature, pressure and non-reacting components on the composition of a system in the state of chemical equilibrium are described in this chapter for one reaction. The process of this calculation for more simultaneously proceeding reactions is described at the close of the chapter.

8.1 Basic terms

- **Chemical reaction** is a process [see **1.4.3**] during which new aggregates of atoms are formed in consequence of a collision (radiation,. . .).

Note: In thermodynamics, phase transformations, e.g. C (graphite) = C (diamond), are sometimes ranked among chemical reactions.

- **Chemical equilibrium** is a special case of thermodynamic equilibrium [see **1.4.1** and **1.4.2**].

- **Equilibrium composition** is the composition of a system which is in the state of chemical equilibrium.
- **One mole of reaction.**
  We speak about one mole of reaction when a moles of substance A, b moles of substance B, … react to form s moles of substance S, t moles of substance T,…, according to the record (8.1) of the given reaction.

8.2 Systems with one chemical reaction

8.2.1 General record of a chemical reaction

In chemistry it is usual to record a chemical reaction as follows [see **5.1**]:

$$aA(f) + bB(f) + \ldots = sS(f) + tT(f) + \ldots \tag{8.1}$$

In this record, A, B, ... represent the **initial** chemical individuals or reactants; S, T, ... represent the **products** of a given chemical reaction; $a, b, \ldots$, and $s, t, \ldots$ represent the respective stoichiometric number. By subtracting the left side in equation (8.1) we obtain an alternative record

$$0 = \sum_{i=1}^{k} \nu_i R_i(f)\,. \tag{8.2}$$

S *Symbols:* Here the chemical individuals are denoted $R_1, \ldots, R_n$(in the first case they are denoted A, B, ..., S, T, ...), and the stoichiometric numbers are denoted ν_i where "i" is the ordinal number of the i-th substance (in the first case they are indicated by the symbol of the substance to which they relate). The stoichiometric numbers of the products are positive while those of the reactants are negative.

The physical state (phase) of a given component is denoted (f) . If $(f) = (s)$, the component is solid, if $(f) = (l)$, it is liquid, and if $(f) = (g)$, it is gas.

Example

Record the chemical reaction

$$SO_2\,(g) + \frac{1}{2}O_2\,(g) = SO_3\,(g)$$

in the alternative way and calculate individual stoichiometric numbers.

Solution

Subtracting the left side yields

$$0 = \mathrm{SO_3\,(g)} - \mathrm{SO_2\,(g)} - \frac{1}{2}\mathrm{O_2\,(g)}\,.$$

If we denote sulphur trioxide with the subscript $_1$, sulphur dioxide with the subscript $_2$ and oxygen with the subscript $_3$, then

$$\begin{aligned} \mathrm{R}_1 &= \mathrm{SO_3}\,, & \nu_1 &= +1\,,\\ \mathrm{R}_2 &= \mathrm{SO_2}\,, & \nu_2 &= -1\,,\\ \mathrm{R}_3 &= \mathrm{O_2}\,, & \nu_3 &= -\tfrac{1}{2}\,. \end{aligned}$$

8.2.2 Material balance

The record of a chemical reaction reflects the mass conservation law in a closed system. Material balance allows for the changes in the amount of substance of individual components participating in a given reaction to be expressed using a single variable ξ which is called the **extent of reaction**

$$\xi = \frac{n_i - n_{i,0}}{\nu_i}\,, \tag{8.3}$$

where $n_{i,0}$ denotes the initial amount of the i-th substance and ξ is the extent of reaction.

Note: The extent of reaction is an extensive quantity.

U *Main unit:* mol.

For the amount of the i-th component in any stage of reaction it holds that

$$n_i = n_{i,0} + \nu_i \xi\,. \tag{8.4}$$

Sometimes also the **degree of conversion α**

$$\alpha = \frac{n_{i,0} - n_i}{n_{i,0}} = -\frac{\xi \nu_i}{n_{i,0}} \tag{8.5}$$

is used.

Note: The degree of conversion is an intensive quantity.

U *Main unit:* dimensionless quantity.

Example

The following reaction proceeds in a closed system

$$0 = \mathrm{SO_3\,(g)} - \mathrm{SO_2\,(g)} - \frac{1}{2}\mathrm{O_2\,(g)}\,.$$

What is the extent of reaction of a system at equilibrium if there is initially
a) 1 mol SO_2 and 1 mol O_2,
b) 2 mol SO_2 and 3 mol O_2, 4 mol SO_3 and 20 mol N_2 in the system?

Solution

If we use ξ to denote the extent of reaction and $n_{i,\mathrm{eq}}$ to denote the amount of the i-th component at equilibrium, then

Substance	$n_{i,0}$ a)	$n_{i,\mathrm{eq}}$ a)	$n_{i,0}$ b)	$n_{i,\mathrm{eq}}$ b)
SO_2	1	$1-\xi$	2	$2-\xi$
O_2	1	$1-\frac{1}{2}\xi$	3	$3-\frac{1}{2}\xi$
SO_3	0	ξ	4	$4+\xi$
N_2	0	0	20	20
$\sum_{i=1}^{k} n_i$	2	$2-\frac{1}{2}\xi$	29	$29-\frac{1}{2}\xi$

In the case a) ξ is a number between 0 and 1. In the case b), when the products are also present in the initial mixture, the reaction may also proceed in the opposite direction and $\xi \in (-4, 2)$.

- Material balance at constant volume

When a reaction proceeds in the gas phase in a closed system at constant temperature and volume with a change in the total amount of substance (and thus also pressure), and if ideal behaviour may be assumed, pressure is often balanced instead.

Example

The reaction

$$0 = \mathsf{SO_3}\,(\mathrm{g}) - \mathsf{SO_2}\,(\mathrm{g}) - \frac{1}{2}\mathsf{O_2}\,(\mathrm{g})\,.$$

is again under way in a closed system. What are the partial pressures of the individual components of the system at equilibrium if initially there is only SO_2 and oxygen in the system at constant temperature and volume? The initial partial pressure of SO_2 is $p^\circ_{\mathsf{SO_2}}$, the partial pressure of oxygen is $p^\circ_{\mathsf{O_2}}$.

Solution

Substance	Initial partial pressure $p_{i,0}$	Partial pressure at equilibrium $p_{i,\mathrm{eq}}$
SO_2	$p_{\mathsf{SO_2},0}$	$p_{\mathsf{SO_2},0} - \Delta p$
O_2	$p_{\mathsf{O_2},0}$	$p_{\mathsf{O_2},0} - \frac{1}{2}\Delta p$
SO_3	0	Δp

If the extent of reaction is ξ then

$$\Delta p = \xi\,\frac{\boldsymbol{R}T}{V}\,.$$

The initial pressure is

$$p_0 = p_{\mathsf{SO_2},0} + p_{\mathsf{O_2},0}\,,$$

and the equilibrium pressure is

$$p = p_{\mathsf{SO_2}} + p_{\mathsf{O_2}} + p_{\mathsf{SO_3}} = p_{\mathsf{SO_2},0} + p_{\mathsf{O_2},0} - \frac{1}{2}\Delta p\,.$$

From the preceding two equations we obtain

$$\Delta p = 2(p_0 - p)\,.$$

By way of measuring the total pressure we may calculate the partial pressures of all components of the mixture.

8.2.3 Gibbs energy of a system

The Gibbs energy of a k-component system is given by the relation

$$G = \sum_{i=1}^{k} n_i\,\mu_i\,, \tag{8.6}$$

where μ_i is the chemical potential of the i-th component in the mixture, for which it holds [see **6.4.2**]

$$\mu_i = \overline{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} = \mu_i^{\rm st} + \boldsymbol{R}T\ln a_i. \tag{8.7}$$

S *Symbols:* We use superscript $^{\rm st}$ to denote a quantity in an unspecified standard state. According to the new IUPAC recommendations, symbol $^{\ominus}$ is used instead.

If changes in the amount of substance occur in a closed system due to a chemical reaction, we may substitute (8.4) into (8.6) to obtain

$$G = \sum_{i=1}^{k}(n_{i,0} + \nu_i\xi)\mu_i\,. \tag{8.8}$$

The Gibbs energy of a closed system in which a chemical reaction proceeds thus depends on the extent of reaction, i.e. on the extent of the initial substances (reactants) transformation to the products.

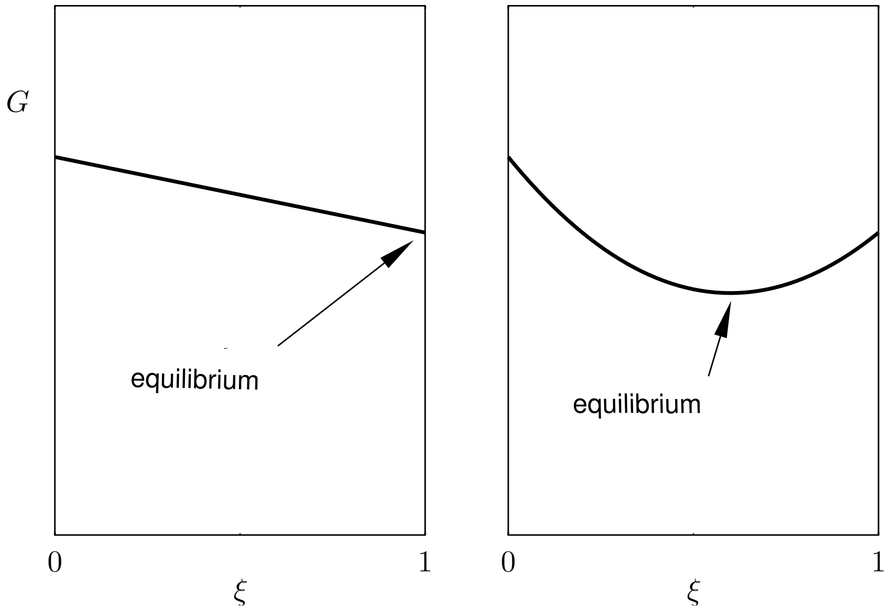
Figure **8.1** shows two possible cases of this dependence at constant temperature and pressure:

a) the Gibbs energy changes linearly with the extent of reaction. This case occurs when all components involved in the reaction are mutually immiscible.

b) the Gibbs energy reaches its minimum in dependence on the extent of reaction. This case always occurs in reactions proceeding in a closed system in a homogeneous mixture.

By differentiating (8.8) with respect to the extent of reaction while taking into account the Gibbs-Duhem equation [see **6.3.2**], we obtain $\Delta_{\rm r}G$, i.e. the **change in Gibbs energy at one mole of reaction** in an infinitely large reactor

$$\Delta_{\rm r}G \equiv \left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \sum_{i=1}^{k}\nu_i\mu_i = \sum_{i=1}^{k}\nu_i(\mu_i^{\rm st} + \boldsymbol{R}T\ln a_i)\,. \tag{8.9}$$



Obr. 8.1: Dependence of the Gibbs energy of a closed system on the extent of reaction.

U *Main unit:* $\mathrm{J\,mol^{-1}}$.

The **Gibbs** or **reaction isotherm** is the relation between the change in the Gibbs energy (at one mole of reaction at constant temperature and pressure) and the activities of the reacting substances (which change in the course of the reaction).

$$\Delta_{\mathrm{r}} G = \Delta_{\mathrm{r}} G^{\mathrm{st}} + \boldsymbol{R} T \ln \prod_{i=1}^{k} a_i^{\nu_i} \,. \tag{8.10}$$

$$\Delta_{\mathrm{r}} G^{\mathrm{st}} = \sum_{i=1}^{k} \nu_i \mu_i^{\mathrm{st}} = \sum_{i=1}^{k} \nu_i G_{\mathrm{m},i}^{\mathrm{st}} \tag{8.11}$$

is the change in the Gibbs energy at one mole of reaction if substances involved in the reaction are in a standard state [see **5.2**].

S *Symbols:* The symbol $\prod_{i=1}^{k} a_i^{\nu_i}$ denotes the product of the activities of substances from 1 to k, raised to the power of their stoichiometric numbers.

Note: For the negative values of $\Delta_{\mathrm{r}}G$, the system composition shifts toward the products, for the positive values it is vice versa, i.e. the amount of products decrease in the reaction mixture. The **affinity** of reaction is sometimes defined using the relation $A = -\Delta_{\mathrm{r}}G$.

Example

Calculate the change in the Gibbs energy of the reaction

$$0 = \mathsf{CO}\,(\mathrm{g}) - \mathsf{C}\,(\mathrm{s}) - \frac{1}{2}\mathsf{O}_2\,(\mathrm{g})$$

at the beginning of the reaction when there is no carbon oxide present in the reacting mixture.

Solution

$$\Delta_{\mathrm{r}}G = \Delta_{\mathrm{r}}G^{\mathrm{st}} + \boldsymbol{R}T\ln\frac{a_{\mathsf{CO}}}{a_{\mathsf{C}}a_{\mathsf{O}_2}^{1/2}}\,,$$

where

$$\Delta_{\mathrm{r}}G^{\mathrm{st}} = G^{\mathrm{st}}_{m,\mathsf{CO}} - \frac{1}{2}G^{\mathrm{st}}_{m,\mathsf{O}_2} - G^{\mathrm{st}}_{m,\mathsf{C}}\,.$$

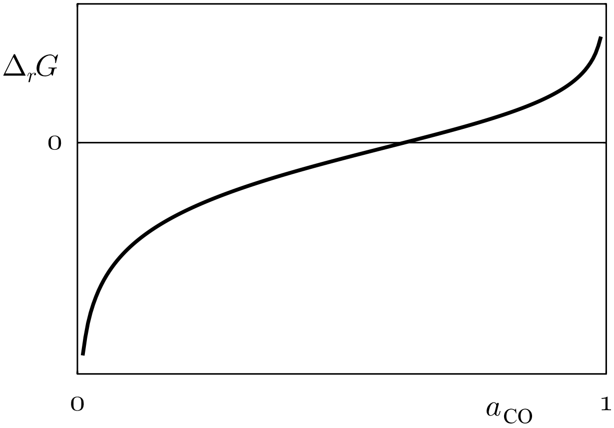
The initial activity of carbon oxide (just like its fugacity, partial pressure and concentration) is zero. Consequently, for any non-zero initial concentrations of the reactants, $\Delta_{\mathrm{r}}G = -\infty$. ($\Delta_{\mathrm{r}}G^{\mathrm{st}}$ always has a finite value).

The dependence of $\Delta_{\mathrm{r}}G$ on the activity of carbon oxide in the reaction mixture is shown in Figure 8.2.3.

8.2.4 Condition of chemical equilibrium

At equilibrium, the Gibbs energy of a closed system reaches its minimum at constant temperature and pressure [see **3.4.6**]. Hence, chemical equilibrium is attained at constant temperature and pressure if

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \Delta_{\mathrm{r}}G = 0 \qquad [\mathrm{eq}] \tag{8.12}$$



Obr. 8.2: Dependence of $\Delta_\mathrm{r} G$ on the activity of carbon oxide

or

$$\sum_{i=1}^{k} \nu_i \mu_i = 0 \qquad [\mathrm{eq}]\,. \tag{8.13}$$

S *Symbols:* [eq] denotes the condition applying at equilibrium.

Example

What relation has to apply at equilibrium between the chemical potentials of substances A and B bound by the reaction

$$0 = \mathsf{B} - 2\,\mathsf{A}.$$

Solution

From (8.13) we obtain

$$\mu_\mathsf{B} = 2\mu_\mathsf{A}.$$

From (8.10) at equilibrium we obtain

$$\Delta_\mathrm{r} G^{\mathrm{st}} = -\boldsymbol{R}T \ln \prod_{i=1}^{k} a_{i,\mathrm{eq}}^{\nu_i}\,, \tag{8.14}$$

where $a_{i,\mathrm{eq}}$ denotes the activities of reacting substances in equilibrium.

Note: If minimum is not reached inside the concentration interval, i.e. if the Gibbs energy of the system monotonously decreases or increases with the extent of reaction , only the products or only the reactants are present in equilibrium [see **8.2.8** and Figure **8.1**].

8.2.5 Overview of standard states

The standard states of individual components may be chosen arbitrarily within certain limits. The first limitation is that the standard temperature is always the temperature of the system. Further on, the standard state of individual components of a system is usually chosen at fixed composition. The standard pressure is either constant, or it changes with the system pressure. Compare with **6.5.3**.

- Standard state: the state of a pure substance in a given state of matter or modification at the temperature of the system and a standard pressure.

S *Symbols:* For this standard state, the superscript $^{\rm st}$ is replaced with the superscript $^\circ$ if $p^{\rm st} =$ 101.325 kPa.

Note: For gases, the superscript $^\circ$ is used to denote the standard state of the gaseous component in the state of an ideal gas at the temperature of the system and a standard pressure ($p^{\rm st} = 101.325$ kPa). The standard fugacity in this case equals the standard pressure [see **3.2.6**].

- Standard state: the state of a pure substance in the same state of matter or modification as in the mixture at the temperature and pressure of the system.

S *Symbols:* For this standard state, the superscript $^{\rm st}$ is replaced with the superscript $^\bullet$.

- Standard state: the state of a hypothetical pure substance at the temperature and pressure of the system obtained by extrapolation from the behaviour of a component in a mixture at infinite dilution.

S *Symbols:* For this standard state, the superscript $^{\rm st}$ is replaced with the superscript $^{[x]}$.

- Standard state: the state a given component would have in a hypothetical ideal mixture whose properties would be extrapolated from infinite dilution at the temperature and pressure of the system to the concentration 1 mol/dm^3; $c^{\rm st}= 1$ mol/dm^3.

S *Symbols:* For this standard state, the superscript $^{\mathrm{st}}$ is replaced with the superscript $^{[c]}$.

- Standard state: the state a given component would have in a hypothetical ideal mixture whose properties would be extrapolated from infinite dilution at the temperature and pressure of the system to the concentration 1 mol/kg of solvent; $\underline{m}^{\mathrm{st}} = 1$ mol/kg of solvent.

S *Symbols:* For this standard state, the superscript $^{\mathrm{st}}$ is replaced with the superscript $^{[m]}$.

Example

What is the activity of nitrogen, whose fugacity at temperature T and pressure 1 MPa is $f_{N_2} =$ 0.505 MPa, if we choose the standard state as follows:

a) nitrogen in the state of an ideal gas at the temperature of the system and the standard pressure 101 kPa,

b) nitrogen in the state of an ideal gas at the temperature and pressure of the system

Solution

a)

$$a_{\mathrm{N_2}} = \frac{f_{\mathrm{N_2}}}{f^{\mathrm{st}}} = \frac{f_{\mathrm{N_2}}}{p^{\mathrm{st}}} = \frac{0.505}{0.101} = 5\,,$$

b)

$$a_{\mathrm{N_2}} = \frac{f_{\mathrm{N_2}}}{f^{\mathrm{st}}} = \frac{f_{\mathrm{N_2}}}{p^{\bullet}} = \frac{0.505}{1} = 0.505\,.$$

Note that the activity of nitrogen changes with the standard state.

8.2.6 Equilibrium constant

The equilibrium constant of reaction (8.2.3) is

$$K \equiv \prod_{i=1}^{k} a_{i,\mathrm{eq}}^{\nu_i}\,. \qquad (8.15)$$

U *Main unit:* dimensionless quantity.

Note: Since further on in this chapter we will deal solely with states at equilibrium, the subscript $_{eq}$ will be omitted.

The relation (8.14) may thus be also written as

$$\Delta_{\mathrm{r}} G^{\mathrm{st}} = -\boldsymbol{R} T \ln K\,. \tag{8.16}$$

The value of the equilibrium constant is determined by:

- the **standard state**
- the **stoichiometric coefficients** in the chemical reaction.

Example

If we multiply a chemical equation by two, we get

$$\Delta_{r,2} G^{\mathrm{st}} = 2\Delta_{r,1} G^{\mathrm{st}}$$

and from this we have for equilibrium constants [compare (8.16)]

$$K_2 = K_1^2\,.$$

8.2.7 Reactions in the gaseous and liquid phases

The exact relations for equilibrium constants, simplified relations for ideal cases, and symbols for individual standard states together with other information are given in tables on pages 241 and 242.

Note: The symbol

$$\Delta\nu = \sum_{i=1}^{k} \nu_i$$

denotes a change in the total amount of substances.

S *Symbols:* For the standard state of a pure component at the temperature and pressure of the system, the superscript $^{\mathrm{st}}$ is replaced with the superscript $^{\bullet}$, the respective γ is without any subscript or superscript.

Note: In an ideal solution, the result for the standard state denoted $^\bullet$ is the same as for that denoted $^{[x]}$.

Example

Write the equilibrium constant of sulphur dioxide oxidation

$$0 = \mathsf{SO_3}\,(\mathrm{g}) - \frac{1}{2}\mathsf{O_2}\,(\mathrm{g}) - \mathsf{SO_2}\,(\mathrm{g})$$

for the standard state of a pure gaseous component in the state of an ideal gas at the temperature of the system and the standard pressure 101.325 kPa if the reaction proceeds at a pressure of 10 kPa.

Solution

$$\begin{aligned} K &= \frac{a_{\mathsf{SO_3}}}{a_{\mathsf{SO_2}}a_{\mathsf{O_2}}^{1/2}} = \frac{\left(\frac{f}{f^{\mathrm{st}}}\right)_{\mathsf{SO_3}}}{\left(\frac{f}{f^{\mathrm{st}}}\right)_{\mathsf{SO_2}}\left(\frac{f}{f^{\mathrm{st}}}\right)_{\mathsf{O_2}}^{1/2}} = \frac{\phi_{\mathsf{SO_3}}}{\phi_{\mathsf{SO_2}}\phi_{\mathsf{O_2}}^{1/2}}\frac{x_{\mathsf{SO_3}}}{x_{\mathsf{SO_2}}x_{\mathsf{O_2}}^{1/2}}\left(\frac{p^{\mathrm{st}}}{p}\right)^{1/2} \\ &= \frac{\phi_{\mathsf{SO_3}}}{\phi_{\mathsf{SO_2}}\phi_{\mathsf{O_2}}^{1/2}}\frac{n_{\mathsf{SO_3}}}{n_{\mathsf{SO_2}}n_{\mathsf{O_2}}^{1/2}}\left(\frac{101.325\sum_{i=1}^{k} n_i}{10}\right)^{1/2}, \end{aligned}$$

where n_i denote the amount of individual components at equilibrium, and ϕ_i their fugacity numbers.

Example

Write the equilibrium constants $K^\bullet$ and $K^{[c]}$ for the reaction of acetic acid with 1-pentene

$$0 = \mathsf{C_7H_{14}O_2}(\mathrm{l}) - \mathsf{C_5H_{10}}(\mathrm{l}) - \mathsf{C_2H_4O_2}(\mathrm{l})\,.$$

Solution

$$K^{\bullet} = \frac{\gamma_{\mathsf{E}}}{\gamma_{\mathsf{P}}\gamma_{\mathsf{A}}}\frac{x_{\mathsf{E}}}{x_{\mathsf{P}}x_{\mathsf{A}}} = \frac{\gamma_{\mathsf{E}}}{\gamma_{\mathsf{P}}\gamma_{\mathsf{A}}}\frac{n_{\mathsf{E}}}{n_{\mathsf{P}}n_{\mathsf{A}}}(n_{\mathsf{E}} + n_{\mathsf{P}} + n_{\mathsf{A}})\,,$$

$$K^{[c]} = \frac{\gamma_{\mathsf{E}}^{[c]}}{\gamma_{\mathsf{P}}^{[c]}\gamma_{\mathsf{A}}^{[c]}}\frac{c_{\mathsf{E}}}{c_{\mathsf{P}}c_{\mathsf{A}}}c_{\mathrm{st}} = \frac{\gamma_{\mathsf{E}}^{[c]}}{\gamma_{\mathsf{P}}^{[c]}\gamma_{\mathsf{A}}^{[c]}}\frac{n_{\mathsf{E}}}{n_{\mathsf{P}}n_{\mathsf{A}}}V c_{\mathrm{st}}\,,$$

where $c_{\mathrm{st}} = 1$ mol/dm^3, and E, A, P as subscripts denote ester, acetic acid and 1-pentene. While the ratio of the amounts of substance at equilibrium is the same in both relations, the ratio of the activity coefficients is different.

Reactions in the

St.state	a_i	K
$\circ$	$\dfrac{\phi_i x_i p}{p^{\mathrm{st}}}$	$\prod_{i=1}^{k} \phi_i^{\nu_i} n_i^{\nu_i} \left(\dfrac{p}{p^{\mathrm{st}} \sum_{i=1}^{k} n_i}\right)^{\Delta\nu} = \prod_{i=1}^{k} \phi_i^{\nu_i} p_i^{\nu_i} \left(\dfrac{1}{p^{\mathrm{st}}}\right)^{\Delta\nu}$
$\bullet$	$\dfrac{\phi_i n_i}{\phi_i^{\bullet} \sum_{i=1}^{k} n_i}$	$\prod_{i=1}^{k} \left(\dfrac{\phi_i n_i}{\phi_i^{\bullet}}\right)^{\nu_i} \left(\dfrac{1}{\sum_{i=1}^{k} n_i}\right)^{\Delta\nu}$
$[c]$	$\dfrac{\phi_i c_i}{c_{\mathrm{st}}}$	$\left(\dfrac{1}{\boldsymbol{R}T c_{\mathrm{st}}}\right)^{\Delta\nu} \prod_{i=1}^{k} f_i^{\nu_i} = \prod_{i=1}^{k} \phi_i^{\nu_i} \left(\dfrac{c_i}{c_{\mathrm{st}}}\right)^{\nu_i}$

Reactions in the

St.state	a_i	K
$\bullet$	$\gamma_i\, x_i$	$\prod_{i=1}^{k} \gamma_i^{\nu_i} n_i^{\nu_i} \left(\dfrac{1}{\sum_{i=1}^{k} n_i}\right)^{\Delta\nu}$
$[x]$	$\gamma_i^{[x]} x_i$	$\prod_{i=1}^{k} \left(\gamma_i^{[x]}\right)^{\nu_i} n_i^{\nu_i} \left(\dfrac{1}{\sum_{i=1}^{k} n_i}\right)^{\Delta\nu}$
$[c]$	$\gamma_i^{[c]} \frac{c_i}{c_{\mathrm{st}}}$	$\prod_{i=1}^{k} \left(\gamma_i^{[c]}\right)^{\nu_i} c_i^{\nu_i} \left(\dfrac{1}{c_{\mathrm{st}}}\right)^{\Delta\nu}$
$[m]$	$\gamma_i^{[m]} \frac{\underline{m}_i}{\underline{m}_{\mathrm{st}}}$	$\prod_{i=1}^{k} \left(\gamma_i^{[m]}\right)^{\nu_i} \underline{m}_i^{\nu_i} \left(\dfrac{1}{\underline{m}_{\mathrm{st}}}\right)^{\Delta\nu}$

see next page →

gaseous phase

K^*	*	Comments
$\prod_{i=1}^{k} n_i^{\nu_i} \left(\frac{p}{p^{\mathrm{st}} \sum_{i=1}^{k} n_i} \right)^{\Delta\nu}$	For a mixture of ideal gases	Used for almost ideal gaseous systems. The equilibrium constant does not depend on pressure, the composition does.
$\prod_{i=1}^{k} x_i^{\nu_i}$	For an ideal mixture of real gases	Both the equilibrium constant and composition are the function of pressure.
$\prod_{i=1}^{k} \left(\frac{c_i}{c_{\mathrm{st}}} \right)^{\nu_i}$	For a mixture of ideal gases	Used particularly in connection with chemical kinetics.

liquid phase

K^*	*	Comments
$\prod_{i=1}^{k} n_i^{\nu_i} \left(\frac{1}{\sum_{i=1}^{k} n_i} \right)^{\Delta\nu}$	For an ideal solution	Used in the thermodynamics of non-electrolytes.
$\prod_{i=1}^{k} n_i^{\nu_i} \left(\frac{1}{\sum_{i=1}^{k} n_i} \right)^{\Delta\nu}$	For an ideal solution	It applies that $\gamma_i = \gamma_i^{\infty} \cdot \gamma_i^{[x]}$, where $\gamma_i^{\infty} = \lim\limits_{x_i \to 0} \gamma_i$.
$\prod_{i=1}^{k} c_i^{\nu_i} \left(\frac{1}{c_{\mathrm{st}}} \right)^{\Delta\nu}$	For an ideal solution	Used in the thermodynamics of solutions of electrolytes (dissociation constants, solubility products).
$\prod_{i=1}^{k} \underline{m}_i^{\nu_i} \left(\frac{1}{\underline{m}_{\mathrm{st}}} \right)^{\Delta\nu}$	For an ideal solution	Used in the thermodynamics of the solutions of electrolytes.

← see previous page

8.2.8 Reactions in the solid phase

- Choosing as the standard state a pure substance at the temperature and pressure of the system, the activity of solids which do not form solid solutions equals 1.

For a reaction between immiscible solids we have

$$\Delta_{\mathrm{r}} G = \Delta_{\mathrm{r}} G^{\bullet} \qquad [T, p] \tag{8.17}$$

and the reaction proceeds in the direction of decrease in the Gibbs energy until at least one of the reacting substances disappears from the mixture. The reactants are in equilibrium with the products only if $\Delta_{\mathrm{r}} G^{\bullet} = 0$.

- **Solid solutions** (e.g. amalgams) are processed in the same way as liquids [see the preceding section].

Example

Say whether red (1) and white (2) phosphor can be in equilibrium at 298 K and 101.325 kPa if you know that under these conditions the molar Gibbs energies of the pure substances are $G^{\bullet}_{m,1} = -6.804\,\mathrm{kJ\ mol^{-1}}$ and $G^{\bullet}_{m,2} = 5.2\,\mathrm{kJ\ mol^{-1}}$.

Solution

For the reaction

$$0 = \mathrm{P}(\mathrm{red}, s) - \mathrm{P}(\mathrm{white}, s)$$

we have $\Delta_{\mathrm{r}} G^{\bullet} = G^{\bullet}_{m,1} - G^{\bullet}_{m,2} = -12.004\,\mathrm{kJ\ mol^{-1}}$. For the sake of the unit activities of both solid substances it follows

$$\Delta_{\mathrm{r}} G = \Delta_{\mathrm{r}} G^{\bullet} < 0$$

and therefore equilibrium cannot be attained, but the reaction proceeds until all white phosphor transforms into red phosphor. In the same way it can be shown that

$$G = (n_1^{\circ} + \xi) G_1^{\bullet} + (n_2^{\circ} - \xi) G_2^{\bullet}$$

will linearly decrease with increasing ξ.

8.2.9 Heterogeneous reactions

In the case of heterogeneous reactions, different standard states are often chosen for individual components of the reacting system. For condensed components, this is most often the standard state of a pure component at the temperature and pressure of the system, for gaseous components it is the standard state of a pure gaseous component in the state of an ideal gas at the temperature of the system and a pressure of 101.325 kPa.

Example

Write the equilibrium constant for the reaction

$$0 = \mathsf{Si}(\mathrm{s}) + 2\,\mathsf{H_2O}(\mathrm{l}) - \mathsf{SiO_2}(\mathrm{s}) - 2\,\mathsf{H_2}(\mathrm{g}).$$

Solution

It holds that

$$K = \frac{a^2_{\mathsf{H_2O}}\, a_{\mathsf{Si}}}{a_{\mathsf{SiO_2}}\, a^2_{\mathsf{H_2}}}\,.$$

If we choose the standard state of a pure substance at the temperature and pressure of the system for condensed components, their activities equal 1 because neither Si nor SiO_2 is soluble in water. For hydrogen, we choose the standard state of a pure substance in the state of an ideal gas at a standard pressure. Then

$$K = \frac{1}{a^2_{\mathsf{H_2}}} = \left(\frac{p^{\mathrm{st}}}{\phi_{\mathsf{H_2}}\, p_{\mathsf{H_2}}}\right)^2 .$$

Decomposition temperature is the temperature at which the sum of the partial pressures of gaseous components originating by the decomposition of a solid reaches the value of the ambient pressure. It is the lowest temperature at which a reaction can be performed at a sufficient rate because below this temperature the rate of reaction is determined by the rate of diffusion of gaseous products toward the surface (an analogy to boiling).

Example

The equilibrium constant of the reaction

$$0 = \mathsf{FeO}(\mathrm{s}) + \mathsf{CO}_2(\mathrm{g}) - \mathsf{FeCO}_3(\mathrm{s})$$

at a temperature of 25°C is $K = 0.000216$ (the chosen standard state: pure component at the temperature and pressure of the system for the solids, and an ideal gas at the temperature of the system and standard pressure $p^{\mathrm{st}} = 101.325$ kPa for carbon dioxide). At what pressure would this temperature be the decomposition temperature?

Solution

$$K = \frac{a_{\mathsf{CO}_2} a_{\mathsf{FeO}}}{a_{\mathsf{FeCO}_3}} = \frac{\phi_{\mathsf{CO}_2} p_{\mathsf{CO}_2}}{p^{\mathrm{st}}}\,.$$

Assuming ideal behaviour of the gas phase, then

$$p_{\mathsf{CO}_2} = K \cdot p^{\mathrm{st}} = 21.89\,\mathsf{Pa}.$$

The temperature 25°C would be the decomposition temperature of iron (II) carbonate at an ambient pressure of 21.89 Pa.

8.3 Dependence of the equilibrium constant on state variables

8.3.1 Dependence on temperature

It holds that

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta_\mathrm{r} H^\circ}{\boldsymbol{R} T^2}\,, \tag{8.18}$$

where $\Delta_\mathrm{r} H^\circ$ is a change in the standard enthalpy of a given reaction at one mole of reaction. Equation (8.18) is called the **van't Hoff isobar**.

> *Note:* Note that in exothermic reactions ($\Delta_\mathrm{r} H^\circ < 0$) the equilibrium constant decreases with increasing temperature while in endothermic reactions it increases.

8.3.1.1 Integrated form

$$\ln K(T_2) = \ln K(T_1) + \int_{T_1}^{T_2} \frac{\Delta_\mathrm{r} H^\circ}{\boldsymbol{R} T^2} dT\,. \tag{8.19}$$

To calculate the integral on the right side of equation (8.19) it is necessary to know the temperature dependence of $\Delta_\mathrm{r} H^\circ$ [see **5.3**].

- For the simplest case when $\Delta_\mathrm{r} H^\circ$ can be assumed to be independent of temperature, we have

$$\ln K(T_2) = \ln K(T_1) - \frac{\Delta_\mathrm{r} H^\circ}{\boldsymbol{R}} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\,, \tag{8.20}$$

- In general we write (5.16)

$$\Delta_\mathrm{r} H^\circ(T) = \Delta_\mathrm{r} H^\circ(T_o) + \int_{T_o}^{T} \Delta C_p^\circ dT\,.$$

If the temperature dependence of the isobaric molar heat capacities of individual components are expressed in the form

$$C_{pm,i}^\circ = a_i + b_i T + c_i T^2 + d_i T^{-2}\,,$$

we obtain

$$\begin{aligned}\ln K(T_2) &= \ln K(T_1) - \frac{1}{\boldsymbol{R}}\left[A\left(\frac{1}{T_2}-\frac{1}{T_1}\right) - \Delta a \,\ln\frac{T_2}{T_1}\right.\\ &- \left.\frac{\Delta b}{2}\left(T_2-T_1\right) - \frac{\Delta c}{6}\left(T_2^2-T_1^2\right) - \frac{\Delta d}{2}\left(\frac{1}{T_2^2}-\frac{1}{T_1^2}\right)\right], \qquad (8.21)\end{aligned}$$

where T_1 denotes the temperature at which we know the value of the equilibrium constant,

$$A = \Delta_{\rm r}H^\circ(T_o) - \Delta a T_o - \frac{\Delta b}{2}T_o^2 - \frac{\Delta c}{3}T_o^3 + \frac{\Delta d}{T_o}\,,$$

$\Delta_{\rm r}H^\circ(T_o)$ is the value of the standard reaction enthalpy at temperature T_o a $\Delta a = \sum_{i=1}^{k}\nu_i a_i$, $\Delta b = \sum_{i=1}^{k}\nu_i b_i$, $\Delta c = \sum_{i=1}^{k}\nu_i c_i$, $\Delta d = \sum_{i=1}^{k}\nu_i d_i$.

Example

Calculate the equilibrium constant of butane(1) isomerization to 2-methylpropane(2) at 500 K if the equilibrium constant for this reaction at 300 K is 4.5 (standard state: ideal gas at the temperature of the system and a pressure of 101.325 kPa).

Input data: $\Delta_{\rm r}H^\circ = -8.368$ kJ mol^{-1}at $T = 298$ K, $C^\circ_{pm,1} = 123.1$ J mol^{-1} K^{-1}and $C^\circ_{pm,2} = 123.37$ J mol^{-1} K^{-1}.

Solution

$\Delta C_p = 0.27$ J mol^{-1} K^{-1},

$\Delta_{\rm r}H^\circ(\mathrm{T}) = \Delta_{\rm r}H^\circ(298) + \Delta C_p(\mathrm{T} - 298) = -8448.46 + 0.27\,T$. Substitution to (8.19) and integration yields

$$\begin{aligned}\ln K(500) &= \ln K(300) + \frac{8448.46}{\boldsymbol{R}}\left(\frac{1}{500}-\frac{1}{300}\right) + \frac{0.27}{\boldsymbol{R}}\ln\frac{500}{300}\\ &= 1.504 + 1016.2\left(\frac{1}{500}-\frac{1}{300}\right) + 0.0325\ln\frac{500}{300}\,.\end{aligned}$$

From this we obtain $K(500) = 1.180$.

8.3.2 Dependence on pressure

- The equilibrium constants of reactions in which the standard state at the temperature of the system and an arbitrary **standard pressure** is chosen for all substances are **independent** of pressure. In general, however, the extent of reaction changes with pressure [see **8.5.2**].
- If we choose the standard state at the temperature and pressure of the system, then

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta_r V^\bullet}{\boldsymbol{R}T}\,, \tag{8.22}$$

where

$$\Delta_r V^\bullet = \sum_{i=1}^{k} \nu_i V^\bullet_{\mathrm{m},i}$$

and $V^\bullet_{\mathrm{m},i}$ s the molar volume of the i^{th} component at the temperature and pressure of the system.

Note: If different standard states are chosen for different components of a system, the summation is only performed over those system components for which the standard state at the temperature and pressure of the system has been chosen.

8.3.2.1 Integrated form

$$\ln K(p_2) = \ln K(p_1) - \int_{p_1}^{p_2} \frac{\Delta_r V^\bullet}{\boldsymbol{R}T}\mathrm{d}p\,. \tag{8.23}$$

In condensed systems, $\Delta_r V^\bullet$ can be mostly assumed to be independent of pressure. Then

$$\ln K(p_2) = \ln K(p_1) - \frac{\Delta_r V^\bullet}{\boldsymbol{R}T}(p_2 - p_1)\,, \tag{8.24}$$

Note: The pressure dependence of the equilibrium constant in condensed systems is usually very small.

8.4 Calculation of the equilibrium constant

8.4.1 Calculation from the equilibrium composition

If we know the system composition at equilibrium at a given temperature and pressure, we can also calculate its equilibrium constant.

> *Note:* In order to accurately determine the equilibrium constant of liquid or solid solutions we need to know the activity coefficients, in addition to the equilibrium composition. For gaseous mixtures we need to know the fugacity coefficients.

8.4.2 Calculation from tabulated data

Pressure and absolute temperature have natural zero. The entropy of a pure substance in its most stable crystalline modification is also zero at absolute zero, and hence it may be calculated absolutely [see **3.5.5**]. The energy functions U, H, G and F do not have natural zero. In tables, the **enthalpy of elements in a stable modification at a pressure of 101.325 kPa and a reference temperature** of either **0 K** or **298.15 K** is chosen as a reference state. It is the same as if the enthalpy of elements in stable modifications under reference conditions **equalled zero**.

At a temperature other than the reference temperature, the enthalpy of elements can be calculated provided that we know their C_p and the standard enthalpy of their modification transformations [see **3.5.3**]. At the reference temperature, the enthalpy of a compound equals its enthalpy of formation. Other energy functions are calculated from the defining relations.

In order to calculate the equilibrium constant we need to know $\Delta_\mathrm{r} G^\mathrm{st}$ because

$$K = \exp\left(-\frac{\Delta_r G^\mathrm{st}}{\boldsymbol{R}T}\right) . \tag{8.25}$$

However, in tables we can find only the quantities from which $\Delta_\mathrm{r} G^\circ$ can be calculated. This must be then converted to other standard states.

- Calculation from $H^\circ_{\mathrm{m},i}$ and $S^\circ_{\mathrm{m},i}$

From the given data we may calculate $G^\circ_{\mathrm{m},i}$ of every component

$$G^\circ_{\mathrm{m},i} = H^\circ_{\mathrm{m},i} - T S^\circ_{\mathrm{m},i} \tag{8.26}$$

and

$$\Delta_\mathrm{r} G^\circ = \sum_{i=1}^{k} \nu_i G^\circ_{\mathrm{m},i} \,, \tag{8.27}$$

where the summation is performed over all substances involved in the reaction.

- Calculation from $\Delta_f H_i^\circ$ and $S^\circ_{\mathrm{m},i}$

Using this data we may calculate $\Delta_\mathrm{r} H^\circ$ and $\Delta_r S^\circ$ for a given temperature [see **5.1**]. Hence

$$\Delta_\mathrm{r} G^\circ = \Delta_\mathrm{r} H^\circ - T \Delta_r S^\circ \tag{8.28}$$

Note: The same procedure could be also applied in the preceding case.

Note: At the standard temperature, $\Delta_f H_i^\circ$ equals $H^\circ_{\mathrm{m},i}$ for the most stable modification. $\Delta_f H_i^\circ$ of elements are zero at all temperatures.

- Calculation from $\Delta_f G_i^\circ$ or $G^\circ_{\mathrm{m},i}$

We again calculate $\Delta_\mathrm{r} G^\circ$ from relation (8.27) or, alternatively

$$\Delta_\mathrm{r} G^\circ = \sum_{i=1}^{k} \nu_i \Delta_f G_i^\circ \tag{8.29}$$

and the equilibrium constant from relation (8.25).

Note: $\Delta_f G_i$ of elements in their most stable modification equals zero, $G^\circ_{\mathrm{m},i}$ of elements is not zero, not even at the standard temperature (if this is not zero absolute temperature) due to the non-zero entropy.

- Calculation from the **logarithms of the equilibrium constants of formation**

$$K_{f,i} = \exp\left(-\frac{\Delta_f G_i^\circ}{\boldsymbol{R}T}\right) . \tag{8.30}$$

For the equilibrium constant of the given reaction it holds

$$\ln K = \sum_{i=1}^{k} \nu_i \ln K_{f,i} \,. \tag{8.31}$$

- Calculation from the Giauque **G-functions**, which are usually tabulated for individual chemical substances either as
$$\left(-\frac{G^\circ_{\mathrm{m},i}(T)-H^\circ_{\mathrm{m},i}(298)}{T}\right) \quad \text{or} \quad \left(-\frac{G^\circ_{\mathrm{m},i}(T)-H^\circ_{\mathrm{m},i}(0)}{T}\right) ,$$

where
$$\left(-\frac{G^\circ_{\mathrm{m},i}(T)-H^\circ_{\mathrm{m},i}(298)}{T}\right) = S^\circ_{\mathrm{m},i}(T) - \frac{H^\circ_{\mathrm{m},i}(T)-H^\circ_{\mathrm{m},i}(298)}{T} \tag{8.32}$$

or
$$\left(-\frac{G^\circ_{\mathrm{m},i}(T)-H^\circ_{\mathrm{m},i}(0)}{T}\right) = S^\circ_{\mathrm{m},i}(T) - \frac{H^\circ_{\mathrm{m},i}(T)-H^\circ_{\mathrm{m},i}(0)}{T} . \tag{8.33}$$

For the calculation of $\Delta_{\mathrm{r}}G^\circ$ or the equilibrium constants we need to know $\Delta_{\mathrm{r}}H^\circ(298)$ in the first case, or $\Delta_{\mathrm{r}}H^\circ(0)$ in the second case.

$$\ln K = \frac{1}{\boldsymbol{R}}\left[\sum_{i=1}^{k}\nu_i\left(-\frac{G^\circ_{\mathrm{m},i}(T)-H^\circ_{\mathrm{m},i}(298)}{T}\right) - \sum_{i=1}^{k}\nu_i\frac{\Delta_f H^\circ_i(298)}{T}\right] \tag{8.34}$$

or
$$\ln K = \frac{1}{\boldsymbol{R}}\left[\sum_{i=1}^{k}\nu_i\left(-\frac{G^\circ_{\mathrm{m},i}(T)-H^\circ_{\mathrm{m},i}(0)}{T}\right) - \sum_{i=1}^{k}\nu_i\frac{\Delta_f H^\circ_i(0)}{T}\right] . \tag{8.35}$$

Example

Calculate the equilibrium constant of water vapour formation

$$0 = \mathrm{H_2O}\,(\mathrm{g}) - \mathrm{H_2}\,(\mathrm{g}) - \frac{1}{2}\mathrm{O_2}\,(\mathrm{g})$$

at 400 K if:

substance	$-\left(\frac{G^\circ(400)-H^\circ(298)}{400}\right)$ /J mol^{-1} K^{-1}
H_2	131.721
O_2	205.029
H_2O	190.079

and $\Delta_f H^\circ(298)$ for water vapour is $-241.827\,\mathrm{kJ\ mol^{-1}}$.

Solution

$$-\Delta_\mathrm{r} G^\circ = 400\,(190.079 - \frac{1}{2}205.029 - 131.721) + 241827 = 224164.2\ \mathsf{J\ mol^{-1}}\,,$$

$$K = \exp(-\frac{\Delta_\mathrm{r} G^\circ}{\boldsymbol{RT}}) = 1.9 \times 10^{29}\,.$$

- Calculation from the **standard electrode potential** of galvanic cells

If a given reaction can be carried out using a reversible electrochemical cell, then it is also possible to calculate $\Delta_\mathrm{r} G^\circ$ from the standard electrode potential of the cell E° because we have

$$\Delta_\mathrm{r} G^\circ = -zFE^\circ\,, \tag{8.36}$$

where F is the Faraday constant and z is the number of electrons exchanged during one mole of reaction [see **11.2.2**].

8.4.3 Calculation from the equilibrium constants of other reactions

For the calculation of $\Delta_\mathrm{r} G^\mathrm{st}$ just like $\Delta_\mathrm{r} H^\circ$, reactions may be combined [see Hess's law, **5.1.2**]

Example

Calculate the equilibrium constant of the reaction

$$0 = \mathsf{CO_2}(\mathrm{g}) + 2\mathsf{H_2}(\mathrm{g}) - \mathsf{C}(\mathrm{s}) - 2\mathsf{H_2O}(\mathrm{g})\,,$$

if K_1 is the equilibrium constant of the reaction

$$0 = \mathsf{CO_2}\,(\mathrm{g}) - \mathsf{C}\,(\mathrm{s}) - \mathsf{O_2}\,(\mathrm{g})$$

and K_2 is the equilibrium constant of the reaction

$$0 = \mathsf{H_2O}\,(\mathrm{g}) - \mathsf{H_2}\,(\mathrm{g}) - \frac{1}{2}\mathsf{O_2}\,(\mathrm{g})\,.$$

Solution

If we use the subscript $_3$ to denote $\Delta_{\mathrm{r}} G^{\mathrm{st}}$ of the reaction whose equilibrium constant we want to calculate, we can write

$$\Delta_r G_3^{\mathrm{st}} = \Delta_r G_1^{\mathrm{st}} - 2\Delta_r G_2^{\mathrm{st}}$$

and by substituting from (8.16) we obtain

$$\ln K_3 = \ln K_1 - 2\ln K_2$$

and thus

$$K_3 = \frac{K_1}{K_2^2}\,.$$

8.4.4 Conversions

- Conversion to another temperature

The dependence of enthalpy, entropy and the Gibbs energy on temperature is given in [**3.5.3** through **3.5.7**]. The temperature dependence of the equilibrium constant is given in [**8.2.1**].

- Conversion to another pressure

The dependence of enthalpy, entropy and the Gibbs energy on pressure is given in [**3.5.3** through **3.5.7**]. The pressure dependence of the equilibrium constant is given in [**8.3.2**].

Example

Oxidation of sulphur dioxide

$$0 = \mathrm{SO_3}\,(\mathrm{g}) - \mathrm{SO_2}\,(\mathrm{g}) - \frac{1}{2}\mathrm{O_2}\,(\mathrm{g})\,,$$

has the equilibrium constant $K = 1.794$ (standard state of the gaseous component in the state of an ideal gas at temperature 1000 K and standard pressure 101.325 kPa). Calculate the equilibrium constant of the same reaction for the standard state of a pure gaseous component at the temperature and pressure of the system if the system pressure is 1 kPa. Assume ideal behaviour.

Solution

$$K^\bullet = K^\circ \left(\frac{p^{\text{st}}}{p}\right)^{\Delta\nu} = 1.794\frac{1}{\sqrt{101.3}} = 0.178\,.$$

If we choose the standard state of a pure component at the temperature and pressure of the system, even if under the given conditions the pure substances would be in another state of matter or structural modification than in a mixture, the following conversions are necessary:

- Conversion of $G^\circ_{\mathrm{m},i}(\mathrm{g})$ to $G^\bullet_{\mathrm{m},i}(\mathrm{l})$

$$G^\bullet_{\mathrm{m},i}(l) = G^\circ_{\mathrm{m},i}(\mathrm{g}) + \boldsymbol{R}T\ln\frac{f^s_i}{f^\circ} + \int_{p^s_i}^{p} V_{\mathrm{m},i}(l)dp\,, \tag{8.37}$$

where p^s_i denotes the saturated vapour pressure of substance i at a standard temperature, f^s_i denotes the fugacity of the same substance at a standard temperature and a pressure equal to the saturated vapour pressure, and $f^\circ = 101.325$ kPa.

Example
Calculate $\Delta_f G^\bullet_{\mathsf{H_2O}}(\mathrm{l})$ at 25°C and pressure 0.3 MPa. The value $\Delta_f G^\circ_{\mathsf{H_2O}}(\mathrm{g}) = -228.590$ $\mathrm{k\,J\,mol^{-1}}$for this temperature, and the saturated vapour pressure of water at 25°C is $p^s = 3.168$ kPa.

Solution
Substituting in the above relation while assuming ideal behaviour of water vapour yields

$$\begin{aligned}\Delta_f G^\bullet_{\mathsf{H_2O}}(\mathrm{l}) &= -228590 + \boldsymbol{R}\cdot 298.15\ln\frac{3.168}{101.25} + 18\cdot 10^{-3}(300-3.168)\\ &= -237174\ \mathrm{J\,mol^{-1}}\,.\end{aligned}$$

We assumed that the density of liquid water (1 g $\mathrm{cm^{-3}}$) did not depend on pressure.

- Conversion of $G^\bullet_{\mathrm{m},i}$ to $G^{[c]}_{\mathrm{m},i}$

$$G^{[c]}_{\mathrm{m},i} = G^\bullet_{\mathrm{m},i} - \boldsymbol{R}T\ln\frac{\gamma^{[c]}_i c_i}{c^s{}_{\text{st}}}\,. \tag{8.38}$$

8.5 Le Chatelier's principle

Chemists are usually interested in what effect a change of temperature, pressure or the initial composition of a mixture would have on its equilibrium composition. For the study of these changes we use Le Chatelier's principle which may be formulated as follows:

When a system in the state of equilibrium is subjected to a change, it strives to minimize the effect of this change.

8.5.1 Effect of initial composition on the equilibrium extent of reaction

At a given temperature and pressure and at a constant amount of substance entering the reaction, the equilibrium extent of reaction depends on the initial composition.

- The maximum extent of reaction at a given temperature and pressure and for a constant total amount of initial substances can be attained when initial substances enter the reaction in a stoichiometric ratio.
- When one reactant is rarer (more expensive), its higher conversion is attained by adding other reactants in excess.

Note: At a considerable dilution in reactions with $\Delta\nu < 0$, however, the initial increase in the equilibrium extent of reaction is followed by its decline. This is so because the excess second component starts to act as an inert [see **8.5.4**].

- Addition of any product to the initial mixture suppresses the reaction.

8.5.2 Effect of pressure

Reactions with ideal gaseous components

- If the reaction proceeds without any change in the total amount of substances ($\Delta\nu^{(\mathrm{g})} = 0$), **pressure has no effect** on the equilibrium composition of the mixture.
- If the reaction proceeds with an increasing total amount of substances ($\Delta\nu^{(\mathrm{g})} > 0$), the equilibrium extent of the reaction **decreases** with increasing pressure.
- If the reaction proceeds with a decreasing total amount of substances ($\Delta\nu^{(\mathrm{g})} < 0$), the equilibrium extent of the reaction **increases** with increasing pressure.

Example

Assess the change in the extent of the reaction

$$0 = \mathsf{N_2O_4}\,(\mathrm{g}) - 2\,\mathsf{NO_2}\,(\mathrm{g})$$

at temperature 298 K if pressure changes from $p_1 = 101$ kPa to $p_2 = 600$ kPa. Assume ideal behaviour of both gases.

substance	$G^\circ_m(298)\,/\mathrm{kJmol}^{-1}$
NO_2	-38.4
N_2O_4	-81.6

Solution

The total Gibbs energy equals

$$G = \xi \left(G^\circ_{\mathsf{N_2O_4}} + \boldsymbol{R}T \ln \frac{p\xi}{p^{\mathrm{st}}(2-\xi)} \right) + 2(1-\xi) \left(G^\circ_{\mathsf{NO_2}} + \boldsymbol{R}T \ln \frac{2p(1-\xi)}{p^{\mathrm{st}}(2-\xi)} \right) .$$

The course of the dependence $G = G(\xi)$ for both pressures is shown in Figure **8.3**. Due to stoichiometry, the equilibrium extent of the reaction increases from about 0.92 at 101 kPa to 0.95 at 600 kPa in this case.

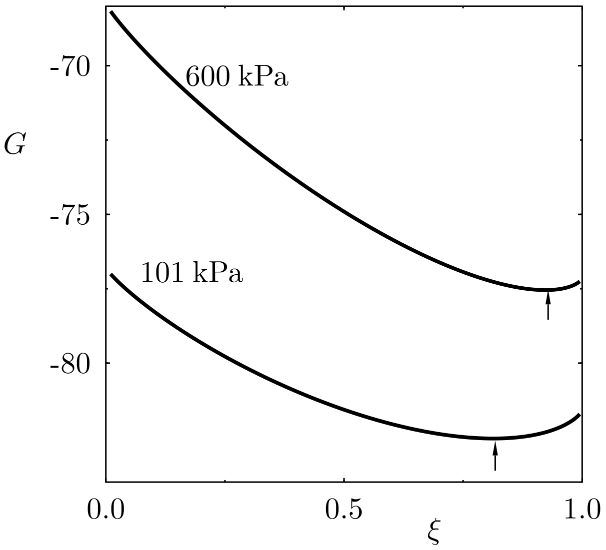
8.5.2.1 Reactions in condensed systems

are not very susceptible to a change of pressure because the effect of pressure on the equilibrium constant [see **8.3.2**] and the activity coefficients [see **6.5.5**] is rather small.

8.5.3 Effect of temperature

The change of temperature affects the value of the equilibrium constant [see **8.2.1**].

- If the reaction is **exothermic**, both the equilibrium constant and the equilibrium extent of the reaction **decrease** with increasing temperature.



Obr. 8.3: Change in the extent of reaction with pressure for the formation of dinitrogen tetraoxide.

- If the reaction is **endothermic**, both the equilibrium constant and the equilibrium extent of the reaction **increase** with increasing temperature.

8.5.4 Effect of inert component

The word **inert** is used for all components in a mixture which do not participate in a given reaction. These components dilute the reaction mixture. Let us consider only homogeneous system in this subsection.

- If the reaction proceeds without any change in the total amount of substances ($\Delta\nu = 0$), the inert **has no effect** on the equilibrium extent of the reaction.
- If the reaction proceeds with an increasing total amount of substances ($\Delta\nu^{(g)} > 0$), the equilibrium extent of the reaction **increases** with increasing concentration of the inert.
- If the reaction proceeds with an deceasing total amount of substances ($\Delta\nu^{(g)} < 0$), the, the equilibrium extent of the reaction **decreases** with increasing concentration of the inert.

Note: These conclusions apply for the extent of reaction only in the case of an ideal mixture. This is so because in systems with real behaviour, a change of the equilibrium extent of reaction may be also affected by changes in the ratio of the activity or fugacity coefficients, which are the functions of temperature, pressure and composition.

8.6 Simultaneous reactions

If several chemical reactions proceed simultaneously in the initial mixture, we speak about **simultaneous reactions**.

8.6.1 Material balance

For simultaneous reactions we may expand the procedure described for a single reaction [see **8.2.2**] by introducing as many extents of reaction as is the number of independent reactions proceeding in the system. An **independent reaction** is a reaction that cannot be obtained by a linear combination [see **5.1.1**] of other reactions.

Example
Derive expressions for the equilibrium constants of two isomerization reactions proceeding in an ideal gas phase. Proceed from 1 mole of a pure substance A_1.

Solution

Let us use ξ_1 to denote the equilibrium extent of the first isomerization reaction, which can be recorded as

$$0 = \mathsf{A}_2 - \mathsf{A}_1$$

and K_1 to denote its equilibrium constant.
Similarly for the second reaction

$$0 = \mathsf{A}_3 - \mathsf{A}_1$$

we use ξ_2 to denote the equilibrium extent of reaction and K_2 to denote the equilibrium constant. The material balance can be carried out in two steps: at first the first reaction proceeds until equilibrium, and only then the second reaction starts.

Substance	$n_{i,0}$	amount of substances after 1st reaction	amount of substances at equilibrium
A_1	1	$1-\xi_1$	$1-\xi_1-\xi_2$
A_2	0	ξ_1	ξ_1
A_3	0	0	ξ_2

For the equilibrium constants we write [see (8.15)]

$$K_1 = \frac{\xi_1}{1-\xi_1-\xi_2}\left(\frac{p}{p^{\mathrm{st}}\sum_{i=1}^{k} n_i}\right)^0 = \frac{\xi_1}{1-\xi_1-\xi_2}$$

and

$$K_2 = \frac{\xi_2}{1-\xi_1-\xi_2}\left(\frac{p}{p^{\mathrm{st}}\sum_{i=1}^{k} n_i}\right)^0 = \frac{\xi_2}{1-\xi_1-\xi_2}$$

8.6.2 Chemical equilibrium of a complex system

When solving the task of finding the equilibrium composition in a system in which m chemical reactions may proceed with k chemical substances involved, we search for the minimum Gibbs energy of the system

$$G = \sum_{j=1}^{m} \sum_{i=1}^{k} (n_{i,0} + \nu_{j,i}\xi_j)\, G_{\mathrm{m},i} \tag{8.39}$$

while obeying the material balance equations. In relation (8.39), ξ_j is the extent of the j^{th} reaction.

The ways of solving chemical equilibrium of a complex system are studied within the physical chemistry specialization at the Institute of Chemical Technology, Prague.

Chapter 9

Chemical kinetics

9.1 Basic terms and relations

Chemical kinetics is focused on the study of chemical reactions prior to the attainment of a chemical equilibrium. Kinetics studies in particular the rate of reactions, changes in the reactants concentrations with time, and the mechanisms of reactions, i.e. their real course at the molecular level. The field of chemical kinetics also embraces catalysis.

9.1.1 Rate of chemical reaction

Let us consider the general one-way chemical reaction

$$a\mathrm{A} + b\mathrm{B} + \cdots \;\rightarrow\; s\mathrm{S} + t\mathrm{T} + \cdots\,. \tag{9.1}$$

The **rate of consumption** of a reactant A is defined by the relation

$$r_\mathrm{A} = -\frac{\mathrm{d}\, c_\mathrm{A}}{\mathrm{d}\,\tau}\,, \quad [V, T]\,. \tag{9.2}$$

The **rate of formation** of a product S is

$$r_\mathrm{S} = \frac{\mathrm{d}\, c_\mathrm{S}}{\mathrm{d}\,\tau}\,, \quad [V, T]\,. \tag{9.3}$$

The **rate of reaction** (9.1) is

$$r = -\frac{1}{a}\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = -\frac{1}{b}\frac{\mathrm{d}\,c_{\mathrm{B}}}{\mathrm{d}\,\tau} = \cdots \frac{1}{s}\frac{\mathrm{d}\,c_{\mathrm{S}}}{\mathrm{d}\,\tau} = \frac{1}{t}\frac{\mathrm{d}\,c_{\mathrm{T}}}{\mathrm{d}\,\tau} = \cdots\,, \quad [V,\,T]\,, \tag{9.4}$$

where c_i stands for the reactants concentrations and τ for time. If we re-write the general chemical reaction (9.1) to the form

$$0 = \sum_{i=1}^{n} \nu_i \mathrm{R}_i\,,$$

we may write equations (9.4) in the form:

$$r = \frac{1}{\nu_i}\frac{\mathrm{d}\,c_{\mathrm{R_i}}}{\mathrm{d}\,\tau}\,, \quad [V,\,T]\,. \tag{9.5}$$

The rate of reaction does not depend on the choice of substance, but it does depend on the way in which the chemical reaction (9.1) is written. The rates of consumption and formation are different for individual substances; they do not, however, depend on the form of reaction record. Since the rates are easy to convert to one another, it is not so important which one we use.

The following relations apply between the rate of reaction and the rates of consumption and formation of the components:

$$r_{\mathrm{A}} = a\,r\,, \quad r_{\mathrm{B}} = b\,r\,, \quad r_{\mathrm{S}} = s\,r\,, \quad r_{\mathrm{T}} = t\,r\,. \tag{9.6}$$

The rate of consumption of substance A is determined experimentally by approximating the derivative in relation (9.2) by the ratio of (sufficiently small) differences

$$\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} \approx \frac{\Delta c_{\mathrm{A}}}{\Delta \tau}\,. \tag{9.7}$$

The rates of formation of products are determined in a similar way.

Example

The reaction

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

proceeded in a closed autoclave of the volume $V = 5\,\mathrm{dm}^3$. In the course of $1\,\mathrm{s}$, 0.01 moles of nitrogen reacted.

a) Estimate the rates of consumption of nitrogen and hydrogen, the rate of formation of ammonia, and the rate of the reaction.

b) Find out how these rates will change if we write the reaction in the form

$$\frac{1}{2}\,\mathsf{N_2} + \frac{3}{2}\,\mathsf{H_2} \;\rightarrow\; \mathsf{NH_3}\,.$$

Solution

a) The change in the concentration of nitrogen is
$\Delta c_{\mathsf{N_2}} = \Delta n_{\mathsf{N_2}}/V = -0.01/5 = -0.002\ \mathrm{mol\,dm^{-3}}$.
The rate of consumption of nitrogen is

$$r_{\mathsf{N_2}} = -\frac{\mathrm{d}\,c_{\mathsf{N_2}}}{\mathrm{d}\,\tau} \doteq -\frac{\Delta c_{\mathsf{N_2}}}{\Delta \tau} = -\frac{-0.002}{1} = 0.002\ \mathrm{mol\,dm^{-3}\,s^{-1}}\,.$$

According to (9.4) and (9.5) we have
$r_{\mathsf{N_2}} = r = 0.002\,\mathrm{mol\,dm^{-3}\,s^{-1}}$
$r_{\mathsf{H_2}} = 3\,r = 0.006\,\mathrm{mol\,dm^{-3}\,s^{-1}}$
$r_{\mathsf{NH_3}} = 2\,r = 0.004\,\mathrm{mol\,dm^{-3}\,s^{-1}}$
b) For the same reaction written in the form

$$\frac{1}{2}\,\mathsf{N_2} + \frac{3}{2}\,\mathsf{H_2} \;\rightarrow\; \mathsf{NH_3}$$

the rate of reaction will be double, the rates $r_{\mathsf{N_2}}$, $r_{\mathsf{H_2}}$, $r_{\mathsf{NH_3}}$ will not change.

Note: Note that the rates in equations (9.2) through (9.5) are defined at constant volume. The concentration of component i, $c_i = n_i/V$, can change in consequence of a change in the amount of substance or in the volume. Here, however, we are interested in changes concerning the amount of substance. We will assume again constant volume and point out only those cases in which it changes. The rate of reaction also depends on temperature. If not otherwise stated, we will assume that the reaction proceeds at constant temperature.

9.1.2 Kinetic equation

The kinetic equation is a differential equation representing the relation between the concentrations of substances and time. For the reaction (9.1) it may be written in the form

$$r_{\mathrm{A}} = -\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = f(c_{\mathrm{A}},\, c_{\mathrm{B}},\, \ldots,\, c_{\mathrm{S}},\, c_{\mathrm{T}},\, \ldots) \tag{9.8}$$

or in similar forms, with the rate of formation of the product or the rate of reaction appearing on the left side of the equation. By solving kinetic equations we obtain the time dependence of the reactants concentrations. These solutions [see **9.1.6**] will be referred to as the **integrated forms of the kinetic equation**.

9.1.3 Simple reactions, order of reaction, rate constant

We will use the term “simple” for such a chemical reaction whose kinetic equation has the form

$$r_{\mathrm{A}} = -\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = k_{\mathrm{A}}\, c_{\mathrm{A}}^{\alpha} c_{\mathrm{B}}^{\beta} \ldots\,, \tag{9.9}$$

where A, B,... are the *reactants*. The exponent α is called the **order of reaction with respect to component** A, β is the order of reaction with respect to B, etc. The sum of the exponents $n = \alpha + \beta + \ldots$ is called the **(overall) order of reaction**.

The constant k_{A} in the kinetic equation (9.9) is called the **rate constant**. It is the function of temperature [see **9.159**]. The dimension of the rate constant depends on the reaction order.

U *Main unit:* $\mathrm{s}^{-1}\,(\mathrm{mol\,m}^{-3})^{1-n}$, where n is the order of reaction.

The kinetic equation in the relation (9.9) is written for the rate of consumption of substance A. Similarly we may write kinetic equations for the rate of consumption of substance B, the rate of formation of substance S, or for the rate of reaction, e.g.

$$r_{\mathrm{B}} = -\frac{\mathrm{d}\, c_{\mathrm{B}}}{\mathrm{d}\, \tau} = k_{\mathrm{B}}\, c_{\mathrm{A}}^{\alpha} c_{\mathrm{B}}^{\beta} \dots .$$

The partial orders of reaction and the overall order of reaction remain the same, but the numerical values of the rate constants k_{A}, k_{B} are different and depend on the way in which the reaction is recorded. From relation (9.5) it follows that

$$k_{\mathrm{B}} = \frac{b}{a}\, k_{\mathrm{A}} .$$

Example

The simple reaction

$$\mathrm{A} + 2\mathrm{B} \rightarrow \mathrm{C}$$

is of the half-order with respect to substance A and of the second-order with respect to substance B. Determine the overall order of the reaction, and write the kinetic equation for the rate of consumption of substance A, for the rate of formation of substance C, and the relation between the respective rate constants.

Solution

The overall order of the reaction is $n = \frac{1}{2} + 2 = \frac{5}{2}$. The kinetic equation for the rate of consumption of substance A is

$$-\frac{\mathrm{d}\, c_{\mathrm{A}}}{\mathrm{d}\, \tau} = k_{\mathrm{A}} c_{\mathrm{A}}^{1/2} c_{\mathrm{B}}^{2} .$$

The kinetic equation for the rate of formation of substance C is

$$\frac{\mathrm{d}\, c_{\mathrm{C}}}{\mathrm{d}\, \tau} = k_{\mathrm{C}} c_{\mathrm{A}}^{1/2} c_{\mathrm{B}}^{2} .$$

The rate constants are identical in this case, $k_{\mathrm{C}} = k_{\mathrm{A}}$.

Determination of the rate constants, the order of reaction and the partial orders of reaction from experimental kinetic data is discussed in section (9.3). In elementary reactions [see (9.5)], the partial orders of reactions equal their stoichiometric coefficients.

Symbols: When there is no risk of confusion, we will use simple k instead of the more correct k_i.

9.1.4 Reaction half-life

The half-life of a reaction is the time in which the concentration of a chosen reactant falls to one half. It is denoted $\tau_{1/2}$ or $\tau_{0.5}$.

> *Note:* When there is only one reactant in the reaction, or when the initial concentrations of reactants are in a stoichiometric ratio, the half-life of reaction can be determined unambiguously. When there are more reactants and their initial concentrations are not in a stoichiometric ratio, the half-life is usually defined with respect to the key component (a compounds which would first disappear is usually chosen as the key component).

Example

The initial concentration of substance A reacting according to the equation

$$\mathrm{A} \longrightarrow \mathrm{R}$$

was 2 $\mathrm{mol\,dm^{-3}}$. After 20 minutes it fell to 1 $\mathrm{mol\,dm^{-3}}$. Calculate the half-life of the reaction.

Solution

From the definition of the reaction half-life it follows that $\tau_{1/2} = 20$ min.

9.1.5 Material balance

When the concentrations of more than one substance act in a kinetic equation, we cannot solve this equation unambiguously because we have only one equation and several dependent variables. In order to obtain a differential equation for one dependent variable, we carry out material balance.

The concentrations of substances reacting according to equation (9.1) are bound by the material balance equations

$$\begin{aligned} c_\mathrm{A} &= c_\mathrm{A0} - a\,x\,, \\ c_\mathrm{B} &= c_\mathrm{B0} - b\,x\,, \\ &\vdots \qquad\qquad\qquad [V] \\ c_\mathrm{R} &= c_\mathrm{R0} + r\,x\,, \\ c_\mathrm{S} &= c_\mathrm{S0} + s\,x\,, \\ &\vdots \end{aligned} \tag{9.10}$$

where c_{i0} are the initial concentrations, i.e. the concentrations at time $\tau = 0$.

For a chemical reaction written in a compact form,

$$0 = \sum_{i=1}^{n} \nu_i \mathrm{R}_i\,,$$

we may summarize equations (9.10) into:

$$c_i = c_{i0} + \nu_i x\,, \quad i = 1, 2, \ldots, n\,, \tag{9.11}$$

where n is the number of the reacting components and ν_i are their stoichiometric coefficients (negative for the reactants and positive for the products).

> *Note:* The material balance equations are an analogy to equations (8.4) in Chapter 8, which was devoted to chemical equilibrium. The formal difference between them is that here they are written for concentrations (i.e. amounts of substance in unit volume) and not for amounts of substance.

Using material balance equations we may rewrite the kinetic equation of a simple reaction (9.9) into the form

$$a\frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k_\mathrm{A}(c_\mathrm{A0} - ax)^\alpha (c_\mathrm{B0} - bx)^\beta \ldots\,. \tag{9.12}$$

Thus we obtain a differential equation between a single dependent variable x and an independent variable τ. The initial condition is $x = 0$ at time $\tau = 0$.

Example

Consider the chemical reaction

$$\mathsf{A} + 2\,\mathsf{B} \rightarrow 3\,\mathsf{C}.$$

The initial concentrations of substances A and B are $c_{\mathrm{A}0}$ and $c_{\mathrm{B}0}$. The initial concentration of substance C is zero. Write the material balance equations for the concentrations of these substances at time τ. Write the kinetic equation of the reaction if it is half-order with respect to component A and third-order with respect to B.

Solution

The material balance equations are: $c_{\mathrm{A}} = c_{\mathrm{A}0} - x$, $c_{\mathrm{B}} = c_{\mathrm{B}0} - 2x$, $c_{\mathrm{C}} = c_{\mathrm{C}0} - 3x$. The kinetic equation is

$$-\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = k_{\mathrm{A}} c_{\mathrm{A}}^{1/2} c_{\mathrm{B}}^{3}\,.$$

Using the quantity x we may rewrite this kinetic equation into the form

$$\frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k_{\mathrm{A}} (c_{\mathrm{A}0} - x)^{1/2} (c_{\mathrm{B}0} - 2x)^{3}\,.$$

9.1.6 Methods of solving kinetic equations

From the mathematical point of view, the kinetic equation (9.8) is a first-order ordinary differential equation. Time is an independent variable, the concentrations of the reactants, or the quantity x in equation (9.12), are dependent variables.

In all simple reactions and in a number of other cases, the kinetic equation has the form

$$\frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = \phi(x)\,. \qquad (9.13)$$

This differential equation is solved using the method of separation of variables, see basic course of mathematics.

$$\frac{\mathrm{d}\,x}{\phi(x)} = \mathrm{d}\,\tau\,. \qquad (9.14)$$

At time $\tau = 0$ is $x = 0$ and, thus we obtain

$$\int_0^x \frac{\mathrm{d}\,x}{\phi(x)} = \tau\,. \tag{9.15}$$

Example

Solve the kinetic equation $-\frac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = kc_\mathrm{A}$ for a first-order reaction A → products. The initial concentration of the reactant A is $c_{\mathrm{A}0}$.

Solution

From the initial condition and from the material balance equation (9.11) we have

$$\frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k(c_{\mathrm{A}0} - x)\,.$$

This differential equation is of the type (9.13) and we solve it using the method of separation of variables

$$\int_0^x \frac{\mathrm{d}\,x}{c_{\mathrm{A}0} - x} = k\tau \quad \Longrightarrow \quad -\ln\frac{c_{\mathrm{A}0} - x}{c_{\mathrm{A}0}} = k\tau \quad \Longrightarrow \quad c_\mathrm{A} = c_{\mathrm{A}0}\,\mathrm{e}^{-k\tau}\,.$$

We derived the time dependence of the reactant concentration regardless of the number of the reaction products and their stoichiometric coefficients. If, however, we also want to find out the time dependence of the products concentrations, we have to specify the right side of the reaction.

The solution of kinetic equations often leads to the integrals of rational functions of the type

$$\int \frac{\mathrm{d}\,x}{(x-a)^n(x-b)^m\ldots}\,,$$

where n, m, …are natural numbers. We solve these integrals by the integrand decomposition into the sum of fractions, see basic course of mathematics.

Some kinetic equations cannot be solved using the method of separation of variables. Equation (9.130) may serve as a typical example. It is solved using the constant variation method, see basic course of mathematics . In the case of yet more complex kinetic equations we may fail to find any analytical solution at all, and we have to solve these equations numerically.

9.2 Simple reactions systematics

We will assume that a reaction starts at time $\tau = 0$. The initial concentration of the substances involved in the reaction will be denoted using the subscript $_0$, e.g. c_{A0},c_{B0},... In reactions with two or more reactants, we will deal only with those cases in which the partial orders are natural numbers. These cases are most frequent in practice. For the sake of simplicity we will mostly leave the right side of chemical reactions unspecified (i.e. we will write "products").

9.2.1 Zero-order reaction

9.2.1.1 Type of reaction

$$\mathrm{A} \longrightarrow \text{products}\,. \tag{9.16}$$

9.2.1.2 Kinetic equation

$$-\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = k\,. \tag{9.17}$$

9.2.1.3 Integrated form of the kinetic equation

For time as a function of the reactant concentration we have

$$k\tau = c_{\mathrm{A0}} - c_{\mathrm{A}} \quad \text{where} \quad c_{\mathrm{A0}} \geq c_{\mathrm{A}} \geq 0\,. \tag{9.18}$$

For the concentration of substance A as a function of time we have

$$c_{\mathrm{A}} = c_{\mathrm{A0}} - k\tau, \quad \text{where} \quad \tau \leq \frac{\mathrm{c_{A0}}}{\mathrm{k}}\,. \tag{9.19}$$

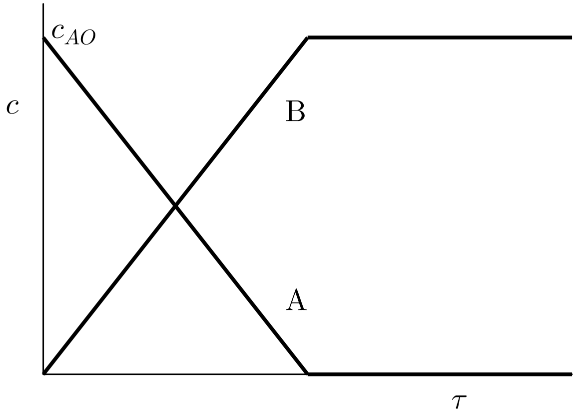
9.2.1.4 Reaction half-life

$$\tau_{1/2} = \frac{c_{\mathrm{A0}}}{2k}\,. \tag{9.20}$$

A zero-order reaction ends at time

$$\tau = \frac{c_{\mathrm{A0}}}{k}\,, \tag{9.21}$$

when the concentration of the reactant falls to zero.



Obr. 9.1: Time dependence of the reactants concentration for a zero-order reaction of the type A → B. The initial concentration of the reactant is c_{A0}, the initial concentration of the product is zero.

Figure **9.1** shows the time dependence of the concentration of the reactant A and product B.

Example

The decomposition of ethanol in the human body is a complex sequence of biochemical reactions. Formally, however, we can describe them using a single zero-order reaction. The rate constant is 0.1 g/hour per 1 kg of the person's mass. How long will it take for a person with a mass of 60 kg to degrade all alcohol left in his or her body after drinking a jar (1/2 litre) of light beer? Assume that a half-litre jar of beer contains 12 g of ethanol. Instead of the usual definition of concentration, consider the number of grams of ethanol per 1 kg of the person's mass to be the "concentration" in this case.

Solution

The initial "concentration" is $c_{\mathrm{A0}} = 12/60 = 0.2$ g/kg. We use relation (9.21) to obtain

$$\tau_{\mathrm{end}} = \frac{0.2}{0.1} = 2\,\mathrm{hours}.$$

9.2.2 First-order reactions

9.2.2.1 Type of reaction

$$\mathrm{A} \rightarrow \text{products}\,. \tag{9.22}$$

9.2.2.2 Kinetic equation

$$-\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = k c_{\mathrm{A}}\,. \tag{9.23}$$

9.2.2.3 Integrated form of the kinetic equation

For time as a function of the reactant concentration we have

$$\tau = \frac{1}{k} \ln \frac{c_{\mathrm{A}0}}{c_{\mathrm{A}}}\,. \tag{9.24}$$

For the concentration of substance A as a function of time we have

$$c_{\mathrm{A}} = c_{\mathrm{A}0} \exp(-k\tau)\,. \tag{9.25}$$

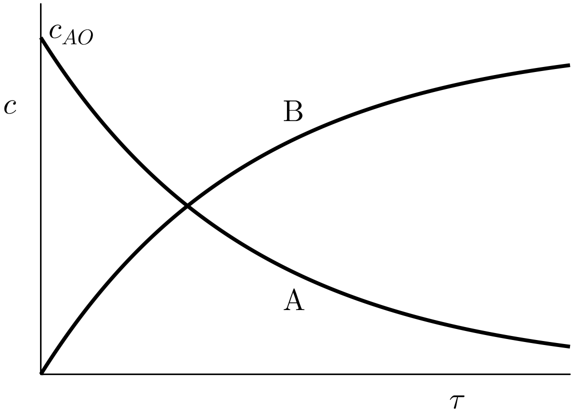
9.2.2.4 Reaction half-life

$$\tau_{1/2} = \frac{\ln 2}{k}\,. \tag{9.26}$$

Figure **9.2** shows the time dependence of the concentration of the reactant A and product B.

Example

The half-life of a certain first-order reaction at a certain temperature is $\tau_{1/2} = 693$ s. The initial concentration of the reactant A is $c_{\mathrm{A}0} = 0.1\ \mathrm{mol\,dm^{-3}}$. Calculate the rate constant of the reaction and the concentration of substance A five minutes after the start of the reaction.



Obr. 9.2: Time dependence of the reactants concentration for a first-order reaction of the type A → B. The initial concentration of the reactant is c_{A0}, the starting concentration of the product is zero.

Solution

We calculate the rate constant using equation (9.26)

$$k = \frac{\ln 2}{\tau_{1/2}} = \frac{0.693}{693} = 0.001\ \mathsf{s}^{-1}\,.$$

The concentration at time $\tau = 5$ min is calculated from relation (9.25)

$$c_{\mathrm{A}} = 0.1\ \exp\left(-0.001 \cdot 300\right) = 0.074\ \mathsf{mol\,dm}^{-3}\,.$$

9.2.3 Second-order reactions

We will deal with three types of second-order reactions:

a) Type

$$2\,\mathrm{A} \rightarrow \text{products}\,. \tag{9.27}$$

b) Type

$$\mathrm{A} + \mathrm{B} \longrightarrow \text{products}\,, \tag{9.28}$$

when the partial orders equal one and the reactants have unit stoichiometric coefficients;

c) Type

$$a\,\mathrm{A} + b\,\mathrm{B} \longrightarrow \text{products}\,, \tag{9.29}$$

when the partial orders equal one and the reactants have general stoichiometric coefficients.

9.2.3.1 Type

$$2\,\mathrm{A} \longrightarrow \text{products}\,. \tag{9.30}$$

9.2.3.2 Kinetic equation

$$-\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = k c_{\mathrm{A}}^2\,. \tag{9.31}$$

9.2.3.3 Integrated forms of the kinetic equation

For time as a function of the reactant concentration we write

$$k\tau = \frac{1}{c_{\mathrm{A}}} - \frac{1}{c_{\mathrm{A0}}}\,. \tag{9.32}$$

For the concentration of substance A as a function of time we write

$$c_{\mathrm{A}} = \frac{c_{\mathrm{A0}}}{1 + c_{\mathrm{A0}} k\tau}\,. \tag{9.33}$$

9.2.3.4 Reaction half-life

$$\tau_{1/2} = \frac{1}{k c_{\mathrm{A0}}}\,. \tag{9.34}$$

Example

The dimerization

$$2\,\mathrm{A} \rightarrow \mathrm{A}_2 \tag{9.35}$$

is a second-order reaction whose rate constant at a certain temperature equals $k = 5 \times 10^{-5}\ \mathrm{dm^{-3}\,mol^{-1}\,s^{-1}}$. The initial monomer concentration is $c_{\mathrm{A}0} = 0.7\ \ \mathrm{mol\,dm^{-3}}$ and the initial dimer concentration is zero. Calculate the time in which the dimer concentration will decrease to 0.1 $\mathrm{mol\,dm^{-3}}$, and the time in which all monomer will be consumed.

Solution

We first carry out material balance. From equations (9.10) we obtain

$$c_{\mathrm{A}} = c_{\mathrm{A}0} - 2x\,, \quad c_{\mathrm{A}_2} = x \quad \Longrightarrow \quad c_{\mathrm{A}} = c_{\mathrm{A}0} - 2c_{\mathrm{A}_2} = 0.7 - 2\cdot 0.1 = 0.5\,\mathrm{mol\,dm^{-3}}\,.$$

We calculate the time needed for the formation of $0.1\,\mathrm{mol\,dm^{-3}}$ of dimer, i.e. the time at which the monomer concentration equals $0.5\,\mathrm{mol\,dm^{-3}}$, from equation (9.32)

$$\tau = \frac{1}{5\cdot 10^{-5}}\left(\frac{1}{0.5} - \frac{1}{0.7}\right) = 11\,429\ \mathrm{s} = 3.175\ \text{hours.}$$

The time needed for all of the monomer to be consumed is calculated as a limit of relation (9.32), with c_{A} approaching zero from the right (from positive values)

$$\lim_{c_{\mathrm{A}}\to 0^+} \tau = \frac{1}{k} \lim_{c_{\mathrm{A}}\to 0^+}\left(\frac{1}{c_{\mathrm{A}}} - \frac{1}{c_{\mathrm{A}0}}\right) = +\infty\,.$$

All of the monomer will be consumed after an infinite time. This result applies in general for all one-way reactions regardless of their reaction order. The only exception is the zero-order reaction where the reactant is consumed after a finite time given by equation (9.21).

9.2.3.5 Type

$$\mathrm{A} + \mathrm{B} \rightarrow \text{products}\,. \tag{9.36}$$

9.2.3.6 Kinetic equation

$$-\frac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = k c_\mathrm{A} c_\mathrm{B} \quad \Longrightarrow \quad \frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k(c_\mathrm{A0} - x)(c_\mathrm{B0} - x)\,. \tag{9.37}$$

9.2.3.7 Integrated forms of the kinetic equation

For time as a function of the reactants concentrations it holds

$$k\tau = \frac{1}{(c_\mathrm{A0} - c_\mathrm{B0})} \ln \frac{c_\mathrm{B0}\, c_\mathrm{A}}{c_\mathrm{A0}\, c_\mathrm{B}} = \frac{1}{(c_\mathrm{A0} - c_\mathrm{B0})} \ln \frac{c_\mathrm{B0}(c_\mathrm{A0} - x)}{c_\mathrm{A0}(c_\mathrm{B0} - x)}\,. \tag{9.38}$$

For concentration as a function of time we write

$$c_\mathrm{A} = c_\mathrm{A0} - x\,, \quad c_\mathrm{B} = c_\mathrm{B0} - x\,, \quad x = c_\mathrm{A0} c_\mathrm{B0} \frac{1 - \exp[k(c_\mathrm{A0} - c_\mathrm{B0})\tau]}{c_\mathrm{B0} - c_\mathrm{A0} \exp[k(c_\mathrm{A0} - c_\mathrm{B0})\tau]}\,. \tag{9.39}$$

9.2.3.8 Reaction half-life

The half-life of reaction is defined here for the component with a lower initial concentration. When $c_\mathrm{B0} < c_\mathrm{A0}$, then $\tau_{1/2}$ defined with respect to B is

$$\tau_{1/2} = \frac{1}{k(c_\mathrm{A0} - c_\mathrm{B0})} \ln \frac{2c_\mathrm{A0} - c_\mathrm{B0}}{c_\mathrm{A0}}\,. \tag{9.40}$$

Note: When the initial concentrations of the components are identical, $c_\mathrm{A0} = c_\mathrm{B0}$, then their concentrations are identical in any moment, $c_\mathrm{A} = c_\mathrm{B}$. The reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \text{products}\,, \tag{9.41}$$

changes to the type

$$2\,\mathrm{A} \rightarrow \text{products} \tag{9.42}$$

and equations (9.38) and (9.40) simplify to (9.32) and (9.34).

Figure **9.3** illustrates the time dependence of the concentration of the reactants and products.

9.2.3.9 Type

$$a\,\mathrm{A} + b\,\mathrm{B} \rightarrow \text{products}\,. \tag{9.43}$$

9.2.3.10 Kinetic equation

$$-\frac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = k c_\mathrm{A} c_\mathrm{B} \quad \Longrightarrow \quad a\frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k(c_{\mathrm{A}0} - a\,x)(c_{\mathrm{B}0} - b\,x)\,. \tag{9.44}$$

This equation can be rearranged to

$$\frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k'\,(c'_{\mathrm{A}0} - x)(c'_{\mathrm{B}0} - x)\,. \tag{9.45}$$

where $k' = b\,k$, $c'_{\mathrm{A}0} = c_{\mathrm{A}0}/a$ and $c'_{\mathrm{B}0} = c_{\mathrm{B}0}/b$. Comparison of (9.45) with (9.37) shows that the equations are formally identical. Hence in this case we can use equations (9.38) through (9.40) in such a way that we substitute k', $c'_{\mathrm{A}0}$, $c'_{\mathrm{B}0}$ in place of k, $c_{\mathrm{A}0}$ and $c_{\mathrm{B}0}$, respectively. Equation (9.38), e.g., will thus rearrange to

$$k'\tau = \frac{1}{(c'_{\mathrm{A}0} - c'_{\mathrm{B}0})} \ln \frac{c'_{\mathrm{B}0}\,c'_\mathrm{A}}{c'_{\mathrm{A}0}\,c'_\mathrm{B}} = \frac{1}{(c'_{\mathrm{A}0} - c'_{\mathrm{B}0})} \ln \frac{c'_{\mathrm{B}0}(c'_{\mathrm{A}0} - x)}{c'_{\mathrm{A}0}(c'_{\mathrm{B}0} - x)}\,. \tag{9.46}$$

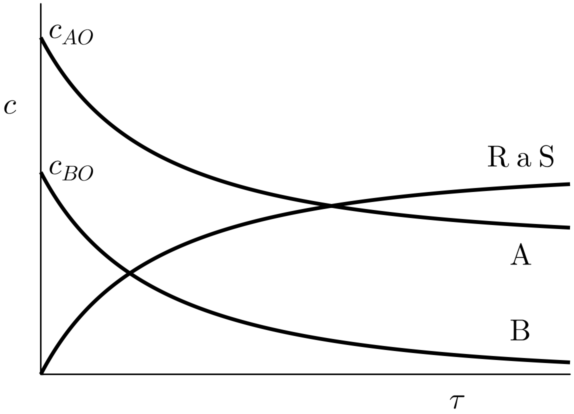
9.2.3.11 Pseudofirst-order reactions

It often happens that one of the reactants, e.g. B, is in large excess at the beginning of the reaction, $c_{\mathrm{B}0} \approx c_{\mathrm{A}0}$. In the course of the reaction, its concentration changes very little and it may be considered constant. The kinetic equation (9.37) then rearranges to

$$-\frac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = k' c_\mathrm{A}\,, \quad \text{where} \quad k' = k c_\mathrm{B}\,.$$

The equation is formally identical with the first-order kinetic equation (9.23), and consequently we speak about a pseudofirst-order reaction.

> *Note:* In literature we sometimes encounter the less correct term “pseudo-unimolecular” reaction.



Obr. 9.3: Time dependence of the reactants concentration for a second-order reaction of the type $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{R} + \mathrm{S}$. The initial concentrations of the reactants are c_{A0} and c_{B0}, the initial concentrations of the products are zero.

9.2.4 Third-order reactions

We will deal with four types of third-order reactions:

a) Type

$$3\,\mathrm{A} \rightarrow \text{products}\,. \tag{9.47}$$

when there is only one reactant.

b) Type

$$2\,\mathrm{A} + \mathrm{B} \rightarrow \text{products}, \tag{9.48}$$

when there are two reactants and their stoichiometric coefficients are equal to the partial orders of the reaction.

c) Type

$$\mathrm{A} + \mathrm{B} + \mathrm{C} \rightarrow \text{products}, \tag{9.49}$$

when there are three reactants and their stoichiometric coefficients are equal to the partial orders of the reaction, i.e. one.

d) Type

$$a\,\mathrm{A} + b\,\mathrm{B} + c\,\mathrm{C} \to \text{products}, \tag{9.50}$$

when there are three reactants with general stoichiometric coefficients and the partial orders equal 1.

9.2.4.1 Type

$$3\,\mathrm{A} \to \text{products} \tag{9.51}$$

9.2.4.2 Kinetic equation

$$-\frac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = k_\mathrm{A} c_\mathrm{A}^3\,. \tag{9.52}$$

9.2.4.3 Integrated forms of the kinetic equation

For time as a function of the reactant concentration we write

$$k\tau = \frac{1}{2}\left(\frac{1}{c_\mathrm{A}^2} - \frac{1}{c_\mathrm{A0}^2}\right)\,. \tag{9.53}$$

For the concentration of substance A as a function of time we write

$$c_\mathrm{A} = \frac{c_\mathrm{A0}}{\sqrt{1 + 2c_\mathrm{A0}^2 k\tau}}\,. \tag{9.54}$$

9.2.4.4 Reaction half-life

$$\tau_{1/2} = \frac{3}{2kc_\mathrm{A0}^2}\,. \tag{9.55}$$

9.2.4.5 Type

$$2\,\mathrm{A} + \mathrm{B} \to \text{products}\,. \tag{9.56}$$

9.2.4.6 Kinetic equation

$$-\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = k_{\mathrm{A}} c_{\mathrm{A}}^2 c_{\mathrm{B}} \quad \Longrightarrow \quad 2\frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k_{\mathrm{A}} (c_{\mathrm{A}0} - 2x)^2 (c_{\mathrm{B}0} - x)\,. \tag{9.57}$$

9.2.4.7 Integrated forms of the kinetic equation

For time as a function of the variable x it holds

$$k_{\mathrm{A}}\tau = \frac{1}{2c_{\mathrm{B}0} - c_{\mathrm{A}0}} \left(\frac{1}{c_{\mathrm{A}0} - 2x} - \frac{1}{c_{\mathrm{A}0}} \right) + \frac{1}{(2c_{\mathrm{B}0} - c_{\mathrm{A}0})^2} \ln \left[\frac{c_{\mathrm{B}0}(c_{\mathrm{A}0} - 2x)}{c_{\mathrm{A}0}(c_{\mathrm{B}0} - x)} \right]. \tag{9.58}$$

For the concentrations of the reactants we write

$$c_{\mathrm{A}} = c_{\mathrm{A}0} - 2x\,, \quad c_{\mathrm{B}} = c_{\mathrm{B}0} - x\,, \tag{9.59}$$

where x has to be determined from equation (9.58) numerically, see basic course of mathematics.

9.2.4.8 Type

$$\mathrm{A} + \mathrm{B} + \mathrm{C} \rightarrow \text{products}\,. \tag{9.60}$$

9.2.4.9 Kinetic equation

$$-\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = k c_{\mathrm{A}} c_{\mathrm{B}} c_{\mathrm{C}} \quad \Longrightarrow \quad \frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k (c_{\mathrm{A}0} - x)(c_{\mathrm{B}0} - x)(c_{\mathrm{C}0} - x)\,. \tag{9.61}$$

9.2.4.10 Integrated forms of the kinetic equation

For time as a function of the variable x we write

$$\begin{aligned} k\tau &= \frac{1}{(c_{\mathrm{A}0} - c_{\mathrm{B}0})(c_{\mathrm{A}0} - c_{\mathrm{C}0})} \ln \frac{c_{\mathrm{A}0}}{c_{\mathrm{A}0} - x} \\ &+ \frac{1}{(c_{\mathrm{B}0} - c_{\mathrm{A}0})(c_{\mathrm{B}0} - c_{\mathrm{C}0})} \ln \frac{c_{\mathrm{B}0}}{c_{\mathrm{B}0} - x} \\ &+ \frac{1}{(c_{\mathrm{C}0} - c_{\mathrm{A}0})(c_{\mathrm{C}0} - c_{\mathrm{B}0})} \ln \frac{c_{\mathrm{C}0}}{c_{\mathrm{C}0} - x}\,. \end{aligned} \tag{9.62}$$

For the concentrations of the reactants we write

$$c_{\mathrm{A}} = c_{\mathrm{A}0} - x\,, \quad c_{\mathrm{B}} = c_{\mathrm{B}0} - x\,, \quad c_{\mathrm{C}} = c_{\mathrm{C}0} - x\,, \tag{9.63}$$

where x is obtained by the numerical solution of equation (9.62)

9.2.4.11 Reaction half-life

The reaction half-life is defined with respect to that component whose initial concentration is the lowest. If, e.g. $c_{\mathrm{A}0} \le c_{\mathrm{B}0} \le c_{\mathrm{C}0}$, the half-life is defined with respect to component A and we write

$$\begin{aligned} k\tau_{1/2} &= \frac{1}{(c_{\mathrm{A}0}-c_{\mathrm{B}0})(c_{\mathrm{A}0}-c_{\mathrm{C}0})}\ln 2 \\ &+ \frac{1}{(c_{\mathrm{B}0}-c_{\mathrm{A}0})(c_{\mathrm{B}0}-c_{\mathrm{C}0})}\ln\frac{2c_{\mathrm{B}0}}{2c_{\mathrm{B}0}-c_{\mathrm{A}0}} \\ &+ \frac{1}{(c_{\mathrm{C}0}-c_{\mathrm{A}0})(c_{\mathrm{C}0}-c_{\mathrm{B}0})}\ln\frac{2c_{\mathrm{C}0}}{2c_{\mathrm{C}0}-c_{\mathrm{A}0}}\,. \end{aligned} \tag{9.64}$$

9.2.4.12 Type

$$a\,\mathrm{A} + b\,\mathrm{B} + c\,\mathrm{C} \rightarrow \text{products}\,. \tag{9.65}$$

9.2.4.13 Kinetic equation

$$-\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = k_{\mathrm{A}}c_{\mathrm{A}}c_{\mathrm{B}}c_{\mathrm{C}} \quad\Longrightarrow\quad a\frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k_{\mathrm{A}}(c_{\mathrm{A}0}-a\,x)(c_{\mathrm{B}0}-b\,x)(c_{\mathrm{C}0}-c\,x)\,. \tag{9.66}$$

Similarly as in section **9.2.3** we rewrite this equation to

$$\frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k'(c'_{\mathrm{A}0}-x)(c'_{\mathrm{B}0}-x)(c'_{\mathrm{C}0}-x)\,, \tag{9.67}$$

where $k' = k_{\mathrm{A}}bc$, $c'_{\mathrm{A}0} = c_{\mathrm{A}0}/a$, $c'_{\mathrm{B}0} = c_{\mathrm{B}0}/b$, $c'_{\mathrm{C}0} = c_{\mathrm{C}0}/c$.

9.2.4.14 Integrated forms of the kinetic equation

For time as a function of x we write

$$\begin{aligned} k'\tau &= \frac{1}{(c'_{\mathrm{A0}}-c'_{\mathrm{B0}})(c'_{\mathrm{A0}}-c'_{\mathrm{C0}})}\ln\frac{c'_{\mathrm{A0}}}{c'_{\mathrm{A0}}-x} \\ &+ \frac{1}{(c'_{\mathrm{B0}}-c'_{\mathrm{A0}})(c'_{\mathrm{B0}}-c'_{\mathrm{C0}})}\ln\frac{c'_{\mathrm{B0}}}{c'_{\mathrm{B0}}-x} \\ &+ \frac{1}{(c'_{\mathrm{C0}}-c'_{\mathrm{A0}})(c'_{\mathrm{C0}}-c'_{\mathrm{B0}})}\ln\frac{c'_{\mathrm{C0}}}{c'_{\mathrm{C0}}-x}\,. \end{aligned} \tag{9.68}$$

For the concentrations of the reactants we have

$$c_{\mathrm{A}} = c_{\mathrm{A0}} - ax\,, \quad c_{\mathrm{B}} = c_{\mathrm{B0}} - bx\,, \quad c_{\mathrm{C}} = c_{\mathrm{C0}} - cx\,, \tag{9.69}$$

where x is determined by the numerical solution of equation (9.68).

9.2.5 n^{th}-order reactions with one reactant

9.2.5.1 Type of reaction

$$\mathrm{A} \to \text{products}\,. \tag{9.70}$$

9.2.5.2 Kinetic equation

$$-\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = kc_{\mathrm{A}}^{n}\,. \tag{9.71}$$

9.2.5.3 Integrated forms of the kinetic equation

For time as a function of the reactant concentration we have

$$k\tau = \frac{1}{n-1}\left(\frac{1}{c_{\mathrm{A}}^{n-1}} - \frac{1}{c_{\mathrm{A0}}^{n-1}}\right)\,. \tag{9.72}$$

For the concentration of substance A as a function of time we have

$$c_{\mathrm{A}} = c_{\mathrm{A0}}\left[1+(n-1)c_{\mathrm{A0}}^{n-1}k\tau\right]^{\frac{1}{1-n}}\,. \tag{9.73}$$

9.2.5.4 Reaction half-life

$$\tau_{1/2} = c_{\mathrm{A}0}^{1-n}\,\frac{2^{n-1}-1}{(n-1)k}\,. \tag{9.74}$$

9.2.6 n^{th}-order reactions with two and more reactants

The general case of an n^{th}-order reaction with two reactants is

$$a\,\mathrm{A} + b\,\mathrm{B} \longrightarrow \text{products.} \tag{9.75}$$

9.2.6.1 Kinetic equation

$$-\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = k c_{\mathrm{A}}^{\alpha} c_{\mathrm{B}}^{\beta} \quad\Longrightarrow\quad a\frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k(c_{\mathrm{A}0} - a\,x)^{\alpha}(c_{\mathrm{B}0} - b\,x)^{\beta}\,, \tag{9.76}$$

where α and β are the partial orders of reaction; the overall order is $n = \alpha + \beta$. For individual specific cases when we know the partial orders of reaction and the stoichiometric coefficients of the equation, we obtain the integrated forms of kinetic equations using the method of separation of variables [see **9.1.6**].

The general case of an n^{th}-order reaction with three reactants is

$$a\mathrm{A} + b\mathrm{B} + c\mathrm{C} \longrightarrow \text{products.} \tag{9.77}$$

The partial orders of reaction with respect to components A, B, C are α, β, γ ($\alpha + \beta + \gamma = n$), and the initial concentrations of the components are $c_{\mathrm{A}0}$, $c_{\mathrm{B}0}$, $c_{\mathrm{C}0}$.

The kinetic equation of the reaction is

$$-\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = k c_{\mathrm{A}}^{\alpha} c_{\mathrm{B}}^{\beta} c_{\mathrm{C}}^{\gamma}\,. \tag{9.78}$$

Using material balance we rewrite the equation to

$$a\,\frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k(c_{\mathrm{A}0} - ax)^{\alpha}(c_{\mathrm{B}0} - bx)^{\beta}(c_{\mathrm{C}0} - cx)^{\gamma} \tag{9.79}$$

and separate variables

$$\int_0^x \frac{a}{(c_{\mathrm{A}0} - ax)^{\alpha}(c_{\mathrm{B}0} - bx)^{\beta}(c_{\mathrm{C}0} - cx)^{\gamma}}\mathrm{d}\,x = \int_0^{\tau} k\mathrm{d}\,\tau = k\tau\,. \tag{9.80}$$

If the partial orders of reaction are integers, we can solve the integral by way of the integrand decomposition (rational function) into the sum of fractions, see basic course of mathematics.

The same procedure can be used when there are more reactants.

9.2.7 Summary of relations

Let us consider the chemical reaction

$$a\,\mathrm{A} + b\,\mathrm{B} + c\,\mathrm{C} \rightarrow \text{products}. \tag{9.81}$$

The following table sums up the integrated forms of the kinetic equations presented in this section. The column “Eq.” gives the number for the integrated form of the kinetic equation. The partial orders of reaction with respect to components A, B, C are denoted by symbols α, β, γ. If the relation applies for arbitrary values of stoichiometric coefficients, these coefficients are denoted using the symbols a, b, c. The initial composition of the reacting mixture $c_{\mathrm{A}0}$, $c_{\mathrm{B}0}$, $c_{\mathrm{C}0}$ is either stoichiometric (S) or arbitrary (A).

order	α	β	γ	stoich. coeff.			init. comp.	Eq.
0	0	0	0	a	-	-	A	(9.18)
1	1	0	0	a	-	-	A	(9.24)
2	2	0	0	a	-	-	A	(9.32)
2	1	1	0	1	1	-	S	(9.32)
2	1	1	0	1	1	-	A	(9.38)
2	1	1	0	a	b	-	A	(9.46)
3	3	0	0	a	-	-	A	(9.53)
3	2	1	0	2	1	-	S	(9.53)
3	2	1	0	2	1	-	A	(9.58)
3	1	1	1	1	1	1	S	(9.53)
3	1	1	1	1	1	1	A	(9.62)
3	1	1	1	a	b	c	A	(9.68)
n	n	0	0	a	-	-	A	(9.72)
n	α	β	γ	a	b	c	A	(9.80)

9.3 Methods to determine reaction orders and rate constants

9.3.1 Problem formulation

In order to be able to use kinetic equations, we need to know the reaction order, the partial orders with respect to individual components, and the rate constant. Theoretical methods to determine these quantities are not yet sufficiently elaborated, and consequently we have to resort to the measurement of the reaction kinetics.

When we have at our disposal a table giving the values of:

a) concentrations of reactants in dependence on time, or
b) reaction half-life in dependence on the initial concentrations, or
c) rates of reaction in dependence on concentrations,

the further procedure consists in the choice of an appropriate numerical method.

9.3.2 Integral method

Let us have a table giving the values of the concentrations of reactants in dependence on time[1].

We choose a kinetic equation and from its integral form calculate the rate constant for all items in the table. If the calculated values of the rate constant do not depend *systematically* on time, the chosen kinetic equation is correct. This determines both the rate constant and the reaction order. The method is suitable particularly for reactions of integer orders, but it may be used for non-integer orders as well, as is shown in the following example.

Example

Kinetic data have been measured for the thermal decomposition of dioxan: dioxan → products at a temperature of 777 K. The results are shown in the following table:

τ [s]	0	240	660	1200	1800	2400
$c \cdot 10^3$ [mol dm^{-3}]	8.46	7.20	5.55	4.04	3.05	2.41

Determine the reaction order and the rate constant.

---

[1] It is sufficient enough to know the concentration of one reactant. The concentrations of other reacting components are then given by initial conditions and the material balance.

Solution

We first try whether this is a first-order reaction. From equation (9.24) we express the rate constant as

$$k = \frac{1}{\tau} \ln \frac{c_{\rm A0}}{c_{\rm A}}\,.$$

The initial concentration is given by the first item in the table: $c_{\rm A0} = 8.46 \times 10^{-3}\,$mol dm^{-3}. We calculate the constant for the other 5 items; it systematically falls with time:

τ [s]	240	660	1200	1800	2400
$k \cdot 10^4$ [s^{-1}]	6.72	6.39	6.16	5.67	5.23

Hence the reaction is not of first order. We then try the second order. In this case we have from relation (9.32)

$$k = \frac{1}{\tau}\left(\frac{1}{c_{\rm A}} - \frac{1}{c_{\rm A0}}\right)\,.$$

The constant increases systematically with time:

τ [s]	240	660	1200	1800	2400
$k \cdot 10^5$ [s^{-1}dm^{3}mol^{-1}]	8.62	9.39	10.78	11.65	12.36

We can thus expect the reaction order to be lower than 2 but higher than 1. We now try one and half order. From relation (9.72) we have for n = 1.5

$$k = \frac{2}{\tau}\left[\left(\frac{1}{c_{\rm A}}\right)^{1/2} - \left(\frac{1}{c_{\rm A0}}\right)^{1/2}\right]\,.$$

The constant does not change systematically with time:

τ [s]	240	660	1200	1800	2400
$k \cdot 10^4$[s^{-1} (dm^3 mol^{-1})$^{(1/2)}$]	2.41	2.44	2.56	2.54	2.50

Hence the order of the reaction is one and half. The average value of the rate constant is $k = 2.49 \times 10^{-4}\,$s^{-1} (dm^3 mol^{-1})$^{(1/2)}$.

Note: In view of experimental errors in the measured concentration values, the rate constant is not the same at all points, but it fluctuates around the mean value. We will consider the arithmetic mean of the calculated rate constants to be the correct value.

9.3.3 Differential method

Let us have a table giving the values of the reaction rates in dependence on concentrations. In this case the reaction order and the rate constant are determined from the differential forms of kinetic equations.

If there is only one reactant in the reaction,

$$\mathrm{A} \longrightarrow \text{products},$$

we use equation (9.71)

$$r = k c_\mathrm{A}^n\,,$$

where $r = -\dfrac{\mathrm{d}\, c_\mathrm{A}}{\mathrm{d}\,\tau}$. In order to determine n and k it is sufficient enough to know the rate of reaction at two concentrations:

$$n = \frac{\ln r_1/r_2}{\ln c_{\mathrm{A},1}/c_{\mathrm{A},2}}\,, \quad k = \frac{r_1}{(c_{\mathrm{A},1})^n}\,. \tag{9.82}$$

When there are two reactants, then

$$r = k c_\mathrm{A}^\alpha c_\mathrm{B}^\beta\,.$$

In order to determine the partial orders of the reaction and its rate constants, we need at least three values of the reaction rates. We will obtain the constants α, β and k by solving the following set of three equations

$$\begin{aligned}
\ln r_1 &= \ln k + \alpha \ln c_{\mathrm{A},1} + \beta \ln c_{\mathrm{B},1}\,,\\
\ln r_2 &= \ln k + \alpha \ln c_{\mathrm{A},2} + \beta \ln c_{\mathrm{B},2}\,,\\
\ln r_3 &= \ln k + \alpha \ln c_{\mathrm{A},3} + \beta \ln c_{\mathrm{B},3}\,.
\end{aligned} \tag{9.83}$$

The procedure is similar in the case of three and more reactants.

Note: The drawback of this method is the difficult determination of reaction rates from experimental data. The rate can be estimated by substituting the derivative of concentration with respect to time with the ratio of differences, see relation (9.7)

$$\frac{\mathrm{d}\, c}{\mathrm{d}\, \tau} \approx \frac{\Delta c}{\Delta \tau}\,.$$

When $\Delta\tau$ is small, Δc is subject to considerable error; if $\Delta\tau$ is large, the substitution of the derivative with the ratio of differences may be rather inaccurate.
It is possible determine the rate of reaction more accurately based on measurements in a stirred flow reactor [see **9.7.3**].

Example
The rate of the reaction

$$\mathsf{A} \longrightarrow \text{products}$$

is 0.01 mol dm^{-3} min^{-1} at $c_{\mathrm{A}} = 1$ mol dm^{-3}, and 0.005 mol dm^{-3} min^{-1} at $c_{\mathrm{A}} = 0.5$ mol dm^{-3}. Determine the reaction order and the rate constant.

Solution
We substitute into equations (9.82)

$$n = \frac{\ln 0.01/0.005}{\ln 1/0.5} = \frac{\ln 2}{\ln 2} = 1\,, \quad k = \frac{0.01}{1^1} = 0.01\,\mathrm{min}^{-1}\,.$$

9.3.4 Method of half-lives

This method is usually applied in the case of reactions with one reactant. The initial data are the reaction half-lives for at least two different initial concentrations of the reactant.

If the reaction half-life does not depend on the initial concentration, the reaction is first order [see equations (9.26)]. If it does depend on the initial concentration, we use relation (9.74) which we write for two initial concentrations $(c_{\mathrm{A}0})_1$ and $(c_{\mathrm{A}0})_2$. This set of two equations for two unknowns is solved as follows:

$$n = 1 - \frac{\ln\left[\left(\tau_{1/2}\right)_1 / \left(\tau_{1/2}\right)_2\right]}{\ln\left[(c_{\mathrm{A}0})_1 / (c_{\mathrm{A}0})_2\right]}\,, \tag{9.84}$$

$$k = \frac{2^{n-1}-1}{(n-1)\,(c_{\mathrm{A}0})_1^{n-1}\left(\tau_{1/2}\right)_1}\,. \tag{9.85}$$

9.3.5 Generalized integral method

For the reaction

$$\mathrm{A} \longrightarrow \text{products},$$

we have a table of the measured values $\tau_i, i = 1, 2, \ldots, M$. The integrated form of the kinetic equation for this reaction is [see equations (9.73)].

$$c_{\mathrm{A}} = c_{\mathrm{A}0}\left[1 + (n-1)c_{\mathrm{A}0}^{n-1}k\tau\right]^{\frac{1}{1-n}}\,.$$

We determine the unknown constants n and k using the least squares method, see basic course of mathematics. The method consists in finding the minimum of the function

$$S(n,k) = \sum_{i=1}^{M}\left(c_{\mathrm{A},i}^{\mathrm{exp}} - c_{\mathrm{A},i}^{\mathrm{calc}}\right)^2 = \sum_{i=1}^{M}\left\{c_{\mathrm{A},i}^{\mathrm{exp}} - c_{\mathrm{A}0}\left[1 + (n-1)c_{\mathrm{A}0}^{n-1}k\tau\right]^{\frac{1}{1-n}}\right\}^2\,. \tag{9.86}$$

The condition of the minimum is for the first derivatives to be zero. Hence we solve a system of two equations for two unknowns

$$\left(\frac{\partial S}{\partial n}\right)_k = 0\,, \qquad \left(\frac{\partial S}{\partial k}\right)_n = 0\,. \tag{9.87}$$

The method is suitable when using a PC, but it is too laborious for “manual” calculation.

9.3.6 Ostwald's isolation method

The methods presented above are not very suitable for determining the partial orders of reactions. Ostwald's isolation method is an experimental procedure which transfers the task of finding the partial order of a reaction to that of finding the overall order of a reaction. We will show the principle on the example of the reaction

$$\mathrm{A} + \mathrm{B} + \mathrm{C} \rightarrow \text{products} \tag{9.88}$$

whose kinetic equation is [compare with equation (9.79)]

$$-\frac{\mathrm{d}\, c_{\mathrm{A}}}{\mathrm{d}\, \tau} = k c_{\mathrm{A}}^{\alpha} c_{\mathrm{B}}^{\beta} c_{\mathrm{C}}^{\gamma} \quad \Longrightarrow \quad \frac{\mathrm{d}\, x}{\mathrm{d}\, \tau} = k(c_{\mathrm{A}0} - x)^{\alpha} (c_{\mathrm{B}0} - x)^{\beta} (c_{\mathrm{C}0} - x)^{\gamma}\,.$$

If we choose for a kinetic experiment such initial concentrations that $c_{\mathrm{A}0} \ll c_{\mathrm{B}0}$, $c_{\mathrm{A}0} \ll c_{\mathrm{C}0}$, then $c_{\mathrm{B}0} - x \approx c_{\mathrm{B}0}$ and $c_{\mathrm{C}0} - x \approx c_{\mathrm{C}0}$ (compare with the section on pseudofirst-order reactions in **9.2.3**). The kinetic equation rearranges to

$$\frac{\mathrm{d}\, x}{\mathrm{d}\, \tau} = k(c_{\mathrm{A}0} - x)^{\alpha} c_{\mathrm{B}0}\, c_{\mathrm{C}0} = k'(c_{\mathrm{A}0} - x)^{\alpha}$$

and the partial order α with respect to substance A is determined using one of the preceding methods. Then we perform a kinetic experiment with the excess of substances A and C and determine β from the data. Finally we take substances A and B in excess and determine γ.

9.4 Simultaneous chemical reactions

We speak about simultaneous reactions when there are several reactions in progress in a system and these reactions have at least one substance in common. In this section we will focus on cases with only two reactions taking place in a system. More complex simultaneous reactions will be discussed in section **9.5**. For the sake of simplicity we will assume that the partial orders of the reactions equal their stoichiometric coefficients, i.e. that the reactions are elementary [see **9.5.1**].

S *Symbols:* We will use the symbol

$$\mathrm{A} \xrightarrow{k} \mathrm{B}$$

to indicate that the reaction rate constant is k.

Example

The following reactions proceed in a system at the same time:

$$\mathsf{A} + \mathsf{B} \xrightarrow{k_1} 2\mathrm{C} \quad \text{and} \quad \mathrm{R} \xrightarrow{k_2} \mathrm{S}\,. \tag{9.89}$$

Are they simultaneous reactions?

Solution

The answer is that they are not. The reactions do not have any reactant in common. Hence they may be studied separately.

9.4.1 Types of simultaneous reactions

We distinguish the following types of simultaneous reactions:

a) **Parallel** or **side** reactions. The initial substances react in competing reactions to form various products. The simplest case is the decomposition of one reactant into two products

$$\begin{array}{l} \mathrm{A} \rightarrow \mathrm{R}_1 \\ \mathrm{A} \rightarrow \mathrm{R}_2 \end{array} \quad \text{i.e.} \quad \mathrm{A} \begin{array}{l} \nearrow \mathrm{R}_1 \\ \searrow \mathrm{R}_2 \end{array} \,. \tag{9.90}$$

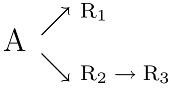
b) **Reversible** or **opposing** reactions. These reactions proceed in both directions. The simplest case is

$$\begin{array}{ccc} \mathrm{A} & \rightarrow & \mathrm{R} \\ \mathrm{R} & \rightarrow & \mathrm{A} \end{array} \quad \text{i.e.} \quad \mathrm{A} \rightleftharpoons \mathrm{R}\,. \tag{9.91}$$

c) **Consecutive** reactions. The reactants react to form intermediates from which the reaction products are formed. The simplest case is

$$\begin{array}{ccc} \mathrm{A} & \rightarrow & \mathrm{B} \\ \mathrm{B} & \rightarrow & \mathrm{C} \end{array} \quad \text{i.e.} \quad \mathrm{A} \rightarrow \mathrm{B} \rightarrow \mathrm{C}\,. \tag{9.92}$$

d) **More complex** reactions. These are the combinations of parallel, reversible and consecutive reactions. For example,



(9.93)

is a parallel and consecutive reaction at the same time.

9.4.2 Rate of formation of a substance in simultaneous reactions

In section **9.1** we defined the rates of consumption and formation of a substance for one single reaction. If a substance A reacts in n chemical reactions whose rates are r_1, r_2, …, r_n, we write for the rate of formation of the substance A (the rate of consumption of a substance is the negatively expressed rate of formation).

$$r_{\mathrm{A}} = \frac{\mathrm{d}\, c_{\mathrm{A}}}{\mathrm{d}\, \tau} = \sum_{i=1}^{n} \nu_{\mathrm{A}i} r_i\,, \tag{9.94}$$

where $\nu_{\mathrm{A}i}$ is the stoichiometric coefficient of substance A in reaction i.

Example

Two simultaneous reactions proceed in a system:

$$\begin{aligned} \mathrm{A} &\xrightarrow{k_1} \mathrm{R} + 2\mathrm{S} + \mathrm{B}\,, \qquad (1)\\ \mathrm{A} + \mathrm{B} &\xrightarrow{k_2} \mathrm{M} + \mathrm{S}\,. \qquad (2) \end{aligned}$$

The reaction (1) is first order. The reaction (2) is second order, i.e. first order with respect to both A and B. Write the relations for the rate of formation of substances A, B and S.

Solution

The rate of the first reaction is $r_1 = k_1 c_\mathrm{A}$, and the rate of the second reaction is $r_2 = k_2 c_\mathrm{A} c_\mathrm{B}$. From relation (9.94) we obtain

$$\begin{aligned} \frac{\mathrm{d}\, c_\mathrm{A}}{\mathrm{d}\,\tau} &= -r_1 - r_2 = -k_1 c_\mathrm{A} - k_2 c_\mathrm{A} c_\mathrm{B}\,,\\ \frac{\mathrm{d}\, c_\mathrm{B}}{\mathrm{d}\,\tau} &= r_1 - r_2 = k_1 c_\mathrm{A} - k_2 c_\mathrm{A} c_\mathrm{B}\,,\\ \frac{\mathrm{d}\, c_\mathrm{S}}{\mathrm{d}\,\tau} &= 2r_1 + r_2 = 2k_1 c_\mathrm{A} + k_2 c_\mathrm{A} c_\mathrm{B}\,. \end{aligned}$$

9.4.3 Material balance in simultaneous reactions

For simultaneous reactions, the material balance equations (9.10) generalize to

$$c_\mathrm{A} = c_{\mathrm{A}0} + \sum_{i=1}^{n} \nu_{\mathrm{A}i} x_i\,, \tag{9.95}$$

where ν_Ai has the same meaning as in equation (9.94), and x_i is an analogy to the quantity x in equation (9.10) for the i-th reaction.

Example

Consider the same reactions as in the preceding example:

$$\begin{aligned} \mathrm{A} &\xrightarrow{k_1} \mathrm{R} + 2\mathrm{S} + \mathrm{B}\,, & (1)\\ \mathrm{A} + \mathrm{B} &\xrightarrow{k_2} \mathrm{M} + \mathrm{S}\,. & (2) \end{aligned}$$

The initial concentrations of substances A and B are $c_{\mathrm{A}0}$ and $c_{\mathrm{B}0}$. The initial concentrations of the other substances participating in the reactions are zero. Write the material balance equations for all substances involved in the reactions.

Solution

$$\begin{aligned} c_\mathrm{A} &= c_{\mathrm{A}0} - x_1 - x_2\,,\\ c_\mathrm{B} &= c_{\mathrm{B}0} + x_1 - x_2\,,\\ c_\mathrm{R} &= x_1\,,\\ c_\mathrm{S} &= 2x_1 + x_2\,,\\ c_\mathrm{M} &= x_2\,. \end{aligned}$$

9.4.4 First-order parallel reactions

9.4.4.1 Type of reaction

$$\begin{aligned} \mathrm{A} &\xrightarrow{k_1} \mathrm{B}\,,\\ \mathrm{A} &\xrightarrow{k_2} \mathrm{C}\,. \end{aligned}$$

9.4.4.2 Kinetic equations

$$\frac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = -(k_1 + k_2)c_\mathrm{A}\,, \tag{9.96}$$

$$\frac{\mathrm{d}\,c_{\mathrm{B}}}{\mathrm{d}\,\tau} = k_1 c_{\mathrm{A}}\,, \tag{9.97}$$

$$\frac{\mathrm{d}\,c_{\mathrm{C}}}{\mathrm{d}\,\tau} = k_2 c_{\mathrm{A}}\,. \tag{9.98}$$

9.4.4.3 Integrated forms of the kinetic equations

$$c_{\mathrm{A}} = c_{\mathrm{A0}}\exp[-(k_1+k_2)\tau]\,, \tag{9.99}$$

$$c_{\mathrm{B}} = c_{\mathrm{B0}} + c_{\mathrm{A0}}\frac{k_1}{k_1+k_2}\left\{1-\exp[-(k_1+k_2)\tau]\right\}\,, \tag{9.100}$$

$$c_{\mathrm{C}} = c_{\mathrm{C0}} + c_{\mathrm{A0}}\frac{k_2}{k_1+k_2}\left\{1-\exp[-(k_1+k_2)\tau]\right\}\,. \tag{9.101}$$

From equations (9.100) and (9.101) it follows that

$$\frac{c_{\mathrm{B}}-c_{\mathrm{B0}}}{c_{\mathrm{C}}-c_{\mathrm{C0}}} = \frac{k_1}{k_2}\,. \tag{9.102}$$

The concentrations of products B and C are usually zero at the start of the reaction, $c_{\mathrm{B0}} = c_{\mathrm{C0}} = 0$, and the equation simplifies to

$$\frac{c_{\mathrm{B}}}{c_{\mathrm{C}}} = \frac{k_1}{k_2}\,. \tag{9.103}$$

9.4.4.4 Wegscheider's principle

The ratio of the concentrations of side reactions products does not depend on time. This principle applies if the side reactions are of the same order and if the initial concentrations of their products are zero.

9.4.5 Second-order parallel reactions

9.4.5.1 Type of reaction

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{C}\,,$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_2} \mathrm{D}\,.$$

9.4.5.2 Kinetic equations

$$\frac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = \frac{\mathrm{d}\,c_\mathrm{B}}{\mathrm{d}\,\tau} = -(k_1+k_2)c_\mathrm{A}c_\mathrm{B} \Longrightarrow \frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = (k_1+k_2)(c_\mathrm{A0}-x)(c_\mathrm{B0}-x)\,, \tag{9.104}$$

$$\frac{\mathrm{d}\,c_\mathrm{C}}{\mathrm{d}\,\tau} = k_1 c_\mathrm{A} c_\mathrm{B} = k_1(c_\mathrm{A0}-x)(c_\mathrm{B0}-x)\,, \tag{9.105}$$

$$\frac{\mathrm{d}\,c_\mathrm{D}}{\mathrm{d}\,\tau} = k_2 c_\mathrm{A} c_\mathrm{B} = k_2(c_\mathrm{A0}-x)(c_\mathrm{B0}-x)\,. \tag{9.106}$$

9.4.5.3 Integrated forms of the kinetic equations

$$c_\mathrm{A} = c_\mathrm{A0} - x\,, \tag{9.107}$$

$$c_\mathrm{B} = c_\mathrm{B0} - x\,, \tag{9.108}$$

$$c_\mathrm{C} = c_\mathrm{C0} + \frac{k_1}{k_1+k_2}\,x\,, \tag{9.109}$$

$$c_\mathrm{D} = c_\mathrm{D0} + \frac{k_2}{k_1+k_2}\,x\,, \tag{9.110}$$

where

$$x = c_\mathrm{A0}c_\mathrm{B0}\frac{z-1}{z c_\mathrm{A0} - c_\mathrm{B0}} \quad \text{and} \quad z = \exp\left[(k_1+k_2)(c_\mathrm{A0}-c_\mathrm{B0})\tau\right]\,. \tag{9.111}$$

We may explicitly express time from equation (9.111) as

$$\tau = \frac{1}{(c_\mathrm{A0}-c_\mathrm{B0})(k_1+k_2)}\ln\frac{c_\mathrm{B0}c_\mathrm{A}}{c_\mathrm{A0}c_\mathrm{B}} = \frac{1}{(c_\mathrm{A0}-c_\mathrm{B0})(k_1+k_2)}\ln\frac{c_\mathrm{B0}(c_\mathrm{A0}-x)}{c_\mathrm{A0}(c_\mathrm{B0}-x)}\,. \tag{9.112}$$

If the concentrations of products C and D are zero at the start of the reaction, the ratio of their concentrations at an arbitrary time is given by equation (9.103) and Wegscheider's principle applies.

9.4.6 First- and second-order parallel reactions

9.4.6.1 Type of reaction

$$\mathrm{A} \xrightarrow{k_1} \mathrm{C}\,,$$

$$\mathrm{A} + \mathrm{B} \quad \xrightarrow{k_2} \quad \mathrm{D}\,.$$

9.4.6.2 Kinetic equations

$$-\frac{\mathrm{d}\,c_{\mathrm{A}}}{\mathrm{d}\,\tau} = k_1 c_{\mathrm{A}} + k_2 c_{\mathrm{A}} c_{\mathrm{B}}\,, \tag{9.113}$$

$$-\frac{\mathrm{d}\,c_{\mathrm{B}}}{\mathrm{d}\,\tau} = k_2 c_{\mathrm{A}} c_{\mathrm{B}}\,, \tag{9.114}$$

$$\frac{\mathrm{d}\,c_{\mathrm{C}}}{\mathrm{d}\,\tau} = k_1 c_{\mathrm{A}}\,, \tag{9.115}$$

$$\frac{\mathrm{d}\,c_{\mathrm{D}}}{\mathrm{d}\,\tau} = k_2 c_{\mathrm{A}} c_{\mathrm{B}}\,. \tag{9.116}$$

Using the material balance equations

$$c_{\mathrm{A}} = c_{\mathrm{A0}} - x - y\,, \quad c_{\mathrm{B}} = c_{\mathrm{B0}} - y\,, \quad c_{\mathrm{C}} = c_{\mathrm{C0}} + x\,, \quad c_{\mathrm{D}} = c_{\mathrm{D0}} + y\,, \tag{9.117}$$

we may rewrite the kinetic equations (9.115) and (9.116) into the form

$$\frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k_1(c_{\mathrm{A0}} - x - y)\,, \tag{9.118}$$

$$\frac{\mathrm{d}\,y}{\mathrm{d}\,\tau} = k_2(c_{\mathrm{A0}} - x - y)(c_{\mathrm{B0}} - y)\,. \tag{9.119}$$

9.4.6.3 Integrated forms of the kinetic equations

From (9.118) and (9.119) it follows that

$$y = c_{\mathrm{B0}}\left[1 - \exp\left(-\frac{k_2}{k_1}x\right)\right]\,, \tag{9.120}$$

$$\tau = \frac{1}{k}\int_0^x \frac{\mathrm{d}\,x}{c_{\mathrm{A0}} - x - c_{\mathrm{B0}}\left[1 - \exp\left(-\frac{k_2}{k_1}x\right)\right]}\,. \tag{9.121}$$

The integral does not have an analytical solution and hence it has to be solved numerically when calculating the reactants concentrations, see basic course of mathematics.

Note: Wegscheider's principle does not apply for this type of parallel reactions.

9.4.7 First-order reversible reactions

9.4.7.1 Type of reaction

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}\,,$$
$$\mathrm{B} \xrightarrow{k_2} \mathrm{A}\,.$$

9.4.7.2 Kinetic equations

$$-\frac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = k_1 c_\mathrm{A} - k_2 c_\mathrm{B} \quad\Longrightarrow\quad \frac{\mathrm{d}\,x}{\mathrm{d}\,\tau} = k_1(c_{\mathrm{A}0} - x) - k_2(c_{\mathrm{B}0} + x)\,. \tag{9.122}$$

9.4.7.3 Integrated forms of the kinetic equations

$$x = \frac{k_1 c_{\mathrm{A}0} - k_2 c_{\mathrm{B}0}}{k_1 + k_2}\left[1 - \exp\left(-(k_1 + k_2)\tau\right)\right]\,, \tag{9.123}$$

$$c_\mathrm{A} = c_{\mathrm{A}0} - x\,, \quad c_\mathrm{B} = c_{\mathrm{B}0} + x\,. \tag{9.124}$$

9.4.8 Reversible reactions and chemical equilibrium

Let us consider the reversible reaction

$$a\mathrm{A} + b\mathrm{B} + \cdots \xrightarrow{k_1} s\mathrm{S} + tT + \cdots\,, \tag{9.125}$$

$$s\mathrm{S} + tT \cdots \xrightarrow{k_2} a\mathrm{A} + b\mathrm{B} + \cdots \tag{9.126}$$

We will assume that, as was mentioned at the beginning of this section, the stoichiometric coefficients are equal to the partial orders of the reaction, i.e. that both reactions are elementary [see **9.5.1**]. The rate of the direct reaction (9.125) is $r_1 = k_1 c_\mathrm{A}^a c_\mathrm{B}^b \cdots$ and the rate of the reverse reaction (9.126) is $r_2 = k_2 c_\mathrm{S}^s c_T^t \cdots$ At time $\tau \to \infty$ the reaction reaches the state of chemical equilibrium and we can write

$$r_1 = r_2 \quad\Longrightarrow\quad k_1 c_{\mathrm{A},eq}^a c_{\mathrm{B},eq}^b \cdots = k_2 c_{\mathrm{S},eq}^s c_{T,eq}^t \cdots\,, \quad [\text{equilibrium}]\,, \tag{9.127}$$

where $c_{i,eq}$ are the concentrations of the reactants in the state of chemical equilibrium. From this it follows

$$\frac{c^s_{\mathrm{S},eq}c^t_{T,eq}\cdots}{c^a_{\mathrm{A},eq}c^b_{\mathrm{B},eq}\cdots} = \frac{k_1}{k_2} = K\,, \quad [\text{equilibrium}]\,, \tag{9.128}$$

where K is the equilibrium constant on choosing the standard state of unit concentration, $c^{\mathrm{st}} = 1\,\mathrm{mol\,dm^{-3}}$, provided that the equilibrium mixture forms an ideal solution.

Chemical equilibrium is thus the resulting state of reversible reactions. One-way reactions, as yet the primary focus of our attention, represent special cases when the equilibrium is shifted entirely in favor of the products.

> *Note:* Stoichiometric coefficients are equal to the partial orders of reaction only in elementary reactions [see **9.5.1**]. In addition, equation (9.128) is not thermodynamically consistent because it contains concentrations and not activities [see equations (8.15)]. Activities are equal to concentrations only in ideal solutions.

9.4.9 First-order consecutive reactions

9.4.9.1 Type of reaction

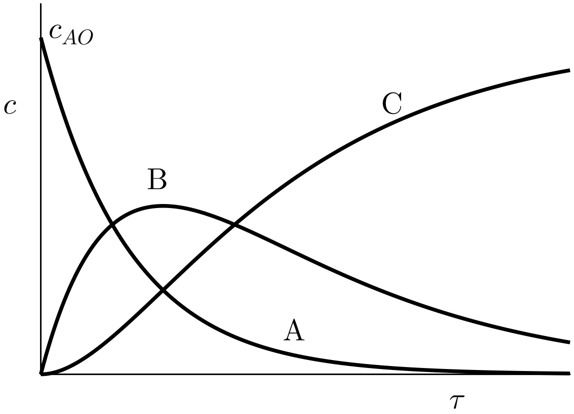
$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}\,,$$
$$\mathrm{B} \xrightarrow{k_2} \mathrm{C}\,.$$

We will consider a reaction with the initial concentration of substances B and C being zero.

9.4.9.2 Kinetic equations

$$-\frac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = k_1 c_\mathrm{A}\,, \tag{9.129}$$

$$\frac{\mathrm{d}\,c_\mathrm{B}}{\mathrm{d}\,\tau} = k_1 c_\mathrm{A} - k_2 c_\mathrm{B}\,. \tag{9.130}$$



Obr. 9.4: Time dependence of the reactants concentrations in the consecutive reaction A → B → C.

9.4.9.3 Integrated forms of the kinetic equations

$$
\begin{aligned}
c_{\mathrm{A}} &= c_{\mathrm{A0}}\mathrm{e}^{-k_1\tau}\,, & (9.131)\\
c_{\mathrm{B}} &= \frac{k_1}{k_2-k_1}\,c_{\mathrm{A0}}\left[\mathrm{e}^{-k_1\tau}-\mathrm{e}^{-k_2\tau}\right]\,, & (9.132)\\
c_{\mathrm{C}} &= c_{\mathrm{A0}}-c_{\mathrm{A}}-c_{\mathrm{B}}=c_{\mathrm{A0}}\left(1+\frac{k_1}{k_2-k_1}\mathrm{e}^{-k_2\tau}-\frac{k_2}{k_2-k_1}\mathrm{e}^{-k_1\tau}\right)\,. & (9.133)
\end{aligned}
$$

Substance B is the intermediate of the reaction. Its concentration first increases with time and then decreases [see Figure 9.4]. It acquires its maximum value $c_{\mathrm{B,max}}$ at time τ_{max}, where

$$c_{\mathrm{B,max}}=c_{\mathrm{A0}}\left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2-k_1}}\,,\quad \tau_{\mathrm{max}}=\frac{\ln\left(k_2/k_1\right)}{k_2-k_1}\,. \qquad (9.134)$$

The time dependence of the substances A, B and C is illustrated in Figure **9.4**.

9.4.9.4 Special cases

a) Both rate constants are the same, $k_1 = k_2 = k$. Then

$$c_{\mathrm{A}} = c_{\mathrm{A0}}\mathrm{e}^{-k\tau}\,, \quad c_{\mathrm{B}} = kc_{\mathrm{A0}}\tau\mathrm{e}^{-k\tau}\,. \tag{9.135}$$

b) The first reaction is much faster than the second, $k_1 \gg k_2$. Then

$$c_{\mathrm{A}} \approx 0\,, \quad c_{\mathrm{B}} \approx c_{\mathrm{A0}}\mathrm{e}^{-k_2\tau}\,, \quad c_{\mathrm{C}} \approx c_{\mathrm{A0}} - c_{\mathrm{B}}\,. \tag{9.136}$$

c) The second reaction is much faster than the first, $k_1 \ll k_2$. Then

$$c_{\mathrm{A}} = c_{\mathrm{A0}}\mathrm{e}^{-k_1\tau}\,, \quad c_{\mathrm{B}} = c_{\mathrm{A0}}\frac{k_1}{k_2} \approx 0\,, \quad c_{\mathrm{C}} \approx c_{\mathrm{A0}} - c_{\mathrm{A}}\,. \tag{9.137}$$

9.5 Mechanisms of chemical reactions

The simplest mechanisms [see **9.5.1**] were described in section **9.4**. In this section we will deal with some more complex cases.

9.5.1 Elementary reactions, molecularity, reaction mechanism

Chemical reactions as we write them usually do not show the real course of processes on the molecular level but merely the stoichiometric ratios between the reactants.

The reactions proceeding on a molecular level are called **elementary reactions**. The number of molecules participating in an elementary reaction is called the **molecularity** of the reaction. Based on molecularity we classify elementary reactions as:

a) **unimolecular**—the reaction occurs due to the decomposition of a molecule,
b) **bimolecular**—the reaction occurs when two molecules collide,
c) **trimolecular**—the reaction occurs when three molecules collide.

Radioactive decay represents a typical unimolecular reaction.

Most elementary reactions are bimolecular. Trimolecular reactions are very rare. Higher than trimolecular reactions have not been observed.

If a reaction is not elementary, it proceeds as a sequence of elementary reactions. This sequence is called the **mechanism of reaction**.

Note: The reaction

$$\mathrm{H} + \mathrm{Br_2} \;\rightarrow\; \mathrm{HBr} + \mathrm{Br}$$

is elementary. It is a bimolecular reaction. Hydrogen burning

$$2\,\mathrm{H_2} + \mathrm{O_2} \rightarrow 2\,\mathrm{H_2O}$$

is not an elementary reaction. Its mechanism is given by the following sequence of elementary reactions:

$$\begin{aligned}
\mathrm{H_2} + \mathrm{O_2} &\rightarrow \mathrm{HO_2}^{\bullet} + \mathrm{H}\,,\\
\mathrm{H_2} + \mathrm{HO_2}^{\bullet} &\rightarrow \mathrm{H_2O} + \mathrm{OH}^{\bullet}\,,\\
\mathrm{H_2} + \mathrm{OH}^{\bullet} &\rightarrow \mathrm{H_2O} + \mathrm{H}^{\bullet}\,,\\
\mathrm{H}^{\bullet} + \mathrm{O_2} &\rightarrow \mathrm{O}^{\bullet} + \mathrm{OH}^{\bullet}\,,\\
\mathrm{H_2} + \mathrm{O}^{\bullet} &\rightarrow \mathrm{H}^{\bullet} + \mathrm{OH}^{\bullet}\,.
\end{aligned}$$

All elementary reactions fall in the group of simple reactions, but far from all simple reactions are elementary. The order of an elementary reaction is identical with its molecularity, the orders with respect to individual components are equal to their stoichiometric coefficients and acquire the value of 1, 2 or 3.

9.5.2 Kinetic equations for elementary reactions

For elementary reactions, the kinetic equation (9.8) has the following form:

$$-\frac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = k\,c_\mathrm{A}^a c_\mathrm{B}^b\ \ldots\ , \tag{9.138}$$

where a, b, ... are the stoichiometric coefficients of the reactants. There are six basic types of elementary reactions. Their kinetic equations are given in Table **9.1**.

9.5.3 Solution of reaction mechanisms

Setting up the mechanism of a chemical reaction is a complex experimental and theoretical task which we will not discuss here. A set-up mechanism of a chemical reaction (a sequence

Tabulka 9.1: Types of elementary reactions and their kinetic equations.

molecularity	elementary reaction	kinetic equation
1	$\mathrm{A} \rightarrow$ products	$-\dfrac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = k\,c_\mathrm{A}$
2	$2\,\mathrm{A} \rightarrow$ products	$-\dfrac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = k\,c_\mathrm{A}^2$
	$\mathrm{A}+\mathrm{B} \rightarrow$ products	$-\dfrac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = k\,c_\mathrm{A}c_\mathrm{B}$
3	$3\,\mathrm{A} \rightarrow$ products	$-\dfrac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = k\,c_\mathrm{A}^3$
	$2\,\mathrm{A}+\mathrm{B} \rightarrow$ products	$-\dfrac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = k\,c_\mathrm{A}^2c_\mathrm{B}$
	$\mathrm{A}+\mathrm{B}+\mathrm{C} \rightarrow$ products	$-\dfrac{\mathrm{d}\,c_\mathrm{A}}{\mathrm{d}\,\tau} = k\,c_\mathrm{A}c_\mathrm{B}c_\mathrm{C}$

of elementary reactions) has a corresponding set of kinetic equations, i.e. first-order ordinary differential equations. **Solving the reaction mechanism** is no less complex task. By this we mean finding integral forms of a set of (differential) kinetic equations describing the given mechanism. A solution in an analytic form is usually required, which is not always possible. In the case of more complex mechanisms we have to put up either with a numerical solution of kinetic equations, or with only an *approximate* analytic solution.

Another complication is the fact that radicals (denoted $\mathrm{A}^\bullet$), "activated molecules" (denoted A^*), etc. often act as intermediates in elementary reactions. The concentrations of these reactive components of chemical reactions are usually small and experimentally difficult to obtain or unobtainable. The numerical values of the rate constants of the reactions in which they participate are not known, either. It is thus undesirable for these concentrations to occur in the resulting integrated forms of kinetic equations.

In order to simplify the solution of reaction mechanisms, the following approximations are used:

- rate-determining process principle,
- Bodenstein’s steady-state principle,
- pre-equilibrium principle.

9.5.4 Rate-determining process

In simultaneously proceeding reactions, the reaction whose rate has the decisive effect on the rate of formation of products is called the rate-determining reaction or the rate-determining process. The rate-determining process is usually either the fastest or the slowest of the simultaneously proceeding reactions.

In parallel reactions, the rate-determining process is the fastest reaction while in consecutive reactions it is the slowest reaction.

Example

Which of reactions (9.93) is the rate-determining process?

Solution

Let the rate constant of the reaction $\mathrm{A} \rightarrow \mathrm{R}_1$ be denoted k_1, the rate constant of the reaction $\mathrm{A} \rightarrow \mathrm{R}_2$ be denoted k_2, and the rate constant of the reaction $\mathrm{R}_2 \rightarrow \mathrm{R}_3$ be denoted $k_{3.}$ We assume that the values of the rate constants are different in order because otherwise the term rate-determining process would not make sense. Several cases may occur:

- $k_1 \gg k_2$: the rate-determining process is the reaction $\mathrm{A} \rightarrow \mathrm{R}_1$ regardless of the value of the constant k_3.
- $k_1 \ll k_2$:
  - $k_2 \ll k_3$: the rate-determining process is the reaction $\mathrm{A} \rightarrow \mathrm{R}_2$,
  - $k_2 \gg k_3$: the rate-determining process is the reaction $\mathrm{R}_2 \rightarrow \mathrm{R}_3$.

9.5.5 Bodenstein’s steady-state principle

Except for a short initial and final stage of reaction, the concentrations of radicals, activated molecules and other reactive components of elementary reactions vary relatively little with time, i.e. the rate of formation of these species is almost equal to their rate of consumption. If we assume that the concentration of these components does not change with time, we obtain

$$\frac{\mathrm{d}\, c_{\mathrm{A}^*}}{\mathrm{d}\, \tau} = 0\,. \tag{9.139}$$

This assumption is called Bodenstein's principle or the steady-state principle. It does not apply absolutely accurately but it is often used as a good approximation.

9.5.6 Lindemann mechanism of first-order reactions

Some reactions of the type A → B proceed neither as unimolecular nor as bimolecular (i.e. those in which a molecule reacts on colliding with another molecule). Lindemann suggested the following mechanism for these reactions:

$$\mathrm{A} + \mathrm{A} \xrightarrow{k_1} \mathrm{A} + \mathrm{A}^*\,, \tag{9.140}$$

$$\mathrm{A}^* + \mathrm{A} \xrightarrow{k_2} \mathrm{A} + \mathrm{A}\,, \tag{9.141}$$

$$\mathrm{A}^* \xrightarrow{k_3} \mathrm{B}\,, \tag{9.142}$$

where A^* is the **activated molecule**, a molecule endowed with a substantially higher energy than its fellow-molecules.

The rate of formation of the product according to (9.142) is

$$\frac{\mathrm{d}\, c_{\mathrm{B}}}{\mathrm{d}\, \tau} = k_3 c_{\mathrm{A}^*}\,. \tag{9.143}$$

The concentrations of activated molecules are determined using Bodenstein's principle:

$$\frac{\mathrm{d}\, c_{\mathrm{A}^*}}{\mathrm{d}\, \tau} = k_1 c_{\mathrm{A}}^2 - k_2 c_{\mathrm{A}^*} c_{\mathrm{A}} - k_3 c_{\mathrm{A}^*} = 0 \quad \Longrightarrow \quad c_{\mathrm{A}^*} = \frac{k_1 c_{\mathrm{A}}^2}{k_3 + k_2 c_{\mathrm{A}}}\,. \tag{9.144}$$

By substituting the concentrations of activated molecules from (9.144) into (9.143) we obtain the resulting kinetic equation

$$\frac{\mathrm{d}\, c_{\mathrm{B}}}{\mathrm{d}\, \tau} = \frac{k_1 k_3 c_{\mathrm{A}}^2}{k_3 + k_2 c_{\mathrm{A}}}\,. \tag{9.145}$$

From the form of the kinetic equation it is obvious that the reaction A → B is not a simple reaction [see **9.1.3**]. At low concentrations of the substance A, when $k_2 c_A \ll k_3$, equation (9.145) rearranges to a second-order equation

$$\frac{\mathrm{d}\, c_B}{\mathrm{d}\, \tau} = \frac{k_1 k_3}{k_2} c_A \,.$$

while at high concentrations or high values of k_2, when $k_2 c_A \gg k_3$, equation (9.145) rearranges to a first-order equation

$$\frac{\mathrm{d}\, c_B}{\mathrm{d}\, \tau} = \frac{k_1 k_3}{k_2} c_A \,.$$

9.5.7 Pre-equilibrium principle

Let us consider the reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$$

and its mechanism as a sequence of reactions

$$\mathrm{A} + \mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{X}\,,$$

$$\mathrm{X} \xrightarrow{k_3} \mathrm{C}\,,$$

where X is an unstable intermediate of the reaction. The rate of formation of substance C is determined by the kinetic equation

$$\frac{\mathrm{d}\, c_C}{\mathrm{d}\, \tau} = k_3 c_X \,, \tag{9.146}$$

where c_X is the concentration of the unstable intermediate, which mostly cannot be obtained experimentally. If the rate of X decomposition into the product C is much lower than the rate of formation of X and its decomposition into the reactants A and B, i.e. if $k_3 \ll k_2$ and $k_3 \ll k_1$, we may approximate the concentration c_X using the relation

$$K = \frac{c_X}{c_A c_B} \,, \tag{9.147}$$

where K is the equilibrium constant of formation of the intermediate. This relation is a mathematical expression of the assumption of pre-equilibrium. Combining equations (9.146) and (9.147) yields

$$\frac{\mathrm{d}\, c_\mathrm{C}}{\mathrm{d}\, \tau} = k_3 K c_\mathrm{A} c_\mathrm{B}\,. \tag{9.148}$$

9.5.8 Mechanism of some third-order reactions

If the third-order reaction (second-order with respect to A and first-order with respect to B)

$$2\,\mathrm{A} + \mathrm{B} \;\rightarrow\; 2\,\mathrm{C} \tag{9.149}$$

were trimolecular [see **9.5.1**], there would have to be two molecules of substance A and one molecule of substance B coming into contact. However, a collision of three molecules is a rare event. Consequently, a mechanism has been suggested explaining some reactions of the type (9.149) as a sequence of bimolecular reactions

$$2\,\mathrm{A} \;\overset{k_1}{\rightarrow}\; \mathrm{A}_2\,, \quad \mathrm{A}_2 \;\overset{k_2}{\rightarrow}\; 2\,\mathrm{A}\,, \quad \mathrm{A}_2 + \mathrm{B} \;\overset{k_3}{\rightarrow}\; 2\,\mathrm{C}\,. \tag{9.150}$$

The rate of formation of the product is

$$\frac{\mathrm{d}\, c_\mathrm{C}}{\mathrm{d}\, \tau} = k_3 c_{\mathrm{A}_2} c_\mathrm{B}\,. \tag{9.151}$$

Provided that the pre-equilibrium principle (see the preceding subsection) applies for the intermediate A_2, its concentration is given by the relation

$$\frac{c_{\mathrm{A}_2}}{c_\mathrm{A}^2} = \frac{k_1}{k_2} = K\,. \tag{9.152}$$

Substituting into relation (9.151) for c_{A_2} from (9.152) leads us to

$$\frac{\mathrm{d}\, c_\mathrm{C}}{\mathrm{d}\, \tau} = k_3 K c_\mathrm{A}^2 c_\mathrm{B}\,. \tag{9.153}$$

Example

The above mechanism is used to explain the oxidation of nitrogen oxide to nitrogen dioxide

$$2\,\mathsf{NO} + \mathsf{O}_2 \rightarrow 2\,\mathsf{NO}_2,$$

which is a third-order reaction. Write the mechanism of the reaction, find out which substance is the intermediate, and what has to apply for the rate constants of the partial reactions in order that we could calculate the concentration of the intermediate from relation (9.152).

Solution

The oxidation mechanism is

$$\begin{aligned} 2\,\mathsf{NO} &\rightleftharpoons \mathsf{N}_2\mathsf{O}_2\,, \\ \mathsf{N}_2\mathsf{O}_2 + \mathsf{O}_2 &\rightarrow 2\,\mathsf{NO}_2\,. \end{aligned}$$

The intermediate of the reaction is nitrogen oxide dimer N_2O_2. Relation (9.152) is based on the assumption of pre-equilibrium, see the preceding section. In this case it is assumed that the dimerization of nitrogen oxide quickly reaches the state of thermodynamic equilibrium, and that the dimer oxidation to nitrogen dioxide is relative slow, i.e. $k_3 \ll k_1$ and $k_3 \ll k_2$.

9.5.9 Chain reactions

Chain reactions are complex consecutive reactions characterized by a cyclic consumption and formation of reactive intermediates, most often radicals. We distinguish three stages of a chain reaction:

a) **Initiation** or formation of reactive intermediates. Usually it occurs when the reactants are heated (thermal initiation) or irradiated (photoinitiation).

b) **Propagation**. This is a cyclically proceeding reaction or a sequence of reactions (cycle). We distinguish:

   - Unbranched-chain reactions, in which the same number of reactive intermediates is formed as consumed in the course of the cycle.

  - Branched-chain reactions, in which more reactive intermediates are formed than consumed in the course of the cycle.

c) **Termination** or end of reaction during which the reactive intermediates cease to exist in consequence of either their mutual reaction or their adsorption on the walls of the containing vessel.

Kinetic chain length is the number of cycles in the stage of propagation induced by one reactive intermediate.

> *Note:* In branched-chain reactions, the reaction in the stage of propagation permanently accelerates. If its termination is not sufficiently fast, the reaction ends up in an explosion. The reaction
>
> $$\mathrm{H_2} + \frac{1}{2}\,\mathrm{O_2} \rightarrow \mathrm{H_2O}$$
>
> may serve as an example of an explosive reaction of this type.
> Another type of explosion is thermal explosion in which the heat evolved by an exothermic reaction increases temperature and consequently also the rate of reaction.

An example of an unbranched-chain reaction is hydrogen burning in chlorine with hydrogen chloride formed.

$$\mathrm{H_2} + \mathrm{Cl_2} \rightarrow 2\,\mathrm{HCl}\,.$$

The reaction is initiated thermally

$$\mathrm{Cl_2} \rightarrow 2\,\mathrm{Cl}^{\bullet}\,.$$

(Analogous dissociation of the hydrogen molecule does not occur; it is substantially more energy-consuming.) One propagation cycle is comprised of two reactions

$$\mathrm{Cl}^{\bullet} + \mathrm{H_2} \rightarrow \mathrm{HCl} + \mathrm{H}^{\bullet}\,,$$
$$\mathrm{H}^{\bullet} + \mathrm{Cl_2} \rightarrow \mathrm{HCl} + \mathrm{Cl}^{\bullet}\,.$$

The number of these cycles, or the kinetic chain length is approx. 10^6. One chlorine radical yields millions of hydrogen chloride molecules! The step

$$2\,\mathrm{Cl}^{\bullet} \rightarrow \mathrm{Cl_2}\,.$$

terminates this reaction.

9.5.10 Radical polymerization

Radical polymerization is a special case of a chain reaction in which a monomer molecule M reacts with a polymer radical $\mathrm{M}_n^{\bullet}$,whose chain permanently grows. In the stage of propagation, the following reactions take place

$$\begin{aligned} \mathrm{M}^{\bullet} + \mathrm{M} &\rightarrow \mathrm{M_2}^{\bullet}\,, \\ \mathrm{M_2}^{\bullet} + \mathrm{M} &\rightarrow \mathrm{M_3}^{\bullet}\,, \\ &\vdots \\ \mathrm{M_n}^{\bullet} + \mathrm{M} &\rightarrow \mathrm{M_{n+1}}^{\bullet}\,. \end{aligned} \tag{9.154}$$

9.5.11 Photochemical reactions

Photochemical reactions are initiated by electromagnetic radiation. This type of reactions comprises photosynthesis, the reaction causing the tanning of the skin during sunbathing, photographic processes, and a number of organic syntheses.

9.5.11.1 Energy of a photon ϵ

The Planck relation applies for this energy

$$\epsilon = h\nu = h\frac{c}{\lambda} = hc\tilde{\nu}\,, \tag{9.155}$$

where h is the Planck constant, c is the light velocity, ν is the frequency, λ is the wave length, and $\tilde{\nu}$ is the radiation wavenumber.

Example

Light of the wave length $\lambda = 299.3$ nm was supplied to a system. The system absorbed 10 J of energy. How many photons were absorbed?

Solution

The energy of one photon was

$$\epsilon = hc/\lambda = 6.626 \cdot 10^{-34} \cdot 2.993 \cdot 10^{8}/(299.3 \cdot 10^{-9}) = 6.626 \cdot 10^{-19}\ \mathsf{J}\,.$$

The number of the absorbed photons was

$$N = \frac{10}{\epsilon} = \frac{10}{6.626 \cdot 10^{-19}} = 1.509 \cdot 10^{19}\,\mathsf{photons}\,.$$

9.5.11.2 Quantum yield of reaction

is defined by the relation

$$\phi = \frac{\text{number of molecules changed}}{\text{number of photons absorbed}}\,. \tag{9.156}$$

In simple reactions the quantum yield is in the interval $\phi \in [0, 1]$. In chain reactions, if a photon initiates the formation of a radical, it may be $\phi > 1$.

9.5.11.3 Rate of a photochemical reaction

The rate of reaction of the type

$$\mathrm{A} + \text{photon} \xrightarrow{k} \mathrm{B} \tag{9.157}$$

is

$$\frac{\mathrm{d}\,c_{\mathrm{B}}}{\mathrm{d}\,\tau} = kI_{\mathrm{abs}}\,, \tag{9.158}$$

where I_{abs} is the energy absorbed per unit time in unit volume.

9.6 Temperature dependence of the rate of a chemical reaction

The rate of reaction depends on temperature via the rate constant. In a simple reaction, both the rate constant and the rate of reaction increase with temperature. The rate of parallel and consecutive reactions also increases with temperature. In reactions proceeding by more complex mechanisms, the rate may decrease with temperature.

Example

When does the rate of formation of a product proceeding according to the Lindemann mechanism [see 9.5.6] decrease with increasing temperature?

Solution

The rate is given by the kinetic equation (9.145)

$$\frac{\mathrm{d}\,c_\mathrm{B}}{\mathrm{d}\,\tau} = \frac{k_1 k_3}{k_3 + k_2 c_\mathrm{A}}\, c_\mathrm{A}^2 \,.$$

When the temperature is raised, all the three rate constants k_1, k_2, k_3 will increase. However, the overall rate of reaction will decrease if the denominator in the kinetic equation increases more than the numerator.

9.6.1 Van't Hoff rule

With the temperature raised by 10°C, the rate of a chemical reaction increases 1.5- to 3-times. This qualitative rule often allows for distinguishing chemical reactions from physical processes and from biochemical reactions proceeding in living organisms. If the rate of reaction obeys the van't Hoff rule, it is highly probable that the reaction in question is chemical. If, on the contrary, the rate of reaction increases substantially less, the studied process is most likely of a physical nature. This may be, e.g., gas diffusion or adsorption on a solid surface. A typical physical process is a radioactive decay where the rate does not depend on temperature at all. However, this may be also a chemical reaction with a more complex mechanism (see the example in the preceding section). If a reaction ceases to proceed above a certain limit when the temperature increases, it is highly probable that it is a reaction mediated by living organisms decaying at higher temperatures. Fermentation is a typical example of such a reaction.

9.6.2 Arrhenius equation

For the dependence of the rate constant on temperature, Arrhenius suggested the relation

$$k = A\mathrm{e}^{-E^*/(\boldsymbol{R}T)}\,, \tag{9.159}$$

where A and E^* are constants independent of temperature. The constant A is called the pre-exponential factor, constant E^* is the activation energy. The constant A is always positive, the activation energy is positive in simple reactions (the rate constant increases with temperature). In radioactive decays, $E^* = 0$ because in this case the rate constant does not depend on temperature [see **9.6.1**].

If we know the values of the rate constant at two temperatures, we can determine A and E^* from the equations

$$E^* = \boldsymbol{R}\frac{T_2 T_1}{T_2 - T_1}\ln\frac{k(T_2)}{k(T_1)}\,, \quad A = k(T_1)\mathrm{e}^{E^*/(\boldsymbol{R}T_1)}\,. \tag{9.160}$$

Note: If we know the values of the rate constant at more temperatures, we determine A and E^* using the least squares method. This procedure is more reliable than the use of equations (9.160).

In reversible reactions the difference between the activation energy of the direct reaction $\overrightarrow{E}^*$ and that of the reverse reaction $\overleftarrow{E}^*$ equals the internal energy of reaction

$$\Delta_\mathrm{r} U = \overrightarrow{E}^* - \overleftarrow{E}^*\ . \tag{9.161}$$

Example

For the decomposition of acetone

$$\mathrm{CH_3COCH_3 \rightarrow CH_2{=}CO + CH_4}$$

we know the values of the pre-exponential factor $A = 1.5 \times 10^{15}\,\mathrm{s}^{-1}$ and the activation energy $E^* = 286.6\ \mathrm{kJ\,mol^{-1}}$. Calculate the rate constant of this reaction at temperature $T = 850\,\mathrm{K}$.

Solution

Substituting into relation (9.159) yields

$$k = 1,5 \cdot 10^{15} \mathrm{e}^{-286600/(8.314 \cdot 850)} = 3.657 \cdot 10^{-3}\ \mathsf{s}^{-1}\,.$$

9.6.3 Collision theory

The collision theory was suggested for the calculation of the rate of reactions in the gas phase. In this theory the reacting molecules are modelled using hard spheres. It is assumed that the rate of reaction equals the number of collisions between molecules per unit time multiplied by the probability that the collision will result in a reaction. It may be deduced that the number of collisions is proportional to the concentrations of the reactants and to the root of temperature. The probability that the reaction will take place is approximated by the term $\exp[-E^*/(\boldsymbol{R}T)]$, where E^* is the lowest value of energy sufficient for the reaction to take place.

For the temperature dependence of the rate constant it follows from the collision theory that

$$k = A\sqrt{T}\mathrm{e}^{-B/T}\,, \tag{9.162}$$

where A and B are constants.

9.6.4 Theory of absolute reaction rates

The theory of absolute reaction rates (also called the "activated-complex theory" or the "transition-state theory") is an attempt at theoretical modelling of an elementary reaction. It assumes that the molecules of reactants approach each other and form an unstable formation called the **activated complex**. This complex can either decompose back to the reactants, or it can change into the reaction products. In the model it is assumed that the activated complex is in the state of pre-equilibrium with the reactants [see section **9.5.7**]. The model may be symbolically described using the sequence of "reactions"

$$\text{reactants} \rightleftharpoons \text{activated complex} \rightarrow \text{products}\,, \tag{9.163}$$

For the temperature dependence of the reaction rate constant (9.163) we then have

$$k = (c^{\mathrm{st}})^{(n-1)} \frac{\boldsymbol{R}T}{N_A h} \, \mathrm{e}^{\frac{\Delta S^\#}{\boldsymbol{R}}} \, \mathrm{e}^{-\frac{\Delta H^\#}{\boldsymbol{R}T}} \,, \tag{9.164}$$

where $c^{\mathrm{st}} = 1\ \mathrm{mol\,dm^{-3}}$ is the standard concentration, n is the order of reaction, N_A is the Avogadro constant, and h is the Planck constant. The activation enthalpy $\Delta H^\#$ and the activation entropy $\Delta S^\#$ are the reaction enthalpy and reaction entropy of a hypothetical chemical reaction reactants $\rightleftharpoons$ activated complex. In the first approximation they are considered independent of temperature.

Example

The reaction

$$2\,\mathrm{HI} \rightarrow \mathrm{H_2} + \mathrm{I_2}$$

was studied at two temperatures. At $T_1 = 556$ K, the rate constant $k_1 = 3.517 \times 10^{-7}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$, and at $T_2 = 781$ K , the rate constant $k_2 = 3.954 \times 10^{-2}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$. Calculate the values of $\Delta H^\#$ and $\Delta S^\#$.

Solution

We take the logarithm of equation (9.164) and substitute for T_i, k_i

$$\begin{aligned}\ln k_1 &= \ln\left(\frac{\boldsymbol{R}T_1c^{\mathrm{st}}}{N_Ah}\right) + \frac{\Delta S^{\#}}{\boldsymbol{R}} - \frac{\Delta H^{\#}}{\boldsymbol{R}T_1}\,,\\ \ln k_2 &= \ln\left(\frac{\boldsymbol{R}T_2c^{\mathrm{st}}}{N_Ah}\right) + \frac{\Delta S^{\#}}{\boldsymbol{R}} - \frac{\Delta H^{\#}}{\boldsymbol{R}T_2}\,.\end{aligned}$$

The solution of this set of two equations for two unknowns is

$$\Delta H^{\#} = \boldsymbol{R}\frac{T_1T_2}{T_2-T_1}\ln\frac{T_1k_2}{T_2k_1} = 8.314\frac{556\cdot 781}{781-556}\ln\frac{556\cdot 3.954\cdot 10^{-2}}{781\cdot 3.517\cdot 10^{-7}} = 181\,160\ \mathsf{J\,mol^{-1}}\,,$$

$$\begin{aligned}\Delta S^{\#} &= \frac{\Delta H^{\#}}{T_1} + \boldsymbol{R}\ln\frac{k_1N_Ah}{\boldsymbol{R}T_1c^{\mathrm{st}}} =\\ &= \frac{181\,160}{556} + 8.314\ln\frac{3.517\cdot 10^{-7}\cdot 6.022\cdot 10^{23}\cdot 6.626\cdot 10^{-34}}{8.314\cdot 556\cdot 1} =\\ &= -47.814\ \mathsf{J\,mol^{-1}\,K^{-1}}\,.\end{aligned}$$

9.6.5 General relation for temperature dependence of the rate constant

The temperature dependence of the rate constant may be written in the form

$$k = a\,T^b\,\mathrm{e}^{-c/T}\,. \tag{9.165}$$

The relations discussed in the preceding sections are special cases of this dependence. For $b = 0$ we obtain the Arrhenius equation (9.159), where $a = A$ and $c = E^*/\boldsymbol{R}$. For $b = 1/2$ we obtain the relation (9.162) from the collision theory, where $a = A$ and $c = B$. For $b = 1$ we obtain the relation (9.164) from the absolute-rates theory, where $a = (c^{\mathrm{st}})^{(n-1)}\frac{\boldsymbol{R}}{N_Ah}\exp(\Delta S^{\#}/\boldsymbol{R})$ and $c = \Delta H^{\#}/\boldsymbol{R}$.

In practice, the Arrhenius equation is used most often. The more general relation (9.165) with adjustable values of the constants a, b, c is used in the case of a broad temperature range and for complex reactions. The relation derived from the collision theory is used rarely. The relation following from the absolute-rates theory is applied primarily in theoretical chemical kinetics.

Note: If none of these relations is able to describe the experimental dependence of the rate constant on temperature well, then either the reaction is not a chemical reaction or its mechanism is more complicated or the experimental data are faulty.

9.7 Chemical reactors

A chemical reactor is a device, most often industrial, in which a chemical reaction takes place.

9.7.1 Types of reactors

Based on the way of the reactants transport, we distinguish the following types of reactors:

a) **Batch reactors**—reactants are put in the reactor of a fixed volume (autoclave, beaker) and products are withdrawn after the reaction is terminated.

b) **Flow reactors**—reactants enter the reactor and products (more accurately a mixture of products and reactants) are withdrawn continuously. Flow reactors are further classified as:

   - **plug flow reactors**—the reactants flow laminarly, the concentration of the products changes with their position (it is zero at the entry and the highest at the exit);
   - **stirred flow reactors**—the concentration of the reactants is the same in all parts of the reactor.

Based on the thermodynamic conditions under which the reaction takes place, we distinguish the following three types of chemical reactors:

- isothermal,
- adiabatic,
- polytropic.

9.7.2 Batch reactor

Here we are interested in the relations between the reactor volume V, the amount of substance of the product n_p, and the reaction time τ. The ratio of the amount of substance and volume is the concentration, $c_p = n_P/V$. The relations between the concentrations of the reactants and time—integrated forms of kinetic equations—were discussed in sections **9.2**, **9.4** and **9.5**.

Example

A first-order reaction $\mathrm{A} \xrightarrow{k} \mathrm{P}$, where $k = 0.1$ hour^{-1}, proceeds in a batch reactor. The initial concentration of the reactant is $c_{\mathrm{A}0} = 2.6$ mol dm^{-3}. The reaction terminates when the concentration of the substance A falls to $c_{\mathrm{A}} = 0.1$ mol dm^{-3}. A total of $n_{\mathrm{P}} = 250$ moles of the product is to be produced. What must be the reactor volume and how long will the reaction proceed?

Solution

$$c_{\mathrm{P}} = c_{\mathrm{A}0} - c_{\mathrm{A}} = 2.5\,\mathrm{mol\,dm^{-3}} \quad \Longrightarrow \quad V = n_{\mathrm{P}}/c_{\mathrm{P}} = 250/2.5 = 100\ \mathrm{dm}^3\,.$$

The reaction time will be calculated from equation (9.24)

$$\tau = \frac{1}{k} \ln \frac{c_{\mathrm{A}0}}{c_{\mathrm{A}}} = \frac{1}{0.1} \ln \frac{2.6}{0.1} = 32.58 \text{ hours.}$$

9.7.3 Flow reactor

If the reacting mixture flows through the reactor at a constant flow (volume rate), we have

$$\frac{\mathrm{d}\,V}{\mathrm{d}\,\tau} = F\,, \tag{9.166}$$

where F is the **feed**, i.e. the volume of reactants entering the reactor per unit time. By integrating this relation we obtain

$$\tau_r = \frac{V_r}{F}\,, \tag{9.167}$$

where τ_r is the **residence time**, i.e. the time in which the reacting mixture passes through the reactor, and V_r is the reactor volume.

Note: Relation (9.167) and the relations ensuing from it do not apply if the total amount of substance changes in the course of the reaction.

Example

Every hour, two trucks loaded with clay bricks enter a brick kiln and two trucks loaded with burnt bricks leave it. The kiln can hold a total of 100 trucks. What is the truck's residence time in the kiln?

Solution

The process can be modelled using a plug flow reactor. The "feed" is $F = 2$ trucks/hour, and the "volume" is V = 100 trucks. We apply relation (9.167) to obtain

$$\tau_r = \frac{100}{2} = 50 \text{ hours}\,.$$

From the definition of the reaction rate (9.4), from the general reaction (9.1), and from the relation (9.166) it follows that

$$\frac{1}{\nu_i}\frac{\mathrm{d}\,c_i}{\mathrm{d}\,V} = \frac{r}{F}\,. \tag{9.168}$$

From this we obtain a relation for the reactor volume

$$V_r = \frac{1}{\nu_i} F \int_{c_{i0}}^{c_i} \frac{\mathrm{d}\,c_i}{r}\,, \tag{9.169}$$

where c_i in the upper limit of the integral is the concentration of the chosen component i at the exit from the reactor.

Example

Derive the relation for the volume of a reactor in which a first-order reaction $\mathrm{A} \xrightarrow{k} \mathrm{P}\,.$ proceeds.

Solution

The rate of a first-order reaction is $r = kc_{\mathrm{A}}$. We substitute it into (9.169) and integrate

$$V_r = \frac{1}{-1} F \int_{c_{\mathrm{A0}}}^{c_{\mathrm{A}}} \frac{\mathrm{d}\,c_{\mathrm{A}}}{kc_{\mathrm{A}}} = \frac{F}{k} \ln \frac{c_{\mathrm{A0}}}{c_{\mathrm{A}}}\,.$$

In a stirred flow reactor the concentrations of the reactants and the reaction rate are constant. Equation (9.169) thus simplifies to

$$V_r = \frac{1}{\nu_i}\frac{F}{r}(c_i - c_{i0})\,. \tag{9.170}$$

Note: A stirred flow reactor can be used as a source of direct experimental data on reaction rates. The rate is calculated from (9.170) if we know the reactor volume, the feed, the initial and current composition. Compare with the Note in **9.3.3**.

Example

A first-order reaction $\mathrm{A} \xrightarrow{k} \mathrm{P}$, where $k = 0.1$ hour^{-1}, is under way. The initial concentration of the reactant is $c_{\mathrm{A0}} = 2.6\,\mathrm{mol\,dm^{-3}}$, the final concentration is $c_{\mathrm{A}} = 0.1\,\mathrm{mol\,dm^{-3}}$. A total of $n_{\mathrm{P}} = 250$ mol of the product is to be produced in 32.57 hours. Compare the volume of a plug flow reactor, a stirred flow reactor, and a batch reactor which would be needed for the production of the given amount of the product.

Solution

The specification for the batch reactor is the same as in the Example in **9.7.2**. The volume of the batch reactor is 100 cm^3.

For the flow reactors we first calculate the feed. From the material balance we have

$$F = \frac{1}{\tau}\frac{n_p}{c_{\mathrm{A0}} - c_{\mathrm{A}}} = \frac{1}{32.57}\frac{250}{2.6 - 0.1} = 3.07\,\mathsf{dm}^3\,\mathsf{hr}^{-1}.$$

The volume of the stirred flow reactor will be calculated from (9.170)

$$V_r = \frac{1}{\nu_{\mathrm{A}}}\frac{F}{kc_{\mathrm{A}}}(c_{\mathrm{A}} - c_{\mathrm{A0}}) = \frac{1}{-1}\;\frac{3.07}{0.1\cdot 0.1}(0.1 - 2.6) = 767.5\ \mathsf{dm}^3\,.$$

The volume of the plug flow reactor will be calculated from (9.169)

$$V_r = \frac{F}{k}\ln\frac{c_{\mathrm{A0}}}{c_{\mathrm{A}}} = \frac{3.07}{0.1}\ln\frac{2.6}{0.1} = 100\ \mathsf{dm}^3\,.$$

The volumes of the batch and plug flow reactors are the same, the volume of the stirred flow reactor is more than seven-times higher.

9.8 Catalysis

9.8.1 Basic terms

A **catalyst** is a substance whose presence changes the mechanism and consequently also the rate of a chemical reaction. It is not consumed by the reaction but it leaves it unchanged, i.e. in the same state of matter, or in the same crystalline modification in the case of a solid catalyst. The catalyst does not change the composition of an equilibrium mixture.

> *Note:* The last assertion is not entirely true. A catalyst in a larger amount may act as an inert substance [see chapter Chemical equilibrium], and its presence changes the activities of the reactants.

Autocatalysis is a process during which the products of a reaction catalyze its course. An example of autocatalysis is the oxidation of oxalic acid by permanganate ions in an acidic environment

$$5\,(\mathrm{COOH})_2 + 2\,\mathrm{MnO_4}^- + 6\,\mathrm{H}^+ \;\rightarrow\; 8\,\mathrm{H_2O} + 10\,\mathrm{CO_2} + 2\,\mathrm{Mn}^{2+}\,,$$

catalyzed by manganous ions. The initial course of the reaction is very slow, but as soon as a certain amount of Mn^{2+} ions is formed, the rate of reaction increases many times.

Catalysis may be **homogeneous**, in which case the catalyst is in the same phase (gas or liquid) as the reactants (substances participating in the reaction), and **heterogeneous**, in which case the catalyst is usually in the solid phase and the reactants are either gaseous or liquid. **Enzyme catalysis** is a special case in which the catalyst is an enzyme, a (macromolecular) protein whose dimensions are 10 to 100 nm.

9.8.2 Homogeneous catalysis

The reaction A + B → P proceeds in the presence of catalyst K by the following mechanism:

$$\begin{aligned} \mathrm{A} + \mathrm{K} \quad &\underset{k_2}{\overset{k_1}{\rightleftarrows}} \quad X\,, \\ X + \mathrm{B} \quad &\overset{k_3}{\rightarrow} \quad \mathrm{K} + \mathrm{P}\,. \end{aligned}$$

Substance X is an intermediate for which the Bodenstein principle applies [see **9.5.5**]

$$\frac{\mathrm{d}\, c_X}{\mathrm{d}\, \tau} = k_1 c_\mathrm{A} c_\mathrm{K} - k_2 c_X - k_3 c_X c_\mathrm{B} = 0 \quad \Longrightarrow \quad c_X = \frac{k_1}{k_2 + k_3 c_\mathrm{B}} c_\mathrm{A} c_\mathrm{K} \,.$$

For the rate of formation of product P we have the kinetic equation

$$\frac{\mathrm{d}\, c_\mathrm{P}}{\mathrm{d}\, \tau} = k_3 c_X c_\mathrm{B} = \frac{k_1 k_3}{k_2 + k_3 c_\mathrm{B}} c_\mathrm{A} c_\mathrm{K} c_\mathrm{B} \,, \tag{9.171}$$

from which it follows that the rate of reaction is directly proportional to the catalyst concentration.

Acid-base catalysis is a special case of homogeneous catalysis in which reactions in aqueous solutions are catalyzed by H_3O^+ and OH^- ions.

9.8.3 Heterogeneous catalysis

The reversible reaction

$$\text{reactants} \rightleftharpoons \text{products}\,,$$

during which the reactants are in the gas or liquid phase and the catalyst is in the solid phase, can be divided into the following five consecutive processes:

1. Transport of the reactants toward the catalyst surface.
2. Adsorption of the reactants on the catalyst surface.
3. Chemical reaction on the catalyst surface.
4. Desorption of the products from the catalyst surface.
5. Transport of the product from the catalyst surface.

The description of the whole process can be simplified by writing a kinetic equation solely for the rate-determining process and considering the other processes to be equilibrium. In consecutive processes, the slowest process is the rate-determining process [see **9.5.4**]. It is usually a chemical reaction.

9.8.3.1 Transport of reactants

Starting substances are transported toward the surface and products from the surface by way of **diffusion**. If the diffusion is faster than adsorption (desorption) and chemical reaction, it is not the rate-determining process. If the diffusion is slow, the transport may be accelerated by mixing.

9.8.3.2 Adsorption and desorption

These processes are considered to be in equilibrium and they are discussed in chapter Physical chemistry of surfaces.

9.8.3.3 Chemical reaction

Let's assume the following reaction taking place on the catalyst surface

$$\mathrm{A} \underset{k_\mathrm{B}}{\overset{k_\mathrm{A}}{\rightleftarrows}} \mathrm{B}$$

The rate of the reaction is given by the kinetic equation

$$-\frac{\mathrm{d}\,\theta_\mathrm{A}}{\mathrm{d}\,\tau} = k_\mathrm{A}\theta_\mathrm{A} - k_\mathrm{B}\theta_\mathrm{B}\,, \tag{9.172}$$

where θ_i is the surface concentration of substance i. Surface concentrations may be determined e.g. from the Langmuir adsorption isotherm, see equations (13.39).

> *Note:* The only difference between kinetic equations for reactions on the surface of the solid phase and common kinetic equation is that in the former case we write surface concentrations, i.e. amounts of substance, related to unit surface.

9.8.4 Enzyme catalysis

The Michaelis-Menten mechanism models the reaction of a reactant (substrate) S to product P amid the catalytic effect of enzyme E in the following way

$$\mathrm{E} + \mathrm{S} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{ES} \xrightarrow{k_3} \mathrm{E} + \mathrm{P}\,, \tag{9.173}$$

where ES is a complex of the enzyme with the substrate. It is assumed that the concentration of the enzyme-substrate complex, ES, does not vary with time (steady state principle, see **9.5.5**), i.e. that

$$\frac{\mathrm{d}\ c_{\mathrm{ES}}}{\mathrm{d}\ \tau} = k_1 c_{\mathrm{E}} c_{\mathrm{S}} - k_2 c_{\mathrm{ES}} - k_3 c_{\mathrm{ES}} = 0\,.$$

From this we obtain

$$c_{\mathrm{ES}} = \frac{k_1}{k_2 + k_3} c_{\mathrm{E}} c_{\mathrm{S}}\,.$$

The kinetic equation of the product formation is

$$\frac{\mathrm{d}\,c_{\mathrm{P}}}{\mathrm{d}\,\tau} = \frac{k_3 k_1}{k_2 + k_3} c_{\mathrm{E}} c_{\mathrm{S}} = \frac{k_3 c_{\mathrm{E0}} c_{\mathrm{S}}}{K_M + c_{\mathrm{S}}}\,, \tag{9.174}$$

where $c_{\mathrm{E0}} = c_{\mathrm{E}} + c_{\mathrm{ES}}$ is the initial concentration of the enzyme and $K_{\mathrm{M}} = \dfrac{k_3 + k_2}{k_1}$ is the **Michaelis constant**.

Chapter 10

Transport processes

This chapter deals with thermal conductivity, viscosity and diffusion. All these phenomena relate to the transport of a certain physical quantity in a system. Diffusion involves mass transport from one part of a system to another; viscosity concerns the transfer of molecules momentum in flowing gas or liquid; thermal conductivity relates to transport of molecules thermal energy.

10.1 Basic terms

10.1.1 Transport process

In a system which is not in the state of thermodynamic equilibrium, spontaneous processes occur under unchanging external conditions which in the end lead to equilibrium [see 1.4.1, 1.4.2, 1.4.4]. During a transport process the value of the observed quantity changes with time at a certain location in the system. The observed quantity may be amount of substance, energy or momentum.

Example

Let us have a metal rod. One end of this rod has an initial temperature of 1000 K and the other 300 K. The rod is not at thermal equilibrium—its temperature is different at different positions. The system undergoes transition to the state of equilibrium during which its temperature changes with time at every location. As the temperatures equalize, energy is transported from areas with a higher temperature to those with a lower temperature.

Note: Processes in which transition to equilibrium is accelerated by external disturbances, e.g. by stirring, are not considered transport processes.

10.1.2 Flux and driving force

The flux J_z in the direction of axis z is defined as the amount of a certain quantity X which passes through unit area perpendicular to this axis per unit time

$$J_z = \frac{1}{S}\,\frac{\mathrm{d}X}{\mathrm{d}\tau}\,. \tag{10.1}$$

In general, the flux is a vector with components $(J_x,\ J_y,\ J_z)$ in the direction of axes x, y, z.

The flux in the direction of axis z is caused by the **driving force** $\mathcal{F}_z$. Driving force means a change of an intensive quantity with location (this quantity will be the same everywhere in the system after equilibrium is attained). To be more precise, if we denote the intensive quantity using the symbol Y, the driving force in the direction of the axis z will be equal to the derivative

$$\mathcal{F}_z = \frac{\mathrm{d}Y}{\mathrm{d}z}\,. \tag{10.2}$$

Note: The term *driving force* indicates that the quantity $\mathcal{F}_z$ should have the physical meaning of strength. This, however, is not always so.

In general, driving force is a gradient of the quantity Y, i.e. a vector with components $(\mathcal{F}_x, \mathcal{F}_y, \mathcal{F}_z)$ in the direction of axes x, y, z.

Example

In the preceding example, the flux was the amount of heat, related to unit cross-section of the rod, which passed through a given location per unit time. Heat was the intensive quantity Y, the change of temperature with location, or more accurately $\frac{\mathrm{d}T}{\mathrm{d}z}$, was the driving force.

10.1.3 Basic equations of transport processes

It is postulated that the flux is proportional to the driving force

$$J_z = -C\,\mathcal{F}_z\,, \tag{10.3}$$

where the proportionality constant C depends on temperature, pressure, and in mixtures also on composition. This postulate is usually fulfilled well. Deviations from proportionality may be observed only in some materials or in the states very far from equilibrium.

Relation (10.3) is used when the flux occurs in only one direction (e.g. through a rod), or in isotropic situations, i.e. when all directions are equivalent (heat spreading from a point source in a thermally homogeneous environment may serve as an example).

10.2 Heat flow—thermal conductivity

10.2.1 Ways of heat transfer

Heat may be transferred in three ways: by convection, conduction or radiation.

Convection is a heat transfer driven by the transfer of mass. This type of heat transfer occurs in single-storey heating systems in which hot water from a boiler is driven by a pump to the radiators.

Radiation is a heat transfer driven by electromagnetic radiation (photons). This way heat is transferred from the Sun to the Earth.

Conduction is a heat transfer without any mass transferred. In this case the molecules endowed with more energy pass heat to those with less energy. Heat transfer through a wall from a warm room to the colder surroundings may serve as an example.

10.2.2 Fourier's law

For the heat flux, equation (10.1) acquires the form

$$J_z = \frac{1}{S}\frac{\mathrm{d}Q}{\mathrm{d}\tau}\,. \tag{10.4}$$

The heat flow in a system is caused by temperature differences. The driving force is a change of temperature with location, or more accurately the derivative of temperature with respect to location, $\frac{\mathrm{d}T}{\mathrm{d}z}$. The general equation (10.3) becomes

$$\frac{1}{S}\frac{\mathrm{d}Q}{\mathrm{d}\tau} = -\lambda\frac{\mathrm{d}T}{\mathrm{d}z}\,. \tag{10.5}$$

This equation is called the **Fourier's law**. The quantity λ is the **coefficient of thermal conductivity**, or more briefly **thermal conductivity**.

10.2.3 Thermal conductivity

The coefficient of thermal conductivity is the amount of heat that passes through unit surface per unit time at unit temperature gradient. The higher the value of λ, the faster the temperatures in the system equalize, or the faster the given environment conducts heat. Thermal conductivity is a property of material.

U *Main unit:* $\mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}}$.

10.2.3.1 Dependence on state variables

According to kinetic theory, the thermal conductivity in gases at low and medium pressures increases with temperature and does not depend on pressure, see section **10.5.3**, relation (10.22). The behaviour of real gases qualitatively corresponds to kinetic theory results. Only at high pressures the thermal conductivity of gases increases with pressure.

Thermal conductivity of liquids is higher than that of gases. It decreases with temperature and (slightly) increases with pressure.

Thermal conductivity of solids is higher than that of liquids; in metals it is usually higher than in non-metals. Diamond exhibits an anomalously high thermal conductivity.

Example

Let us consider a dual window of an area of $4\,\mathrm{m}^2$. The inside window has the temperature of the room $25\,^\circ\mathrm{C}$, the outside window has a temperature of $-10\,^\circ\mathrm{C}$. The space between the two windows is 20 cm. What is the amount of heat that passes through the air layer between the two windows in one hour? The thermal conductivity coefficient of air under the given conditions is $\lambda = 2.41 \times 10^{-2}\,\mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}}$.

Solution

We use equation (10.5) rewritten into the form

$$\mathrm{d}\,Q = -S\,\lambda \frac{\mathrm{d}T}{\mathrm{d}z}\,d\tau$$

and integrate

$$Q = -S\lambda \frac{\mathrm{d}T}{\mathrm{d}z}\,\tau\,.$$

We estimate the temperature gradient, i.e. the derivative of temperature with respect to location

$$\frac{\mathrm{d}T}{\mathrm{d}z} \doteq \frac{\Delta T}{\Delta z} = \frac{263.15 - 298.15}{0.20} = -175\,\mathsf{K\,m}^{-1}$$

and substitute

$$Q = -4 \times 2.41 \times 10^{-2} \times (-175) \times 3600 = 60732\,\mathsf{J}\,.$$

Note: When solving the above example we neglected the heat conduction through the glass and through the glass-air interface. We assumed that the windows were perfectly sealed, and that the air between the two windows was motionless. We also neglected the heat transfer by convection. This assumption was not fully justified. The cold air at the outer window went down while the warm air at the inside window went up. This air flow could significantly affect the result, i.e. increase the heat transfer.

10.2.4 Fourier-Kirchhoff law

For the dependence of temperature on time τ and location z we use the following partial differential equation

$$\frac{\partial T}{\partial \tau} = \frac{\lambda}{c\,C_{pm}} \frac{\partial^2 T}{\partial z^2}\,, \quad [p] \qquad (10.6)$$

where c is the molar density (see **2.1.1**) and C_{pm} is the molar isobaric heat capacity (see **3.2.4**). If we want to solve this equation we need to know the initial conditions (for $\tau = 0$) and boundary conditions (for $z = 0$). The solution yields temperature as a function of time τ and location z. Specific cases are solved within the course in Chemical Engineering.

10.3 Flow of momentum—viscosity

10.3.1 Newton's law

Let us consider a fluid flowing laminarly through a tube in the direction of axis x. In the middle of the tube, the velocity of the fluid in the direction of the flow is the highest while at the tube walls it is zero. However, the molecules do not travel only in the direction of the flow but also in the perpendicular direction, i.e. from the middle of the tube toward its walls and vice versa, while transporting their momentum. For the flux of momentum it follows from (10.1)

$$J_z = \frac{1}{S}\,\frac{\mathrm{d}p_x}{\mathrm{d}\tau}\,, \tag{10.7}$$

where $p_z = mv_x$ is the momentum component in the direction of the flux, m is the molecule mass, and v_x is the velocity component in the direction of the flux. The driving force is the change of the velocity component in the direction of the flux with the distance z from the middle of the tube, $\frac{\mathrm{d}v_x}{\mathrm{d}z}$. The general equation (10.3) rearranges to

$$\frac{1}{S}\,\frac{\mathrm{d}p_x}{\mathrm{d}\tau} = -\eta\,\frac{\mathrm{d}v_x}{\mathrm{d}z}\,. \tag{10.8}$$

This equation is called **Newton's law**. The quantity η is the **viscosity coefficient**, or briefly **viscosity**.

Note: Fluids obeying equation (10.8) are called the **Newtonian fluids**. There is a large group of substances (macromolecular fluids, suspensions. . .) for which relation (10.8) does not apply, and these are called the **non-Newtonian** fluids. Their study is the focus of *rheology*.

The derivative on the left side of equation (10.8) is the force F_z

$$F_z = -S\,\eta\,\frac{\mathrm{d}v_x}{\mathrm{d}z}\,. \tag{10.9}$$

F_z is called the **internal friction force** (acting on the molecule in the direction of the axis z).

10.3.2 Viscosity

Viscosity is the measure of internal friction between molecules in a flowing fluid. The higher the value of η the slower is the flow of the fluid (under otherwise identical conditions).

U *Main unit:* $\mathrm{kg\,m^{-1}\,s^{-1} = Pa\,s}$.
Older unit: 1 poise (P); $1\ \mathrm{P} = 10^{-1}\,\mathrm{kg\,m^{-1}\,s^{-1}}$; a hundred-times smaller unit, a centipoise, 1 cP = 1 mPa s used to be in common use.

> *Note:* Make sure that you do not confuse the terms viscosity and density. Mercury density is much higher than that of honey or puree. Viscosity of honey or puree, on the contrary, is much higher than that of mercury. Honey or puree would take much longer to flow spontaneously out through a hole in the bottom of a pot as compared with mercury.

10.3.2.1 Dependence on state variables

According to kinetic theory, viscosity in gases at low and medium pressures increases with temperature and does not depend on pressure, see section **10.5.3**, relation (10.21). The description of the viscosity of real gases by kinetic theory is relatively correct.

The viscosity of liquids is higher than that of gases. It increases (slightly) with pressure[1] and decreases with increasing temperature. The following empirical relation is often used for the temperature dependence of viscosity

$$\ln \eta = A - \frac{B}{T}\,, \quad [p] \tag{10.10}$$

where A and B are adjustable constants.

Glass and macromolecular substances exhibit extremely high viscosity. For solid crystalline substances, however, viscosity is effectively infinite.

The most widely spread helium isotope ^{4}He represents a special case. In the range of very low temperatures, 0–2 K and in the pressure range from 0 to about 2.5 MPa, this isotope forms a **superfluid liquid** called **helium II** (helium I is a liquid of common properties, stable at temperatures above 2 K). The viscosity of superfluid helium II is zero; it is the only liquid

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[1] Water is an exception: at low temperatures and moderate pressures, its viscosity decreases with increasing pressure.

without any internal friction. It would flow out through the smallest possible hole in the bottom of a vessel instantaneously.

Note: The ratio of viscosity and density η/ϱ is called the **kinematic viscosity**. In order to distinguish the two, the viscosity η is sometimes called the **dynamic viscosity**.

10.3.3 Poiseuille's equation

Let us consider a fluid flowing laminarly through a tube of diameter r, length L and volume $V = \pi r^2 L$. At its beginning there is pressure p_1 and at its end pressure p_2. For the volume flow rate $\dot{V} \equiv \frac{\mathrm{d}V}{\mathrm{d}\tau}$ we have from (10.9)

$$\dot{V} = \frac{\pi\, r^4}{8\,\eta} \frac{\mathrm{d}p}{\mathrm{d}\ell}\,, \tag{10.11}$$

where $\frac{\mathrm{d}p}{\mathrm{d}\ell}$ is the change of pressure with the distance from the beginning of the tube. By integrating this equation with respect to ℓ and τ, on condition that neither $\dot{V}$ nor η depends on pressure, we obtain **Poiseuille's equation**:

$$V = \frac{\pi\, r^4\,(p_1 - p_2)}{8\,\eta\, L}\,\tau\,, \quad [T, \text{incompressible liquid}] \tag{10.12}$$

If Boyle's law applies for the pressure dependence of the gas volume (fluid is an ideal gas), we obtain by integrating (10.11)

$$V = \frac{\pi\, r^4\,(p_1^2 - p_2^2)}{16\,\eta\, L\, p_0}\,\tau\,, \quad [T, \text{ideal gas}] \tag{10.13}$$

where p_0 is the pressure at which the volume V is measured.

Note: Relations (10.12) and (10.13) are used to measure viscosity. r, L, p_1, p_2 are known, V and τ are measured, η is calculated. Relation (10.12) is suitable for liquids at common temperatures and pressures, relation (10.13) can be used for gases in the temperature and pressure range in which the state equation of an ideal gas applies.

Example

A total of 90.2 cm^3 of air flew through a tube with a length of one metre and a radius of 1 mm in 100 seconds. The pressure at the beginning of the tube was 102 kPa and at its end 101 kPa. The volume was measured at a pressure of 101 kPa. Calculate the viscosity of air at a given temperature.

Solution

Under the given conditions, equation (10.13) can be used for air:

$$\eta = \frac{\pi\, r^4\,(p_1^2 - p_2^2)}{16\, V\, L\, p_0}\,\tau = \frac{3.14 \times (10^{-3})^4\,(102\,000^2 - 101\,000^2)}{16 \times 90.2 \times 10^{-6} \times 1 \times 101\,000}\,100 = 1.8 \times 10^{-5}\,\mathrm{kg\,m^{-1}\,s^{-1}}.$$

10.4 Flow of matter—diffusion

Diffusion is a process during which concentrations are spontaneously equalized in a system with different concentrations. For the sake of simplicity we will deal solely with diffusion in binary mixtures.

10.4.1 Fick's first law of diffusion

The flow of substance is caused by differences in its concentration. The driving force is a change of a component concentration with location, or, to be more precise, a derivative of concentration with respect to location, $\frac{\mathrm{d}c_i}{\mathrm{d}z}$.

In a binary mixture we have

$$\frac{1}{S}\frac{\mathrm{d}n_i}{\mathrm{d}\tau} = -\,D_{ij}\frac{\mathrm{d}c_i}{\mathrm{d}z}\,, \quad i,j = 1,2 \quad [T,p] \tag{10.14}$$

where D_{ij} is the diffusion coefficient of component i in a mixture with component j, while

$$D_{12} = D_{21}\,. \tag{10.15}$$

10.4.2 Diffusion coefficient

The diffusion coefficient gives the number of moles of a given component in a mixture which passes through unit area per unit time at unit concentration gradient of the component.

U *Main unit:* $\mathrm{m}^2\,\mathrm{s}^{-1}$.

10.4.2.1 Dependence on state variables

In gases, the diffusion coefficient increases with temperature and decreases with pressure; according to kinetic theory the diffusion coefficient does not depend on the mixture composition, see section **10.5.3**, equations (10.24) and (10.23).

The diffusion coefficients in liquids are smaller than in gases (diffusion is slower). In solids they are yet smaller than in liquids.

In dilute solutions of component i in solute j the diffusion coefficient may be estimated from the **Einstein relation**

$$D_{ij} = \frac{\boldsymbol{R}T}{6\,\pi\,N_A\,\eta_j\,r_i}\,, \tag{10.16}$$

where η_j is the viscosity of solvent j and r_i is the effective radius of the diffusing molecule i. The relation applies on condition that the radius of diffusing molecules is much larger than the radius of the molecules of the solvent. This relation is typically used for the diffusion of colloid particles in a low-molecular solvent.

10.4.3 Fick's second law of diffusion

The dependence of a component concentration on time and location is described by the partial differential equation

$$\frac{\partial c_i}{\partial \tau} = D_{ij}\frac{\partial^2 c_i}{\partial z^2}\,, \tag{10.17}$$

which is referred to as **Fick's second law of diffusion**. By solving this equation given initial and boundary conditions we may determine the concentration of a substance in dependence on time and location.

> *Note:* Compare relation (10.17) with (10.6). Both partial differential equations have the same form. The Navier-Stokes equations describing fluid flow are more complex.

10.4.4 Self-diffusion

Self-diffusion is a processes during which molecules diffuse in an environment formed by identical molecules. Fick's first and second laws apply for self-diffusion, with the binary diffusion coefficient D_{ij} being replaced with the **self-diffusion coefficient** D.

> *Note:* Strictly speaking, it is impossible to measure self-diffusion because it is impossible to distinguish the diffusing molecules from the molecules of the environment. Self-diffusion is therefore determined using radioactive isotopes of the given substance which are considered identical with non-radioactive isotopes.

10.4.5 Thermal diffusion

Let us consider a mixture of gases in a system with a temperature gradient. The lighter gas diffuses in the direction of increasing temperature and the heavier gas in the direction of decreasing temperature. This phenomenon is called thermal diffusion. It may be used for the separation of gases.

10.5 Kinetic theory of transport processes in dilute gases

Kinetic theory views transport processes as a consequence of processes going on at the molecular level.

10.5.1 Molecular interpretation of transport processes

Thermal conductivity is interpreted as the result of the transport of energy which molecules pass to one another in mutual collisions. Faster molecules, which travel from places with a higher temperature, pass part of their kinetic energy on collision with slower molecules at places with a lower temperature and thus provide for energy transport in the system. The result of these mutual collisions is the equalization of temperatures, i.e. attainment of thermal equilibrium.

Viscosity is the result of the chaotic movement of molecules during which the particles travelling from areas with a higher flow rate of the fluid pass part of their momentum to the slower molecules on collision. This leads to the equalization of the flow rates, which is macroscopically manifested as internal friction in the flowing fluid.

Diffusion is also the result of the chaotic movement of molecules. By random moves the molecules travel from higher-concentration areas to lower-concentration areas. This causes spontaneous equalization of concentrations in the system.

Accuracy of the molecular description of transport processes depends primarily on the accuracy of the model used for the description of forces acting between the molecules. We will present only the two simplest models: an ideal gas and the hard spheres model.

10.5.2 Molecular models

An **ideal gas** is the simplest model of intermolecular forces. It assumes that molecules are mass points which do not interact at all.

This model is not very successful in relation to transport properties—no energy or momentum transport by way of collisions between molecules occurs because the probability of a collision of two mass points is zero. In this case the heat flow is caused solely by molecules collisions with the warmer or colder walls of the containing vessel. The heat flow mechanism is thus radiation rather than conduction.

Note: In literature, we may sometimes encounter the term “Kinetic theory of an ideal gas”. This, however, never relates to an ideal gas but to the hard spheres model.

Hard spheres. The second simplest model is a gas whose molecules are replaced with hard spheres, particles which do not attract each other but cannot permeate each other. This model provides a qualitatively correct description of the behaviour of real gases. In the region of low densities, where collisions between three and more molecules can be neglected, explicit relations for transport quantities can be derived for this model.

10.5.3 Basic terms of kinetic theory

The **collision diameter** σ is the diameter of the range of repulsive forces of a molecule. In the model of an ideal gas it is zero, in the hard spheres model it equals the diameter of the sphere. In real molecules it is determined experimentally. For example, the collision diameter of an argon atom is roughly 3.4×10^{-10} m.

The **mean free path** ℓ is the average distance a molecule travels between two collisions. We have

$$\ell = \frac{1}{\sqrt{2}\,\pi\,\sigma^2\,\mathcal{N}}\,, \tag{10.18}$$

where $\mathcal{N}$ is the number of molecules in unit volume. For an argon atom at a temperature of 273 K and pressure 101 kPa, the mean free path equals approximately 10^{-7} m.

The **collision frequency** Z, the number of collisions made by a single molecule per unit time, is given by the relation

$$Z = \frac{\overline{u}}{\ell} = \pi\,\sigma^2\,\mathcal{N}\,, \tag{10.19}$$

where $\overline{u}$ is the **mean velocity** of the molecule. An argon atom at a temperature of 273 K and pressure 101 kPa collides about five-thousand-million-times in one second.

The **collision density** $\mathcal{Z}$ is the total number of collisions per unit volume per unit time.

$$\mathcal{Z} = \frac{Z\,\mathcal{N}}{2} = \pi\,\sigma^2\,\overline{u}\,\frac{\mathcal{N}^2}{2}\,. \tag{10.20}$$

For argon under normal conditions we obtain an unimaginably high number $\mathcal{N} = 6{\times}10^{34}$ $\mathrm{m^{-3}\,s^{-1}}$.

10.5.4 Transport quantities for the hard spheres model

For viscosity at low pressures we may derive the following relation from the hard spheres model

$$\eta = \frac{5}{16\, N_A\, \sigma^2} \sqrt{\frac{M\boldsymbol{R}T}{\pi}}\,, \tag{10.21}$$

where σ is the collision diameter of the molecule and M is its molar mass. The formula clearly shows that the viscosity of a diluted gas increases linearly with the second root of temperature, and that it does not depend on pressure.

For thermal conductivity we may derive the following relation from the hard spheres model

$$\lambda = \frac{5}{2}\,\frac{\eta}{M}\, C_{V\mathrm{m}}\,, \tag{10.22}$$

where $C_{V\mathrm{m}}$ is the molar isochoric heat capacity. The viscosity η is given by relation (10.21). From this relation it follows that the thermal conductivity of a dilute gas does not depend on pressure but only on temperature, through η and $C_{V\mathrm{m}}$.

For the diffusion coefficient of a binary mixture we have

$$D_{12} = \frac{3\boldsymbol{R}T}{16\,\sigma_{12}^2\, N_A\, p} \sqrt{\frac{2\boldsymbol{R}T(M_1 + M_2)}{\pi\, M_1\, M_2}}\,, \tag{10.23}$$

where $\sigma_{12} = \dfrac{\sigma_1 + \sigma_2}{2}$.

For the self-diffusion coefficient we have

$$D = \frac{3\,\boldsymbol{R}T}{8\,\sigma^2\, N_A\, p} \sqrt{\frac{\boldsymbol{R}T}{\pi\, M}}\,. \tag{10.24}$$

It follows from relations (10.23) and (10.24) that the diffusion and self-diffusion coefficients of a gas at low densities increase with temperature and decrease with increasing pressure; the diffusion coefficient does not depend on composition.

> *Note:* The hard spheres model is a good approximation for the description of viscosity and diffusion of gases. In the case of thermal conductivity, however, it provides results which are correct only within orders of magnitude.

10.5.5 Knudsen region

The relation (10.18) for the mean free path can be rewritten to the form

$$\ell = \frac{\boldsymbol{R}\,T}{\sqrt{2}\,\pi\,\sigma^2\,p\,N_A}\,, \tag{10.25}$$

where N_A is the Avogadro constant. The mean free path is thus inversely proportional to pressure, and at very low pressures it may exceed the dimensions of the containing vessel. In this case we speak about the **Knudsen pressure region**. In the Knudsen region the formulas of the preceding section are inapplicable. In this region, collisions between molecules do not occur and transport quantities lose their physical meaning, just like in an ideal gas.

Example

Calculate the pressure at which the mean free path of argon molecules at a temperature of 300 K would equal 1 cm. Substitute argon molecules with hard spheres of 0.34 nm in diameter.

Solution

From equation (10.25) we obtain

$$p = \frac{8.31 \times 300}{\sqrt{2} \times 3.14 \times (0.34 \times 10^{-9})^2 \times 0.01 \times 6.02 \times 10^{23}} = 0.8\,\mathsf{Pa}.$$

Chapter 11

Electrochemistry

Electrochemistry is part of physical chemistry focused on the study of thermodynamic and kinetic processes in the solutions of electrolytes and melts, and in processes related to electrolysis and those occurring in galvanic cells.

11.1 Basic terms

11.1.1 Electric current conductors

Electric current conductors are materials allowing for the transport of electric charge. Conductors may be divided into three classes:

- **First-class conductors**—the electric charge is carried by electrons; metals are typical representatives of this class.
- **Second-class conductors**—the electric charge is carried by ions; typical representatives of this class are the solutions of electrolytes and melts (see **11.1.2**).
- **Third-class conductors**—the electric charge is carried by both ions and electrons; this class is typically represented by ionized gas (plasma).

11.1.2 Electrolytes and ions

Electrolytes are chemical substances which are present in melts or solutions partially or fully in the form of ions. The positively charged ion is called the cation, the negatively charged ion is the anion. We will also use the term electrolyte for electrolyte solutions and melts.

Note: Water is the most common solvent of electrolytes. Some polar compounds, e.g. methanol, formaldehyde, acetonitrile, or ammonia can be also used as solvents.

A **strong electrolyte** is a substance that is present in a melt or solvent solely in the form of its ions. Typical strong electrolytes are aqueous solutions of most salts, strong inorganic acids (nitric, hydrochloric, . . .), hydroxides of alkaline metals and alkaline earth (sodium hydroxide, calcium hydroxide, . . .).

Example

An example of a strong electrolyte is a sodium chloride melt in which complete dissociation to ions occurs according to the reaction

$$\mathrm{NaCl} \rightarrow \mathrm{Na}^+ + \mathrm{Cl}^- \,,$$

where Na^+ is a sodium cation and Cl^- is a chloride anion. Sodium chloride dissolved in water dissociates according to the same reaction.

A **weak electrolyte** is a substance that is present in a melt or solvent both in the form of its ions and in the form of undissociated molecules. Typical weak electrolytes are water, aqueous solutions of weak inorganic acids (carbonic acid, boric acid, . . .), most aqueous solutions of organic acids (acetic acid, oxalic acid, . . .), and solutions of weak hydroxides (ammonium hydroxide, . . .).

Example

An example of a weak electrolyte is the solution of acetic acid in water. During the reaction

$$\mathrm{CH_3COOH} = \mathrm{CH_3COO^-} + \mathrm{H^+}$$

chemical equilibrium is established between the undissociated acid and its ions.

S *Symbols:* When writing chemical equations we will use the symbol " → " to indicate complete dissociation, and the symbol " = " to indicate a reaction proceeding until the state of a chemical equilibrium.

Note: The reaction mentioned in the above example is often written in a different way:

$$\mathrm{CH_3COOH + H_2O = CH_3COO^- + H_3O^+}$$

where H_3O^+ is called the **oxonium cation**. The reason given for this procedure is that the hydrogen cation H^+ is actually a proton which cannot exist independently in the solution and is always bound to water. On the other hand, we cannot say for sure whether it is linked with one molecule of water (H_3O^+), two ($H_5O_2^+$), or more. For the sake of simplicity we will write H^+ while being aware of this ambiguity.

Note: The boundary line between strong and weak electrolytes is not sharp. The term strong electrolyte is usually applied when more than 90% of molecules are dissociated, the term weak electrolyte indicates that the dissociation is less extensive.
The kind of solvent used is one of several factors deciding whether a substance is a strong or a weak electrolyte. The solution of nitric acid in water, e.g., is a strong electrolyte, the solution of nitric acid in methanol is a weak electrolyte.

11.1.3 Ion charge number

The ion charge number is given by the ratio of the ion charge and the absolute value of the electron charge. For example, the charge number of a bivalent zinc cation is +2, the charge number of a sulfate anion is –2. Instead of the term "ion charge number" we will write simply "*ion charge*" when there is no risk of ambiguity.

S *Symbols:* The symbols z^+ and z^- will be used to denote the *absolute values* of charge numbers.

11.1.4 Condition of electroneutrality

It is obvious that after partial or complete dissociation of an electrolyte into ions the system stays outwardly electrically neutral. This fact is called the **global condition of electroneu-**

trality. Every part of a system also stays electroneutral, which is called the **local condition of electroneutrality**.

> *Note:* On the molecular level, the local condition of electroneutrality means that in the near vicinity of a given ion there are primarily ions of the opposite charge which partly neutralize the given ion charge. In this connection we say that every ion is surrounded by **ionic atmosphere**.

The condition of electroneutrality can be expressed mathematically: let us have a compound $\mathrm{K}_{\nu^+}\mathrm{A}_{\nu^-}$ which dissociates according to the equation

$$\mathrm{K}_{\nu^+}\mathrm{A}_{\nu^-} = \nu^+\,\mathrm{K}^{z^+} + \nu^-\,\mathrm{A}^{z^-}\,, \tag{11.1}$$

where K^{z^+} is a cation carrying charge z^+, and A^{z^-} is an anion carrying charge z^-. We thus have

$$\nu^+\,z^+ = \nu^-\,z^-\,. \tag{11.2}$$

This relation can be rewritten to the form

$$c^+\,z^+ = c^-\,z^-\,, \tag{11.3}$$

where c^+ is the concentration of cations and c^- the concentration of anions. When there are several kinds of ions present in a system, the generalized condition applies

$$\sum_i c_i^+ z_i^+ = \sum_i c_i^- z_i^-\,. \tag{11.4}$$

11.1.5 Degree of dissociation

The **degree of dissociation** α is a special case of the degree of conversion, see **8.2.2**, for the dissociation reactions of the type (11.1). If we divide the numerator and the denominator in relation (8.5) by the volume, we obtain the degree of dissociation expressed using the initial and equilibrium concentrations of the dissociating substance

$$\alpha = \frac{c_{i0} - c_i}{c_{i0}}\,. \tag{11.5}$$

Example
The initial concentration of acetic acid was 1 mol dm^{-3}. Part of the molecules dissociated into ions. At equilibrium, the concentration of H$^+$ ions equalled 0.1 mol dm^{-3}. Calculate the degree of dissociation.

Solution
The concentration of acetic acid at equilibrium is $c_i = 1$—$0.1 = 0.9$ mol dm^{-3}. By substituting into relation (11.5) we obtain

$$\alpha = \frac{1-0.9}{1} = 0.1\,.$$

11.1.6 Infinitely diluted electrolyte solution

An infinitely diluted solution is formed by 1 molecule of an electrolyte $\mathrm{K}_{\nu^+}\mathrm{A}_{\nu^-}$ in a large amount of solvent. This system is the basic model applied when describing the behaviour of dilute solutions.

In an infinitely diluted solution, ions do not influence one another. The degree of dissociation equals one, regardless of the nature of the electrolyte.

11.1.7 Electrochemical system

An electrochemical system is comprised of a vessel containing an electrolyte into which two electrodes are dipped. The electrodes are connected by first-class conductors either with a source of electric current—in this case we speak about **electrolysis**, or with an electrical device—in this case we speak about a **galvanic cell**. During electrolysis, chemical reactions of ions occur at the electrodes due to the passage of electric current. In a galvanic cell, on the other hand, electric current is generated in consequence of chemical reactions proceeding at the electrodes.

The **cathode** is an electrode at which reduction occurs. **Reduction** in this context means a reaction during which electrons are consumed. An example of a reduction is the reaction

$$\mathrm{Cu}^{2+} + 2\,\mathrm{e}^- = \mathrm{Cu}.$$

The **anode** is an electrode at which oxidation proceeds. **Oxidation** in this context means a reaction during which electrons are released. An example of an oxidation is the reaction

$$\mathrm{Cu} = \mathrm{Cu}^{2+} + 2\,\mathrm{e}^{-}.$$

11.2 Electrolysis

During electrolysis, the anode carries a positive charge and the cathode a negative charge due to the influence of an external source. Anions travel through the electrolyte toward the anode, cations travel toward the cathode. Electrochemical reactions take place at the electrodes.

11.2.1 Reactions occurring during electrolysis

Electrochemical reactions depend primarily on the nature of the electrolyte, on temperature, the current density, and on the material of the electrodes. In terms of the material used, we classify electrodes as **inert** and **active**. Inert electrodes do not participate in electrochemical reactions proceeding at them—a platinum electrode is a typical example of an inert electrode. At these electrodes, the products of oxidation or reduction are either discharged or they participate in further reactions, most often with the solvent. Active electrodes take part in electrochemical reactions. They may either dissolve or their material may react with the corresponding ions.

Example

Examples of products discharging at an inert electrode:

$$\begin{aligned} \mathrm{Zn}^{2+} + 2\,\mathrm{e}^- &= \mathrm{Zn}\,, \\ 2\,\mathrm{Cl}^- &= \mathrm{Cl}_2 + 2\,\mathrm{e}^-\,. \end{aligned}$$

Examples of the reactions of products at an inert electrode:

$$\begin{aligned} \mathrm{Na}^+ + \mathrm{e}^- &= \mathrm{Na}, & \mathrm{Na} + \mathrm{H_2O} &= \mathrm{NaOH} + \tfrac{1}{2}\,\mathrm{H}_2, \\ \mathrm{OH}^- &= \mathrm{OH}^{\bullet} + \mathrm{e}^-, & \mathrm{OH}^{\bullet} &= \tfrac{1}{2}\mathrm{H_2O} + \tfrac{1}{4}\mathrm{O}_2, \\ \mathrm{SO}_4^{2-} &= \mathrm{SO}_4^{\bullet} + 2\,\mathrm{e}^-, & \mathrm{SO}_4^{\bullet} + \mathrm{H_2O} &= \mathrm{H_2SO_4} + \tfrac{1}{2}\,\mathrm{O}_2, \\ \mathrm{NO}_3^- &= \mathrm{NO}_3^{\bullet} + \mathrm{e}^-\,, & \mathrm{NO}_3^{\bullet} + \tfrac{1}{2}\mathrm{H_2O} &= \mathrm{HNO_3} + \tfrac{1}{4}\,\mathrm{O}_2. \end{aligned}$$

Example

During electrolytic refining of copper, raw copper forms the anode and an aqueous solution of copper sulfate forms the electrolyte. Copper dissolution occurs at the anode

$$\mathrm{Cu} = \mathrm{Cu}^{2+} + 2\,\mathrm{e}^{-}.$$

while electrolytically pure copper is discharged at the cathode. The anode is the active electrode and the cathode is the inert electrode in this case.

11.2.2 Faraday's law

Faraday's law relates the electric charge Q, which passes through a system during electrolysis, with the amount of substance of the ion n_i discharged at the electrode

$$n_i = \frac{Q}{z_i\,\boldsymbol{F}}\,, \tag{11.6}$$

where z_i is the ion charge. $\boldsymbol{F}$ is the **Faraday constant** which is, but for the sign, equal to the charge of 1 mole of electrons

$$\boldsymbol{F} = \boldsymbol{N}_{\mathbf{A}}\,|e^{-}| = 96485.3\,\mathrm{C\,mol}^{-1}\,. \tag{11.7}$$

Given that the charge is the product of the electric current I and the time of electrolysis τ,

$$Q = I\,\tau\,,$$

$$m_i = \frac{M_i\,I\,\tau}{z_i\,\boldsymbol{F}}\,, \tag{11.8}$$

where M_i is the molecular mass of the ion.

Note: If a charge of 1 $\boldsymbol{F}$ passes through a system, then 1 mole of univalent anions (or 1/2 mole of bivalent anions, etc.) reacts at the anode, and at the same time 1 mole of univalent cations (or 1/2 mole of bivalent cations, etc.) reacts at the cathode.

When we are interested in finding the total mass m of substance $\mathrm{K}_{\nu^+}\mathrm{A}_{\nu^-}$ used up at the electrodes (in the form of ions), we can use Faraday's law in the form

$$m = \frac{M\,I\,\tau}{z^+\,\nu^+\,\boldsymbol{F}} = \frac{M\,I\,\tau}{z^-\,\nu^-\,\boldsymbol{F}}\,, \tag{11.9}$$

where M is the molar mass of the substance $\mathrm{K}_{\nu^+}\mathrm{A}_{\nu^-}$.

Faraday's law can be also used when the products of oxidation or reduction react at the electrode further on. In such cases we first have to write the overall reaction and then use the relation

$$m_i = \frac{M_i\,I\,\tau}{z_e\,\boldsymbol{F}}\,\nu_i\,, \tag{11.10}$$

where z_i is the number of electrons in the reaction and ν_i is the stoichiometric coefficient of substance i.

Example

An aqueous solution of aluminium sulfate was electrolyzed for one hour by an electric current of 0.1 A. The molar mass of aluminium is $M_{\mathrm{Al}} = 27\,\mathrm{g\,mol^{-1}}$ and the molar mass of aluminium sulfate is $M = 343\,\mathrm{g\,mol^{-1}}$.

a) Calculate the mass of aluminium discharged at the cathode.

b) Calculate the mass of aluminium sulfate that dissociated at the electrodes.

c) Calculate the mass of oxygen discharged at the anode.

Solution

a) We calculate the mass of discharged aluminium from relation (11.8)

$$m_{\mathrm{Al}} = \frac{27 \times 0.1 \times 3600}{3 \times 96485.3} = 0.034\,\mathsf{g}\,.$$

b) The mass of aluminium sulfate that was used up during the electrolysis will be calculated from relation (11.9)

$$m = \frac{343 \times 0.1 \times 3600}{3 \times 2 \times 96485.3} = 0,213\,\mathsf{g}\,.$$

c) Oxidation of the anion SO_4^{2-} and the reaction of the radical $SO_4^{\cdot}$ with water occur at the anode. Overall we may write

$$\mathrm{SO}_4^{2-} + H_2O = H_2SO_4 + \frac{1}{2}\,O_2 + 2\,\mathrm{e}^-\,.$$

If we use relation (11.10), where $\nu_{\mathrm{O}_2} = 1/2$ and $z_e = 2$, we have

$$m_{\mathrm{O}_2} = \frac{32 \times 0.1 \times 3600}{2 \times 96485.3} \times \frac{1}{2} = 0.030\,\mathsf{g}\,.$$

11.2.3 Coulometers

Coulometers are devices measuring the electric charge that has passed through an electric circuit. In these apparatuses electrolysis proceeds while either the gain in the electrode mass (coulometer for silver or copper) or the volume of gas discharged during the electrolysis (electrolytic-gas coulometer) is measured. The charge passed through the circuit is measured using Faraday's law.

Example

(Acidified) water is electrolyzed in a coulometry monitor for explosive gas. The volume of the discharged stoichiometric mixture of oxygen and hydrogen, the so-called explosive gas, is measured. Determine the volume of the discharged explosive gas if a charge of 1 $\boldsymbol{F}$ passes through the circuit at a temperature of 300 K and pressure 100 kPa. Assume that under the given conditions, the equation of state of an ideal gas can be applied.

Solution

The following reactions occur during the electrolysis of water:

$$\begin{array}{lcll} H_2O & = & H^+ + OH^- & \text{dissociation of water,} \\ H^+ + e^- & = & \frac{1}{2}H_2 & \text{reduction at the cathode,} \\ OH^- & = & \frac{1}{2}H_2O + \frac{1}{4}O_2 + e^- & \text{oxidation at the anode.} \end{array}$$

A total of 1/2 mole of H_2 and 1/4 mole of O_2, i.e. 3/4 moles of electrolytic gas were discharged by a charge of 1 $\boldsymbol{F}$. From the state equation of an ideal gas we obtain

$$V = \frac{n\,\boldsymbol{R}\,T}{p} = \frac{3/4\ \times 8.314\ \times 300}{100} = 18.706\,\mathrm{dm}^3\,.$$

11.2.4 Transport numbers

During electrolysis, the electric charge is carried in the electrolyte by both cations and anions, but the amount of charge they transport is different. The **cation transport number** t^+ is defined as the ratio of the charge carried by the cations Q^+ and the total charge $Q = Q^+ + Q^-$

$$t^+ = \frac{Q^+}{Q}\,. \tag{11.11}$$

Similarly, the **anion transport number** is defined as

$$t^- = \frac{Q^-}{Q}\,. \tag{11.12}$$

It is obvious that

$$t^+ + t^- = 1\,. \tag{11.13}$$

The amount of the transported charge relates to the velocity with which the ions travel through the electrolyte. We have

$$t^+ = \frac{v^+}{v^+ + v^-}\,, \quad t^- = \frac{v^-}{v^+ + v^-}\,, \tag{11.14}$$

where v^+ is the velocity of the cation and v^- is that of the anion.

The velocity of ions in a solution of a given concentration, temperature and pressure depends on the voltage between the two electrodes and on the distance between them. The higher the voltage and the closer the electrodes to each other, the higher is the ions velocity. The **ionic mobility** is defined as the velocity of an ion at a potential gradient of $1\,\mathrm{V\,m^{-1}}$.

$$u^+ = \frac{\ell}{E}\,v^+\,, \quad u^- = \frac{\ell}{E}\,v^-\,, \tag{11.15}$$

where u^+ is the cation mobility, u^- is the anion mobility, E is the voltage and ℓ is the distance between the electrodes. The same relations as (11.14) apply between transport numbers and ionic mobilities

$$t^+ = \frac{u^+}{u^+ + u^-}\,, \quad t^- = \frac{u^-}{u^+ + u^-}\,. \tag{11.16}$$

Relations (11.11) through (11.16) can be easily extended to cases when there are more kinds of anions and cations in an electrolyte. For example, generalized equation (11.13) becomes

$$\sum_i t_i^+ + \sum_j t_j^- = 1\,. \tag{11.17}$$

Transport numbers and ionic mobilities depend on the concentration of the electrolyte, temperature and (to a small extent) pressure.

11.2.5 Concentration changes during electrolysis

In consequence of unequal velocity of ions, concentration changes in the vicinity of the electrodes occur during electrolysis. If the ions are discharged at the electrode, their concentration in the vicinity of the opposite electrode decreases. If the ions reaction at the electrode is such that they return to the solution, their concentration in the vicinity of the given electrode increases. In both cases, the condition of local electroneutrality, relation (11.3), is always fulfilled.

11.2.6 Hittorf method of determining transport numbers

The Hittorf method of determining transport numbers is based on the measurement of concentration changes. Let us consider an electrolyte dissociating into ions according to relation (11.1). The vessel containing the electrolyte is divided into two compartments: the anode compartment and the cathode compartment. We use the symbol Δn_{an} to denote the change in the amount of substance of the electrolyte in the anode compartment (the amount after the termination of the electrolysis minus the amount prior to its start). Similarly the symbol Δn_{cat} will be used to denote the change in the amount of substance of the electrolyte in the cathode compartment. Some of the following relations apply for transport numbers:

$$t^+ = -\frac{z^+ \nu^+ \Delta n_{\mathrm{an}}}{Q/\boldsymbol{F}}\,, \tag{11.18}$$

$$t^+ = \frac{z^+ \nu^+ \Delta n_{\mathrm{cat}}}{Q/\boldsymbol{F}}\,, \tag{11.19}$$

$$t^- = -\frac{z^- \nu^- \Delta n_{\mathrm{cat}}}{Q/\boldsymbol{F}}\,, \tag{11.20}$$

$$t^- = \frac{z^- \nu^- \Delta n_{\mathrm{an}}}{Q/\boldsymbol{F}}\,. \tag{11.21}$$

- Relation (11.18) is used when the cation is discharged at the cathode.
- Relation (11.19) is used when the cation reacts at the cathode and returns back to the electrolyte.
- Relation (11.20) is used when the anion is discharged at the anode.
- Relation (11.21) is used when the anion reacts at the anode and returns back to the electrolyte.

Note: The Hittorf method cannot be used directly when ions are formed during reactions at the electrodes which were not present in the initial electrolyte. During the electrolysis of sodium chloride, e.g. the ions OH^- are formed and start to participate in the charge transport together with the initially present ions Na^+ and Cl^-. In this case the Hittorf method does not allow for determining what amount of charge has been transported by the Cl^- and OH^- anions.

Example

During the electrolysis of HCl, the charge $Q = 1\,\boldsymbol{F}$ passes through the system. The transport number of the cation H^+ is $t^+ = 0.82$. Determine the concentration changes in the anode and cathode compartments.

Solution

Hydrochloric acid dissociates into ions according to the reaction

$$\mathsf{HCl} = \mathrm{H}^+ + \mathrm{Cl}^- .$$

It thus holds that $z^+ = \nu_+ = z^- = \nu_- = 1$. Both ions are discharged at the electrodes, i.e. relations (11.18) and (11.20) apply. From the first of them we obtain

$$\Delta n_{\mathrm{an}} = -\,t^+\,\frac{Q/\boldsymbol{F}}{z^+\,\nu^+} = -0.82\,\mathsf{mol}.$$

A total of 0.82 moles of hydrochloric acid were used up in the anode compartment.
Now we first calculate the anion transport number from relation (11.13)

$$t^- = 1 - t^+ = 1 - 0.82 = 0.18\,.$$

and finally use relation (11.20) to obtain

$$\Delta n_{\mathrm{cat}} = -\,t^-\,\frac{Q/\boldsymbol{F}}{z^-\,\nu^-} = -0.18\,\mathsf{mol}.$$

A total of 0.18 moles of hydrochloric acid were used up in the cathode compartment.

11.3 Electric conductivity of electrolytes

Ohm's law applies in electrolytes just like in first-class conductors:

$$R = \frac{E}{I}\,, \tag{11.22}$$

where R stands for resistance, E for voltage, and Idenotes electric current.

> *Note:* To be more precise, Ohm's law applies in cases where no polarization of electrodes occurs, see **11.9**. In order to suppress the effect of polarization, alternate current is used when measuring resistance.

11.3.1 Resistivity and conductivity

The **resistivity** ρ is the resistance of a conductor of unit length and unit cross-section. It is defined by the relation

$$\rho = R\,\frac{A}{\ell}\,, \tag{11.23}$$

where A is the cross-section and ℓ is the length of the conductor.

U *Main unit:* $\Omega\,\mathrm{m}$

The **conductivity** κ is the reciprocal value of resistivity.

$$\kappa = \frac{1}{\rho}\,. \tag{11.24}$$

U *Main unit:* $\Omega^{-1}\,\mathrm{m}^{-1} = \mathrm{S\,m^{-1}}$.

Example

The resistance $R = 100\,\Omega$ was measured in a potassium chloride solution. Each of the electrodes had a surface area of 4 cm^2, and the distance between them was 2 cm. Calculate the conductivity.

Solution

From relations (11.23) and (11.24) we obtain

$$\kappa = \frac{\ell}{R\,A} = \frac{2\times10^{-2}}{100\times4\times10^{-4}} = 0.5\,\mathrm{S\,m^{-1}}\,.$$

11.3.2 Conductivity cell constant

Calculating conductivity from relations (11.23) and (11.24) is impractical in electrolytes due to problems related to the determination of accurate values of the electrodes surface area A and the distance between them ℓ. For this reason, conductivity is usually calculated using the relation

$$\kappa = \frac{C}{R}\,. \tag{11.25}$$

The quantity C is called the **conductivity cell constant**, and it is determined by calibration.

U *Main unit:* m^{-1}.

Example
The conductivity of a potassium chloride solution of the concentration $c = 0.1\,\mathrm{mol\,dm}^{/3}$ is $\kappa = 1.288\,\mathrm{S\,m}^{-1}$. The resistance of this solution was measured in a conductivity cell and the value $R = 220\,\Omega$ was found. Calculate the conductivity cell constant.

Solution
From equation (11.25) we obtain

$$C = R\,\kappa = 220 \times 1.228 = 540.9\,\mathrm{m}^{-1}\,.$$

11.3.3 Molar electric conductivity

The **molar electric conductivity** Λ (or shortly molar conductivity) is defined by the relation

$$\Lambda = \frac{\kappa}{c}\,, \tag{11.26}$$

where c is the electrolyte concentration in the units $\mathrm{mol\,m}^{-3}$.

U *Main unit:* $\mathrm{S\,m^2\,mol}^{-1}$.

Example
The resistance of a copper sulfate of the concentration $c = 0.02\,\mathrm{mol\,dm}^{-3}$ is $R = 1440\,\Omega$, and the conductivity cell constant is $C = 541\,\mathrm{m}^{-1}$. Calculate the molar conductivity of the solution.

Solution

The first step is to determine the conductivity from relation (11.25)

$$\kappa = \frac{541}{1440} = 0.3757\,\mathsf{S\,m^{-1}}\,.$$

Then we use relation (11.26) to calculate the molar conductivity—we make sure that we converted the molar concentration value to the SI system

$$\Lambda = \frac{0.3757}{0.02 \times 10^3} = 187.8 \times 10^{-4}\,\mathsf{S\,m^2\,mol^{-1}}\,.$$

Molar conductivity depends on concentration, temperature and pressure. Its concentration dependence is dealt with in section **11.3.7**. The value of Λ usually increases with temperature. The pressure dependence is very low and it is usually neglected.

11.3.4 Kohlrausch's law of independent migration of ions

The **molar conductivity at infinite dilution** Λ_∞ is defined by the relation

$$\Lambda_\infty = \lim_{c \to 0} \Lambda\,. \qquad (11.27)$$

It applies that

$$\Lambda_\infty = \nu^+\,\Lambda^+_\infty + \nu^-\,\Lambda^-_\infty\,, \qquad (11.28)$$

where Λ^+_∞ is the **molar conductivity of the cation at infinite dilution** and Λ^-_∞ is the **molar conductivity of the anion at infinite dilution**. Relation (11.28) is called **Kohlrausch's law of the independent migration of ions**. It expresses the fact that ions in an infinitely diluted solution do not influence each other, see **11.1.6**.

The molar conductivity of ions at infinite solution can be found in tables. Their values together with relation (11.28) are used to calculate the molar conductivity of electrolytes at infinite dilution.

Note: The term molar conductivity is often used also for the conductivity related to unit concentration of the fractions of molecules and ions containing one positive or negative charge (e.g. $1/2\,H_2SO_4$, $1/3\,Fe^{3+}$, $1/3\,[Fe(CN)_6]^{3-}$), in older literature, referred to as the **equivalent conductivity** Λ_e and **equivalent conductivity of ions**, defined by the relations

$$\Lambda_e = \frac{\Lambda}{z^+\,\nu^+} = \frac{\Lambda}{z^-\,\nu^-}\,, \quad \Lambda^+_{e,\infty} = \frac{\Lambda^+_\infty}{z^+}\,, \quad \Lambda^-_{e,\infty} = \frac{\Lambda^-_\infty}{z^-}\,. \tag{11.29}$$

Thus, e.g., $\Lambda_e(1/3\,Fe^{3+}) = 1/3\,\Lambda(Fe^{3+})$ and $\Lambda_e = (1/2\,H_2SO_4) = (1/2)\,\Lambda(H_2SO_4)$. Kohlrausch's law of the independent migration of ions then acquires the form

$$\Lambda_{e,\infty} = \Lambda^+_{e,\infty} + \Lambda^-_{e,\infty}\,. \tag{11.30}$$

It has to be checked whether the tables we use give molar or equivalent conductivities.

11.3.5 Molar conductivity and the degree of dissociation

The following relation applies between the molar conductivity, the degree of dissociation and the ionic mobility.

$$\Lambda = \alpha\,\boldsymbol{F}\left(\nu^+\,z^+\,u^+ + \nu^-\,z^-\,u^-\right)\,. \tag{11.31}$$

If we use the same relation at an infinite dilution, where $\alpha = 1$, and neglect the concentration dependence of the ionic mobility, we obtain the **Arrhenius relation** for the degree of dissociation

$$\alpha = \frac{\Lambda}{\Lambda_\infty}\,. \tag{11.32}$$

11.3.6 Molar conductivity and transport numbers

The following relations apply at infinite dilution

$$\Lambda^+_\infty = \boldsymbol{F}\,z^+\,u^+\,, \qquad \Lambda^-_\infty = \boldsymbol{F}\,z^-\,u^-\,. \tag{11.33}$$

Their combination with equations (11.16) yields relations for transport numbers at infinite dilution

$$t^+_\infty = \frac{\nu^+\,\Lambda^+_\infty}{\Lambda_\infty}\,, \qquad t^-_\infty = \frac{\nu^-\,\Lambda^-_\infty}{\Lambda_\infty}\,. \tag{11.34}$$

11.3.7 Concentration dependence of molar conductivity

Molar conductivity usually decreases with increasing concentration of the electrolyte. In strong electrolytes it is roughly a linear function of the second root of concentration

$$\Lambda = \Lambda_\infty - a\sqrt{c}\,. \tag{11.35}$$

where a is a temperature-dependent positive number. This relation does not apply for weak electrolytes.

> *Note:* The character of the experimental dependence of Λ on c enables to find out whether an electrolyte is strong or weak.

11.4 Chemical potential, activity and activity coefficient in electrolyte solutions

This section describes thermodynamic behaviour of electrolyte solutions in the absence of an external electric field. We will focus on the description of the chemical potential, activities and activity coefficients.

Electrolyte solutions represent a special case of mixtures whose components may be divided into three groups:

1. *Solvents*, most often water. The quantities relating to the solvent will be denoted using the subscript 1.
2. *Undissociated electrolytes,* e.g. undissociated molecules of a weak acid. This component is missing in the solutions of strong electrolytes.
3. *Ions*.

11.4.1 Standard states

11.4.1.1 Solvent

For the chemical potential of a solvent, the standard state of a pure substance at the temperature and pressure of the system is chosen [see equations (6.72) and section **6.5.3**]. For the solvent activity a_1, equation (6.99) applies, $a_1 = x_1\,\gamma_1$, where x_1 is the molar fraction of the solvent and γ_1 is its activity coefficient.

> *Note:* For the thermodynamic description of non-ideal behaviour of a solvent, the osmotic coefficient defined in **6.5.5** is sometimes used instead of the activity coefficient.

The activity of a solvent will be approximated by one, if not otherwise stated

$$a_1 = 1\,. \tag{11.36}$$

The reason for this approximation is that solvents are usually present in solutions in a large excess and therefore they behave almost as pure substances.

11.4.1.2 Undissociated electrolyte

The standard state of unit molar concentration, $c^{\mathrm{st}} = 1\,\mathrm{mol\,dm^{-3}}$, [see **6.5.3**], or the standard state of unit molality, $\underline{m}^{\mathrm{st}} = 1\,\mathrm{mol\,kg^{-1}}$ [see **6.5.3**] is usually chosen. In the former case the activity coefficient is defined by the relation $a_i^{[c]} = \dfrac{c_i}{c^{\mathrm{st}}}\gamma_i^{[c]}$, [see equation (6.101)], in the latter case by the relation $a_i^{[\underline{m}]} = \dfrac{\underline{m}_i^{[\underline{m}]}}{\underline{m}^{\mathrm{st}}}\gamma_i^{[\underline{m}]}$. [see equation (6.102)].

In aqueous solutions of electrolytes at room temperature, the molar concentration in $\mathrm{mol\,dm^{-3}}$ is approximately equal to the molality. In that case also the respective activities and activity coefficients are approximately equal.

Example
An aqueous solution of acetic acid has the concentration $c = 0.3334\,\mathrm{mol\,dm^{-3}}$. Its density at $t = 20\,°\mathrm{C}$ is $\rho = 1.0012\,\mathrm{kg\,dm^{-3}}$. The molar mass of the acid is $M = 60.05\,\mathrm{g\,mol^{-1}}$. Calculate the molality of acetic acid.

Solution
The mass of $1\,\mathrm{dm^3}$ of the solution $m = \rho = 1.0012\,\mathrm{kg}$; the mass of the acetic acid is $m_{\mathrm{a}} = c\,M = 0.3334 \times 60.05 = 20.024\ \mathrm{g} = 0.020\ \mathrm{kg}$. The mass of the water is thus $m_{\mathrm{H_2O}} = m - m_{\mathrm{a}} = 1.0012 - 0.020 = 0.9812\ \mathrm{kg}$. From the definition of molality, see **1.6.5**, it follows that

$$\underline{m}_{\mathrm{a}} = \frac{n_{\mathrm{a}}}{m_{\mathrm{H_2O}}} = \frac{0.3334}{0.9812} = 0.34\ \mathrm{mol\,kg^{-1}}\,.$$

We can see that the difference between the molality and molar concentration is negligible here.

In an infinitely diluted solution we have

$$\gamma_i^{[c]} = \gamma_i^{[\underline{m}]} = 1\,. \tag{11.37}$$

In dilute solutions the activity coefficients of an undissociated electrolyte are usually less than 10% different from one. We will thus mostly consider them to be unity.

S *Symbols:* In order to simplify the writing of this type of equations we will leave out the superscript $[c]$ or $[\underline{m}]$ in activities and activity coefficients whenever it is clear from the context which of the standard states is meant.

11.4.1.3 Ions

The same standard states are chosen for ions in a solution as for an undissociated electrolyte (i.e. unit molar concentrations or unit molalities). For an infinitely diluted solution equation (11.37) applies.

> *Note:* The significant difference between the description of an undissociated substance and that of ions is due to the fact that the activity coefficients of the ions are considerably different from unity even in dilute solutions.

11.4.2 Mean molality, concentration, activity and activity coefficient

Let us consider a strong electrolyte of the molality $\underline{m}$ which dissociates into ions according to equation (11.1)

$$\mathrm{K}_{\nu^+}\mathrm{A}_{\nu^-} = \nu^+\,\mathrm{K}^{z^+} + \nu^-\,\mathrm{A}^{z^-}\ .$$

The mean molality of the ions $\underline{m}_\pm$ is defined by the relation

$$\underline{m}_\pm = \left[\left(\underline{m}^+\right)^{\nu^+}\left(\underline{m}^-\right)^{\nu^-}\right]^{\frac{1}{\nu}}\ , \tag{11.38}$$

where $\nu = \nu^+ + \nu^-$, $\underline{m}^+ = \nu^+\underline{m}$ and $\underline{m}^- = \nu^-\underline{m}$. From this it follows that

$$\underline{m}_\pm = \underline{m}\left[\left(\nu^+\right)^{\nu^+}\left(\nu^-\right)^{\nu^-}\right]^{\frac{1}{\nu}}\ . \tag{11.39}$$

The mean concentration $c_\pm$, the mean activities $a_\pm^{[c]}$, $a_\pm^{[\underline{m}]}$ and the mean activity coefficients $\gamma_\pm^{[c]}$, $\gamma_\pm^{[\underline{m}]}$ are defined in a similar way.

$$c_\pm = \left[\left(c^+\right)^{\nu^+}\left(c^-\right)^{\nu^-}\right]^{\frac{1}{\nu}}\ ,\ a_\pm = \left[\left(a^+\right)^{\nu^+}\left(a^-\right)^{\nu^-}\right]^{\frac{1}{\nu}}\ ,\ \gamma_\pm = \left[\left(\gamma^+\right)^{\nu^+}\left(\gamma^-\right)^{\nu^-}\right]^{\frac{1}{\nu}}\ . \tag{11.40}$$

> *Note:* The mean activities and mean activity coefficients are introduced because the activities and activity coefficients of ions are experimentally unavailable.

Example

Let us consider a solution of aluminium sulfate of the molality $0.2\,\mathrm{mol\,kg^{-1}}$. Calculate the mean molality of $Al_2(SO_4)_3$ and write the relations for the mean activity and the mean activity coefficient.

Solution

For the molality of ions we have

$$\underline{m}^+ = \nu^+\,\underline{m} = 2 \times 0.2 = 0.4\,, \qquad \underline{m}^- = \nu^-\,\underline{m} = 3 \times 0.2 = 0.6\,.$$

From relation (11.38) we obtain

$$\underline{m}_\pm = (0.4^2 \times 0.6^3)^{1/5} = 0.51\,.$$

We would obtain the same result from relation (11.39). Check it!
From relations (11.40) we have

$$a_\pm = \left[\left(a^+\right)^2 \left(a^-\right)^3\right]^{1/5}\,,$$
$$\gamma_\pm = \left[\left(\gamma^+\right)^2 \left(\gamma^-\right)^3\right]^{1/5}\,.$$

11.4.3 Ionic strength of a solution

The ionic strength of a solution I is defined by the relation

$$I = \frac{1}{2}\sum_i \underline{m}_i\, z_i^2\,, \tag{11.41}$$

where $\underline{m}_i$ is the molality of ions i in a solution, and z_i is the ion charge. Summation is done over <u>all</u> kinds of ions present in the solution. If the solution composition is given in molar concentrations, the ionic strength is approximated using the relation

$$I = \frac{1}{2}\sum_i c_i\, z_i^2\,. \tag{11.42}$$

Example
Calculate the ionic strength of
a) a solution of $FeCl_3$ of the molality $\underline{m} = 0.1\,\mathrm{mol\,kg^{-1}}$,
b) a solution containing KCl of the molality $0.1\,\mathrm{mol\,kg^{-1}}$ and $CuCl_2$ of the molality $0.2\,\mathrm{mol\,kg^{-1}}$.

Solution
a) From the material balance it follows that the molality of the ferric ions is $0.1\,\mathrm{mol\,kg^{-1}}$, the molality of the chloride ions is $3 \times 0.1 = 0.3\,\mathrm{mol\,kg^{-1}}$. From equation (11.41) we obtain

$$I = \frac{1}{2}\left(0.1 \times 3^2 + 0.3 \times 1^2\right) = 0.6\,\mathrm{mol\,kg^{-1}}\,.$$

b) From the material balance it follows that the molality of the potassium ions is $0.1\,\mathrm{mol\,kg^{-1}}$, the molality of the cupric ions is $0.2\,\mathrm{mol\,kg^{-1}}$, and the molality of the chloride ions is

$$0.1 + 2\ \times 0.2 = 0.5\,\mathrm{mol\,kg^{-1}}.$$

From equation (11.41) we obtain

$$I = \frac{1}{2}\left(0.1 \times 1^2 + 0.2 \times 2^2 + 0.5 \times 1^2\right) = 0.7\,\mathrm{mol\,kg^{-1}}\,.$$

11.4.4 Debye-Hückel limiting law

Based on a theoretical model of a dilute solution of a strong electrolyte, Debye and Hückel derived a relation for the calculation of the activity coefficient of an ion i

$$\ln \gamma_i = -A\, z_i^2 \sqrt{I}\,, \tag{11.43}$$

where z_i is the ion charge number and I is the ionic strength of the solution. For the parameter A we have

$$A = \frac{e^3\, \boldsymbol{N_\mathrm{A}}^2 \sqrt{2/\rho_1}}{8\,\pi(\epsilon_0\, \epsilon_r\, \boldsymbol{R}\, T)^{3/2}}\,, \tag{11.44}$$

where e is the absolute value of the electron charge, $\boldsymbol{N_A}$ is the Avogadro constant, ϵ_0 is the permittivity of a vacuum, ϵ_r is the relative permittivity of the solvent, and ρ_1 is the solvent density. It is obvious from the relation that the parameter A depends solely on the properties of the solvent and not on the properties of the ions. Equation (11.43) is called the **Debye-Hückel limiting relation** for the activity coefficient of an ion. It may be also applied for ions in a mixture of electrolytes.

Example
The density of water at the standard pressure and a temperature of 298.15 K is 997.07 kg m^{-3}, its relative permittivity is 78.303, the permittivity of a vacuum is 8.8542×10^{-12} C^2 N^{-1} m^{-2}, and the electron charge is 1.602×10^{-19} C. Calculate the value of the parameter A for water at the given temperature and pressure.

Solution
Substituting into (11.44) yields

$$\begin{aligned} A &= \frac{(1.602 \times 10^{-19})^3 \times (6.022 \times 10^{23})^2 \times \sqrt{2/997.07}}{8 \times 3.1416 \times (8.8542 \times 10^{-12} \times 78.303 \times 8.314 \times 298.15)^{3/2}} \\ &= 1.1762\,(\mathrm{kg\,mol})^{1/2}\,. \end{aligned}$$

By combining equations (11.2), (11.40) and (11.43) we obtain the Debye-Hückel relation for the mean activity coefficient

$$\ln \gamma_{\pm} = -A\, z^{+}\, z^{-}\, \sqrt{I}\,. \qquad (11.45)$$

Relations (11.43) and (11.45) express well the experimental values of activity coefficients in dilute solutions, where $I < 0.01\,\mathrm{mol\,kg^{-1}}$, but they fail at higher ionic strengths of the solution.

Example
Calculate the activity coefficients of the ions and the mean activity coefficients in a solution containing 0.004 mol HCl and 0.002 mol $CaCl_2$ in 1 kg of water at a temperature of 25 °C, given that $A = 1.1762\,(\mathrm{kg\,mol^{-1}})^{1/2}$.

Solution

We first determine the molalities of the ions from the specification and from the material balance. We obtain

$$\underline{m}_{\mathrm{H}^+} = 0.004,\ \underline{m}_{\mathrm{Ca}^{2+}} = 0.002,\ \underline{m}_{\mathrm{Cl}^-} = 0.004 + 2 \times 0.002 = 0.008\,\mathsf{mol\,kg}^{-1}\,.$$

We calculate the ionic strength of the solution from (11.41)

$$I = \frac{1}{2}\left(0.004 \times 1^2 + 0.002 \times 2^2 + 0.008 \times 1^2\right) = 0.01\,\mathsf{mol\,kg}^{-1}\,.$$

The activity coefficients of the ions will be calculated from (11.43)

$$\gamma_{\mathrm{H}^+} = 0.889, \qquad \gamma_{\mathrm{Ca}^{2+}} = 0.624, \qquad \gamma_{\mathrm{Cl}^-} = 0.889\,.$$

The mean activity coefficients of HCl and $CaCl_2$ will be calculated from the results for the ions activity coefficients and from relation (11.40)

$$\gamma_{\pm,\,\mathrm{HCl}} = (0.889 \times 0.889)^{1/2} = 0.889\,,$$

$$\gamma_{\pm,\,\mathsf{CaCl_2}} = \left(0.624 \times 0.889^2\right)^{1/3} = 0.790\,.$$

11.4.5 Activity coefficients at higher concentrations

Several semiempirical expansions of equation (11.45) have been suggested for the range of higher values of the ionic strength, e.g.

$$\ln \gamma_\pm = -\frac{A\,z^+\,z^-\sqrt{I}}{1+\sqrt{I}} + B\,z^+\,z^-\,I\,, \tag{11.46}$$

where B depends on the nature of both the solvent and the ions.

11.5 Dissociation in solutions of weak electrolytes

This section is focused on the dissociation of weak acids, bases and their salts. This is nothing but application of the theory of chemical equilibrium to electrolyte solutions.

11.5.1 Some general notes

When solving dissociation equilibria we observe the following rules:

1. The activity of water is assumed to be unity. For the activity of an undissociated electrolyte and for the activities of ions, the standard state of unit concentration is chosen, see **11.4.1**.
2. The activity coefficient of an undissociated electrolyte is in most calculations assumed to be unity. It is considered only in very accurate calculations, but in that case we have to know its concentration dependence.
3. The activity coefficients of the ions:
   - in less accurate calculations they are considered to be unity,
   - if the ionic strength of the solution is $I < 0.01$, they are calculated from the Debye-Hückel relation,
   - if the ionic strength is higher, we have to know their dependence on this ionic strength or on the concentration.
4. If the concentration of hydrogen ions is comparable in order with their concentration in pure water, we also have to consider equation (11.47) for the dissociation of water when solving a chemical equilibrium.

11.5.2 Ionic product of water

Water dissociates according to the reaction

$$\mathrm{H_2O} = \mathrm{H^+} + \mathrm{OH^-}\,. \tag{11.47}$$

The equilibrium constant of this reaction is called the **ionic product of water** K_w. We have

$$K_\mathrm{w} = \frac{a_{\mathrm{H^+}}\, a_{\mathrm{OH^-}}}{a_{\mathrm{H_2O}}} = \frac{c_{\mathrm{H^+}}\, c_{\mathrm{OH^-}}\, \gamma_\pm^2}{(c^\mathrm{st})^2}\,, \tag{11.48}$$

where the activity of water is considered to be one.

The ionic product of water depends on temperature and pressure. At a temperature of 298.15 K and the standard pressure 101.325 kPa it is $K_\mathrm{w} = 1.005 \times 10^{-14}$. This very low value allows for the simplification of the equation to

$$K_\mathrm{w} = \frac{c_{\mathrm{H}^+}\, c_{\mathrm{OH}^-}}{(c^\mathrm{st})^2}\,. \tag{11.49}$$

Note: Relation (11.49) can be applied only for pure water. If it contains other ions, we have to consider activity coefficients and use relation (11.48).

For the dependence of the ionic product of water on temperature we have, see equation (8.18),

$$\left(\frac{\partial \ln K_\mathrm{w}}{\partial T}\right)_p = \frac{\Delta_\mathrm{r} H^\ominus}{\boldsymbol{R}\, T^2}\,, \tag{11.50}$$

where $\Delta_\mathrm{r} H^\ominus$ is the standard reaction enthalpy of water dissociation. (Symbol $^\ominus$ (or equivalently $^\mathrm{st}$) for an "unspecified standard state" should be replaced by the respective standard state of a compound occurring in the dissociation reaction. It is the state "pure substance in the liquid state ($^\bullet$)" for water and "infinite dilution extrapolated to c^st ($^{[c]}$)" for ions H^+ and OH^-, see **8.2.3** for details.) But for the sign it is equal to the enthalpy of the neutralization of a strong acid by a strong base

$$\Delta_\mathrm{r} H^\ominus = -\Delta_\mathrm{neutr} H^\ominus\,. \tag{11.51}$$

Example

Calculate the ionic product of water at the standard pressure and at temperatures of 0 °C and 100 °C. Assume that in the given temperature range the reaction enthalpy does not depend on temperature and equals $\Delta_\mathrm{r} H^\ominus = 56500\ \mathrm{J\,mol^{-1}}$.

Solution

By integrating equation (11.50) we obtain

$$\begin{aligned}\ln K_\mathrm{w}(T) &= \ln K_\mathrm{w}(298.15) + \frac{\Delta_\mathrm{r} H^\ominus}{\boldsymbol{R}}\left(\frac{1}{298.15} - \frac{1}{T}\right)\\ &= \ln\left(1.005\times 10^{-14}\right) + \frac{56500}{8.314}\left(\frac{1}{298.15} - \frac{1}{T}\right).\end{aligned}$$

For $T = 273.15\,\mathrm{K}$ we obtain

$$K_\mathrm{w}(273.15) = 1.25\times 10^{-15}\,,$$

and for $T = 373.15\,\mathrm{K}$

$$K_\mathrm{w}(273.15) = 9.81\times 10^{-13}\,.$$

The results show that the ionic product of water largely depends on temperature. In the studied temperature range it increased 785-times!

The pressure dependence of the ionic product is low; it exhibits itself only at extremely high pressures.

11.5.3 Dissociation of a week monobasic acid

A weak monobasic acid HA dissociates according to the equation

$$\mathrm{HA} = \mathrm{H}^+ + \mathrm{A}^-\,. \tag{11.52}$$

The equilibrium constant of this reaction is called the **acid dissociation constant**. We write

$$K = \frac{a_{\mathrm{H}^+}\, a_{\mathrm{A}^-}}{a_\mathrm{HA}} = \frac{c_{\mathrm{H}^+}\, c_{\mathrm{A}^-}\, \gamma_\pm^2}{c_\mathrm{HA}\, \gamma_\mathrm{HA}}\, \frac{1}{c^\mathrm{st}}\,. \tag{11.53}$$

If we do not consider any other reaction in the system (e.g. dissociation of water), we may express the composition of an equilibrium mixture using the degree of dissociation:

$$c_\mathrm{HA} = (1-\alpha)\, c, \qquad c_{\mathrm{H}^+} = \alpha\, c, \qquad c_{\mathrm{A}^-} = \alpha\, c\,.$$

Equation (11.53) can then be written in the form

$$K = \frac{\alpha^2\, c\, \gamma_{\pm}^2}{(1-\alpha)\, \gamma_{\rm HA}}\, \frac{1}{c^{\rm st}}\,, \tag{11.54}$$

where c is the initial concentration of the acid.

Example

The dissociation degree of acetic acid of the concentration $c = 0.0025\,\mathrm{mol\,dm^{-3}}$ is $\alpha = 0.0825$. Calculate the dissociation constant of the acid

a) given that $\gamma_{\rm HA} = \gamma_{\pm} = 1$,

b) given that $\gamma_{\rm HA} = 1$ and $\gamma_{\pm} = 0.983$, which is the estimate from relation (11.45).

c) Compare the two results.

Solution

Substituting into relation (11.54) yields

a)

$$K = \frac{0.0825^2 \times 0.0025 \times 1^2}{(1-0.0825)\times 1} = 1.85\times 10^{-5}\,,$$

b)

$$K = \frac{0.0825^2 \times 0.0025 \times 0.983^2}{(1-0.0825)\times 1} = 1.79\times 10^{-5}\,.$$

c) If we neglect the effect of the activity coefficients, the error in the dissociation constant will be about 3 per cent in this case.

Note: The dissociation of a weak acid, equation (11.52), may be also written as

$$\mathrm{HA} + \mathrm{H_2O} = \mathrm{H_3O^+} + \mathrm{A^-}\,,$$

see the Note in section **11.1.2**. Then we have for the dissociation constant

$$K = \frac{c_{\mathrm{H_3O^+}}\, c_{\mathrm{A^-}}\, \gamma_\pm^2}{a_{\mathrm{H_2O}}\, c_{\mathrm{HA}}\, \gamma_{\mathrm{HA}}}\, \frac{1}{c^{\mathrm{st}}}\,.$$

For $a_{\mathrm{H_2O}} = 1$, which applies practically every time, this relation is identical with equation (11.53), since $c_{\mathrm{H_3O^+}} = c_{\mathrm{H^+}}$.

11.5.4 Dissociation of a weak monoacidic base

A weak monoacidic base BOH dissociates according to the equation

$$\mathrm{BOH} = \mathrm{B^+} + \mathrm{OH^-}\,. \tag{11.55}$$

The equilibrium constant of this reaction is called the **base dissociation constant**, for which we have

$$K = \frac{c_{\mathrm{B^+}}\, c_{\mathrm{OH^-}}\, \gamma_\pm^2}{c_{\mathrm{BOH}}\gamma_{\mathrm{BOH}}}\, \frac{1}{c^{\mathrm{st}}}\,. \tag{11.56}$$

If we neglect the contribution of the ions formed in consequence of water dissociation to the concentration of the hydrogen ions, we may rewrite equation (11.56) to

$$K = \frac{\alpha^2\, c\, \gamma_\pm^2}{(1-\alpha)\, \gamma_{\mathrm{BOH}}}\, \frac{1}{c^{\mathrm{st}}}\,, \tag{11.57}$$

where c is the initial concentration of the base and α is the degree of dissociation.

11.5.5 Dissociation of weak polybasic acids and polyacidic bases

A weak dibasic acid $\mathrm{H_2A}$ dissociates in the first stage according to the equation

$$\mathrm{H_2A} = \mathrm{H^+} + \mathrm{HA^-} \tag{11.58}$$

and in the second stage according to the equation

$$\mathrm{HA}^- = \mathrm{H}^+ + \mathrm{A}^{2-}\,. \tag{11.59}$$

If we denote the equilibrium constant of the first reaction K_1 and of the second reaction K_2, we have

$$K_1 = \frac{c_{\mathrm{H}^+}\, c_{\mathrm{HA}^-}\, \gamma_{\mathrm{H}^+}\, \gamma_{\mathrm{HA}^-}}{c_{\mathrm{H_2A}}\, \gamma_{\mathrm{H_2A}}}\, \frac{1}{c^{\mathrm{st}}}\,, \tag{11.60}$$

$$K_2 = \frac{c_{\mathrm{H}^+}\, c_{\mathrm{A}^{2-}}\, \gamma_{\mathrm{H}^+}\, \gamma_{\mathrm{A}^{2-}}}{c_{\mathrm{HA}^-} \gamma_{\mathrm{HA}^-}}\, \frac{1}{c^{\mathrm{st}}}\,. \tag{11.61}$$

Note: In the concentration range in which the Debey-Hückel limiting relation applies, we have

$$\gamma_{\mathrm{H}^+} = \gamma_{\mathrm{HA}^-}\,, \quad \gamma_{\mathrm{A}^{2-}} = \gamma^4_{\mathrm{H}^+}\,.$$

Note: When $K_1 \gg K_2$ (the differences in the values of dissociation constants are of the order of 3 and higher), it is not necessary to consider dissociation in the second and higher stages. The same applies to diacidic bases. Similarly, we also neglect dissociation in higher stages in polybasic acids and polyacidic bases.

11.5.6 Dissociation of strong polybasic acids and polyacidic bases

A strong dibasic acid H_2A dissociates in the first stage completely

$$\mathrm{H_2A} \;\longrightarrow\; \mathrm{H}^+ + \mathrm{HA}^- \tag{11.62}$$

and in the second stage up to the attainment of equilibrium

$$\mathrm{HA}^- = \mathrm{H}^+ + \mathrm{A}^{2-}\,. \tag{11.63}$$

For the dissociation constant of the reaction (11.63) we have

$$K = \frac{c_{\mathrm{H}^+}\, c_{\mathrm{A}^{2-}}\, \gamma^4_{\pm}}{c_{\mathrm{HA}^-}}\, \frac{1}{c^{\mathrm{st}}}\,, \tag{11.64}$$

where we assume, in compliance with the Debye-Hückel limiting relation, that $\gamma_{\mathrm{H}^+} = \gamma_{\mathrm{HA}^-} = \gamma_\pm$ and $\gamma_{\mathrm{A}^{2-}} = \gamma_\pm^4$.

If we do not consider any other ions in the solution but those formed in consequence of reactions (11.62) and (11.63), we may rewrite equation (11.64) to

$$K = \frac{c\,\alpha(1+\alpha)\,\gamma_\pm^4}{1-\alpha}\,\frac{1}{c^{\mathrm{st}}}\,, \tag{11.65}$$

where c is the initial concentration of the acid and α is the degree of dissociation of the anion HA^-.

A strong diacidic base $\mathrm{B(OH)_2}$ dissociates in the second stage completely and in the second stage up to the attainment of equilibrium:

$$K = \frac{c_{\mathrm{B}^{2+}}\,c_{\mathrm{OH}^-}\,\gamma_\pm^4}{c_{\mathrm{BOH}^+}}\,\frac{1}{c^{\mathrm{st}}}\,, \tag{11.66}$$

Equation (11.65) also applies here, with c standing for the initial concentration of the base and α for the degree of dissociation of the cation BOH^+.

We do not present relations describing the dissociation of strong tribasic and higher acids or triacidic and higher bases. We would obtain them in a similar way—it would be enough to write equations for the dissociation in higher stages and the corresponding equilibrium constants.

11.5.7 Hydrolysis of salts

Hydrolysis is a phenomenon that occurs in the salts of strong bases and weak acids (e.g. sodium acetate), in the salts of weak bases and strong acids (e.g. ammonium chloride), and in the salts of weak bases and weak acids (e.g. ammonium acetate). These salts are strong electrolytes and consequently they dissociate in aqueous solutions completely. The dissociation products, i.e. the anion of a weak acid A^- or the cation of a weak base B^+, react further with water until a **hydrolytic equilibrium** is established.

11.5.8 Hydrolysis of the salt of a weak acid and a strong base

If we denote the salt of a strong base and a weak acid using the symbol NaA, the reactions taking place can be written as

$$\mathrm{NaA} \longrightarrow \mathrm{Na}^+ + \mathrm{A}^- \tag{11.67}$$

and

$$A^- + H_2O = HA + OH^- \,. \tag{11.68}$$

The equilibrium constant of the reaction (11.68) is called the **hydrolytic constant**. We write

$$K_h = \frac{a_{HA}\, a_{OH^-}}{a_{A^-}\, a_{H_2O}} \,. \tag{11.69}$$

In dilute solutions the equation simplifies to

$$K_h = \frac{c_{HA}\, c_{OH^-}}{c_{A^-}} \frac{1}{c^{st}} \,. \tag{11.70}$$

The following relation applies between the hydrolytic constant K_h, the ionic product of water K_w and the dissociation constant K of a weak acid HA

$$K_h = \frac{K_w}{K} \,. \tag{11.71}$$

11.5.9 Hydrolysis of the salt of a weak base and a strong acid

The following reactions proceed in the solutions of the salts of a weak base and a strong acid BCl

$$BCl \longrightarrow B^+ + Cl^- \tag{11.72}$$

and

$$B^+ + H_2O = BOH + H^+ \,. \tag{11.73}$$

The equilibrium constant of reaction (11.73) is also called the **hydrolytic constant**. We write

$$K_h = \frac{a_{BOH}\, a_{H^+}}{a_{B^+}\, a_{H_2O}} \,. \tag{11.74}$$

In dilute solutions the equation simplifies to

$$K_h = \frac{c_{BOH}\, c_{H^+}}{c_{B^+}} \frac{1}{c^{st}} \,. \tag{11.75}$$

Relation (11.71) also applies for the hydrolytic constant of reaction (11.72), with K standing for the dissociation constant of a weak base this time.

11.5.10 Hydrolysis of the salt of a weak acid and a weak base

The salt of a weak monoacidic base and a weak monobasic acid BA is a strong electrolyte and it dissociates completely according to the equation

$$\mathrm{BA} \longrightarrow \mathrm{B}^+ + \mathrm{A}^- \,. \tag{11.76}$$

Two hydrolytic reactions proceed in the system

$$\mathrm{B}^+ + \mathrm{H_2O} = \mathrm{BOH} + \mathrm{H}^+ \,, \tag{11.77}$$

$$\mathrm{A}^- + \mathrm{H_2O} = \mathrm{HA} + \mathrm{OH}^- \,. \tag{11.78}$$

In addition to them, the dissociation of water, i.e. the reaction (11.47), also has to be considered.

Let the equilibrium constant of reaction (11.77) be denoted $K_{\mathrm{h},1}$ and the equilibrium constant of reaction (11.78) be denoted $K_{\mathrm{h},2}$. Then we write

$$K_{\mathrm{h},1} = \frac{a_{\mathrm{H}^+}\, a_{\mathrm{BOH}}}{a_{\mathrm{B}^+}\, a_{\mathrm{H_2O}}} \,, \tag{11.79}$$

$$K_{\mathrm{h},2} = \frac{a_{\mathrm{OH}^-} a_{\mathrm{HA}}}{a_{\mathrm{A}^-} a_{\mathrm{H_2O}}} \,. \tag{11.80}$$

In dilute solutions the equation simplifies to

$$K_{\mathrm{h},1} = \frac{c_{\mathrm{H}^+}\, c_{\mathrm{BOH}}}{c_{\mathrm{B}^+}} \frac{1}{c^{\mathrm{st}}} \,, \tag{11.81}$$

$$K_{\mathrm{h},2} = \frac{c_{\mathrm{OH}^-} c_{\mathrm{HA}}}{c_{\mathrm{A}^-}} \frac{1}{c^{\mathrm{st}}} \,. \tag{11.82}$$

When calculating the equilibrium composition we solve a set of three equations: (11.81), (11.82), and (11.49), with the latter describing the dissociation of water.

11.6 Calculation of pH

11.6.1 Definition of pH

The quantity pH is defined by the relation

$$\mathrm{pH} = -\log a_{\mathrm{H}^+}\,, \tag{11.83}$$

where a_{H^+} is the activity of hydrogen ions. For practical calculations it is convenient to rewrite the equation to

$$\mathrm{pH} = -\log\left(\frac{c_{\mathrm{H}^+}}{c^{\mathrm{st}}}\,\gamma_{\mathrm{H}^+}\right)\,. \tag{11.84}$$

The activity coefficient of hydrogen ions is calculated from the Debye-Hückel relation (11.43) at low concentrations. At higher concentrations it is replaced with the mean activity coefficient $\gamma_\pm$.

11.6.2 pH of water

The pH of pure water is calculated from the relation

$$\mathrm{pH} = -\frac{1}{2}\log K_{\mathrm{w}}\,, \tag{11.85}$$

where K_{w} is the ionic product of water, see **11.5.2**.

Example

Calculate the pH of pure water at the standard pressure and at temperatures of 0 °C, 25 °C and 100 °C. The ionic product of water at 25 °C is 1.00×10^{-14}, its values at the other two temperatures are the results of the Example in Section **11.5.2.**

Solution

At 0 °C the ionic product of water is $K_\mathrm{w} = 1.25 \times 10^{-15}$. Substituting into (11.85) yields

$$\mathrm{pH} = -\frac{1}{2}\log(1.25 \times 10^{-15}) = 7.45\,.$$

At 25 °C and the standard pressure the ionic product of water is $K_\mathrm{w} = 1.00 \times 10^{-14}$ and

$$\mathrm{pH} = -\frac{1}{2}\log(1.00 \times 10^{-14}) = 7.00\,.$$

At 100 °C the ionic product of water is $K_\mathrm{w} = 9.81 \times 10^{-13}$ and

$$\mathrm{pH} = -\frac{1}{2}\log(9.81 \times 10^{-13}) = 6.00\,.$$

Note: In the past, water and aqueous solutions were studied almost exclusively at room temperature and atmospheric pressure. This is the reason for the deeply rooted conviction that the pH of pure water equals 7. The results of the above example make it clear that water has its pH = 7 only at a temperature of 25 °C and a pressure of 101.325 kPa.

11.6.3 pH of a neutral solution

A neutral solution is such an aqueous solution of a salt that does not contain any other ions of H^+ and OH^- but those formed in consequence of the dissociation of water. For the pH of a neutral solution, the same relation applies as that for the pH of pure water, i.e. equation (11.85).

Example

Calculate the pH of a solution of NaCl at a temperature of 25 °C and a pressure of 101.325 kPa.

Solution

The presence of sodium chloride does not affect K_w, the equilibrium constant of reaction (11.47) because NaCl is an inert component in this reaction, see **8.5.4**. The pH is thus the same as that of pure water at the given temperature and pressure, i.e. 7.00.

11.6.4 pH of a strong monobasic acid

For a strong monobasic acid HA it applies that $c_{\mathrm{H}^+} = c$, where c is the acid concentration. Then

$$\mathrm{pH} = -\log \frac{c\,\gamma_{\mathrm{H}^+}}{c^{\mathrm{st}}}\,. \tag{11.86}$$

Example
Calculate the pH of a solution of HCl of the concentration $c = 3\,\mathrm{mol\,dm^{-3}}$. The mean activity coefficient at a given temperature and pressure is $\gamma_{\pm} = 1.316$.

Solution
From relation (11.86) we approximate the activity coefficient of hydrogen ions using the mean activity coefficient to obtain

$$\mathrm{pH} = -\log(3 \times 1.316/1) = -0.596\,.$$

Note: It is obvious from the result of the above example that the often heard assertion about pH ranging in the interval from 0 to 14 is not true. Concentrated acids may have their pH negative, concentrated bases may have it higher than 14!

Relation (11.86) applies on condition that the concentration of hydrogen ions formed by the dissociation of water may be neglected. This assumption fails only in relation to the solutions of acids (and bases) of an extremely low concentration.

Example
Calculate the pH of a solution of HCl of the concentration $c = 10^{-8}\,\mathrm{mol\,dm^{-3}}$ at a temperature of 298 K and the standard pressure.

Solution

At a concentration as low as this, the activity coefficient of hydrogen ions is practically equal to one. If, however, we used relation (11.86), we would obtain a nonsensical result

$$\mathrm{pH} = -\log(10^{-8} \times 1) = 8$$

implying that the solution of hydrochloric acid is basic. The error is caused by the neglect of the concentration of hydrogen ions formed by the reaction (11.47). The correct procedure consists in solving a chemical equilibrium. The concentration of hydrogen ions is $c = 10^{-8} + x$, and the concentration of $\mathrm{OH^-}$ ions is $c_{\mathrm{OH^-}} = x$, where x is the concentration of the ions formed by the dissociation of water. We substitute the concentrations into equation (11.49) and set the activity coefficients equal to one

$$K_\mathrm{w} = 10^{-14} = (10^{-8} + x)x \qquad \Longrightarrow \qquad x = 9.5 \times 10^{-8}\,.$$

From this we obtain the correct result

$$c_{\mathrm{H^+}} = 10^{-8} + 9.5 \times 10^{-8} = 1.05 \times 10^{-7}\,\mathrm{mol\,dm^{-3}} \qquad \Longrightarrow \qquad \mathrm{pH} = 6.978\,.$$

11.6.5 pH of a strong monoacidic base

Provided that the concentration of the $\mathrm{OH^-}$ ions formed by the dissociation of water is negligible, it applies for a monoacidic base BOH that $c_{\mathrm{OH^-}} = c$, where c is the base concentration. The pH is determined by the relation

$$\mathrm{pH} = -\log\left(\frac{K_\mathrm{w}\, c^\mathrm{st}}{c\,\gamma_{\mathrm{OH^-}}}\right)\,. \tag{11.87}$$

11.6.6 pH of a strong dibasic acid and a strong diacidic base

For the pH of a strong dibasic acid $\mathrm{H_2A}$ we have

$$\mathrm{pH} = -\log\frac{c\,\gamma_{\mathrm{H^+}}}{c^\mathrm{st}} - \log(1+\alpha)\,, \tag{11.88}$$

where c is the acid concentration and α is the degree of dissociation in the second stage. We obtain it by solving equation (11.65)

$$\alpha = \frac{-(c+K') + \sqrt{(c+K')^2 + 4\,K'\,c}}{2\,c}\,, \qquad K' = \frac{K\,c^{\rm st}\,\gamma_{\rm HA^-}}{\gamma_{\rm H^+}\gamma_{\rm A^{2-}}} \approx \frac{K\,c^{\rm st}}{\gamma_\pm^4}\,, \tag{11.89}$$

where $\gamma_\pm$ is given in **11.5.6**.

> *Note:* If $c \gg K'$ or $c \ll K'$, the numerator of (11.89) is a difference of close numbers. Either use a sufficient number of digits in the evaluation, or a numerically stable equivalent form $\alpha = 2K'/[c+K'+\sqrt{(c+K')^2+4\,K'\,c}]$. The cases of weak acids and bases are similar.

For a strong diacidic base we have

$$\mathrm{pH} = -\,\log\left(\frac{K_{\rm w}\,c^{\rm st}}{c\,\gamma_{\rm OH^-}}\right) + \log\,(1+\alpha)\,, \tag{11.90}$$

where relations (11.89) apply for the degree of dissociation of the base in the second stage α.

Relations (11.88) and (11.90) apply on condition that it is not necessary to consider the dissociation of water. This has to be taken into account only at extremely low concentrations, for $c < 10^{-6}$ in order. In such cases we may assume that the dissociation in the second stage is complete, i.e. $\alpha \to 1$, and proceed similarly as in the Example in section **11.6.4**.

11.6.7 pH of a weak monobasic acid

A weak monobasic acid dissociates up to the attainment of a chemical equilibrium between the ions and undissociated acid molecules, see **11.5.3**. We have

$$\mathrm{pH} = -\,\frac{1}{2}\,\log\left(\frac{K'\,c\,\gamma_\pm^2}{(c^{\rm st})^2}\right) - \frac{1}{2}\,\log\,(1-\alpha)\,, \tag{11.91}$$

where c is the initial concentration of the acid and α is the degree of dissociation for which it follows from equation (11.53)

$$\alpha = \frac{-K' + \sqrt{K'^2 + 4\,K'\,c}}{2\,c}\,, \quad K' = \frac{K\,c^{\rm st}\,\gamma_{\rm HA}}{\gamma_\pm^2}\,, \tag{11.92}$$

where K is the dissociation constant of the acid.

If the dissociation degree is low, $\alpha < 0.1$ in order, relation (11.91) can be simplified to

$$\mathrm{pH} = -\frac{1}{2}\log\left(\frac{K'\,c\,\gamma_{\pm}^{2}}{(c^{\mathrm{st}})^{2}}\right). \tag{11.93}$$

Example

Calculate the pH of a dichloroacetic acid solution in water of the concentration $c = 0.01\,\mathrm{mol\,dm^{-3}}$ at a temperature of 298.15 K and the standard pressure. Under the given conditions the dissociation constant of the acid is $K = 0.0514$. Assume that all the activity coefficients are unity. Compare the result with the value calculated from the simplified relation (11.93).

Solution

We calculate K' and the degree of dissociation from relation (11.92)

$$\begin{aligned} K' &= \frac{0.0514 \times 1 \times 1}{1^2} = 0.0514\,, \\ \alpha &= \frac{-0.0514 + \sqrt{0.0514^2 + 4 \times 0.0514 \times 0.01}}{2 \times 0.01} = 0.857 \end{aligned}$$

and the pH value from (11.91)

$$\mathrm{pH} = -\frac{1}{2}\log\left(0.0541 \times 0.01\right) - \frac{1}{2}\log\left(1 - 0.857\right) = 2.06\,.$$

If we used the simplified relation (11.93), we would obtain

$$\mathrm{pH} = -\frac{1}{2}\log\left(0.0514 \times 0.01\right) = 1.63\,.$$

This value is considerably different from the correct result $\mathrm{pH} = 2.06$. It is so because the condition allowing for applying formula (11.93), i.e. a low degree of dissociation, is not fulfilled.

Equations (11.91) and (11.93) apply on condition that the effect of water dissociation on the pH can be neglected, which is usually so. However, we have to consider water dissociation if by calculation we obtain $\mathrm{pH} > 6$. This happens in two limiting cases:

1. The acid concentration is very low, $c = 10^{-6}$ in order. At very low concentrations a weak acid dissociates completely. The same procedure can be applied as in the Example in section **11.6.4**.
2. The product of the acid dissociation constant and its concentration is low, $K\,c < 10^{-12}$. In this case the set of equations (11.48) and (11.53) has to be solved.

11.6.8 pH of a weak monoacidic base

A weak monoacidic base dissociates up to the attainment of a chemical equilibrium between the ions and undissociated base molecules, see **11.5.4.** We have

$$\mathrm{pH} = -\frac{1}{2}\log\left(\frac{K_\mathrm{w}^2\,(c^\mathrm{st})^2}{K'\,c\,\gamma_\pm^2}\right) + \frac{1}{2}\log\left(1-\alpha\right), \tag{11.94}$$

where c is the initial concentration of the base and α is the degree of dissociation for which it follows from equation (11.57)

$$\alpha = \frac{-K' + \sqrt{K'^2 + 4\,K'\,c}}{2\,c}\,, \qquad K' = \frac{K\;c^\mathrm{st}\;\gamma_\mathrm{BOH}}{\gamma_\pm^2}\,, \tag{11.95}$$

where K is the dissociation constant of the base.

If the dissociation degree is low, $\alpha < 0.1$ in order, relation (11.94) may be simplified to

$$\mathrm{pH} = -\frac{1}{2}\log\left(\frac{K_\mathrm{w}^2\,(c^\mathrm{st})^2}{K'\,c\,\gamma_\pm^2}\right). \tag{11.96}$$

Relations (11.94) and (11.96) apply on condition that the effect of hydrogen ions formed in consequence of water dissociation can be neglected.

11.6.9 pH of weak polybasic acids and polyacidic bases

In weak dibasic acids and diacidic bases, when $K_2 \ll K_1$, it is enough to consider solely dissociation in the first stage. To calculate the pH of a weak acid and a weak base, we use relations (11.93) and (11.96), respectively.

If the conditions are not as above, we have to take into account dissociation in the second stage and solve, in the case of a weak dibasic acid, the set of equations (11.60) and (11.61). We calculate the concentration of hydrogen ions and substitute into relation (11.84). The procedure is similar for weak diacidic bases.

In weak polybasic acids and polyacidic bases, dissociation in the third stage and higher usually does not have any effect on the pH value.

11.6.10 pH of the salt of a weak acid and a strong base

In consequence of hydrolysis, see section **11.5.8**, solutions of the salts of strong bases and weak acids exhibit alkaline reactions. When calculating the pH it is usually necessary to consider not only the hydrolytic equilibrium but also the dissociation of water.

The set of equations (11.70) and (11.49) does not have an analytical solution. When the degree of hydrolysis is low, however, we obtain an analytical relation for the pH

$$\mathrm{pH} = -\frac{1}{2}\log\frac{K_\mathrm{w}\,K\,c^\mathrm{st}}{c}\,, \tag{11.97}$$

where K_w is the ionic product of water, K is the dissociation constant of the acid, and c is the initial concentration of the salt.

Example

Calculate the pH of an aqueous solution of sodium formate of the concentration $c = 0.001\,\mathrm{mol\,dm^{-3}}$ at a temperature of 298 K and the standard pressure. Under these conditions the dissociation constant of formic acid is $K = 1.77\times10^{-4}$, and the ionic product of water is $K_\mathrm{w} = 10^{-14}$.

Solution

Substituting into (11.97) yields

$$\mathrm{pH} = -\frac{1}{2}\log\left(\frac{10^{-14}\times1.77\times10^{-4}}{0.001}\right) = 7.376\,.$$

11.6.11 pH of the salt of a strong acid and a weak base

In consequence of hydrolysis, see section **11.5.9**, solutions of the salts of strong acids and weak bases exhibit acidic reactions. When calculating the pH it is usually necessary to consider not only the hydrolytic equilibrium but also the dissociation of water. We solve the set of equations (11.75) and (11.49), which does not have an analytical solution. When the degree of hydrolysis is low, however, we obtain an analytical relation for the pH

$$\mathrm{pH} = -\frac{1}{2}\log\frac{K_\mathrm{w}\,c}{K\,c^\mathrm{st}}\,, \tag{11.98}$$

where K_w is the ionic product of water, K is the dissociation constant of the base, and c is the initial concentration of the salt.

11.6.12 pH of the salt of a weak acid and a weak base

When calculating the pH, we have to solve the set of three equations (11.81), (11.82) and (11.49), of which the first two describe a hydrolytic equilibrium and the third describes the dissociation of water. This set does not have an analytical solution and thus has to be solved numerically. If, however, the degrees of hydrolysis α_1 and α_2 are low, we obtain a simplified relation for the pH

$$\mathrm{pH} = -\frac{1}{2}\log\frac{K_\mathrm{a}\,K_\mathrm{w}}{K_b}\,, \tag{11.99}$$

where K_a is the dissociation constant of the acid, K_b is the dissociation constant of the base, and K_w is the ionic product of water.

Note: From relation (11.99) it follows that at $K_\mathrm{a} > K_\mathrm{b}$ the solution of the salt solution is acidic while in the opposite case it is alkaline.

11.6.13 Buffer solutions

A **buffer solution** (**buffer**) is a system whose pH changes only a little with the addition of an acid or a base. It is usually an aqueous solution of a weak acid and its salt with a strong base (e.g. $CH_3COOH + CH_3COONa$), or a solution of a weak base and its salt with a strong acid (e.g. $NH_4OH + NH_4Cl$).

We obtain the pH of a buffer solution formed by a weak acid HA of the concentration c and its salt NaA of the concentration c_s by solving equation (11.53)

$$\mathrm{pH} = -\log\left(\frac{\gamma_\pm}{2\,c^\mathrm{st}}\left[-(K'+c_\mathrm{s})+\sqrt{(K'+c_\mathrm{s})^2+4\,K'\,c}\right]\right), \tag{11.100}$$

where $K' = K\,c^\mathrm{st}\,\frac{\gamma_\mathrm{HA}}{\gamma_\pm^2}$, and K is the dissociation constant of the acid. If the degree of dissociation of the acid is very low, the relation simplifies to

$$\mathrm{pH} = -\log\frac{K'\,c\,\gamma_\pm}{c^\mathrm{st}\,c_\mathrm{s}}\,. \tag{11.101}$$

We obtain the pH of a buffer solution formed by a weak base BOH of the concentration c and its salt BCl of the concentration c_s by solving equation (11.57)

$$\mathrm{pH} = -\log\left(\frac{2\,K_\mathrm{w}\,c^\mathrm{st}}{\gamma_\pm\left[-(K'+c_\mathrm{s})+\sqrt{(K'+c_\mathrm{s})^2+4\,K'\,c}\right]}\right), \tag{11.102}$$

where $K' = K\,c^\mathrm{st}\,\frac{\gamma_\mathrm{HA}}{\gamma_\pm^2}$, and K is the dissociation constant of the base. For a low degree of the base dissociation this relation rearranges to

$$\mathrm{pH} = -\log\frac{K_\mathrm{w}\,c_\mathrm{s}\,c^\mathrm{st}}{K'\,c\,\gamma_\pm}\,. \tag{11.103}$$

In relations (11.100) through (11.103) the influence of water dissociation is not considered. If their application leads to a pH close to the pH of pure water, it is a warning signal indicating that their application was not necessarily justified.

> *Note:* The reason for the low sensitivity of the pH of a buffer solution to the addition of an acid or a base relates to Le Chatelier's principle, see **8.5**. In the case of a weak acid and its salt, the following reaction proceeds in the system
>
> $$\mathrm{HA} = \mathrm{H}^+ + \mathrm{A}^-\,,\qquad \mathrm{NaA}\longrightarrow \mathrm{Na}^+ + \mathrm{A}^-\,.$$
>
> The addition of an acid to this system, i.e. H^+ ions, will suppress the dissociation of the acid because H^+ ions are actually the products of the reaction, see **8.5.1** The addition of a base, i.e. OH^- ions, will increase the dissociation of the acid. The hydroxylic ions react with the hydrogen ions and thus withdraw the products of the dissociation.

The **buffer capacity** of a buffer, β_b, related to the added base is defined by the relation

$$\beta_\mathrm{b} = \frac{\mathrm{d}\, c_\mathrm{b}}{\mathrm{d\,pH}}\,, \tag{11.104}$$

where c_b is the concentration of the added base. The buffer capacity β_a related to the added acid of the concentration c_b is

$$\beta_\mathrm{a} = \frac{\mathrm{d}\, c_\mathrm{a}}{\mathrm{d\,pH}}\,, \tag{11.105}$$

The higher the buffer capacities β_b and β_a, the less the buffer solution changes its pH. The highest buffer capacity is that in solutions in which $c_\mathrm{s} = c$, where c is the concentration of an acid or a base.

11.7 Solubility of sparingly soluble salts

If the concentration of a saturated solution of the salt $B_{\nu^+}A_{\nu^-}$ is lower than about 0.01 $\mathrm{mol\,dm^{-3}}$, we speak about a **sparingly soluble salt**. An equilibrium between the undissolved and dissolved salt is established in the system. The dissolved salt dissociates into ions completely. Overall we may write

$$\mathrm{B}_{\nu^+}\mathrm{A}_{\nu^-}(\mathrm{s}) = \nu^+\,\mathrm{B}^{z^+} + \nu^-\,\mathrm{A}^{z^-}\,. \tag{11.106}$$

The equilibrium constant of this reaction is called the **solubility product** K_s. We have

$$K_\mathrm{s} = \frac{a^{\nu^+}_{\mathrm{B}^{z+}}\,a^{\nu^-}_{\mathrm{A}^{z-}}}{a_{\mathrm{B}_{\nu^+}\mathrm{A}_{\nu^-}}} = c^{\nu^+}_{\mathrm{B}^{z+}}\,c^{\nu^-}_{\mathrm{A}^{z-}}\,\gamma^{\nu}_{\pm}\,(c^{\mathrm{st}})^{-\nu}\,, \tag{11.107}$$

where $\nu = \nu^+ + \nu^-$.

Example

The solubility product of silver chromate at a temperature of 298 K and the standard pressure is $K_\mathrm{s} = 9 \times 10^{-12}$. Calculate the solubility of silver chromate

a) given that $\gamma_\pm = 1$,

b) given that the Debye-Hückel relation with the constant $A = 1.176$ applies.

Solution

a) We have

$$\mathsf{Ag_2CrO_4}(\mathrm{s}) = 2\,\mathrm{Ag}^+ + \mathrm{CrO}_4^{2-}\,.$$

From the material balance it follows that $c_{\mathrm{Ag}^+} = 2\,c$ and $c_{\mathrm{CrO}_4^{2-}} = c$, where c is the concentration of the dissolved chromate. By substituting into (11.107) we obtain

$$9\times10^{-12} = (2\times c)^2\times c/(c^{\mathrm{st}})^3 \quad\Longrightarrow\quad c = 1.31\times10^{-4}\,\mathsf{mol\,dm}^{-3}\,.$$

b) We use the preceding result to calculate the ionic strength of the solution, see equations (11.42)

$$I = \frac{1}{2}\,(2\times c\times1^2 + c\times2^2) = 3\times c = 3\times1.37\times10^{-4} = 4.11\times10^{-4}\,.$$

We use relation (11.45) to calculate the mean activity coefficient

$$\ln\,\gamma_\pm = -1.176\times1\times2\times\sqrt{4.11\times10^{-4}} = -0.0477 \quad\Longrightarrow\quad \gamma_\pm = 0.953\,.$$

Now we substitute the mean activity coefficient into (11.107)

$$9\times10^{-12} = (2\times c)^2\times c\times0.953^3/(c^{\mathrm{st}})^3 \quad\Longrightarrow\quad c = 1.37\times10^{-4}\,\mathsf{mol\,dm}^{-3}\,.$$

If we add to a solution of a sparingly soluble salt an electrolyte that shares a cation or an anion with the salt, the solubility of the salt will decrease. If we add a small amount of an electrolyte that does not share an ion with the salt, the solubility of the salt will increase.

Example

Calculate the solubility of silver chromate in a solution of potassium chromate of the concentration $c_{\mathrm{s}} = 0.001\,\mathsf{mol\,dm}^{-3}$. Use the data from the preceding Example and compare the results with its solubility in pure water.

Solution

From the material balance it follows that $c_{\mathrm{Ag}^+} = 2\,c$ and $c_{\mathrm{CrO}_4^{2-}} = c + 0.01$, where c is the concentration of the dissolved chromate. We substitute into (11.107) while assuming that $\gamma_\pm = 1$.

$$9 \times 10^{-12} = (2\,c)^2 \times (c + 0.01) \doteq 4 \times c^2 \times 0.01 \quad \Longrightarrow \quad c = 1.5 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}\,.$$

This result can be made more accurate by considering the mean activity coefficient. As compared with the solubility in pure water, see the preceding Example, the solubility of silver chromate decreased almost 10-times.

11.8 Thermodynamics of galvanic cells

11.8.1 Basic terms

A **galvanic cell** is an electrochemical system, see **11.1.7**, in which a potential difference occurs between the anode and the cathode due to electrochemical reactions. This potential difference is called the **(equilibrium) cell potential**, in older literature also the **electromotive force of the cell**.

The anode, i.e. the electrode at which oxidation takes place, is charged negatively. The cathode, i.e. the electrode at which reduction takes place, is charged positively, compare with the beginning of section **11.2**.

In the simplest case, both electrodes share a single electrolyte. If it is not so, the galvanic cell is made up of two or more half-cells. The **half-cell** is formed by an electrode and an electrolyte that surrounds it.

> *Note:* In electrochemistry the term *electrode* is commonly used as a synonym to the term *half-cell*, e.g. "calomel electrode" or "glass electrode".

The interface between two half-cells is usually a frit which prevents the electrolyte surrounding the anode from mixing with that surrounding the cathode. A potential difference occurring at the interface between the two electrolytes is called the **diffusion** or **liquid junction potential**.

We often seek to suppress this liquid potential. This can be achieved by connecting the electrolytes by a **salt bridge,** which is usually a U-shape tube filled with a saturated solution of potassium chloride or potassium sulfate.

If no electric current passes through a galvanic cell, we say that the cell is in a **zero-current state**. The zero-current state may be attained in two ways:
a) the cell is disconnected,
b) the cell is connected with an external source compensating for the equilibrium cell potential.

From the thermodynamic point of view, we classify galvanic cells as reversible and irreversible. A **reversible cell** is such in which
a) no reaction proceeds in the zero-current state,
b) if the voltage of the external source exceeds the cell potential, the same reactions take place in it as in a cell without any external source, but in the opposite direction.

Example

The Daniell cell is an example of a galvanic cell. It is formed by two half-cells. One of them is a zinc electrode surrounded by a solution of zinc sulfate, and the other is a copper electrode surrounded by a solution of copper sulfate. The zinc electrode is the anode at which oxidation proceeds

$$\mathrm{Zn} = \mathrm{Zn}^{2+} + 2\,\mathrm{e}^- \,.$$

The copper electrode is the cathode at which reduction proceeds

$$\mathrm{Cu}^{2+} + 2\,\mathrm{e}^- = \mathrm{Cu}\,.$$

We add up the reaction at the anode and that at the cathode to obtain the overall reaction taking place in the cell

$$\mathrm{Zn} + \mathrm{Cu}^{2+} = \mathrm{Zn}^{2+} + \mathrm{Cu}\,.$$

If the electrodes are connected by a first-class conductor, electrons travel through the conductor from the anode to the cathode.

If the solutions of $ZnSO_4$ and $CuSO_4$ are separated by a frit, the zinc ions travel through the frit from the anode to the cathode while the sulfate ions travel in the opposite direction. The liquid potential originates at the interface.

11.8.2 Symbols used for recording galvanic cells

Galvanic cells are schematically recorded in a line, with the following conventions applied:

- The anode is written on the left, the cathode on the right. Their charges may, but do not have to, be marked.
- The phase interface is marked by a single vertical bar "|". We find it at the place of contact of the electrode and the electrolyte, two electrolytes separated by a frit, or at the place of contact of an undissolved salt and a metal in the case of electrodes of the second type, see **11.8.10**.
- If there is a salt bridge suppressing the diffusion potential at the place of contact of two electrolytes, we write a double vertical bar "||" instead of a single one.

- With the electrolyte we note its molality or activity in brackets. This may be omitted if it is unimportant in the given case.
- For gas electrodes, the gas pressure or fugacity is given in brackets. For amalgam electrodes, the composition of the amalgam is given in brackets.
- A dash (—) is written between a gas electrode and its carrier.
- In the case of electrodes of the second type, the symbol (s) is written with the chemical formula of undissolved salt, emphasizing that it is not salt in a solution.

Example

Describe the following galvanic cells:

a) $\ominus\ \mathrm{Zn}\,|\,\mathsf{ZnSO_4}(\underline{m}_1)\,||\,\mathsf{CuSO_4}(\underline{m}_2)\,|\,\mathrm{Cu}\ \oplus$

b) $\ominus\ \mathrm{Pt}\text{—}\mathrm{H_2}(p^{\mathrm{st}})\,|\,\mathrm{HCl}(a_\pm = 1)\,|\,\mathrm{AgCl(s)}\,|\,\mathrm{Ag}\ \oplus$

Solution

a) The cell is formed by a zinc anode dipped into a solution of zinc sulfate of the molality $\underline{m}_1$. This half-cell is separated by a salt bridge from another half-cell formed by a solution of copper sulfate of the molality $\underline{m}_2$ into which a copper cathode is dipped.

b) The cell is formed by a hydrogen anode with platinum as its carrier. Hydrogen pressure equals the standard pressure. The electrode is dipped into a solution of hydrochloric acid whose mean activity equals one. A silver electrode covered with solid silver chloride is dipped into the same electrolyte. This electrode is the cathode.

11.8.3 Electrical work

For the electrical work W_{el} we have

$$W_{\mathrm{el}} = -z\,\boldsymbol{F}\,E\,, \qquad (11.108)$$

where z is the number of electrons exchanged during the reaction in the cell, $\boldsymbol{F}$ is the Faraday constant, and E is the cell potential.

> *Note:* Work is related to 1 mole of reaction turnovers, see **8.1**, and consequently depends on the way the reaction is written.

The following relation applies between electrical work and a change in the Gibbs energy during reaction at a given temperature and pressure, see equation (3.15)

$$\Delta_{\mathrm{r}} G = W_{\mathrm{el}} = -\, z\, \boldsymbol{F}\, E\,, \qquad [T, p, \text{reversible process}]\,. \tag{11.109}$$

Example

The following reaction proceeds at the electrodes in a Daniell cell

$$\mathrm{Zn} = \mathrm{Zn}^{2+} + 2\,\mathrm{e}^- \,, \qquad \mathrm{Cu}^{2+} + 2\,\mathrm{e}^- = \mathrm{Cu}\,.$$

The equilibrium potential of the cell is 1 V.
a) Calculate the work done by the cell at one mole of reaction turnovers.
b) Calculate the work done by the cell at one mole of reaction turnovers if the reaction is written in the form

$$\frac{1}{2}\,\mathrm{Zn} = \frac{1}{2}\,\mathrm{Zn}^{2+} + \mathrm{e}^- \,, \qquad \frac{1}{2}\,\mathrm{Cu}^{2+} + \mathrm{e}^- = \frac{1}{2}\,\mathrm{Cu}\,.$$

Solution

a) From the reactions record it follows that $z = 2$. By substituting into (11.108) we obtain

$$W_{\mathrm{el}} = -2 \times 96485.3 \times 1 = -192\,970.6\,\mathrm{J\,mol^{-1}}\,.$$

The work done has an opposite sign and it is equal to $192\,970.6\,\mathrm{J\,mol^{-1}}$.
b) From the reactions record it follows that $z = 1$. The work done is half, 96 485.3 J/mol.

11.8.4 Nernst equation

Let the following overall chemical reaction proceed in a galvanic cell

$$a\,\mathrm{A} + b\,\mathrm{B} \ldots = s\,\mathrm{S} + t\,\mathrm{T} \ldots \tag{11.110}$$

By combining equations (8.10) and (11.109) we obtain for the cell potential

$$E = E^{\circ} - \frac{\boldsymbol{R}\,T}{z\,\boldsymbol{F}} \ln \frac{a_{\mathrm{S}}^{s}\, a_{\mathrm{T}}^{t} \ldots}{a_{\mathrm{A}}^{a}\, a_{\mathrm{B}}^{b} \ldots}\,, \tag{11.111}$$

where a_i is the activity of substance i. Relation (11.111) is called the **Nernst equation** for the equilibrium cell potential (electromotive force of the cell). The quantity $E^{\ominus}$ is called the **standard equilibrium cell potential**. It is the potential of a cell in which reaction (11.110) proceeds with the activities of all substances involved in the reaction being equal to one.

If the cell is in the state of thermodynamic equilibrium, $E = 0$ and we write

$$E^{\ominus} = \frac{\boldsymbol{R}\,T}{z\,\boldsymbol{F}}\,\ln K\,, \tag{11.112}$$

where K is the equilibrium constant of the reaction (11.110).

Note: For the activities of solids acting in the Nernst equation we choose the standard state of a pure substance at the temperature and pressure of the system—then $a_i = 1$. For the activities of ions we choose the standard state of unit molality—then $a_i = \underline{m}_i\,\gamma_{\pm}^{[m]}$. For the activity of gaseous substances we choose the standard state of an ideal gas at a given temperature and the pressure $p^{\mathrm{st}} = 101\,325\,\mathrm{Pa}$—then $a_i = f_i/p^{\mathrm{st}}$.

Relation (11.111) applies on condition that the cell diffusion potential, E_{d}, is zero (either the electrodes share an electrolyte or the diffusion potential is suppressed, e.g. by a salt bridge). If it is not so, then

$$E = E^{\ominus} - \frac{\boldsymbol{R}\,T}{z\,\boldsymbol{F}}\,\ln\frac{a_{\mathrm{R}}^{r}\,a_{\mathrm{S}}^{s}\dots}{a_{\mathrm{A}}^{a}\,a_{\mathrm{B}}^{b}\dots} + E_{\mathrm{d}}\,. \tag{11.113}$$

11.8.5 Electromotive force and thermodynamic quantities

From the relation between the cell potential and the reaction Gibbs energy (11.109) we have the following relations for the reaction enthalpy $\Delta_{\mathrm{r}}H$, the reaction entropy $\Delta_{\mathrm{r}}S$, and the reaction isobaric heat capacity $\Delta_{\mathrm{r}}C_p$

$$\Delta_{\mathrm{r}}H = z\,\boldsymbol{F}\left[T\left(\frac{\partial E}{\partial T}\right)_p - E\right], \tag{11.114}$$

$$\Delta_{\mathrm{r}}S = z\,\boldsymbol{F}\left(\frac{\partial E}{\partial T}\right)_p, \tag{11.115}$$

$$\Delta_{\mathrm{r}}C_p = z\,\boldsymbol{F}\,T\left(\frac{\partial^2 E}{\partial T^2}\right)_p. \tag{11.116}$$

Note: The same relations apply between the standard cell potential (electromotive force) and the standard reaction thermodynamic functions.

In a reversible cell, relation (11.108) applies between the electrical work and equilibrium electromotive force. If the electrodes are connected in a short circuit, the electrical work is zero. If there is an electrical device between the electrodes, the following analogy of relation (11.108) applies for the electrical work

$$W_{\mathrm{el}} = -zFE_{\mathrm{tv}}\,, \tag{11.117}$$

where $E_{\mathrm{tv}} < E$ is the so-called **terminal voltage**, the measured voltage between the electrodes.

If the cell works reversibly, we write for the heat supplied to the cell

$$Q = T\,\Delta_{\mathrm{r}} S = z\,\boldsymbol{F}\,T\left(\frac{\partial E}{\partial T}\right)_p\,, \quad [T, p,\ \text{reversible process}]\,. \tag{11.118}$$

If, however, the anode and the cathode are connected in a short circuit, i.e. there is no electrical device between them and consequently no electrical work is done, the heat is equal to the enthalpy change

$$Q = \Delta_{\mathrm{r}} H = z\,\boldsymbol{F}\left[T\left(\frac{\partial E}{\partial T}\right)_p - E\right]\,, \qquad [T, p, W_{\mathrm{el}} = 0]\,. \tag{11.119}$$

In real (irreversible) cells in which the anode and the cathode are connected via an electrical device, Q is found between the values determined from equations (11.118) and (11.119). We can calculate them using the first law of thermodynamics

$$Q = \Delta_{\mathrm{r}} U - W_{\mathrm{el}}\,, \tag{11.120}$$

where $\Delta_{\mathrm{r}} U$ is the reaction internal energy and W_{el} is the electrical work calculated from relation (11.117).

11.8.6 Standard hydrogen electrode

The standard hydrogen electrode is such at which the following reaction occurs

$$\mathrm{H}^+ + \mathrm{e}^- = \frac{1}{2}\,\mathrm{H}_2(g)\,, \tag{11.121}$$

while the activity of hydrogen ions is equal to one, $a_{\mathrm{H}^+} = 1$, and the fugacity of hydrogen is equal to the standard pressure, $f_{\mathrm{H}_2} = 101325\,\mathrm{Pa}$.

> *Note:* The standard hydrogen electrode consists of a platinum strip covered with platinum black, saturated with hydrogen under a pressure of 101325 Pa, and dipped into a solution of hydrochloric acid of the molality $1.2\,\mathrm{mol\,kg^{-1}}$ (the corresponding activity of hydrogen ions is unity).

11.8.7 Nernst equation for a half-cell

An electrochemical reaction occurs at the electrode in a half-cell, e.g.

$$\mathrm{B}^{z^+} + z^+\mathrm{e}^- = \mathrm{B}\,. \tag{11.122}$$

For this reaction we can write

$$\Phi = \Phi^\ominus - \frac{\boldsymbol{R}T}{z^+\boldsymbol{F}} \ln \frac{a_\mathrm{B}}{a_{\mathrm{B}^{z+}}}\,. \tag{11.123}$$

The quantity Φ is called the **electrode potential**, $\Phi^\ominus$ is the **standard electrode potential**.

The electrode potential is defined as the equilibrium potential (electromotive force) of a galvanic cell in which one electrode is the standard hydrogen electrode and the other is the studied electrode. When oxidation proceeds at the studied electrode, we speak about the **oxidation potential** Φ_ox, when reduction occurs, we speak about the **reduction potential** Φ_red. It applies that

$$\Phi_\mathrm{ox} = -\Phi_\mathrm{red}\,, \quad \Phi^\ominus_\mathrm{ox} = -\Phi^\ominus_\mathrm{red}\,. \tag{11.124}$$

> *Note:* Based on an international agreement, we can find only the values of standard reduction potentials in tables.

11.8.8 Electromotive force and electrode potentials

Electrode potentials allow for the calculation of the potential a cell using the relation

$$E = \Phi_\mathrm{ox} + \Phi_\mathrm{red}\,, \tag{11.125}$$

where Φ_{ox} is the potential of the anode (on which oxidation occurs), and Φ_{red} is the potential of the cathode (on which reduction occurs). The same relation applies for the standard cell potential and the standard electrode potentials

$$E^{\ominus} = \Phi^{\ominus}_{\mathrm{ox}} + \Phi^{\ominus}_{\mathrm{red}}\,. \tag{11.126}$$

In view of relations (11.124) we can rewrite equations (11.125) and (11.126) to the forms in which only reduction potentials appear

$$E = -\Phi_{\mathrm{red}}(\mathrm{anode}) + \Phi_{\mathrm{red}}(\mathrm{cathode})\,, \quad E^{\ominus} = -\Phi^{\ominus}_{\mathrm{red}}(\mathrm{anode}) + \Phi^{\ominus}_{\mathrm{red}}(\mathrm{cathode})\,. \tag{11.127}$$

Note: Equation (11.125) and the first of equations (11.127) apply only for galvanic cells with one electrolyte and for cells without transference. For cells with transference, the diffusion potential has to be added to the cell potential.

11.8.9 Classification of half-cells

Half-cells are divided into several categories:

- A metal electrode, in which the electrolyte contains the ions of the given metal. These half-cells are divided into the following sub-categories:
  - amalgam,
  - first-type,
  - second-type.
- A nonmetal electrode, in which the electrolyte contains the ions of a nonmetal. These half-cells are divided based on the nature of the electrode:
  - gas electrode,
  - solid electrode.
- Reduction-oxidation half-cells
- Ion-selective half-cells.

11.8.10 Examples of half-cells

Presented below are some typical examples of the individual half-cell categories and sub-categories. The reactions at the electrodes and the Nernst equation are given for reduction.

11.8.10.1 Amalgam half-cell

In this half-cell the electrode is formed by mercury in which a metal is dissolved. The electrolyte contains the cations of this metal.

Example

An electrode is formed by cadmium dissolved in mercury. The molality of the dissolved cadmium is denoted $\underline{m}_1$. The electrolyte is an aqueous solution of cadmium sulfate. The molality of the Cd^{2+} ions in the solution is denoted $\underline{m}_2$.

Reaction:

$$\mathrm{Cd}^{2+} + 2\,\mathrm{e}^- = \mathrm{Cd}\,.$$

Nernst equation:

$$\Phi = \Phi^{\ominus} - \frac{\boldsymbol{R}\,T}{2\,\boldsymbol{F}}\,\ln\frac{\underline{m}_1\,\gamma_{\mathrm{Cd}}}{\underline{m}_2\,\gamma_\pm}\,.$$

11.8.10.2 Half-cell of the first type

The electrode is formed by a metal, with the electrolyte containing the cations of this metal.

Example

A copper electrode is dipped into a solution of copper sulfate of the molality $\underline{m}$.

Reaction:

$$\mathrm{Cu}^{2+} + 2\,\mathrm{e}^- = \mathrm{Cu}\,.$$

Nernst equation:

$$\Phi = \Phi^{\ominus} - \frac{\boldsymbol{R}\,T}{2\,\boldsymbol{F}}\,\ln\frac{\underline{m}^{\mathrm{st}}}{\underline{m}\,\gamma_\pm}\,.$$

11.8.10.3 Half-cell of the second type

Half-cells of the second type are formed by a metal electrode coated with a layer of a sparingly soluble salt whose cation is the given metal. The electrode is dipped into an electrolyte which has the same anion as the sparingly soluble salt.

Example

A silver electrode coated with a layer of solid silver chloride (a silver chloride electrode) is dipped into a solution of hydrogen chloride of the molality $\underline{m}$.

Partial reactions:

$$\mathrm{AgCl(s)} = \mathrm{Ag^+} + \mathrm{Cl^-}\,, \quad \mathrm{Ag^+} + \mathrm{e^-} = \mathrm{Ag(s)}\,.$$

Overall reaction:

$$\mathrm{AgCl(s)} + \mathrm{e^-} = \mathrm{Ag(s)} + \mathrm{Cl^-}\,.$$

Nernst equation:

$$\Phi = \Phi^{\ominus} - \frac{\boldsymbol{R}\,T}{\boldsymbol{F}}\,\ln\frac{\underline{m}\,\gamma_{\pm}}{\underline{m}^{\mathrm{st}}}\,.$$

Note: Half-cells of the second type are used as so-called **referential electrodes** to determine standard potentials of other half-cells. Compared with the standard hydrogen electrode (see **11.8.6**) which was chosen for the definition of half-cell potentials, referential electrodes offer a number of practical benefits. Their potentials in relation to the standard hydrogen electrode are measured very accurately.

11.8.10.4 Gas half-cell

An inert electrode is washed by a gas. In the electrolyte there are ions (either anions or cations) of this gas.

Example

An example is the standard hydrogen electrode, see **11.8.6**. Another example is a chlorine electrode—a platinum electrode washed by chlorine of the partial pressure p. The electrode is dipped into a solution of hydrogen chloride of the molality $\underline{m}$.

Reaction:

$$\mathrm{Cl_2} + 2\,\mathrm{e}^- = 2\,\mathrm{Cl}^-\,.$$

Nernst equation:

$$\Phi = \Phi^{\ominus} - \frac{\boldsymbol{R}T}{2\,\boldsymbol{F}}\,\ln\frac{\gamma_\pm^2\,\underline{m}^2/(\underline{m}^{\mathrm{st}})^2}{p\,\varphi/p^{\mathrm{st}}}\,,$$

where φ is the fugacity coefficient of gaseous chlorine.

11.8.10.5 Reduction-oxidation half-cell

This half-cell is comprised of an inert electrode dipped into an electrolyte containing a substance in two different oxidation degrees, e.g. ions Fe^{2+} and Fe^{3+}.

Example

Another example is the so-called quinhydrone electrode. It is a platinum electrode dipped into a saturated solution of quinhydrone, an equimolar mixture of quinon $C_6H_4O_2$ and hydroquinon $C_6H_4(OH)_2$ containing hydrogen ions of the activity a_{H^+}. It is assumed that the activities of quinon and hydroquinon are equal.

Reaction:

$$C_6H_4O_2 + 2\,\mathrm{H}^+ + 2\,\mathrm{e}^- = C_6H_4(OH)_2\,.$$

$$\Phi = \Phi^{\ominus} - \frac{\boldsymbol{R}T}{\boldsymbol{F}}\,\ln\frac{1}{a_{\mathrm{H}^+}}\,.$$

11.8.10.6 Ion-selective half-cell

This is a cell exchanging only ions of one type with another half-cell.

Example

An example is the so-called glass electrode. This half-cell is comprised of a silver chloride electrode dipped into an electrolyte containing a HCl solution of the molality $\underline{m}_1$. This electrolyte is enclosed in a vessel made of special glass permeable only for hydrogen ions. Outside the vessel there is another HCl solution of the molality $\underline{m}_2$. The hydrogen ions are exchanged between these two solutions.

Nernst equation:

$$\Phi = \Phi^{\ominus} - \frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln \frac{\underline{m}_2\, \gamma_{\pm,2}}{\underline{m}_1\, \gamma_{\pm,1}} = \text{const} - \frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln \left(\underline{m}_2\, \gamma_{\pm,2}\right) .$$

In this case $\Phi^{\ominus}$ does not have the physical meaning of the standard potential, but it is a constant dependent on the material of the half-cell.

11.8.11 Classification of galvanic cells

If electric energy is generated in a galvanic cells in consequence of chemical reactions, we speak about a **chemical cell**. If, on the other hand, it is generated in consequence of the equalization of differences in the concentrations of substances present in different parts of the cell, we speak about a **concentration cell**.

Concentration cells are divided into two categories:

- **Electrolyte concentration cells**

  The anodic and cathodic compartments are formed by the same electrolyte of different concentrations. Both electrodes are identical. Electrolyte concentration cells are further divided into

  - cells with transference,
  - cells without transference.
- **Electrode concentration cells**

  The concentration differences occur at the (otherwise identical) electrodes. These are dipped into a shared electrolyte. Electrode concentration cells are further divided into

  - gas concentration cells comprised of two identical gas electrodes with different partial pressures of the gas

- amalgam concentration cells comprised of two mercury electrodes containing a dissolved metal of different concentrations.

11.8.12 Electrolyte concentration cells with transference

The cell is formed by two identical electrodes dipped into the same but unequally concentrated solution. Both half-cells are separated in a way that allows for the transfer of ions.

Example

Consider a galvanic cell formed by two identical hydrogen electrodes dipped into HCl solutions of the activities a_1 and a_2, with $a_1 < a_2$. The solutions are separated by a frit allowing for the transfer of ions:

$$\mathrm{Pt}\text{—}\mathrm{H_2}(p)\,|\,\mathrm{HCl}(a_1)\,|\,\mathrm{HCl}(a_2)\,|\,\mathrm{Pt}\text{—}\mathrm{H_2}(p)\,.$$

Solution

The following partial reactions occur in the cell:

$$\begin{aligned}
&\tfrac{1}{2}\,\mathrm{H_2}(g) &&= \mathrm{H^+}(a_1) + \mathrm{e^-} &&\text{oxidation at the anode}\,,\\
&t^+\,\mathrm{H^+}(a_1) &&= t^+\,\mathrm{H^+}(a_2) &&\text{transfer across the frit}\,,\\
&t^-\,\mathrm{Cl^-}(a_2) &&= t^-\,\mathrm{Cl^-}(a_1) &&\text{transfer across the frit}\,,\\
&\mathrm{H^+}(a_2) + \mathrm{e^-} &&= \tfrac{1}{2}\,\mathrm{H_2}(g) &&\text{reduction at the cathode}\,.
\end{aligned}$$

The Nernst equation:

$$E = 2t^-\frac{\boldsymbol{R}T}{\boldsymbol{F}}\ln\frac{\underline{m}_2\gamma_{\pm,2}}{\underline{m}_1\gamma_{\pm,1}}$$

Note: Since both electrodes are identical, the standard cell potential E° is zero and does not appear in the Nernst equation. This fact is characteristic of all concentration cells.

11.8.13 Electrolyte concentration cells without transference

The cell is formed by two identical electrodes dipped into the solutions of the same electrolyte, but of different concentrations. Both half-cells are separated in a way that enables ion transfer.

Example

Consider the following galvanic cell

$$\mathrm{Pt—H_2}(p)\,|\,\mathrm{HCl}(a_1)\,|\,\mathrm{AgCl(s)}\,|\,\mathrm{Ag—Ag}\,|\,\mathrm{AgCl(s)}\,|\,\mathrm{HCl}(a_2)\,|\,\mathrm{Pt—H_2}(p)\,,$$

where $a_2 > a_1$.

Solution

Its difference from a cell with transference is that instead of a frit it has a silver chloride electrode. It acts as a cathode with respect to the hydrogen electrode on the left of the cell record and as an anode with respect to the hydrogen electrode on the right. The following partial reactions proceed in the cell:

$$\begin{aligned}
&\tfrac{1}{2}\,\mathrm{H_2}(g) &&= \mathrm{H^+}(a_1) + \mathrm{e^-} &&\text{oxidation at the hydrogen anode}\,,\\
&\mathrm{AgCl}(s) + \mathrm{e^-} &&= \mathrm{Ag(s)} + \mathrm{Cl^-}(a_1) &&\text{reduction at the silver chloride electrode}\,,\\
&\mathrm{Ag(s)} + \mathrm{Cl^-}(a_2) &&= \mathrm{AgCl(s)} + \mathrm{e^-} &&\text{oxidation at the silver chloride electrode}\,,\\
&\mathrm{H^+}(a_2) + \mathrm{e^-} &&= \tfrac{1}{2}\,\mathrm{H_2}(g) &&\text{reduction at the hydrogen cathode}\,.
\end{aligned}$$

$$E = 2\,\frac{\boldsymbol{R}T}{\boldsymbol{F}}\,\ln\frac{\underline{m}_2\,\gamma_{\pm,2}}{\underline{m}_1\,\gamma_{\pm,1}}\,.$$

11.8.14 Gas electrode concentration cells

The cell is comprised of two identical gas electrodes containing gas of different partial pressures. The electrodes are dipped into a shared electrolyte.

Example

Let us consider a cell formed by two hydrogen electrodes with the partial pressures of hydrogen p_1 and p_2, with $p_1 > p_2$, dipped into a shared electrolyte.

$$\mathrm{Pt—H_2}(p_1)\,|\,\mathrm{HCl}(a)\,|\,\mathrm{Pt—H_2}(p_2)\,.$$

Solution

The following reactions proceed in the cell:

$$\begin{aligned} \tfrac{1}{2}\,\mathrm{H}_2(p_1) &= \mathrm{H}^+(a) + \mathrm{e}^- && \text{oxidation}\,, \\ \mathrm{H}^+(a) + \mathrm{e}^- &= \tfrac{1}{2}\,\mathrm{H}_2(p_2) && \text{reduction}\,. \end{aligned}$$

Nernst equation:

$$E = \frac{\boldsymbol{R}T}{2\,\boldsymbol{F}}\,\ln\frac{p_1\,\varphi_1}{p_2\,\varphi_2}\,,$$

where φ_1 and φ_2 are the fugacity coefficients of hydrogen.

11.8.15 Amalgam electrode concentration cells

The cell is formed by two mercury electrodes in which the same metal of different concentrations is dissolved. The electrodes are dipped into a shared electrolyte in which there are cations of the given metal.

Example

Let us consider a cell formed by two cadmium amalgam electrodes dipped into a shared electrolyte

$$\mathrm{Cd(Hg)}(a_1)\,|\,\mathsf{CdSO_4}(a)\,|\,\mathrm{Cd(Hg)}(a_2)\,,$$

where $a_1 > a_2$. The following reactions proceed in the cell:

$$\begin{aligned} \mathrm{Cd}(a_1) &= \mathrm{Cd}^{2+}(a) + 2\,\mathrm{e}^- && \text{oxidation}\,, \\ \mathrm{Cd}^{2+}(a) + 2\,\mathrm{e}^- &= \mathrm{Cd}(a_2) && \text{reduction}\,. \end{aligned}$$

Nernst equation:

$$E = \frac{\boldsymbol{R}T}{2\,\boldsymbol{F}}\,\ln\frac{a_1}{a_2}\,.$$

11.9 Electrode polarization

During electrolysis, the products of electrochemical reactions are discharged at the electrodes. These products cause the formation of a galvanic cell whose potential (electromotive force) suppresses the electrolysis (this is another example of Le Chatelier's principle, see **8.5**). This phenomenon is called **electrode polarization**, the respective electrode potential is called the **polarization voltage**, E_p. Ohm's law then acquires the form

$$E - E_p = I\,R\,. \tag{11.128}$$

It is obvious that the electrolysis starts at voltages higher than the polarization voltage.

Example

During the electrolysis of hydrochloric acid, hydrogen is discharged at the cathode and chlorine at the anode. A galvanic cell originates formed by a hydrogen anode, chlorine cathode, and a hydrogen chloride solution. Electrolysis starts only when the voltage of the source is higher than the potential (electromotive force) of the given cell (approximately 1.36 V under laboratory conditions).

In addition, polarization voltage may be due to concentration changes during electrolysis, see **11.2.5**. An electrolyte concentration cell originates, see **11.8.13**, whose potential also suppresses the electrolysis. In this connection we speak about **concentration polarization** while in the above example it was **chemical polarization**.

It is necessary to distinguish between the polarization voltage and the **decomposition voltage**, the real voltage of the source at which undisturbed electrolysis starts to proceed. The difference between the decomposition and polarization voltages is called **overvoltage**. It is caused by complicated kinetic phenomena during electrolysis.

Chapter 12

Basic terms of chemical physics

Chemical physics is an important area of modern physical chemistry embracing theoretical fields on the boundary between chemistry and physics. Chemical physics describes the studied system either as a system of macroscopic phases without any further inner structure, or as a set of elementary particles and the atoms and molecules composed of them, from which the properties of the whole system are then derived by mathematical procedures. Comparison of both the above approaches allows for gaining a lot of information both about the system as a whole and about the properties of the molecules it contains.

12.1 Interaction of systems with electric and magnetic fields

In addition to the classic thermodynamic quantities such as temperature, volume and pressure, other system properties need to be defined for systems interacting with the surrounding fields.

12.1.1 Permittivity

The vector of the intensity of the electric field around a point charge following from the **Coulomb law** is

$$\vec{\mathcal{E}} = \frac{1}{4\pi\varepsilon}\frac{Q\,\vec{r}}{r^3}, \tag{12.1}$$

where Q is the electric charge given in coulombs, $\vec{r}$ is the vector determining the position of the point in relation to the charge, and ε is the **permittivity** of the surrounding environment.

The lowest value of permittivity is that of vacuum, $\varepsilon_0 = 8.854 \times 10^{-12}\,\mathrm{C^2\,N^{-1}\,m^{-2}}$. Other environments exhibit a higher permittivity, which is usually expressed using the **relative permittivity**

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}\,. \tag{12.2}$$

Relative permittivity shows the ability of a substance to weaken the electric field, and it may be determined by measuring the ratio between the capacitance C of a capacitor with the given substance and another with vacuum, C_0,

$$\varepsilon_r = \frac{C}{C_0}\,.$$

Note: In older literature, relative permittivity is called the dielectric constant.

U *Main units:* permittivity: $\mathrm{C^2\,N^{-1}\,m^{-2}}$, relative permittivity is a dimensionless number.

Example

Determine the relative permittivity of water if you know that the capacitance of a capacitor with an empty cell is 5 pF, and that it increases to 390 pF after the cell is filled with water. Assume that the capacitance is determined solely by the filling of the cell.

Solution

The capacitance of the capacitor is proportional to the permittivity of the space between the electrodes. With the cell empty, the permittivity is very close to that of vacuum. The relative permittivity of water is thus equal to the ratio between both capacitances,

$$\varepsilon_r = \frac{C}{C_0} = \frac{390\,\mathrm{pF}}{5\,\mathrm{pF}} = 78\,.$$

12.1.2 Molar polarization and refraction

Molar polarization is another quantity derived from relative permittivity:

$$P_{\mathrm{m}} = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} V_{\mathrm{m}} = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \frac{M}{\rho} \,, \tag{12.3}$$

where V_{m} is the molar volume [see **2.1.1**].

U *Main unit:* $\mathrm{m}^3\,\mathrm{mol}^{-1}$.

Molar refraction is defined in a similar way:

$$R_{\mathrm{m}} = \frac{n^2 - 1}{n^2 + 2} V_{\mathrm{m}} \tag{12.4}$$

where n is the refractive index of the given substance.

In terms of the electric and magnetic properties of substances, electromagnetic radiation can be described as electromagnetic field oscillations. Since non-polar substances, i.e. those without permanent dipole moments [see **12.1.3**] in the range of higher wavelengths, have to satisfy the **Maxwell relation**[1]

$$\varepsilon_r = n^2, \tag{12.5}$$

their molar polarization and refraction acquire the same values.

12.1.3 Dipole moment

A pair of opposite electric charges of magnitude Q at a distance L constitutes an electric dipole. The measure of its magnitude is the dipole moment defined by the relation

$$\vec{\mu} = Q\,\vec{L}\,, \tag{12.6}$$

where vector $\vec{L}$ points from $-Q$ to Q.

U *Main unit:* C m.

Older unit: debye, $1\,\mathrm{D} = 3.33564 \times 10^{-30}\,\mathrm{C\,m}$.

In terms of the electric charge distribution, a molecule represent a much more complicated system containing positive charges (atomic nuclei) and negative charges (electrons). The electric

---

[1] More precisely $\varepsilon_r \mu_r = n^2$ (see (12.11)), where $\mu_r \doteq 1$.

field far enough from the molecule can be regarded as caused by one dipole determined by a combination of charges.

A homonuclear diatomic molecule (a molecule comprised of a pair of identical atoms) exhibits a symmetrical charge distribution and therefore its dipole moment is zero. These substances are called non-polar (N_2, Cl_2). If it is comprised of different atoms (HCl), the charge distribution is asymmetrical, the molecule has a nonzero dipole moment, and the substance is polar. In more complex molecules, the dipole moment depends on the type of atoms and their mutual orientation. The overall dipole moment is the vector sum of the dipole moments of individual bonds.

Example

Explain why CO_2 has a zero dipole moment while H_2O is polar.

Solution

Both the bonds C–O and O–H are polar and have a nonzero dipole moment. However, the CO_2 molecule is linear and the dipole moments of both bonds cancel. The molecule of water is nonlinear and its total dipole moment is the vector sum of the dipole moments of the two bonds.

Note: Also nonpolar molecules create a certain electric field around them, which is usually characterized by higher multipole moments (quadrupole, octupole, etc.).

12.1.4 Polarizability

In the presence of an electric field, the charge distribution in the molecule changes so that even nonpolar molecules acquire a nonzero dipole moment, i.e. they polarize. The magnitude of this **induced** dipole moment ($\vec{\mu}^*$) is proportional[2] to the intensity of the surrounding electric field ($\vec{\mathcal{E}}$). The proportionality constant is called polarizability (α),

$$\mu^* = \alpha\,\mathcal{E}\,. \tag{12.7}$$

---

[2] There are two simplifications here: The field is not too strong and the molecule is approximately rotationally symmetric so that $\vec{\mu}^*$ has the same direction as $\vec{\mathcal{E}}$

U *Main unit:* $\mathrm{C^2\,m\,J^{-1}}$.

> *Note:* Polarizability α is usually converted to the so called **polarizability volume** α',
>
> $$\alpha' = \frac{\alpha}{4\pi\varepsilon_0}\,,$$
>
> traditionally called also "polarizability". It has dimensions of volume and equals very roughly 1/10 of the volume of a molecule.

Polarization also occurs in polar molecules. In this case the total dipole moment is the vector sum of the permanent and induced dipole moments.

12.1.5 Clausius-Mossotti and Debye equations

For nonpolar substances, the molar polarization P_M is related to the polarizability of the molecules by the approximate relation called the **Clausius-Mossotti** equation,

$$P_M = \frac{N_A\,\alpha}{3\,\varepsilon_0}, \tag{12.8}$$

where N_A is the Avogadro constant.

For polar substances, the molar polarization is also influenced by the magnitude of the dipole moment. For not too large dipole moments relation(12.8) becomes

$$P_M = \frac{N_A}{3\,\varepsilon_0}\left(\alpha + \frac{\mu^2}{3k_\mathrm{B}T}\right), \tag{12.9}$$

where k_B is the Boltzmann constant ($k_\mathrm{B} = R/N_A = 1.381\times10^{-23}\,\mathrm{J\,K^{-1}}$). This more general relations is called the **Debye equation**, and it expresses the fact that polar molecules tend to further increase the permittivity of their environment by orienting themselves prevailingly in the direction of the electric field. With increasing temperature, however, the thermal motion of the molecules disturbs this orientation, and the effect of the molecular dipole moments gradually decreases. By measuring the thermal dependence of molar polarization it is possible to determine both the polarizability of molecules and their dipole moment.

Example

The relative permittivity of chlorobenzene at 20°C is $\varepsilon_1 = 5.71$. At 25°C it drops to $\varepsilon_2 = 5.62$. Calculate the polarizability and the dipole moment of chlorobenzene. Its density in the given temperature interval is approximately constant, $\rho = 1.11\,\mathrm{g\,cm^{-3}}$ and $M = 112.5\,\mathrm{g\,mol^{-1}}$.

Solution

By substituting into equations (12.3) and (12.9) for both temperatures while using the constants $k_\mathrm{B} = 1.381\times 10^{-23}\,\mathrm{J\,K^{-1}}$ and $\varepsilon_0 = 8.854\times 10^{-12}\,\mathrm{C^2 J^{-1} m^{-2}}$ we obtain a set of two equations with two unknowns (in SI units)

$$\frac{112.5\times 10^{-3}}{1.11\times 10^{3}}\,\frac{5.71-1}{5.71+2} = \frac{6.022\times 10^{23}}{3\times 8.854\times 10^{-12}}\left(\alpha + \frac{\mu^2}{3\times 1.381\times 10^{-23}\times 293.15}\right)$$

and

$$\frac{112.5\times 10^{-3}}{1.11\times 10^{3}}\,\frac{5.62-1}{5.62+2} = \frac{6.022\times 10^{23}}{3\times 8.854\times 10^{-12}}\left(\alpha + \frac{\mu^2}{3\times 1.381\times 10^{-23}\times 298.15}\right).$$

By solving this set of equations we obtain $\alpha = 1.5\times 10^{-39}\,\mathrm{C^2\,m^2\,J^{-1}}$ ($\alpha' = 1.35\times 10^{-29}\,\mathrm{m^3}$) and $\mu = 3.86\times 10^{-30}\,\mathrm{C\,m} = 1.16\,\mathrm{D}$.

12.1.6 Permeability and susceptibility

The magnetic field[3] $\vec{B}$ produced by a short segment of wire described by vector $\vec{\ell}$ carrying electric current I in the direction of $\vec{\ell}$ is given by the **Biot-Savart law**,

$$\vec{B} = \frac{\mu}{4\pi}\frac{I\,\vec{\ell}\times\vec{r}}{r^3}, \tag{12.10}$$

where $\vec{r}$ is the vector determining the point at which the magnetic field is measured and × indicates the vector product[4]. The proportionality constant μ is the **permeability** of the

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[3] More precisely **induction of the magnetic field** or **magnetic flux density**.

[4] Vector $\vec{c} = \vec{a}\times\vec{b}$ is perpendicular to both $\vec{a}$ and $\vec{b}$, the magnitude of $\vec{c}$ is $|\vec{c}| = c = ab\sin\gamma$, where γ is the angle between vectors $\vec{a}$ and $\vec{b}$, and vectors $\vec{a}$, $\vec{b}$, and $\vec{c}$ form a right-handed system.

surrounding environment. Its value for vacuum is $\mu_0 = 4\pi \times 10^{-7}\,\mathrm{J\,s^2\,C^{-2}\,m^{-1}}$. For other types of environment the permeability is different and it is sometimes expressed by the **relative permeability**

$$\mu_r = \frac{\mu}{\mu_0} \tag{12.11}$$

or more often by the **susceptibility** (more precisely volume magnetic susceptibility)

$$\chi = \mu_r - 1\,. \tag{12.12}$$

U *Main units:* permeability: $\mathrm{J\,s^2\,C^{-2}\,m^{-1}}$, relative permeability and susceptibility are dimensionless numbers.

Since different substances can either weaken or strengthen the magnetic field, magnetic susceptibility may be positive or negative. For most common substances it is very small (of the order of 10^{-3} and lower), and it can be determined by measuring the force acting on the substance in the field of a strong magnet. Materials weakening the field ($\chi < 0$) are called **diamagnetic**, materials strengthening the field ($\chi > 0$) are called **paramagnetic**. Some substances with freely moving electrons (iron, nickel, . . .) strengthen the magnetic field many times ($\chi \approx 10^2$ up to 10^4). These substances are referred to as **ferromagnetic**.

Note: The same symbol μ is used in this chapter for two different physical properties—permeability and molecule dipole moment (see **12.1.3**).

12.1.7 Molar magnetic susceptibility

The quantity called **molar magnetic susceptibility** is the magnetic-field analogy of the molar polarization (see **12.1.2**),

$$\chi_\mathrm{m} = \chi V_\mathrm{m}\,. \tag{12.13}$$

12.1.8 Magnetizability and magnetic moment

For most substances, the temperature dependence of molar magnetic susceptibility can be expressed by the relation

$$\chi_M = N_A \left(\alpha_m + \frac{\mu_0\, m_m^2}{3k_\mathrm{B}T} \right), \tag{12.14}$$

which is analogous to the Debye equation (12.9). In (12.14), α_m is the **magnetizability** of the molecules and m_m is their permanent **magnetic moment**. The magnetic moment of molecules is a consequence of the quantum behaviour of electrons in the electric field of atomic nuclei. It is strong for molecules with unpaired electrons (see **12.2.6**). Magnetizability of molecules reflects their ability to generate an induced magnetic moment by the influence of the surrounding magnetic field. If we substitute these quantities for the given substance into relation (12.14), we obtain the temperature dependence of molar susceptibility

$$\chi_M = A + \frac{B}{T}\,, \tag{12.15}$$

which was discovered empirically as the **Curie law** earlier.

Permanent moments strengthen the magnetic field in a substance (paramagnetic behaviour) while induced moments usually weaken it (diamagnetic behaviour). Consequently, the diamagnetic or paramagnetic behaviour [see **12.1.6**] of a substance is determined by the relative magnitudes of both terms in equation (12.15).

12.1.9 System interaction with light

The last type of a substance interaction with the external field to be discussed is the absorption of light passing through the substance. In order to be able to measure the light attenuation, we first have to define its **intensity** I as the amount of energy transferred by light in one second across an area of $1\,\mathrm{m}^2$, perpendicularly to the direction of the radiation.

Let us observe the behaviour of light passing through a solution of the absorbing substance in a solvent which does not absorb light in the given wavelength range. For a solution of the concentration c (see **1.6.4**), with the light passing through a layer of the thickness ℓ, the **Lambert-Beer** law applies

$$I' = 10^{-\varepsilon\, c\, \ell}\, I\,, \tag{12.16}$$

where I' and I are the light intensities after and before passing through the solution, and ε is the **molar absorption coefficient**. Its value depends on temperature, the type of the dissolved substance and the solvent, and on the wavelength of the passing light (12.42). In addition to the absorption coefficient, also used is the quantity

$$A = \varepsilon\, c\, \ell \tag{12.17}$$

called **absorbance**, and the ratio

$$T = \frac{I'}{I} \tag{12.18}$$

called **transmittance**.

U *Main units:* molar absorption coefficient: $\mathrm{m^2\,mol^{-1}}$, absorbance and transmittance are dimensionless quantities.

Example

Light of the wavelength 600 nm passes through a measuring cell which is 5 mm thick. The solution in the cell contains $CuSO_4$ of the concentration $c = 10\,\mathrm{mol\,m^{-3}}$. The intensity of the light passing through the cell drops to 30 per cent. What is the molar absorption coefficient?

Solution

From equation (12.16) it follows that

$$\varepsilon = -\frac{\log(I'/I)}{c\,\ell} = \frac{\log(0.30)}{10\,\mathrm{mol\,m^{-3}} \times 0.005\,\mathrm{m}} = 10.46\,\mathrm{m^2\,mol^{-1}}.$$

The Lambert-Beer law describes the absorption of light on the macroscopic level. However, it cannot explain why the light is absorbed by the substance. For this purpose the system has to be described as a set of molecules. This microscopic approach is applied in section **12.3**.

12.2 Fundamentals of quantum mechanics

12.2.1 Schrödinger equation

The starting point for describing a system on the microscopic level is the description of a set of particles (elementary particles, atoms and molecules) using their **wavefunction** Ψ. The wavefunction is obtained by solving the **Schrödinger equation**. It is written for time-independent case as follows

$$-\sum_{i=1}^{N}\frac{h^2}{8\pi^2 m_i}\vec{\nabla}_i^2\Psi(\vec{v})+V(\vec{v})\Psi(\vec{v})=E\,\Psi(\vec{v}), \tag{12.19}$$

where $\vec{v}=(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ is the generalized vector giving the position of all particles in the system, and $V(\vec{v})$ is the potential energy of the system. The symbol $\vec{\nabla}_i^2=\partial^2/\partial\vec{r}_i^2=\partial^2/\partial x_i^2+\partial^2/\partial y_i^2+\partial^2/\partial z_i^2$ denotes the **Laplace operator**, and h is the **Planck constant** ($h=6.626\times10^{-34}\,\mathrm{J\,s}$). The Schrödinger equation has a stable solution only for certain values of E, called the **eigenvalues** of energy, with the corresponding wavefunctions Ψ called **eigenfunctions**. The second power of the absolute value of the wavefunction, $|\Psi|^2=\Psi^*\Psi$ (* denotes complex conjugate), gives the probability density of the occurrence of a system in the state defined by the vector $\vec{v}$. These solutions are characterized by one or several integers known as **quantum numbers**[5]. If the same energy corresponds to several different combinations of quantum numbers, we say that the given energy level is **degenerate**. The number of these combinations is called the **degree of degeneracy** (g) of the energy level.

12.2.2 Solutions of the Schrödinger equation

The general solutions of the Schrödinger equation for systems containing more particles is usually very complicated. However, it is often possible to obtain its solution by partitioning the total potential energy of a system into energies corresponding to individual molecules of the system

$$V(\vec{v})=\sum_{i=1}^{N}V_i, \tag{12.20}$$

---

[5] This applies only to the so called bound states. Continuum states, as e.g. freely moving particle, do not have discrete energy levels.

where $V(\vec{v})$ is the total potential energy of a system of N molecules, and V_i are the energies of the individual molecules. For each molecule we then separate the terms corresponding to different types of motion:

- translation,
- rotation,
- vibration,
- movement of electrons around the nuclei,

$$V_i = V_{\text{trans}} + V_{\text{rot}} + V_{\text{vib}} + V_{\text{el}}\,. \tag{12.21}$$

Thus we also separate the wavefunctions and the corresponding energy eigenvalues of these motions from one another. The solution of the Schrödinger equation for basic types of particles motion is presented in the following sections.

12.2.3 Translation

The simplest type of molecular motion is a translation inside a rectangular box—parallelepiped of the sides a, b and c. The Schrödinger equation has the form

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+V_{\text{trans}}(x,y,z)\Psi = E_{\text{trans}}\,\Psi, \tag{12.22}$$

where $V_{\text{trans}}(x,y,z)$ is the potential energy of a particle given by the relation

$$V_{\text{trans}}(x,y,z) = \begin{cases} 0, & \text{inside box} \\ \infty, & \text{outside box.} \end{cases} \tag{12.23}$$

The translational energy of the particle is then given by the eigenvalues

$$E_{\text{trans}} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right)\ , \tag{12.24}$$

where n_x, n_y, and n_z are translational quantum numbers (n_x, n_y, $n_z = 1, 2, 3\ldots$). The wavefunction is uniquely determined by the triplet (n_x, n_y, n_z).

12.2.4 Rotation

Rotation is another type of molecular motion. The simplest model of a molecule is a **rigid rotor**, i.e. a pair of atoms at a fixed distance r. Its energy is given by the relation

$$V_{\text{rot}} = \frac{1}{2} I \omega^2 \,, \tag{12.25}$$

where ω is the angular velocity and

$$I = \mu\, r^2 \,, \tag{12.26}$$

is the **moment of inertia**. It is expressed using the **reduced mass**

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \,, \tag{12.27}$$

where m_1 and m_2 are the masses of the atoms.

Example

Calculate the reduced mass of the molecule $^1\text{H}^{35}\text{Cl}$.

Solution

The mass of an atom is calculated as the ratio of the atomic mass and the Avogadro constant [see **1.5.2**]

$$m_{\text{H}} = \frac{1\,\text{g mol}^{-1}}{6.022 \times 10^{23}\,\text{mol}^{-1}} = 1.66 \times 10^{-24}\,\text{g}\,,$$

$$m_{\text{Cl}} = \frac{35\,\text{g mol}^{-1}}{6.022 \times 10^{23}\,\text{mol}^{-1}} = 5.18 \times 10^{-23}\,\text{g}\,.$$

The reduced mass is thus

$$\mu = \frac{1.66 \times 10^{-24}\,\text{g} \times 5.18 \times 10^{-23}\,\text{g}}{1.66 \times 10^{-24}\,\text{g} + 5.18 \times 10^{-23}\,\text{g}} = 1.61 \times 10^{-24}\,\text{g}\,,$$

i.e. slightly lower than the hydrogen atom mass.

The energy eigenvalues are

$$E_{\text{rot}} = \frac{h^2}{8\pi^2 I}\, l(l+1)\,, \tag{12.28}$$

where $l = 0, 1, \ldots$, is the rotation quantum number, often denoted by symbol J. The energy values for $l > 0$ correspond to several eigenfunctions whose form depends on another quantum number m ($m = -l, -l+1, \ldots, +l$). The energy levels of the rigid rotor are thus degenerate and the degree of degeneracy g is

$$g = 2l + 1\,. \tag{12.29}$$

The general closed solution of the Schrödinger equation for the rotation of more complex molecules does not exist and can be obtained only approximately.

12.2.5 Vibration

Vibration is the last type of molecular motion to be described. The potential energy of the simplest two-atom molecule can be approximately written as the **harmonic oscillator**

$$V_{\mathrm{vib}} = \frac{1}{2}\kappa\,(x - x_{\mathrm{eq}})^2\ , \tag{12.30}$$

where x is the distance of atoms and x_{eq} the equilibrium distance corresponding to the minimum potential energy. The proportionality constant κ is the **force constant** of vibration which is the measure of the force with which the molecule is kept in the equilibrium position. The higher the value of κ the higher is the force returning the particle to the equilibrium position. The eigenvalues of the vibrational energy obtained from the solution of the Schrödinger equation (12.19) are

$$E_{\mathrm{vib}} = h\nu\left(v + \frac{1}{2}\right)\ , \tag{12.31}$$

where v is the vibrational quantum number and ν is the characteristic frequency of vibration given by the relation

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}}\,, \tag{12.32}$$

and μ is again the reduced mass (12.27).

The vibrational quantum number acquires the values $v = 0, 1, 2, \ldots$ The lowest energy level $\frac{1}{2}h\nu$ corresponding to $v = 0$ is usually referred to as the **zero point energy**. The degree of degeneracy of individual levels is $g = 1$.

For the oscillations of polyatomic molecules the following relation applies

$$E_{\text{vib}} = \sum_i h\nu_i \left(v_i + \frac{1}{2} \right) , \tag{12.33}$$

where the summation is over all possible types of independent (so called fundamental) vibrations of molecules.

> *Note:* In a more accurate description of molecular vibrations we would find out that for higher vibrational quantum numbers the energies deviate from the values of the corresponding harmonic oscillations. Formula
>
> $$E_{\text{vib}} = h\nu \left(v + \frac{1}{2} \right) - h\nu x_e \left(v + \frac{1}{2} \right)^2 , \tag{12.34}$$
>
> where x_e is the anharmonic constant, is a better approximation of the energy of an anharmonic oscillator than (12.31).

12.2.6 Motion of electrons around the nucleus

Another important type of motion is that of electrons in the electrostatic field of the atom nucleus. For the interaction of one single electron with a positively charged nucleus, such as occurs in the case of an isolated hydrogen atom or a He^+ cation, the following relation applies for the potential energy

$$V_{\text{el}}(r) = \frac{1}{4\pi\,\varepsilon_0} \frac{Z\,e^2}{r} , \tag{12.35}$$

where r is the distance between the nucleus and the electron, ε_0 is the vacuum permittivity [see **12.1.1**], e is the elementary charge ($e = 1.602 \times 10^{-19}$ C), and Ze is the nucleus charge.

In the absence of an external electromagnetic field, the energy of an atom depends solely on the **principal quantum number** n,

$$E_{\text{el}} = -\frac{\mu\,e^4\,Z^2}{8\,\varepsilon_0^2\,h^2} \frac{1}{n^2} , \tag{12.36}$$

where μ is the reduced mass of the electron-nucleus system and $n = 1, 2, 3, \ldots$

For $n = 1$ the Schrödinger equation has only one possible solution corresponding to the minimum energy of an atom. It is the **ground state** of the electron at equilibrium. The wavefunction is spherically symmetrical with the most probable distance between the electron and the nucleus at

$$r = \frac{\varepsilon_0\, h^2}{\pi\, \mu\, e^2\, Z}\,. \tag{12.37}$$

If we substitute $\mu = m_e = 9.109\times10^{31}\,\mathrm{kg}$ and $Z = 1$ into this equation, we obtain a quantity denoted a_0,

$$a_0 = \frac{\varepsilon_0\, h^2}{\pi\, m_e\, e^2} = 5.292\times10^{-11}\,\mathrm{m}\,. \tag{12.38}$$

It is called the **Bohr radius** and is used as the atomic unit of length.

If the atom absorbs energy, the electron may transit from the state of equilibrium to a state with a higher energy ($n > 1$), called the **excited state**. For these states there are always several wavefunctions of the same energy but differing in the values of the **angular momentum quantum number**[6] (l) and the **magnetic quantum number** (m). Their energies are thus degenerate.

In the presence of a magnetic field the energy of atoms with quantum numbers $m > 0$ slightly changes. The change can be interpreted as an interaction of the magnetic field B with a moving electron creating a current loop around the nucleus. It holds

$$\Delta E_{\mathrm{el}} = \frac{e\, h}{4\pi\, m_e}\, m\, B = m_B\, m\, B\,, \tag{12.39}$$

where $m_B = 9.274\times10^{-24}\,\mathrm{A\,m^2}$ is the magnetic moment of a free electron called the **Bohr magneton**[7]. Since the magnetic quantum number m has both positive and negative values, the energy of the atom may both increase and decrease against (12.36).

During interaction with the magnetic field, the electron and the nucleus display another property called **spin**. The magnitude of the electron spin is $s = 1/2$ while the nucleus spin depends on the number of nucleons and acquires values which are integer multiples of one half. An energy change due to the interaction of the magnetic field with the electron spin is given by

$$\Delta E_{\mathrm{el}} = g_e\, m_B\, m_s\, B\,, \tag{12.40}$$

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[6] also called **azimuthal** quantum number

[7] The magnetic moment of a free electron is actually $g_e/2 = 1.00116$ times larger, see (12.40).

where $g_e = 2.0023193$ is the **spin g-factor** also called **gyromagnetic ratio** of free electron and the spin projection (magnetic quantum number) m_s adopts values from $-s$ to s, i.e. $\pm 1/2$ (cf. (12.29)).

Note: The nucleus itself may interact with an external magnetic field and it may also have its own spin. An energy change caused by the interaction of the magnetic field with the nucleus spin is

$$\Delta E_{\text{nucl}} = g_N \, m_N \, m_S \, B \,, \tag{12.41}$$

where g_N is the nucleus g-factor, $m_S = -S, -S+1, \ldots, +S$, where S is the total spin quantum number of the nucleus, and m_N is the nuclear Bohr magneton, which is defined similarly as in relation (12.39), only the electron mass is replaced by the nucleus mass.

Complete calculation of the energy of atoms containing more electrons is very complicated. The reason is that the potential energy in the Schrödinger equation includes other terms such as the mutual repulsion of electrons, and it can be solved only approximately. For every type of atom there is nevertheless a unique set of possible energy states which can be taken up by its electrons.

12.3 Interaction of molecules with electromagnetic radiation

In section **12.1.9** we dealt with the interaction of substances with radiation (light), and radiation was interpreted as a variable electromagnetic field. Radiation, however, can be also explained as a flow of immaterial particles—**photons**. Given this dual character of electromagnetic radiation, quantities of two kinds, waves and particles, are used for its description.

12.3.1 Wave characteristics of radiation

The basic characteristic of every wave motion is its frequency, ν, defined by the number of oscillations per unit time. Another quantity is the **wavelength**, λ, the distance covered by the wave during one oscillation. The wavelength depends on the speed of radiation. In vacuum it holds

$$\lambda = \frac{c}{\nu}\,, \tag{12.42}$$

where c is the light velocity in vacuum ($c = 3\times 10^8\,\mathrm{m\,s^{-1}}$).

There is yet another quantity used for describing spectra, the **wavenumber**, $\tilde{\nu}$, which represents the number of waves per unit length

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}\,. \tag{12.43}$$

U *Main units:* radiation frequency: $\mathrm{s^{-1}}$=Hz (one oscillation per second), wavelength: m, wavenumber: $\mathrm{m^{-1}}$.

Example

The red light frequency is approximately 4.3×10^{14} Hz. Calculate its wavelength and wavenumber.

Solution

$$\lambda = \frac{c}{\nu} = \frac{3\times 10^8\,\mathrm{m\,s^{-1}}}{4.3\times 10^{14}\,\mathrm{s^{-1}}} = 7\times 10^{-7}\,\mathrm{m} = 700\,\mathrm{nm}\,,$$
$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{7\times 10^{-7}\,\mathrm{m}} = 1.43\times 10^{6}\,\mathrm{m^{-1}}\,.$$

12.3.2 Particle characteristics of radiation

It follows from the particle character of radiation that the energy of radiation is divided into further indivisible amounts—**quanta**, which represent the energies of individual photons. The energy of one photon depends on the radiation frequency, and is given by formula[8]

$$E = h\nu\,, \tag{12.44}$$

where h is Planck's constant [see **12.2**]. The higher the radiation frequency the higher is the energy of individual photons. The radiation intensity [see **12.1.9**] is given by the product of the number of photons passing through unit area per unit time and their energy.

Example

What is the energy of one photon of red light of the wavelength 700 nm?

Solution

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\,\mathrm{J\,s}\times3\times10^{8}\,\mathrm{m\,s^{-1}}}{700\times10^{-9}\,\mathrm{m}} = 2.84\times10^{-19}\,\mathrm{J}\,.$$

12.3.3 Spectrum

Mutual interaction between electromagnetic radiation and a substance is determined by the quantum behaviour of photons [see **12.3.2**] and the quantization of the energy states of molecules [see **12.2**]. The dependence of the strength of this interaction on the wavelength, frequency or the wavenumber of the radiation is called the **spectrum**. E.g., the dependence of the molar absorption coefficient [see **12.1.9**] on the wavelength etc. is the absorption spectrum.

Spectra may be classified based on several criteria:

- Based on the wavelength of the radiation used, spectra are classified as **radiowave**, **microwave**, **infrared**, **visible light**, **ultraviolet** and **X-ray**.

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[8] This formula is occasionally referred to as "Planck quantum hypothesis" or "Planck law"; the latter term is rather reserved for the historically first consequence, the Planck law of black body radiation.

- Based on the source of the photons used, spectra are classified as **emission**, when we measure the characteristics of photons originating in the substance, **absorption**, when we measure the amount of photons absorbed by the substance, and **Raman**, when we measure the change of the photon wavelength after their collision with molecules.
- Based on the type of the quantum states of molecules, spectra are classified as **electron**, **vibrational**, **rotational** and **magnetic resonance**.
- Based on the appearance of the originating spectrum, spectra may be roughly distinguished as **line** spectra, where interaction occurs in narrow wavelength regions (peaks) which are usually clearly separated from each other, and **continuous** spectra, where absorption occurs in broader wavelength regions (bands) which, in addition, often overlap.

Rough connection of different spectra classifications based on the individual categories follows from the following table:

Type of spectrum	Radiation characteristic		Type of quantum transitions
	frequency [Hz]	wavelength [m]	
X-ray	3×10^{16} to 3×10^{20}	1×10^{-12} to 1×10^{-8}	transition of inner electrons
ultraviolet	7.7×10^{14} to 3×10^{16}	1×10^{-8} to 4×10^{-7}	transition of valence electrons
visible	3.8×10^{14} to 7.7×10^{14}	4×10^{-7} to 7.9×10^{-7}	transition of valence electrons
infrared	1×10^{11} to 3.8×10^{14}	7.9×10^{-7} to 3×10^{-3}	vibrations and rotations
microwave	3×10^{8} to 1×10^{11}	3×10^{-3} to 1	ESR[1], rotations of heavy molecules
radiofrequency	3×10^{6} to 3×10^{8}	1 to 100	NMR[1]

12.3.4 Electronic spectra

The simplest spectrum of electron transitions is given by the absorption or emission of a photon in an isolated hydrogen atom. The energy of the hydrogen atom acquires the values given by

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[1] ESR—electron spin resonance and NMR—nuclear magnetic resonance, see **(12.3.7)**

the relation (12.36), and the energy change of the transition between different quantum states is thus

$$\Delta E = \frac{\mu e^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) , \tag{12.45}$$

where n_1 and n_2 are the principal quantum numbers of the states between which an electron jump occurs. The energy of the emitted or absorbed photon is equal to the above change of the atom energy. If we substitute (12.45) into (12.44), we obtain for the radiation wavenumber

$$\tilde{\nu} = \mathcal{R}_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) , \tag{12.46}$$

where

$$\mathcal{R}_H = \frac{\mu\, e^4}{8\,\varepsilon_0^2\, h^3\, c} = 1.09737\times 10^5\,\mathrm{cm}^{-1} \tag{12.47}$$

is the **Rydberg constant** for the hydrogen atom. Individual wavenumbers for the constant quantum number n_1 are arranged in a **spectral line series** of gradually increasing values approaching a limit. The **Lyman series** ($n_1 = 1$) lies in the ultraviolet region of the spectrum, the **Balmer series** ($n_1 = 2$) can be found in the visible region, whereas the **Paschen** ($n_1 = 3$) and other series lie in the region of infrared radiation. Each series limits to the **series edge** as $n_2 \to \infty$. The series edge corresponds to the dissociation energy of the electron.

Other atomic spectra are substantially more complex, owing to the complexity of the energy levels of multielectron atoms. They are nevertheless composed of individual lines. Their positions and intensities are characteristic for each atom and consequently allow for the identification of elements using spectroscopic methods.

In addition, electron transitions may occur in multielectron atoms between the inner and excited electron levels. These transitions correspond to substantially higher energy changes, so that the frequency of the corresponding radiation is in the X-ray region of the spectrum. For the wavenumber we have the relation

$$\tilde{\nu} = \mathcal{R}_H\,(Z-\sigma)^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) , \tag{12.48}$$

where Z is the atomic number of the element and σ is a constant corresponding to the given series. The preceding relation can be rewritten into the form of the **Moseley's law**

$$\sqrt{\tilde{\nu}} = a\,Z + b\,, \tag{12.49}$$

where a and b are constants characteristic for the series.

The electron spectra of molecules are yet more complex. Owing to the mutual influence of many electrons and nuclei in the molecule, interaction with photons occurs at many wavelengths, and the resulting spectrum does not have the form of lines but that of the absorption coefficient [see **12.1.9**] dependence on the wavelength. The maximum values on this curve usually correspond to the transitions of bonding electrons between different energy states.

12.3.5 Vibrational and rotational spectra

In di- and polyatomic molecules, photons are also absorbed due to the quantization of the molecules vibrational energy [see **12.2.5**]. Transitions between individual quantum states can occur only when the vibrational quantum number changes by one, $\Delta v_i = \pm 1$. Due to this **selection rule**, each vibrational frequency has thus only one single maximum where the photons with a frequency corresponding to the characteristic frequency of vibration (12.33) are absorbed. In addition, the absorption line is active (have measurable intensity) only if the electric dipole moment changes in the course of vibration; homonuclear diatomic molecules therefore are inactive. Since in the case of more complex (particularly organic) molecules individual vibration frequencies can be assigned to certain functional groups, it is possible to use the vibrational spectrum to identify the structure of molecules. The vibrational spectra lie in infrared region.

Note: When applying anharmonic terms in calculating energy, (12.34), the single peak splits into a band composed of several lines close to each other.

Similarly as vibrations, the rotations of molecules are also quantized [see **12.2.4**]. Since, however, the differences between the energy quantum levels for rotations are relatively small, pure rotational spectra lie in the microwave region. Rotations also affect the appearance of vibrational spectra. In low-resolution spectra the range of frequencies where absorption occurs expands and an **absorption band** is formed. Spectra with a high resolution split into several absorption maxima.

The selection rule for a rotational transition is the change if the rotational quantum number l by one. In addition, the rotating molecule must have nonzero dipole moment. It follows from

(12.28) for $l \to l-1$ that the frequencies form a band with

$$\nu = \frac{h}{4\pi^2 I}\, l\,. \tag{12.50}$$

Lines in the bands in rotational (and also rotation-vibration) spectra are thus separated by $\Delta\nu = h/(4\pi^2 I)$.

Example

What is the distance between atoms in a $^{1}\mathrm{H}\,^{35}\mathrm{Cl}$ molecule if the lines in rotation-vibration bands are separated by 2060 $\mathrm{m^{-1}}$?

Solution

From relation (12.50) it follows for the rotational moment

$$I = \frac{h}{4\pi^2\,\Delta\nu} = \frac{h}{4\pi^2\,c\,\Delta\tilde{\nu}} = \frac{6.63\times10^{-34}\,\mathrm{J\,s}}{4\times 3.14^2\times 3\times10^{8}\,\mathrm{m\,s^{-1}}\times 2060\,\mathrm{m^{-1}}} = 2.72\times10^{-47}\,\mathrm{kg\,m^2}.$$

Since the reduced mass of the molecule is 1.61×10^{-27} kg (see the example in section 12.2.4), the interatomic distance is

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.72\times10^{-47}\,\mathrm{kg\,m^2}}{1.61\times10^{-27}\,\mathrm{kg}}} = 1.30\times10^{-10}\,\mathrm{m} = 0.13\,\mathrm{nm}.$$

12.3.6 Raman spectra

Molecules may also interact with electromagnetic radiation in a way other than the photon absorption or emission. A photon colliding with a molecule may be scattered. It means that it changes its frequency (and therefore energy) as well as the direction of motion. A change in the photon energy determines the change in energy of a molecule before and after the collision,

$$\Delta E = h\,\Delta\nu\,. \tag{12.51}$$

Photons of visible or ultraviolet light interact readily with rotational and vibrational states of molecules. The spectrum of scattered light is then called the **Raman spectrum**.

If the photon loses part of its energy during the collision, and its frequency after the collision is thus lower, we speak about the **Stokes radiation**. If, on the contrary, the photon gains further energy on colliding with a previously excited molecule, we speak about the **anti-Stokes radiation**.

The condition for a peak in a Raman spectrum is either a change of the molecule polarizability due a change of the vibrational state [see **12.1.4**], or anisotropic polarizability, i.e. the change of polarizability (in selected direction) due to rotation. The Raman spectra thus add to information gained using the absorption or emission rotation-vibration spectra.

12.3.7 Magnetic resonance spectra

In the presence of a magnetic field the energy of electrons and nuclei may change in dependence on the spin quantum number [see (12.40) and (12.41)]. Consequently, photons with appropriately chosen frequency may be absorbed, and subsequently again emitted, in transition between the spin quantum states. The name "resonance" comes from a classical picture of the spin as rotation of electrons giving rise to a magnetic moment. Interaction of this magnetic moment with a magnetic field creates a torque causing a precession of the rotating object (flywheel). When the frequency of the incident radiation matches the frequency of the precession, a resonance occurs and a signal is detected.

If a molecule with an odd number of electrons transits between the states given by the quantum numbers $m_s = -\frac{1}{2}$ and $m_s = +\frac{1}{2}$, we speak about **electron spin resonance** (ESR), and the resonance frequency is given by

$$\nu = \frac{g_e\, m_B\, B}{h}\,. \tag{12.52}$$

The resulting frequency depends on the magnitude of the magnetic field, and it is usually in the range of microwave radiation. The ESR is primarily employed in detecting free radicals in chemical kinetics.

If it is the nucleus spin that interacts with the magnetic field, we speak about **nuclear magnetic resonance** (NMR). The resonance frequency is given by the relation

$$\nu = \frac{g_N\, m_N\, B}{h} \tag{12.53}$$

and it occurs in atoms with a nonzero spin of the nucleus, particularly in hydrogen. Magnetic field acting on the nucleus is, however, influenced by the magnetic moment of the surrounding electrons. The accurate value of the resonance frequency is thus different for different functional groups containing hydrogen (e.g. OH, CH_3, CH_2). The relative change in the resonance frequency

$$\delta = \frac{\nu - \nu_{\mathrm{ref}}}{\nu_{\mathrm{ref}}} \tag{12.54}$$

is called the **chemical shift**, and ν_{ref} is the resonance frequency of a reference substance, usually tetramethylsilane $Si\,(CH_3)_4$, commonly referred to as TMS.

Example

What is the resonance frequency shift of a substance whose chemical shift is $\delta = 1\,\mathrm{ppm}$ if the spectrometer works at a frequency of 500 MHz?

Solution

The chemical shift of 1 ppm corresponds to a relative frequency shift by 10^{-6}, and we have

$$\nu - \nu_{\mathrm{ref}} = \delta\,\nu_{\mathrm{ref}} = 10^{-6} \times 500 \times 10^{6}\,\mathrm{Hz} = 500\,\mathrm{Hz}.$$

The resonance frequency thus has to be measured very accurately.

Chapter 13

Physical chemistry of surfaces

13.1 Phase interface

When a system contains more phases (see **1.1.4**), the area where two phases come in contact is referred to as the **interface**. It is characterized by its area, and for curved interfaces also by the surface curvature. If the interface area is relatively small, its influence on the overall behaviour of the system can be usually neglected. If, however, the interface is larger, its properties have to be considered in the overall description of the system.

13.1.1 Interfacial tension

The surface work needed for the creation of an interface of an infinitesimally small area $\mathrm{d}A$ is

$$đw = \gamma_{ff}\,\mathrm{d}A\,, \tag{13.1}$$

where the proportionality constant γ_{ff} is the **interfacial tension**.

S *Symbols:* The subscript $_{ff}$ denotes the type of phases meeting at the interface, e.g. $\gamma_{s\ell}$ would be used for a solid-liquid interface.

U *Main unit:* $\mathrm{J\,m^{-2} = N\,m^{-1}}$.

> *Note:* The term interfacial tension is used because its numerical value is equal to the force acting perpendicularly on 1 m of length in the direction of the surface (tangential force) against its expansion.

The value of interfacial tension depends on temperature, pressure and the composition of both phases in contact. The temperature dependence is described in section (**13.1.8**). In a one-component system, the interfacial tension thus depends only on temperature and pressure is equal to the equilibrium pressure. The composition dependence in multicomponent systems is described in section (**13.1.9**). The pressure dependence is relatively low and usually can be neglected.

13.1.2 Generalized Gibbs equations

By including surface work in the Gibbs equations (see **3.4.1**), which represent combined formulations of the first and second laws of thermodynamics in a closed system, we obtain

$$\mathrm{d}U = T\mathrm{d}S - p\,\mathrm{d}V + \gamma_{ff}\mathrm{d}A\,, \tag{13.2}$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \gamma_{ff}\mathrm{d}A\,, \tag{13.3}$$

$$\mathrm{d}F = -S\mathrm{d}T - p\,\mathrm{d}V + \gamma_{ff}\mathrm{d}A\,, \tag{13.4}$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \gamma_{ff}\mathrm{d}A\,. \tag{13.5}$$

From these relations we may define interfacial tension by

$$\gamma_{ff} = \left(\frac{\partial U}{\partial A}\right)_{S,V} = \left(\frac{\partial H}{\partial A}\right)_{S,p} = \left(\frac{\partial F}{\partial A}\right)_{T,V} = \left(\frac{\partial G}{\partial A}\right)_{T,p}\,. \tag{13.6}$$

13.1.3 Interfacial energy

The energy of an interface σ_{ff} is comprised of the work needed for its creation and the heat connected with the change of the surface area. It is given by the relation

$$\sigma_{ff} = \left(\frac{\partial U}{\partial A}\right)_{T,V}\,. \tag{13.7}$$

By applying the Maxwell relations (see **3.4.3**) to the Gibbs equations we obtain

$$\sigma_{ff} = \gamma_{ff} - T\left(\frac{\partial \gamma_{ff}}{\partial T}\right)_{V,A}\,. \tag{13.8}$$

The value $-T(\partial\gamma_{ff}/\partial T)$ corresponds to the heat exchanged with the surroundings and related to unit area. On changing the area by ΔA we obtain

$$Q = -T\left(\frac{\partial\gamma_{ff}}{\partial T}\right)\Delta A\,. \tag{13.9}$$

Note: The total interfacial energy is far less dependent on temperature than the interfacial tension itself.

Example

Determine the work, heat and internal energy change of water if its liquid-vapour interface area increases by $2\,\mathrm{m}^2$ at a temperature of $291\,\mathrm{K}$. For water at $291\,\mathrm{K}$ we have:

$$\gamma = 73\,\mathrm{mN\,m^{-1}},\ (\partial\gamma_{\ell g}/\partial T) = -0.145\,\mathrm{mN\,m^{-1}K^{-1}}.$$

Solution

Work is given by relation (13.1), i.e. $w = \gamma_{\ell g}\Delta A$, and thus

$$w = 73\times10^{-3}\cdot 2 = 0.146\,\mathrm{N\,m} = 0.146\,\mathrm{J}.$$

Heat may be calculated from

$$Q = -2\cdot 291\,(-0.145\times10^{-3}) = 84.4\times10^{-3}\,\mathrm{J}.$$

From the first law of thermodynamics $(\Delta U = Q + W)$ we obtain

$$\Delta U = 0.146 + 0.0844 = 0.2304\,\mathrm{J}.$$

It is obvious from the result that under normal circumstances, when the change of the surface area is relatively small, we do not have to consider surface changes in relation to energy.

13.1.4 Surface tension and surface energy

When we are concerned with a liquid-gas (vapour) interface, we use the term surface tension rather than interfacial tension.

S *Symbols:* When denoting the surface tension, the subscripts indicating the phases in contact are often left out, i.e. $\gamma_{\ell g} \equiv \gamma$.

In a one-component system the surface tension depends only on temperature (pressure is equal to the vapour equilibrium pressure), and the surface energy is

$$\sigma = \gamma - T\left(\frac{\mathrm{d}\gamma}{\mathrm{d}T}\right) . \tag{13.10}$$

Example

Explain why a liquid in a zero-gravity space occupies spontaneously the shape of a sphere.

Solution

Since the sphere is a body that has a minimum outer surface area for a given volume, its surface energy is also the lowest. Any other shape of a body has a higher energy and consequently would be less advantageous as far as energy is concerned.

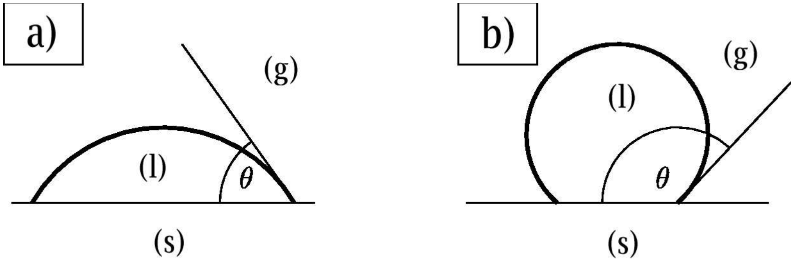
13.1.5 Work of cohesion, work of adhesion, and spreading coefficient

In addition to interfacial tension and energy, some other quantities are also employed for interfaces description. The work needed for pulling apart a continuous liquid column of a unit cross-section in a way that allows for the formation of vapour in the space between them is called the **work of cohesion**, w_c. It is related to surface tension by the relation

$$w_\mathrm{c} = 2\,\gamma_{\ell g} = 2\,\gamma\,. \tag{13.11}$$

The work needed for pulling apart a liquid and a solid phase liquid-vapour and solid-vapour interfaces is called the **work of adhesion**, w_a. It is related to unit area,

$$w_\mathrm{a} = \gamma_{\ell g} + \gamma_{sg} - \gamma_{s\ell}\,. \tag{13.12}$$



Obr. 13.1: Two examples of the “wetting” of a solid.

The difference between the work of cohesion and the work of adhesion is called the **spreading coefficient**, S_s,

$$S_\mathrm{s} = w_\mathrm{a} - w_\mathrm{c} = \gamma_{sg} - \gamma_{s\ell} - \gamma_{\ell g}\,. \tag{13.13}$$

13.1.6 Contact angle

If the spreading coefficient of a liquid on a solid is positive, i.e. the work of adhesion is greater than the work of cohesion, the liquid spreads across the solid surface and it is said to **wet the solid completely**. If, however, the spreading coefficient is negative, the liquid forms drops on the surface (see Figure 13.1), with the following relation applying between the interfacial tensions

$$\gamma_{sg} = \gamma_{s\ell} + \gamma_{\ell g}\cos\theta\,, \tag{13.14}$$

where θ is the **contact angle**, i.e. the angle formed by the liquid phase on contact with the surface. Based on the value of this angle we distinguish two cases:

- $\theta < \pi/2$, the solid surface is (incompletely) “wetted” (Figure 13.1a),
- $\theta > \pi/2$, the body surface does not wet (Figure 13.1b).

If there are two mutually partially miscible liquids present in a system in addition to the gas phase, we may also use relation (13.13), while the lower liquid phase takes over the role of the solid phase.

Example

Ascertain the spreadability of n-octanol (oct) on water (w) and that of water on bromoform (brm) at 20 °C if you have the following data (20 °C):
$\gamma_{\rm w} = \gamma_{\rm w,(g)} = 72.5\,\mathrm{mN\,m^{-1}}$, $\gamma_{\rm oct} = \gamma_{\rm oct,(g)} = 27.5\,\mathrm{mN\,m^{-1}}$, $\gamma_{\rm brm} = \gamma_{\rm brm,(g)} = 41.5\,\mathrm{mN\,m^{-1}}$,
$\gamma_{\rm w,oct} = 8.5\,\mathrm{mN\,m^{-1}}$, $\gamma_{\rm brm,w} = 40.8\,\mathrm{mN\,m^{-1}}$.

Solution

For the air+octanol+water system we substitute into (13.13) to obtain (the lower layer is water)

$$S_{\rm s} = \gamma_{\rm w,(g)} - \gamma_{\rm w,oct} - \gamma_{\rm oct,(g)} = 72.5 - 8.5 - 27.5 = 36.5 > 0$$

and see that n-octanol spreads on water and does not form separate drops.
In the air+water+bromoform system (bromoform is the lower phase),

$$S_{\rm s} = \gamma_{\rm brm,(g)} - \gamma_{\rm brm,w} - \gamma_{\rm w,(g)} = 41.5 - 40.8 - 72.5 = -71.8 < 0$$

and consequently water will not spread on bromoform and, when there is only a small amount of water, drops will be formed.

13.1.7 Laplace-Young equation and Kelvin equation

The interfacial tension affects also other thermodynamic properties of a system when the interface surface is curved.

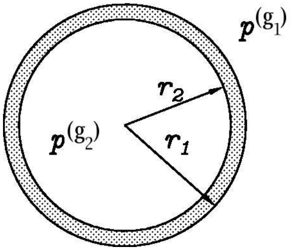
If, e.g., the liquid is in the form of droplets of the radius r which are surrounded by the gas phase, the **Laplace-Young equation** applies for the pressure in both phases

$$p^{(\rm l)} - p^{(\rm g)} = \Delta p = \frac{2\,\gamma}{r}\,, \tag{13.15}$$

where $p^{(\rm l)}$ and $p^{(\rm g)}$ stand for the pressures in the liquid and in the surrounding gas. The pressure in the liquid is thus higher than in the gas.

Correspondingly, the pressure inside a bubble surrounded by a liquid is higher than that in the liquid

$$p^{(\rm g)} - p^{(\rm l)} = \Delta p = \frac{2\,\gamma}{r}\,. \tag{13.16}$$



Obr. 13.2: Pressure inside a bubble

Example

Determine the difference between the pressure inside a soap bubble (Figure 13.2) of the radius r and the surrounding atmospheric pressure. The surface tension of the soap solution forming the cover of the bubble is γ.

Solution

According to the Laplace-Young equation (13.15) the following relation applies between the atmospheric pressure and the pressure in the liquid making up the cover of the bubble

$$p^{(\mathrm{l})} - p^{(\mathrm{g1})} = \frac{2\,\gamma}{r_1}$$

whereas between the pressure in the liquid and inside the bubble we have

$$p^{(\mathrm{g2})} - p^{(\mathrm{l})} = \frac{2\,\gamma}{r_2}\,.$$

By summing up the two equations, on condition that $r_1 \approx r_2 \approx r$, we obtain

$$p^{(\mathrm{g2})} - p^{(\mathrm{g1})} = \frac{4\,\gamma}{r}\,.$$

Given that the liquid inside a droplet has a higher pressure than the liquid over the non-curved surface, it also has a higher chemical potential or fugacity.

S *Symbols:* The chemical potential or fugacity for a curved surface will be denoted using the subscript r. The same quantities for a flat surface are denoted using the superscript $^{\oslash}$.

13.1.7.1 Kelvin's equation

applies

$$\Delta\mu = \mu_r - \mu^{\oslash} = \boldsymbol{R}\,T\ln\frac{f_r}{f^{\oslash}} = \int_{p^{\oslash}}^{p^{\oslash}+2\,\gamma/r} V_{\mathrm{m}}^{(\mathrm{l})}\,\mathrm{d}p = \frac{2\,\gamma\,V_{\mathrm{m}}^{(\mathrm{l})}}{r}\,, \qquad (13.17)$$

where f_r is the fugacity of a substance in a droplet of the radius r, $f^{\oslash} = f(T)$ is the fugacity of a substance in the saturated state with a non-curved surface, γ is the surface tension, and V_{m} is the molar volume of the liquid.

> *Note:* If a system contains both a liquid in the form of droplets and a common liquid (e.g. in a beaker), the fugacity of the liquid in droplets is higher than that of vapour or of the equilibrium liquid over the non-curved surface. The droplets will thus gradually evaporate until they vanish completely.

The behaviour between a liquid and a solid phase may be described in a similar way (if we assume a spherical shape of the crystals). In this case, however, we have to employ the interfacial tension $\gamma_{s\ell}$ and the chemical potential. An analogy to Kelvin's equation is the relation

$$\Delta\mu = \mu_r - \mu^{\oslash} = \boldsymbol{R}\,T\ln\frac{f_r}{f^{\oslash}} = \frac{2\,\gamma_{s\ell}{V_{\mathrm{m}}}^{(\mathrm{s})}}{r}\,, \qquad (13.18)$$

where μ_r is the chemical potential of a solid substance in a crystal of the radius r, $\mu^{\oslash}$ is the chemical potential of a solid in an infinitely large crystal, $\gamma_{s\ell}$ is the interfacial tension between the solution and the solid phase, and ${V_{\mathrm{m}}}^{(\mathrm{s})}$ is the molar volume of the solid.

> *Note:* In an exact description, the non-spherical shape of the crystal and the different surface tensions on its different planes have to be taken into account.

13.1.8 Temperature dependence of surface tension

The surface tension of a liquid that is in equilibrium with its vapour usually decreases with temperature and is zero at the critical point.

Eötvös and later Ramsay-Shields found out that in a very broad temperature interval (up to almost critical temperature) the following empirical relation applies

$$\left(\frac{\mathrm{d}}{\mathrm{d}T}\right)\left[\gamma\,(V_\mathrm{m}^{(\mathrm{l})})^{2/3}\right] = \text{const}\ , \tag{13.19}$$

which can be rewritten into the form of the Ransay-Shields equation

$$\gamma\,(V_\mathrm{m}^{(\mathrm{l})})^{2/3} = k\,(T_\mathrm{c} - T - \delta)\,, \tag{13.20}$$

where $V_\mathrm{m}^{(\mathrm{l})}$ is the molar volume of a saturated liquid at temperature T, T_c is the critical temperature of a substance, and k, δ are empirical constants which for nonassociated liquids have the values

$$k = 2.12\ (\mathrm{mN\,m^{-1}})(\mathrm{cm^3\,mol^{-1}})^{2/3}\,, \qquad \delta = 6\,\mathrm{K}\,. \tag{13.21}$$

Relation (13.20) does not apply for substances such as water, alcohols, organic acids, etc.

Another empirical relation between temperature and surface tension was found by Mac Leod

$$[P] = \frac{M\gamma^{1/4}}{\rho^{(\mathrm{l})} - \rho^{(\mathrm{g})}}\,, \tag{13.22}$$

where M is the molar mass, $\rho^{(\mathrm{l})}$ and $\rho^{(\mathrm{g})}$ are the densities of a saturated liquid and a saturated vapour.[1] The quantity $[P]$ is called the **parachor**. It is practically independent of temperature, and it may be estimated on the basis of atomic and structural contributions. This means that if we know the temperature dependence of the density, we may also estimate the temperature dependence of the surface tension.

13.1.9 Dependence of surface tension on solution composition

The surface tension of mixtures largely depends on their composition, and there is not yet any exact method for its calculation. For a mixture of substances of a similar character we may at least approximately use the empirical equation for the parachor, from which it follows that

$$\gamma^{1/4} = \rho^{(\mathrm{l})} \sum_{i=1}^{k} \frac{x_i\,\gamma_i^{1/4}}{\rho_i^{(\mathrm{l})}}\,, \tag{13.23}$$

---

[1] At low temperatures we may naturally neglect the density of the gas phase as compared with that of the liquid phase.

where k is the number of components in the mixture, and $\rho^{(1)}$ and $\rho_i^{(1)}$ are the densities of the mixture and its components.

For solutions with a low concentration of the dissolved component we may apply the relation

$$\gamma = \gamma(c=0) + k\,c\,, \tag{13.24}$$

where c is the concentration of the dissolved substance, $\gamma(c=0)$ is the surface tension of the solvent, and k is a temperature-dependent constant. k usually has a negative value, and consequently the surface tension decreases with the concentration c. Substances with a high absolute value of k are called **surfactants** or **surface-active agents**.

For aqueous solutions of alcohols, acids, aldehydes or other organic substances with a polar group at the end of a non-polar hydrocarbon skeleton, another empirical equation, found by Szyszkowski, applies in a broad concentration interval

$$\gamma = \gamma(c=0) - a\ln(1+b\,c)\,, \tag{13.25}$$

where a and b are constants which are little temperature-dependent.

13.1.10 Gibbs adsorption isotherm

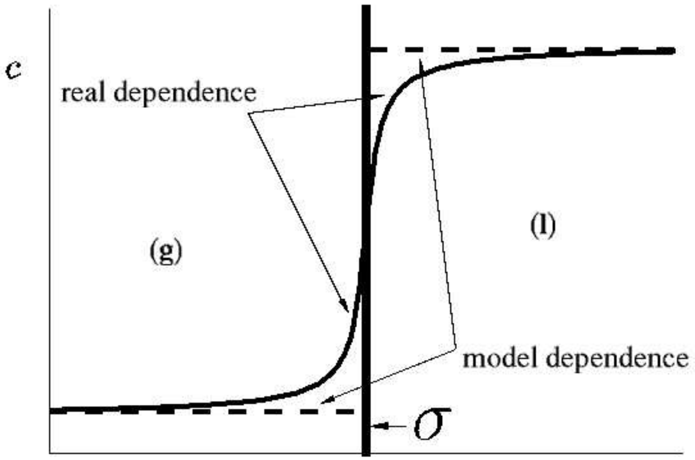
A detailed microscopic description of an interface in mixtures is very complicated. It is therefore expedient to model the overall system as a set of volume phases of a constant composition, and the surface phase (Figure 13.3). The **surface phase,** σ, is defined here as an infinitesimally thin layer of a negligible volume separating the volume phases. This layer, however, contains certain amounts of all system components. The amount of substance i in the surface phase is characterized by **adsorption**

$$\Gamma_i = \frac{n_i^{(\sigma)}}{A}\,, \tag{13.26}$$

where $n_i^{(\sigma)}$ is the amount of substance i and A is the area of the interface.

U *Main unit:* $\mathrm{mol\,m^{-2}}$

The surface phase can be placed in the region of the volume phases transition arbitrarily. Its position is usually chosen for the adsorption of the solvent or the main unit of the mixture to equal zero ($\Gamma_1 = 0$). The adsorption of other mixture components is then referred to as the **relative adsorption** with respect to component 1, $\Gamma_{i,1}$.



Obr. 13.3: Substance concentration in the vicinity of an interface.

Note: At a liquid-vapour interface, a positive value of $\Gamma_{i,1}$ indicates that the amount-of-substance ratio between the dissolved substance i and the solvent in the surface layer is higher than in the liquid phase. The dissolved substance thus concentrates on the liquid surface. If ($\Gamma_{i,1} = 0$, the concentration ratio of both substances in the surface and liquid phases is identical.

The relation between relative adsorption and surface tension is called the **Gibbs adsorption isotherm**

$$\Gamma_{i,1} = -\left(\frac{\partial \gamma}{\partial \mu_i}\right)_T . \qquad (13.27)$$

Using relations (6.71) and (6.101), we may express this equation by the relation[2]

$$\left(\frac{\partial \gamma}{\partial c_i}\right)_T = -\frac{\boldsymbol{R}T}{c_i}\,\Gamma_{i,1}\left[1 + c_i\left(\frac{\partial \ln \gamma_i^{[c]}}{\partial c_i}\right)_T\right] . \qquad (13.28)$$

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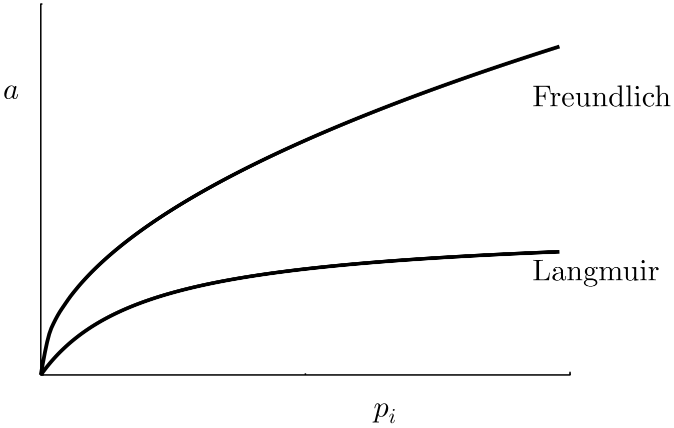
[2] We have to distinguish between the surface tension, γ, and the activity coefficient of component i, $\gamma_i^{[c]}$.



Obr. 13.4: Adsorption isotherms

For an ideal mixture $c_i \left(\frac{\partial \ln \gamma_i^{[c]}}{\partial c_i}\right)_T \to 0$ we have

$$\Gamma_{i,1} = -\frac{c_i}{\boldsymbol{R}T}\left(\frac{\partial \gamma}{\partial c_i}\right)_T \,. \tag{13.29}$$

This equation allows for determining the relative adsorption of a dissolved component in the surface layer provided that we know $\gamma = \gamma(c_i)$.

Example

Given that Szyszkowski's equation (13.25) applies, derive relations for $\Gamma_{2,1}$ at low, medium and high concentrations. Assume ideal behaviour of the solution.

Solution

From Szyszkowski's equation (13.25) we obtain

$$\left(\frac{\partial \gamma}{\partial c_2}\right) = -\frac{a\,b}{1 + b\,c_2}\,.$$

For low concentrations $(c_2 \to 0)$ we then have

$$\Gamma_{2,1} = -\frac{a\,b}{\boldsymbol{R}T}\,c_2\,.$$

For medium concentrations we obtain

$$\Gamma_{2,1} = -\frac{c_2}{\boldsymbol{R}T}\left(-\frac{a\,b}{1 + b\,c_2}\right) = \left(\frac{a}{\boldsymbol{R}T}\right)\frac{b\,c_2}{1 + b\,c_2}\,.$$

For high concentrations $(b\,c_2 >> 1)$ it applies that

$$\Gamma_{2,1} = \frac{a}{\boldsymbol{R}T}\,.$$

13.1.11 Surface films

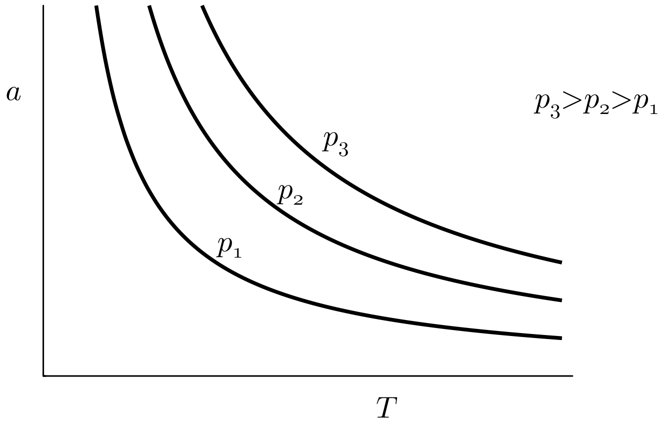
Some surfactants practically do not dissolve in a liquid but stay on the surface. This surface phase is known as the **surface film**. Surfactants cause a **surface pressure**, $p_{\rm sur}$, on the liquid surface, which is given by the relation

$$p_{\rm sur} = \gamma(c_i = 0) - \gamma\,, \qquad (13.30)$$

where $\gamma(c_i = 0)$ is the surface tension of a pure liquid and γ is the surface tension of a mixture.

When there is a relatively small amount of a surfactant on the liquid surface, i.e. at low values of the relative adsorption $\Gamma_{i,1}$, the behaviour of the surface film can be expressed by a two-dimensional analogy of the equation of state of an ideal gas that may be written in the form

$$p_{\rm sur} = \Gamma_{i,1}\,\boldsymbol{R}T\,. \qquad (13.31)$$



Obr. 13.5: Adsorption isobars

At higher adsorption values the dependence of $p_{\rm sur}$ becomes more complicated, due to the occurrence of phenomena corresponding to condensation etc.

Example

Calculate the pressure created by a surface film containing $C_{18}H_{37}NH_2{\cdot}HCl$ and spread on an area of $14 \times 35\,\mathrm{cm}^2 = 0.049\,\mathrm{m}^2$ in an amount of 1.1×10^{-8} mol at a temperature of $22\,^\circ$C. Assume that the given substance practically does not dissolve in water, and that equation (13.31) applies.

Solution

Since the substance does not dissolve, all of it is absorbed in the surface phase and $\Gamma_{2,1} = \Gamma_2 = n_2/A$. By substituting into (13.31) we obtain

$$p_{\rm sur} = \frac{1.1\times10^{-8}}{0.049}\,8.314 \cdot 295.15 = 0.551\times10^{-3}\,\mathrm{N\,m^{-1}} = 0.551\,\mathrm{mN\,m^{-1}}\,.$$

13.2 Adsorption equilibria

Substances adsorbing from a gas to a solid also create a usually thin surface phase on the solid surface.

The solid phase that adsorbs the gas is called the **adsorbent**, and the adsorbed gas is referred to as the **adsorbate**.

The amount of adsorbate is most often expressed by way of

- The dimensionless mass ratio a
$$a = \frac{\text{adsorbate mass}}{\text{adsorbent mass}} = \frac{m_{\text{adsorbate}}}{m_{\text{adsorbent}}}\,, \tag{13.32}$$
- The amount of substance of the adsorbate per unit mass of the adsorbent
$$a_n = \frac{n_{\text{adsorbate}}}{m_{\text{adsorbent}}}\,, \tag{13.33}$$
- The gas volume adsorbed per unit mass of the adsorbent under specified conditions (most often at $T_{\text{ref}} = 273.15\,\text{K}$ and pressure $p_{\text{ref}} = 101.325\,\text{kPa}$)
$$a_v = \frac{V_{\text{adsorbate}}(T_{\text{ref}}, p_{\text{ref}})}{m_{\text{adsorbent}}}\,, \tag{13.34}$$
- If we know the adsorbent surface area, we can also express its amount as
$$a_A = \frac{\text{adsorbate mass}}{\text{adsorbent surface area}} = \frac{m_{\text{adsorbat}}}{A}\,. \tag{13.35}$$

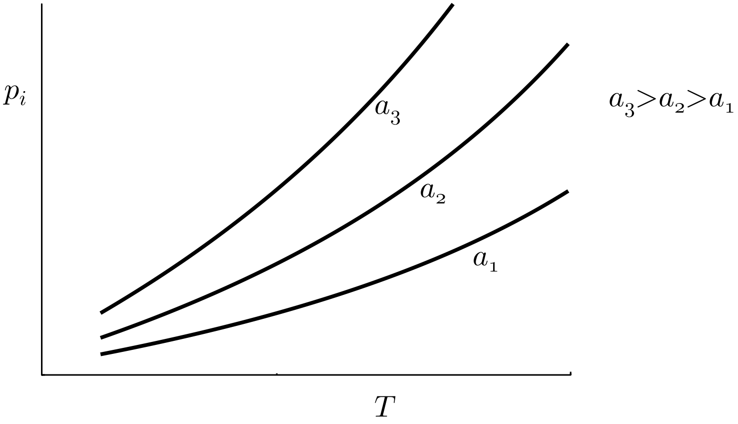
U *Main units:* a is a dimensionless quantity, a_n : $\text{mol}\,\text{kg}^{-1}$, a_v : $\text{m}^3\,\text{kg}^{-1}$, a_A : $\text{kg}\,\text{m}^{-2}$.

13.2.1 Qualitative description of adsorption

The **adsorption isotherm** expresses the dependence of the adsorbed amount of the gas component on its partial pressure at constant temperature. Figure 13.4 shows the basic types of adsorption isotherms. It is obvious that the adsorbed amount monotonously increases with pressure.

The **adsorption isobar** expresses the dependence of the adsorbed amount of gas on temperature at constant partial pressure. Figure 13.5 shows the most typical course of adsorption isobars. It makes it clear that the adsorbed amount of gas decreases with temperature.

The **adsorption isostere** shows the dependence of the partial pressure of the gas on temperature at a constant adsorbed amount. Three isosteres are drawn in Figure 13.6. If we draw $\ln p_i$ in dependence on $1/T$, the isosters become practically straight lines.



Obr. 13.6: Adsorption isosteres

13.2.2 Adsorption heat

The course of the isosteres allows for the determination of the **adsorption heat** (enthalpy), which is given by the relation

$$\left(\frac{\partial \ln p_i}{\partial T}\right)_{a_i} = -\frac{\Delta_{\rm ads} H}{\boldsymbol{R} T^2} = -\frac{H^{(a)}_{{\rm m},i} - H^{({\rm g})}_{{\rm m},i}}{\boldsymbol{R} T^2}\,, \tag{13.36}$$

where $H^{(a)}_{\rm m,i}$ is the molar enthalpy of the adsorbed gas, and $H^{({\rm g})}_{\rm m,i}$ is the molar enthalpy of the gas phase.

13.2.3 Physical adsorption and chemisorption

There are two possible types of bond between the adsorbent and adsorbate molecules:

a) Mutual interactions such as those between molecules in the liquid phase, the van der Waals forces, prevail between the adsorbent and adsorbate molecules. This phenomenon is referred to as **physical adsorption**.

b) A very strong, almost chemical bond exists between the adsorbent and adsorbate atoms. This phenomenon is referred to as **chemisorption**.

The basic differences between physical adsorption and chemisorption are shown in the following table.

	Physical adsorption	Chemisorption
Specificity	unspecific	specific
Number of adsorbed layers	> 1	1
Adsorption heat in $\mathrm{kJ\,mol^{-1}}$	5–50	50–800
Rate of adsorption	high	relatively low
Desorption	by decreasing pressure	by increasing temperature

13.2.4 Quantitative description of the adsorption isotherm in pure gases

Quantitative description of adsorption is most often performed using an adsorption isotherm equation. For pure gases, the following isotherms are used in simple cases:

a) Empirical **Freundlich isotherm**

$$a = \alpha\, p^{\beta}\,, \tag{13.37}$$

where α, β are temperature-dependent parameters. It usually applies that $\beta < 1$. This equation provides a good description of both physical adsorption and chemisorption at medium pressures. The following limits follow from this equation

$$\lim_{p\to 0}\left(\frac{\partial a}{\partial p}\right)_T = \infty \quad [\text{for}\ \beta < 0]\,, \qquad \lim_{p\to\infty} a = \infty\,, \tag{13.38}$$

b) **Langmuir isotherm**

$$a = a_{\max}\frac{b\,p}{1 + b\,p}\,, \tag{13.39}$$

where $a_{\max}$, b are parameters, and $a_{\max}$ has the physical meaning of the maximum amount of adsorbate at $p \to \infty$.

Note: This isotherm can be derived on condition that:

- Only one single layer of adsorbed molecules is formed.
- The adsorbent surface is homogeneous.
- The adsorbed molecules do not influence each other.

Example

Nitrogen adsorption on charcoal at 0 °C in the pressure range up to 100 kPa is expressed by the Langmuir isotherm with the parameters $a_{\max} = 36\,\mathrm{cm^3\,g^{-1}}$, $b = 0.053\,\mathrm{kPa^{-1}}$ (the adsorbed amount of nitrogen is expressed by volume converted to $T_{\mathrm{ref}} = 273.15\,\mathrm{K}$, and pressure $p_{\mathrm{ref}} = 101.32\,\mathrm{kPa}$). Calculate the amount of nitrogen adsorbed per 10 g of charcoal at a pressure of 5 kPa.

Solution

From relation (13.39) we obtain

$$a_v = 36\,\frac{0.053\cdot 5}{1+0.053\cdot 5} = 9.54\,\mathrm{cm^3\,g^{-1}}\,,$$

$$n = m_{\mathrm{adsorbent}}\,\frac{a_v\,p_{\mathrm{ref}}}{\boldsymbol{R}\,T_{\mathrm{ref}}} = 10\,\frac{0.00954\cdot 101.32}{8.314\cdot 273.15} = 0.004256\,\mathrm{mol}\,.$$

13.2.5 Langmuir isotherm for a mixture of gases

For a k-component mixture of gases we obtain by expanding equation (13.39)

$$a_i = a_{\max,i}\,\frac{b_i p_i}{1+\sum_{j=1}^{k} b_j p_j}\,, \tag{13.40}$$

where p_i is the partial pressure of component i in the mixture.

13.2.6 Capillary condensation

Sometimes the description of gas adsorption merely as a thin layer formed on the outer surface of a solid does not suffice. Adsorption of gases which are under critical temperature and which wet the adsorbent surface may occur in narrow pores of the adsorbent. This phenomenon is known as **capillary condensation**. It is a process during which vapour condensation on a liquid occurs at pressures lower than the saturated vapour pressure of gases, while satisfying the following relation

$$\ln \frac{f}{f^{\oslash}} \approx \ln \frac{p}{p^{\oslash}} = -\frac{2\,\gamma\, V_{\mathrm{m}}^{(\mathrm{l})}}{r\,\boldsymbol{R}\,T}\,, \tag{13.41}$$

where r is the pore radius, and $p^{\oslash}$ is the saturated vapour pressure.

Note: Capillary condensation is used to explain differences in the course of the adsorption isotherm recorded in measurements performed while gradually increasing and subsequently decreasing the gas pressure (the so-called hysteresis of the adsorption isotherm).

13.2.7 Adsorption from solutions on solids

On the surface of solids which are in contact with a solution, adsorption of both the solvent and the solute occurs. We speak about adsorption of a solute in the narrow sense of the word when the solute is adsorbed much more than the solvent.

In simple cases, both the Freundlich and Langmuir isotherms are employed for the quantitative description of adsorption. For this purpose they are used in the form of equations (13.37) and (13.39)), only this time concentrations are used in place of partial pressures

$$a_2 = \alpha\, c_2^{\beta}\,, \qquad a_2 = a_{\max}\,\frac{b\,c_2}{1 + b\,c_2}\,, \tag{13.42}$$

where α, β, $a_{\max}$ are temperature-dependent parameters which are characteristic of the given trio of substances, i.e. the solvent, the solute and the adsorbate, a_2 is the amount of solute (adsorbate) adsorbed by unit mass of the adsorbent, and c_2 is the equilibrium concentration of the solute.

Example

Adsorption of acetone(2) from an aqueous solution on charcoal at $18\,°\mathrm{C}$ can be expressed using the Freundlich isotherm $a_2(\mathrm{mmol\,g^{-1}}) = 5.12\,c_2^{0.52}$, where the acetone concentration c_2 is given in $\mathrm{mol\,dm^{-3}}$. Calculate the adsorbed amount of substance of acetone for $c_2 = 0.2\,\mathrm{mol\,dm^{-3}}$.

Solution

By substituting into the above relation we obtain $a_2 = 5.12 \cdot 0.2^{0.52} = 2.217\,\mathrm{mmol\,g^{-1}}$.

Chapter 14

Dispersion systems

Dispersion systems are systems containing at least two phases, with one phase being dispersed in the other phase in the form of small particles.

14.1 Basic classification

A dispersed phase is referred to as the **dispersion ratio** or **dispersion phase**. The phase whose continuity remains preserved is referred to as the **dispersion environment**. Dispersion systems may be classified using several criteria:

- State of matter of the dispersion environment and the dispersion phase
- Size of particles of the dispersion phase
- Structure of the dispersion phase.

Classification based on the phases state of matter is summarized in the following table:

Dispersion environment	Dispersion phase	Term used for the system
Gas	Liquid	Mist
Gas	Solid	Smoke (Dust)
Liquid	Gas	Foam
Liquid	Liquid	Emulsion
Liquid	Solid	Colloid solution, suspension
Solid	Solid	Solid foam, porous substance
Solid	Liquid	Solid emulsion
Solid	Solid	Solid sol, eutectic alloy

Based on the particle size, dispersion systems are classified as

- Analytical dispersions with the particle size less than 5 nm,
- Colloid dispersions with the particle size ranging from 5 to 100 nm.
- Microdisperions with the particle size ranging from 100 nm to 10 μm,
- Coarse dispersions with the particle size over 10 μm.

Note: Analytical dispersion systems rank rather among homogeneous systems. Microdispersions and coarse dispersions are usually ranked among suspensions.

The above list was only a simplified classification of dispersion systems. Only very rarely do these systems contain only one single size of particles. Such systems are classified as **monodispersions**. In most systems, the dispersion ratio exists simultaneously in a continuous distribution of different particle sizes, and the system is termed **polydispersion**.

Based on the **dispersed ratio structure**, dispersion systems may be classified as:

- systems with isolated (often roughly spherical) particles called **sols**,
- systems with an interlinked structure of the dispersion phase forming a net structure in the dispersion environment, which are called **gels**.

The names given to individual dispersion systems often combine the particle shape and the phase of the dispersion environment. Sols with air as the dispersion environment are referred to as aerosols while those with liquid as the dispersion environment are called lyosols (lyos = liquid).

When describing the properties of dispersion systems, we may characterize them using other criteria too. Lyosols, e.g., may be lyophilic (liquid-loving) or lyophobic (liquid-hating), according to Freundlich.

Lyophilic sols are such colloid systems which are (almost) stable on any change of the dispersion environment content (e.g. water evaporation). In the case of lyophobic sols, on the other hand, the dispersion environment may be removed only to a small extent, otherwise the sol would irreversibly change to a coagulate. During coagulation the isolated particles of the dispersion phase unite to form a more extensive macroscopic phase. Glue+water may serve as an example of a lyophylic system, while a lyophobic system may be represented by a colloid solution of gold in water.

14.2 Properties of colloid systems

Systems containing colloid particles are in some properties different from systems which are homogeneous or composed of macroscopic phases.

14.2.1 Light scattering

If light passes through a system containing colloid particles, part of the light is scattered and consequently the ray passage through the environment can be observed (the Tyndall effect). For the intensity I of light passing through a dispersion environment we write (compare with relation (12.16)

$$\ln \frac{I}{I_0} = -\tau\, l\,, \tag{14.1}$$

where l is the length of the dispersion environment through which the light passes (optic path), τ is the turbidity coefficient, I_0 is the intensity of the initial light. A decrease in the light intensity in the original direction is not due to the absorption of light by the molecules of the substance, but it is caused by its scattering to all directions by reflection from the colloid particles. The initial wavelength of the light remains preserved during its scattering.

For the total intensity of scattered light $I_{\rm scat}$

$$I_{\rm scat} = I_0 - I \tag{14.2}$$

the **Rayleigh formula** applies

$$\frac{I_{\rm scat}}{I_0} = 24\,\pi^3\,\frac{N\,v^2_{\rm particle}}{\lambda^4}\left(\frac{n_1^2 - n_0^2}{n_1^2 + 2\,n_0^2}\right)^2\,, \tag{14.3}$$

where N is the number of particles of the volume $v_{\rm particle}$ in unit volume, λ is the wavelength of the incident light, n_0 is the refraction index or the dispersion environment, and n_1 is refraction index of the dispersion ratio. From this relation it is obvious that

- In order for scattered light to originate, the diffraction index of the dispersion ratio and that of the dispersion environment have to be different.
- Light scattering is proportional to the number of particles in the system,
- The scattered light is proportional to the quadrate of the particles volume,

- The scattering is inversely proportional to the fourth power of the wavelength of the incident light.

Example

Explain why the sky is blue and the setting sun is red.

Solution

The sunlight is scattered in the atmosphere by way of the Rayleigh scattering. Since the blue light has a shorter wavelength, it is scattered more and the sky is blue. If we observe the sun directly, we observe unscattered light which has a complementary red colour. This effect is evident particularly during the sunrise and sunset when the sunlight has to pass through a thick layer of the atmosphere.

14.2.2 Sedimentation of colloid particles

Another effect observed in colloid systems is their gradual sedimentation and attainment of a sedimentation equilibrium.

The rate of **sedimentation in the gravitational filed**, v, for sedimenting spherical particles of the radius r is given by the following relation (provided that Stoke's law $F_{\mathrm{resistance}} = 6\,\pi\,r\,\eta\,v$)

$$v = \frac{\mathrm{d}h}{\mathrm{d}\tau} = \frac{m\,g}{6\,\pi\,\eta\,r}\left(1 - \frac{\rho_0}{\rho}\right) = \frac{2}{9}\,\frac{g\,r^2}{\eta}(\rho - \rho_0)\,, \tag{14.4}$$

where $m = (4/3)\,\pi\,r^3$ is the mass of the spherical particle, ρ is the particle density, ρ_0 is the density of the dispersion environment, η is its viscosity and g is the gravitational acceleration.

Example

Calculate the sedimentation rate of quartz particles of the radius 5×10^{-6} m in water at 25 °C ($\eta \doteq 1$ mPa s, $\rho_0 \doteq 1\,\mathrm{g\,cm^{-3}}$). The quartz density is $2.6\,\mathrm{g\,cm^{-3}}$.

Solution

By substituting into the second relation (14.4) we obtain

$$v = \frac{2 \times 9.81 \times (5 \times 10^{-6})^2}{9 \times 0.001}(2.6 - 1) \times 10^3 = 8.72 \times 10^{-5}\,\mathsf{m\,s^{-1}} = 31.4\,\mathsf{cm\,h^{-1}}\,,$$

The rate of **sedimentation in the centrifugal field** in an ultracentrifuge rotating with the angular velocity ω is given by the relation

$$v = \frac{\mathrm{d}h}{\mathrm{d}\tau} = \frac{m\,\omega^2\,h}{6\,\pi\,\eta\,r}\left(1 - \frac{\rho_0}{\rho}\right) = \frac{2\,\omega^2\,r^2\,h}{9\,\eta}(\rho - \rho_0)\,, \tag{14.5}$$

where h is the distance from the axis of rotation. In this case the rate of sedimentation is proportional to the distance from the axis of rotation h.

Example

The sedimentation rate of quartz particles ($\rho \doteq 2.6\,\mathsf{g\,cm^{-3}}$) of the radius $r = 1 \times 10^{-7}\,\mathsf{m}$ in water ($\eta \doteq 1\,\mathsf{mPa\,s}$, $\rho_0 \doteq 1\,\mathsf{g\,cm^{-3}}$) is $1\,\mathsf{cm}$ in about 80 hours. What must be the angular velocity and the number of rotations in an ultracentrifuge for the particles to sediment at a rate of $1\,\mathsf{cm\,min^{-1}}$ at a distance of $10\,\mathsf{cm}$ from the axis of rotation?

Solution

From relation (14.5) we obtain

$$w^2 = v\,\frac{9\,\eta}{2\,r^2\,h\,(\rho - \rho_0)} = \frac{0.01}{60}\,\frac{9 \times 0.001}{2 \times 10^{-14} \times (2.6 - 1) \times 1000} = 4.6875 \times 10^5\,\mathsf{s^{-2}}\,,$$

$$w = 684.6\,\mathsf{s^{-1}},\ n = \frac{\omega}{2\pi} = 108.96\,\mathsf{s^{-1}} = 6538\,\mathsf{min^{-1}}\,.$$

After a certain time the rate of sedimentation starts to decrease because the diffusion flow of particles caused by their different concentrations begins to assert itself against the gravitational or centrifugal force. After a sufficiently long time the rate drops to zero and a **sedimentation equilibrium** is attained. For sedimentation in the gravitational field this equilibrium is expressed by the relation

$$\ln\frac{c_{h_2}}{c_{h_1}} = -\frac{m\,\boldsymbol{N}_{\mathbf{A}}\,g}{\boldsymbol{R}T}\left(1-\frac{\rho_0}{\rho}\right)(h_2-h_1) = -\frac{4\,\pi\,r^3\,\boldsymbol{N}_{\mathbf{A}}\,g}{3\,\boldsymbol{R}\,T}\,(\rho-\rho_0)\,(h_2-h_1) \tag{14.6}$$

where c_{h_2} and c_{h_1} represent the number of particles of the mass m in unit volume, at the height h_2 and h_1. Other symbols have their usual meanings.

Example

Calculate the concentration ratio of quartz particles of the radius $r = 5\times10^{-6}$ m scattered in water as established at equilibrium in layers distant 1 cm from one another. The density of water and quartz is $\rho_0 = 1\,\mathrm{g\,cm^{-3}}$ and $\rho = 2.6\,\mathrm{g\,cm^{-3}}$, respectively.

Solution

Substituting into (14.6) yields

$$\begin{aligned}\ln\frac{c_{h_2}}{c_{h_1}} &= -\frac{4\times3.146\times(5\times10^{-6})^3\times6.022\times10^{23}\times9.81}{3\times8.314\times298.15}\,(2.6-1)\times10^3\times0.01\\ &= -7.625\times10^4\,.\end{aligned}$$

These particles will sediment practically completely.

In the centrifugal field of the ultracentrifuge, a sedimentation equilibrium is attained which is described by the relation

$$\ln\frac{c_{h_2}}{c_{h_1}} = \frac{m\,\boldsymbol{N}_{\mathbf{A}}\,\omega^2}{2\,\boldsymbol{R}T}\left(1-\frac{\rho_0}{\rho}\right)(h_2^2-h_1^2) = \frac{2\,\pi\,r^3\,\boldsymbol{N}_{\mathbf{A}}\,\omega^2}{3\,\boldsymbol{R}\,T}\,(\rho-\rho_0)\,(h_2^2-h_1^2)\,, \tag{14.7}$$

where c_{h_2} denotes the number of particles of the mass m or radius r in unit volume, and at the distance h_2 from the axis of rotation.

14.2.3 Membrane equilibria

Different properties of colloid systems are also evident when we observe those comprised of two subsystems separated by a semipermeable membrane.

The osmotic pressure is given by a relation analogous to that for molecular solutions (7.11). If the system contains a low-molecular electrolyte KA, in addition to a high-molecular electrolyte KR whose anion R^- does not pass through the membrane, a different equilibrium is established in the system. It is influenced by the activity of the electric charges of ions, and it is known as the **Donnan equilibrium**. The equilibrium is conditioned by equal activity of the electrolyte KA in both subsystems (denoted by the subscripts I and II)

$$(a_{\mathrm{K}^+} a_{\mathrm{A}^-})_{\mathrm{I}} = (a_{\mathrm{K}^+} a_{\mathrm{A}^-})_{\mathrm{II}} . \tag{14.8}$$

Example

A subsystem I contains a polymerous electrolyte NaR of the concentration $c_1 = 0.1\,\mathrm{mmol\,dm^{-3}}$, and an NaCl electrolyte of the concentration $c_2 = 1\,\mathrm{mmol\,dm^{-3}}$. Another subsystem, II, of the same volume, separated from the first one by a membrane, contains pure water. Assuming unit activity coefficients and complete dissociation, determine the equilibrium concentration of NaCl in the second subsystem.

Solution

We use x to denote the amount of substance of the Na^+ and Cl^- ions which pass through the membrane to the second subsystem. For the first subsystem we thus have

$$(a_{\mathrm{Na}^+} a_{\mathrm{Cl}^-})_{\mathrm{I}} \approx (c_{\mathrm{Na}^+} c_{\mathrm{Cl}^-})_{\mathrm{I}} = (c_1 + c_2 - x)\,(c_2 - x)\,,$$

for the second subsystem we write

$$(a_{\mathrm{Na}^+} a_{\mathrm{Cl}^-})_{\mathrm{II}} \approx (c_{\mathrm{Na}^+} c_{\mathrm{Cl}^-})_{\mathrm{II}} = x \times x\,.$$

If we set both activities of the electrolytes equal, we obtain

$$x = \frac{c_2\,(c_2 + c_1)}{c_1 + 2\,c_2} = \frac{1 \times 10^{-3}\,(1 \times 10^{-3} + 1 \times 10^{-4})}{1 \times 10^{-4} + 2 \times 10^{-3}} = 0.524\,\mathrm{mmol\,dm^{-3}}\,.$$

If there is only the strong high-molecular electrolyte KR on one side of the membrane, which is actually present in the form of the K^+ and R^- ions, the K^+ ions also pass to the other subsystem. In order to preserve electroneutrality of both subsystems, the OH^- ions by the dissociation of water pass to the other part of the system together with the K^+ ions. The solution in the first subsystem becomes acidic and that in the other subsystem becomes alkaline. The equilibrium condition may be written in the form

$$(a_{K^+}a_{OH^-})_I = (a_{K^+}a_{OH^-})_{II} \; . \tag{14.9}$$

Example

A subsystem I contains a high-molecular electrolyte NaR of the molar concentration $c_1 = 0.1\,\text{mmol}\,\text{dm}^{-3}$. A subsystem II, separated from the subsystem I by a membrane, contains pure water at the beginning. Determine the equilibrium concentration of hydroxyl ions in both subsystems at 25 °C ($K_w = 1\times10^{-14}$, $\gamma_i = 1$).

Solution

Substituting into (14.9) yields

$$(c_1 - x)\,\frac{K_w}{x} = x\cdot x\,.$$

For the first estimate of x we may use the relation

$$x = \sqrt[3]{c_1 K_w} = \sqrt[3]{1\times10^{-4}\times10^{-14}} = 1\times10^{-6}\,\text{mol}\,\text{dm}^{-3}\,.$$

The exact solution of the equation $x^3 + K_w x - c_1 K_w = 0$ would yield $x = 0.9966\times10^{-6}\,\text{mol}\,\text{cm}^{-3}$. In the second subsystem, $(c_{OH^-})_{II} = x = 0.9966\times10^{-6}\,\text{mol}\,\text{dm}^{-3}$. In the first subsystem the concentration of the OH^- ions will be $(c_{OH^-})_{II} = \frac{K_w}{x} = 1.0034\times10^{-8}\,\text{mol}\,\text{dm}^{-3}$.

For a high-molecular electrolyte RB, which dissociates into R^+ and B^-, equation (14.9) rearranges to

$$(a_{R^+}a_{B^-})_I = (a_{R^+}a_{B^-})_{II} \; . \tag{14.10}$$

Appendix

Fundamental constants

According to CODATA 2002. The values in parentheses are estimated standard deviations in the units of the last significant digit.

Quantity	Symbol, formula	Value	Note
Speed of light in vacuum	c	$299792458\,\mathrm{m\,s^{-1}}$	defined
Gas constant	R	$8.314472(15)\,\mathrm{J\,mol^{-1}\,K^{-1}}$	
Avogadro constant	$N_\mathrm{A} = L$	$6.0221415(10)\times10^{23}\,\mathrm{mol^{-1}}$	
Boltzmann constant	$k = k_\mathrm{B} = R/N_\mathrm{A}$	$1.3806505(24)\times10^{-23}\,\mathrm{J\,K^{-1}}$	
Elementary charge	e	$1.60217653(14)\times10^{-19}\,\mathrm{C}$	
Faraday constant	$F = eN_\mathrm{A}$	$96485.3383(83)\,\mathrm{C\,mol^{-1}}$	
Planck constant	h	$6.6260693(11)\times10^{-34}\,\mathrm{J\,s}$	
Vacuum permeability	μ_0	$4\pi\times10^{-7}\,\mathrm{J\,s^2\,C^{-2}\,m^{-1}}$	defined
Vacuum permittivity	$\varepsilon_0 = 1/(c^2\mu_0)$	$8.8541878176\ldots\times10^{-12}$	defined
Fine structure constant	$\alpha = \mu_0 e^2 c/(2h)$	$7.297352568(24)\times10^{-3}$	
Rydberg constant	$R_\infty = \alpha^2 m_\mathrm{e} c/(2h)$	$10973731.568525(73)\,\mathrm{m}$	
Stephan-Boltzmann const.	$\sigma = 2\pi^5 k^4/(15h^3c^2)$	$5.67040(4)\times10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}}$	
Mass of electron (atomic mass unit)	m_e	$9.1093826(16)\times10^{-31}\,\mathrm{kg}$	
Mass of proton	m_p	$1.67262171(29)\times10^{-27}\,\mathrm{kg}$	
Unified atomic mass unit	$u = 1\,\mathrm{g\,mol^{-1}}/N_\mathrm{A}$	$1.66053886(28)\times10^{27}\,\mathrm{kg}$	
Bohr radius	$a_0 = \varepsilon_0 h^2/(\pi m_\mathrm{e} e^2)$	$0.5291772108(18)\times10^{10}\,\mathrm{m}$	
Bohr magneton	$\mu_\mathrm{B} = eh/(4\pi m_\mathrm{e})$	$9.27400949(80)\times10^{-24}\,\mathrm{J\,T^{-1}}$	
Nuclear magneton	$\mu_\mathrm{B} = eh/(4\pi m_\mathrm{p})$	$5.05078343(43)\times10^{-27}\,\mathrm{J\,T^{-1}}$	
Gravitational constant	G	$6.6742(10)\times10^{-11}\,\mathrm{m^3\,kg^{-1}\,s^{-2}}$	
Standard acceleration of free fall	g	$9.80665\,\mathrm{m\,s^{-1}}$	defined
Standard pressure	p^st	$101.325\,\mathrm{kPa}$ or $100\,\mathrm{kPa}$	defined
Standard concentration	c^st	$1\,\mathrm{mol\,dm^{-3}}$	defined
Standard molality	$\underline{m}^\mathrm{st}$	$1\,\mathrm{mol\,kg^{-3}}$	defined
Temperature of water triple point	T_tr	$273.16\,\mathrm{K} = 0.01\,^\circ\mathrm{C}$	defined