Thermodynamics

10

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The insight, that heat is just one of several forms of energy and can be explained by a mechanical model, is today common knowledge, but it is only about 170 years old. The physician *Julius Robert Mayer* (1814–1878) formulated in 1842 his ideas about the energy conservation for the conversion of mechanical energy into heat, and he could already give a numerical value for the thermal energy equivalent (Sect. 10.1.5). However, only after the development of the kinetic gas theory (see Sect. 7.3) the microscopic explanation of heat of a macroscopic body as the total energy (kinetic plus potential energy) of all molecules of the body was possible. As has been explained in Sect. 7.3, a measure of the mean kinetic energy of all particles with mass m in a gas volume, which have three degrees of freedom for their motion is the absolute temperature

$$T = \frac{1}{k} \cdot \frac{2}{3} \cdot \frac{m}{2} \cdot \overline{v^2} \,. \tag{10.1}$$

With this definition of the temperature all macroscopic phenomena and the general laws derived from them (Boyle.-Marriott, general gas law) could be reduced to microscopic models describing matter as composed of atoms and molecules.

In this chapter, we will discuss in more detail the measurement of temperature, the definition of temperature scales, the experimental findings of energy transport and conversion, of material changes with temperature such as thermal expansion and phase transitions. An important subject is the formulation of basic laws of thermodynamics which can be regarded as a summary of many experimental results. We try to explain all macroscopic phenomena as far as possible by microscopic models, where, however, some explanations need a deeper knowledge of atomic physics, which will be imparted in volume 3 of this textbook series.

At the end of this chapter a short excursion to the thermodynamics of real gases and liquids is presented, which might be helpful for the explanation of many phenomena observed in nature.

10.1 Temperature and Amount of Heat

The definition of the absolute temperature, given in (10.1), is for most practical applications of temperature measurements not very helpful. One has to use measuring techniques that are reliable, accurate and easy to handle.

Qualitative information about the temperature can be already obtained with the heat sensibility of our body. Our skin has sensors that inform us whether a body is cold or hot. This sensing is, however, not very accurate and depends on the previous experience, as the following experiment illustrates: Three containers with (1) hot water, (2) lukewarm water and (3) cold water are placed side by side. Dipping a finger at first into (1) and then into (2) the lukewarm water seem to be cold, but dipping at first into (3) and then into (2) the same lukewarm water seems to be warm.

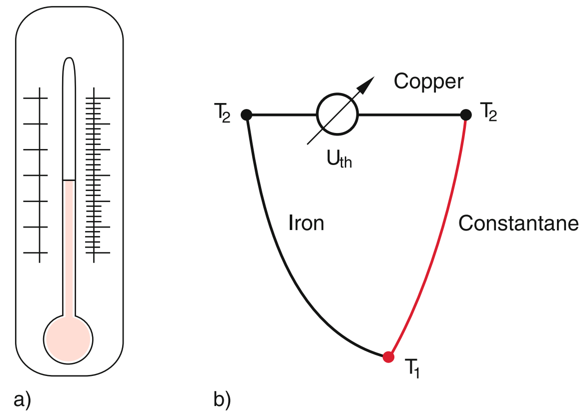


Figure 10.1 **a** Liquid thermometer; **b** thermo couple

This demonstrates that the sensing of our body is not reliable and cannot be used for quantitative measurements. In order to measure temperatures and the amount of heat, measuring instruments and techniques have to be developed that are for practical applications sufficiently easy to handle and which give reliable and reproducible results.

10.1.1 Temperature Measurements, Thermometer, and Temperature Scales

For the measurement of temperatures in principal all physical effects can be used that depend on the temperature. These are for instance:

- The geometrical dimensions of solid, liquid or gaseous bodies, which generally increase with the temperature. Metal wires become longer, liquid or gas volumes expand with increasing temperature at constant pressure.
- The electrical resistance of a body changes with the temperature T. For metals it increases with T for semiconductors it decreases (see Vol. 2, Chap. 2)
- The electric contact potential difference between two different metals in contact changes with temperature (Thermovoltage see Vol. 2, Sect. 2.9)
- The radiation power emitted by a hot body increases with T^4 and can be used for the measurement of the temperature of remote bodies such as stars (Radiation Pyrometer see Vol. 2 Chap. 12).

Devices for the measurement of temperatures are called **thermometers** (Tab. 10.1). For daily practice the expansion of liquids are generally used (liquid thermometer, Fig. 10.1a) or the change of the contact voltage (thermo-elements, Fig. 10.1b).

For the quantitative specification of a temperature, numerical values for fixed temperatures have to be defined that can be accurately reproduced under readily realizable external conditions (temperature fix points). Furthermore, a temperature scale has to be defined. This has been historically realized in different ways.

Table 10.1 The mostly used thermometers

Thermometer type	Temperature range / °C	Measuring principle	Error limits
Liquid thermometers:			
Mercury	−38 to +800	Thermal expansion of liquid in glas capillary	depending on scale division 0.1–1 °C
Alcohol	−110 to +210		
Pentane mixture	−200 to ≈+30		
Solid state thermometers:			
Metal rod	−150 to +1000 dependent on specific metal	Thermal expansion of metals	1–2% of scale range
Bimetal	−150 to +500	Length expansion difference	Dependent on model
Resistance thermometers:			
Metal wire	−250 to +1000	Temperature dependence of electric resistance	0.1–1 °C
Semiconductor	−273 to +400		
Thermo couple:			
Fe-CuNi (iron-constantan)	−200 to +760	Temperature dependence of thermovoltage	0.1–1 °C
Ni-CrNi	−270 to +1000		
Ni-CrNi	−200 to +1370		
Pt-PtRh	−50 to +1700		
W-WMo	−200 to +3000		
Pyrometer	+800 to +3000	Heat radiation	2–10 °C

10.1.1.1 The Celsius Scale

The astronomer *Anders Celsius* (1701–1744) proposed 1742 to use the expansion of a mercury column for the measurement of temperatures (mercury thermometer). Two fix points were defined for the temperature scale: The melting point of ice ($T_C = 0\,°C$) and the boiling point of water ($T_C = 100\,°C$ at a pressure of $1\,\text{atm} = 1013.25\,\text{hPa}$). The range between these two fix points is divided into 100 equal units, where each unit corresponds to 1 °C.

Note: We will label the Celsius temperature with T_C in order to distinguish it from the Fahrenheit temperature (T_F) and Kelvin temperature T.

10.1.1.2 The Fahrenheit Scale

The Fahrenheit scale, which was proposed by Daniel Gabriel Fahrenheit (1686–1736) is still used in the USA. It defines as fix points the melting point of a defined ice-water-ammonia chloride solution at $T_F = 0\,°F$ ($-17.8\,°C$) and the normal body temperature at $T_F = 100\,°F$ ($+37.7\,°C$). The range between the two fix points is equally divided into 100 units where 1 unit corresponds to 1 °F. From this definition it follows that $0\,°C = 32\,°F$ and $100\,°C = 212\,°F$. The conversion between the two scales is as follows (Fig. 10.2):

$$\begin{aligned} T_C/\,°C &= \tfrac{5}{9}\,(T_F/\,°F - 32) \\ T_F/\,°F &= \tfrac{9}{5}\,(T_C/\,°C + 32)\ . \end{aligned} \tag{10.2}$$

10.1.1.3 The Absolute Temperature Scale

The absolute temperature scale needs only one fix point, which is the triple point of water (see below). It is measured with gas thermometers.

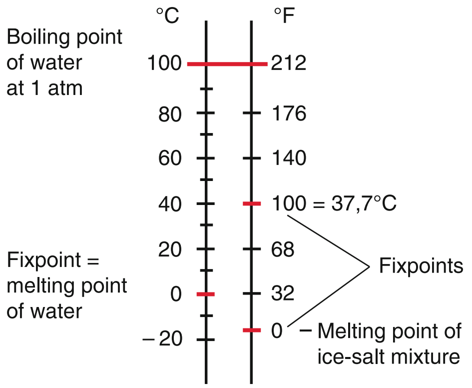


Figure 10.2 Comparison of Celsius and Fahrenheit scale. For the Kelvin scale there is only one fixpoint (triple point of water at 0.01 °C)

Its definition is: The Kelvin is the unit of the thermodynamic temperature scale. 1 K is the 273.16th part of the temperature T_p of the triple point of water. The zero point of the Kelvin scale is the lower absolute limit of possible temperatures and is defined by general laws of thermodynamics (see Sect. 10.3).

10.1.1.4 Accuracy of Thermometers

The temperature scale of liquid thermometers depends on the choice of the liquid and also of the glass of the thermometer capillary, because not only the liquid but also the glass expands with rising temperature. The thermal expansion of liquids and solids is generally not constant over the temperature range measured by thermometers and is not necessarily linear (see next Section). For mercury, the deviation from linearity is small. The comparison with an alcohol thermometer shows that its scale differs from that for the mercury thermometer and is not equidistant (Fig. 10.3).

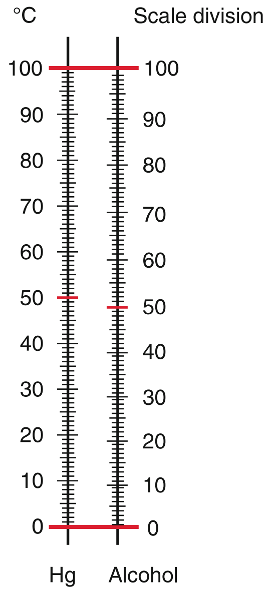


Figure 10.3 Demonstration of non-uniform expansion of liquids by comparing mercury and alcohol themometers

If higher accuracy is demanded, other thermometers have to be found which have a better linear temperature scale. A possible solution is the thermal expansion of gas volumes at constant pressure or the pressure increase at constant volume that are utilized in the gas thermometer (see Sect. 10.1.3). They are used for the definition of the absolute temperature scale (Kelvin scale, Sect. 10.1.4).

10.1.2 Thermal Expansion of Liquids and Solids

The length L of a rod changes with temperature. Experiments show that the relative length change $\Delta L/L$ within a restricted temperature range is approximately proportional to the temperature change ΔT:

$$L(T_C) = L(0) \cdot (1 + \alpha T_C) \, . \tag{10.3}$$

The expansion coefficient

$$\alpha = (\mathrm{d}L/\mathrm{d}T)/L \tag{10.4}$$

gives the relative length change for a temperature change $\Delta T = 1\,°\mathrm{C}$.

Integration of (10.4) gives

$$L(T) = L(0) \cdot e^{\alpha \Delta T} \quad \text{with} \quad \Delta T = T - T_0 \, . \tag{10.4a}$$

Table 10.2 Thermal expansion of solids and liquids at $T = 293\,\mathrm{K} = 20\,°\mathrm{C}$

Solids	Linear expansion coefficient $\alpha/(10^{-6}\,\mathrm{K}^{-1})$	Liquids	Volume expansion coefficient $\gamma/(10^{-4}\,\mathrm{K}^{-1})$
Aluminium	23.8	Water	2.07
Iron	12	Ethanol	11
V2A Steel	16	Acetone	14.3
Copper	16.8	Benzene	10.6
Sodium	71	Mercury	1.8
Tungsten	4.3	Glycerin	5.0
Invar	1.5	*N*-Pentane	15
Cerodur	<0.1	Water at	
Hard rubber	75–100	$T = 0\,°\mathrm{C}$	–0.7
		$T = 20\,°\mathrm{C}$	+2.07

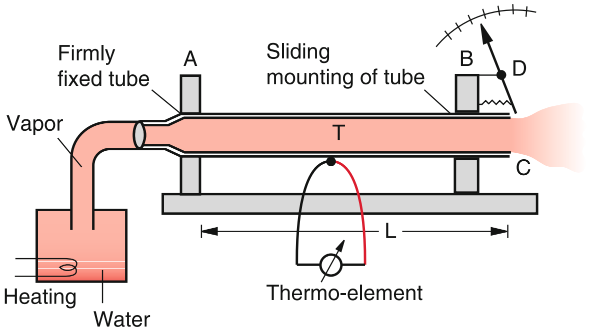


Figure 10.4 Demonstration of thermal expansion of metal tubes

Table 10.2 compiles numerical values of α for some materials. One can see that for most materials α is positive, i. e. the length L increases with T. The coefficients α can be measured with the device shown in Fig. 10.4. A tube made of the material to be inspected, is clamped on one end A, but can freely slide on the other end B where a turnable tongue is connected to the rod that shows the length change on a calibrated scale. When hot water vapour streams through the tube, it expands and turns the tongue. The scale is set to zero at $T_C = 20\,°\mathrm{C}$. The temperature of the tube is measured with a calibrated thermo-element. Metal tubes can be also heated by an electric current through the tube.

The reason for the thermal expansion is the asymmetric potential of the interaction between neighbouring atoms (Fig. 10.5). The atoms of a solid are not fixed at a constant value r_0 of the distance between neighbouring atoms but oscillate around r_0 (see Vol. 3). The length L of a rod is determined by the mean distance $\langle r \rangle$ of this oscillation. Increasing the temperature causes an increase of the vibrational energy and of the oscillation amplitude $r(t)$. Because of the asymmetric potential the mean value $\langle r \rangle$ increases with increasing amplitude $r(t)$ thus causing an increase of the length L.

More detailed measurements prove that the thermal expansion is not strictly linear. Expansion of (10.4a) gives

$$L(T) = L(0)(1 + \alpha \cdot \Delta T + \tfrac{1}{2}(\alpha \Delta T)^2 + \ldots) \, . \tag{10.4b}$$

This nonlinear expansion can be also expressed by a temperature-dependent expansion coefficient α

$$\alpha(T_C) = \alpha(T_C = 0) + \beta \cdot T_C = \alpha_0 + \beta \cdot T_C \, . \tag{10.4c}$$

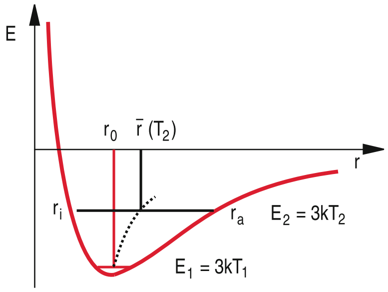


Figure 10.5 Atomic model of thermal expansion due to the anharmonic interaction potential

Instead of (10.3) the more accurate equation is then

$$L(T_\mathrm{C}) = L_0\left(1 + \alpha_0 T_\mathrm{C} + \beta T_\mathrm{C}^2\right) . \qquad (10.5)$$

However, within the temperature range between 0 °C and 100 °C the deviation from linearity is very small, i. e. $\beta \cdot T_\mathrm{C} \ll \alpha_0$. For small temperature intervals ΔT the length $L(T_\mathrm{C})$ can be approximated by a straight line with a slope $\mathrm{d}L/\mathrm{d}T = \alpha_0 + \beta \cdot T_\mathrm{C}$ that slightly depends on T_C.

Example

At room temperature the expansion coefficients of aluminium are $\alpha(T_\mathrm{C} = 20\,°\mathrm{C}) = 23.8 \cdot 10^{-6}/°\mathrm{C}$, $\beta = 1.8 \cdot 10^{-8}/(°\mathrm{C})^2$.

The relative proportion of the nonlinear expansion is therefore $\beta \cdot T_\mathrm{C}/\alpha = 7.5 \cdot 10^{-4}$. This implies that the coefficient α changes within a temperature range $\Delta T = 100\,°\mathrm{C}$ only by 7.5%. ◀

For some alloys the expansion coefficient is very small. Examples are INVAR (64% iron and 36% nickel) or the glass ceramics CERODUR (see Tab. 10.2 and 10.3) [10.1].

Since all length dimensions of a three-dimensional body vary with the temperature, also the volume of the body must change.

Table 10.3 Dependence of mean thermal expansion coefficient $\alpha/10^{-6}\,\mathrm{K}^{-1}$ on temperature (given in K)

T/K	Al	Cu	Fe	Al_2O_3	SiO_2
50	3.5	3.8	1.3	0.0	−0.86
100	12.0	10.5	5.7	0.2	−0.80
150	17.1	13.6	8.4	1.0	−0.45
200	20.2	15.2	10.1	2.8	−0.1
250	22.4	16.1	11.1	4.0	+0.2
300	23.8	16.8	12.0	5.0	+0.4
350	24.1	17.3	12.6	6.0	+0.5
400	24.9	17.6	13.2	6.4	+0.55
500	26.5	18.3	14.3	7.2	+0.58

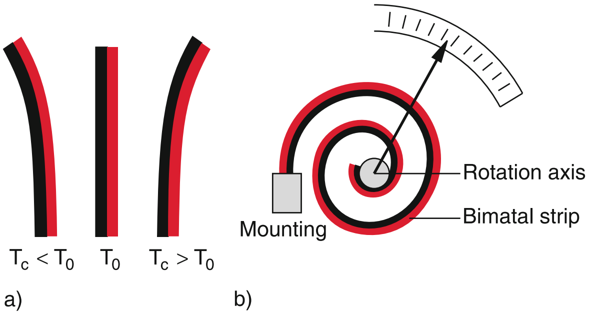


Figure 10.6 Bimetal thermometer. **a** Principle, **b** technical design

For homogenous and isotropic bodies applies

$$\begin{aligned} V(T_\mathrm{C}) &= V_0(1 + \alpha T_\mathrm{C})^3 && \text{with} \quad V_0 = V(T_\mathrm{C} = 0\,°\mathrm{C}) \\ &\approx V_0(1 + 3\alpha T_\mathrm{C}) && \text{for} \quad \alpha T_\mathrm{C} \ll 1 \\ &= V_0(1 + \gamma T_\mathrm{C}) && \text{with} \quad \gamma = 3\alpha \, . \end{aligned} \qquad (10.6)$$

For non-isotropic bodies the expansion may differ for the different directions and one obtains, instead of (10.6), the equation

$$\begin{aligned} V(T_\mathrm{C}) &= V_0(1 + \alpha_1 T_\mathrm{C}) \cdot (1 + \alpha_2 T_\mathrm{C}) \cdot (1 + \alpha_3 T_\mathrm{C}) \\ &\approx V_0\left[1 + (\alpha_1 + \alpha_2 + \alpha_3) T_\mathrm{C}\right] \\ &= V_0(1 + 3\overline{\alpha} T_\mathrm{C}) \quad \text{with} \quad \overline{\alpha} = \tfrac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3) \, . \end{aligned} \qquad (10.6a)$$

The difference of expansion coefficients of different metals is utilized for bimetal thermometers (Fig. 10.6). When two metal strips of different materials are bonded (e. g. by welding or soldering) the double strip will bend when the temperature changes. A special device converts the bending, which is proportional to the temperature change ΔT, into the turn of a hand with a scale (Fig. 10.6b) where after calibration the temperature can be read on the scale.

If the thermal expansion should be prevented by an external force very large forces are necessary, as the following experiment demonstrates (Fig. 10.7). A thick rod S made of wrought iron, is clamped between two stable mountings L_1 and L_2. On one end a bolt B with 5 mm diameter fixes the rod S to the mounting L_1. Now the rod is heated with a Bunsen burner until it is red glowing. The resulting thermal expansion loosens the screw M on the right side at L_2, which is tightened again at the highest temperature of the rod. Now the rod cools down and contracts. The contraction force is so large that the bold at the left side cracks.

A quantitative calculation of the forces necessary to prevent thermal expansion or contraction proceeds as follows:

The force necessary to achieve an elongation of a rod with length L and cross section $A \ll L^2$ and with an elastic modulus E is according to (6.2) and (10.4)

$$F = E \cdot A \cdot \Delta L/L = E \cdot A \cdot \alpha \cdot \Delta T \, . \qquad (10.7)$$

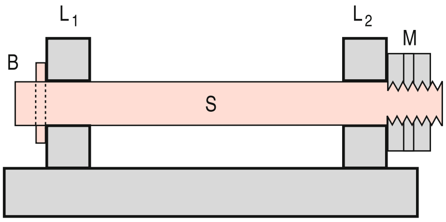


Figure 10.7 Bolt cracker. Demonstration of large forces when the thermal expansion is hindered. (B = bolt, S = hot rod, L_1, L_2 = mounts, M = screw nut)

If the thermal expansion should be prevented by application of external pressure, we obtain from (6.7) and (10.7) the required pressure

$$p = \frac{\alpha \cdot E}{1 - 2\mu} \cdot \Delta T \,, \tag{10.8}$$

where μ is the transverse contraction ratio (Poisson number).

Examples

1. A steel rod ($E = 120\,\mathrm{GN/m^2}$, $\alpha = 16 \cdot 10^{-6}/\,^\circ\mathrm{C}$) with the cross section $A = 100\,\mathrm{cm^2}$ suffers a temperature change $\Delta T = 30\,^\circ\mathrm{C}$. In order to prevent its expansion a force $F = 5.76 \cdot 10^5\,\mathrm{N}$ is necessary.
2. A section of a railroad track of steel with $L = 20\,\mathrm{m}$ and $\alpha = 16 \cdot 10^{-6}/\,^\circ\mathrm{C}$ expands for a temperature difference $\Delta T = 40\,^\circ\mathrm{C}$ by $\Delta L = \alpha \cdot L \cdot \Delta T = 1.3\,\mathrm{cm}$. For modern railroad tracks all sections are welded together at $T = 20\,^\circ\mathrm{C}$ without gap. Without strong mountings each section between the welding spots would bend in such a way, that the length expansion $\Delta L = \alpha \cdot L \Delta T$ could be realized. This would give for $\Delta T = 60\,^\circ\mathrm{C}$ a maximum deviation from the straight line of about 30 cm. This bending is prevented by strong supports where at every meter the rails are mounted. The force on the welding surfaces with a cross section $A = 0.02\,\mathrm{m^2}$ ($d = 10\,\mathrm{cm}$, $b = 20\,\mathrm{cm}$) is then (see Probl. 10.2) $F = 1.5 \cdot 10^6\,\mathrm{N}$. When the rail track cools down to $T = -20\,^\circ\mathrm{C}$ a tensile force of the same magnitude acts onto the welding surfaces which corresponds to a tensile stress of $8 \cdot 10^7\,\mathrm{N/m^2}$. This is still sufficiently far below the break stress of $7 \cdot 10^8\,\mathrm{N/m^2}$. ◀

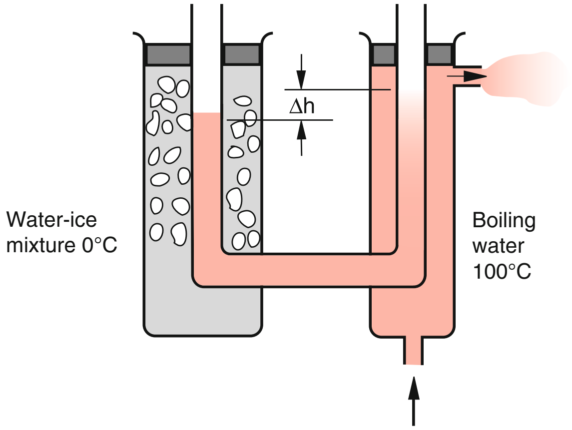


Figure 10.8 Design of Dulong–Petit for the measurement of thermal expansion of liquids

For the thermal expansion of liquids only the volume expansion can be given. When measuring this volume expansion one has to take into account that the solid container also expands. For the measurement of thermal expansion of liquids a device proposed by *Dulong* and *Petit* (Fig. 10.8) has been developed. The liquid is contained in a U-shaped tube where one side is encased in a jacket containing melting ice, while the other side is heated to 100 °C by water vapour. Of course the inspected liquid should not boil at 100 °C and should not freeze at 0 °C. Since the total mass $M = \varrho \cdot V$ of the liquid is constant, independent of the temperature, the density

$$\varrho(T_\mathrm{C}) = \frac{\varrho_0}{1 + \gamma T_\mathrm{C}}$$

does depend on T: It is smaller in the hot side and larger in the cold side. The height h_0 of the liquid surface will be therefore lower in the cold side by Δh. Rearrangement of the equation yields

$$\gamma = \frac{1}{T_\mathrm{C}} \left(\frac{\varrho_0}{\varrho(T_\mathrm{C})} - 1 \right) = \frac{1}{T_\mathrm{C}} \cdot \frac{\Delta\varrho}{\varrho(T_\mathrm{C})} \,.$$

From the equilibrium condition

$$h_0 \cdot \varrho_0 \cdot g = h(T_\mathrm{C}) \cdot \varrho(T_\mathrm{C}) \cdot g$$

gives

$$\varrho_0/\varrho = h/h_0 \,.$$

The thermal volume expansion coefficient γ is then

$$\gamma = \frac{1}{T_\mathrm{C}} \cdot \frac{\Delta h}{h_0} \,. \tag{10.9}$$

Table 10.2 compiles some values of γ.

Note, that they are much larger than the volume expansion coefficients 3α of solids. This justifies the neglect of the glass tube expansion for liquid thermometers.

10.1.3 Thermal Expansion of Gases; Gas Thermometer

Experiments show that the volume of ideal gases (see Sect. 7.3) increases at constant pressure proportional to the temperature.

$$V(T_\mathrm{C}) = V_0(1 + \gamma_\mathrm{V} \cdot T_\mathrm{C}) \,, \tag{10.10}$$

where the temperature is measured in °C and $V_0 = V(T_\mathrm{C} = 0\,^\circ\mathrm{C})$.

Table 10.4 Thermal expansion coefficient of some gases

Gas	$\gamma/(10^{-3}/\mathrm{K})$
Ideal Gas	3.661
He	3.660
Ar	3.671
O_2	3.674
CO_2	3.726

The expansion coefficient

$$\gamma_V = \frac{V(T_C) - V_0}{V_0 \cdot T_C} \qquad (10.11)$$

gives the relative change $\Delta V/V_0$ per 1 °C. The experimentally obtained numerical values of γ_V are compiled in Tab. 10.4.

For Helium, which comes closest to an ideal gas, one finds

$$\gamma_V = \frac{1}{273.15}\,{}^\circ\mathrm{C}^{-1} = 3.661 \cdot 10^{-3}\,{}^\circ\mathrm{C}^{-1} .$$

Accurate experiments performed at a constant gas volume give for the temperature dependence of the pressure the completely analogue relation

$$\begin{aligned} &p = p_0(1 + \gamma_p \cdot T_C) \\ &\quad \text{with} \quad \gamma_p = \gamma_V = \gamma = \frac{1}{273.15}\,{}^\circ\mathrm{C}^{-1} . \end{aligned} \qquad (10.12)$$

(**Law of Gay-Lussac**).

The gas thermometer (Fig. 10.9) utilizes this pressure dependence for the measurement of temperatures. The volume V is connected with a U-shaped tube filled with mercury. The height of Hg in the left side of the U-tube can be changed by up- and down lifting of the right side, which is connected with the left side by a flexible tube. When the gas volume is heated, the pressure rises. In order to keep the gas volume constant, the level of the Hg in the left side is always kept at the same height. The pressure is then indicated by the difference Δh between the left and the right side. It is $p = \varrho_{\mathrm{Hg}} \cdot g \cdot \Delta h$. The temperature, obtained from (10.12)

$$T_C = \frac{1}{\gamma} \cdot \frac{p - p_0}{p_0} = 273.15 \frac{\Delta p}{p_0}\,{}^\circ\mathrm{C} \qquad (10.13)$$

is therefore determined by a pressure measurement. At the temperature $T_C = 0$ which is realized by immersing the gas volume into a melting ice-water mixture, the height difference is adjusted to $\Delta h = 0$. The pressure in the gas volume V is then $p = p_0$.

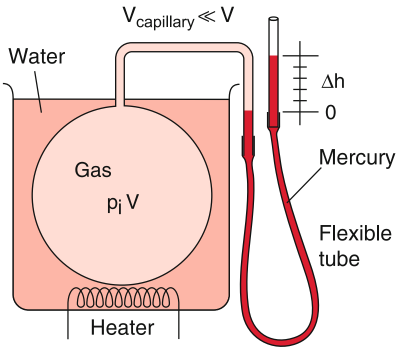


Figure 10.9 Gas thermometer

10.1.4 Absolute Temperature Scale

We will now discuss the relation between the Celsius scale and the absolute temperature scale, which is also called (after its creator Lord Kelvin) **Kelvin scale** or **thermo-dynamical temperature scale**. In Sect. 7.3 the absolute temperature T was used in the general gas equation

$$p \cdot V = N \cdot k \cdot T , \qquad (10.14a)$$

relating pressure p, particle number N in the gas volume V with T. The absolute temperature T was defined by Eq. 10.1, which is based on the results of the kinetic gas theory (see Sect. 7.3). The general gas equation (10.14a) states that for constant pressure and temperature the gas volume has a definite value, which is the same for all ideal gases independent of the specific kind.

At a temperature T_0 (at 0 °C) and a pressure $p_0 = 1\,\mathrm{bar} = 10^3\,\mathrm{hPa}$ (normal conditions) Eq. 10.14a becomes

$$p_0 \cdot V_0 = N \cdot k \cdot T_0 . \qquad (10.14b)$$

From (10.14a) and (10.14b) we can conclude

$$p = p_0 \cdot \frac{V_0}{V} \cdot \frac{T}{T_0} . \qquad (10.14c)$$

In the gas thermometer the volume $V = V_0$ is kept constant. The comparison of (10.14c) with (10.12) yields

$$p = p_0 \cdot \frac{T}{T_0} = p_0(1 + \gamma \cdot T_C) . \qquad (10.15)$$

This gives with the experimental value $\gamma = (273.15)^{-1}$ the relation

$$T = T_0 \cdot (1 + \gamma T_C) = T_0 + \frac{T_0}{273.15} \cdot T_C \qquad (10.16)$$

between the absolute temperature T and the Celsius scale T_C.

Note: ***The unit oft the absolute temperature scale is the Kelvin. It is the 273.16th part of the thermodynamic temperature of the triple point of water.***

A definition of the absolute temperature that is independent of the specific substance, can be given with their help of the Carnot-Cycle (see Sect. 10.3.5)

10.1.5 Amount of Heat and Specific Heat Capacity

When a defined energy ΔW is transferred to a body, its temperature rises by $\Delta T \sim \Delta W$. A simple demonstration (Fig. 10.10) uses an immersion heater which is immersed into water in a thermally isolated Dewar flask and heated for a time Δt. The electric energy $\Delta W = I \cdot U \cdot \Delta t$ (I = electric current, U = voltage, see Vol. 2 Chap. 2) causes a temperature rise ΔT that depends on the mass of the water. The increase ΔQ of the heat Q (often also called the amount of heat) is given by

$$\Delta Q = \Delta W = c \cdot M \cdot \Delta T \,. \tag{10.17}$$

The proportional constant c is the *specific heat*. It depends on the specific material of the heated body. It gives the amount of heat that increases the temperature of a body with $M = 1\,\text{kg}$ by $\Delta T = 1\,\text{K}$. The product $C = c \cdot M$ is the *heat capacity* of a body with mass M.

In former times the unit was the large calorie (1 kcal). This is the amount of heat that increases the temperature of 1 kg water from 14.5 to 15.5 °C. Nowadays the unit is 1 Joule ($1\,\text{J} = 1\,\text{W} \cdot \text{s} = 1\,\text{N} \cdot \text{m}$). It has the great advantage, that for the conversion of heat into electrical or mechanical energy the same units are used and therefore the conversion factor is 1. This is not the case, if the unit calorie is used. Here measurements give the electrical heat equivalent

$$\text{WE}_{\text{el}} = \frac{\Delta Q\,[\text{cal}]}{\Delta W_{\text{el}}\,[\text{W s}]} = 0.23885\,[\text{cal/W s}] \,. \tag{10.18}$$

This equation means: If ΔW_{el} is measured in Joule, but ΔQ in calories, the ratio $\Delta Q/\Delta W_{\text{el}}$ has the numerical value 0.23885 i. e. $1\,\text{W s} = 0.2389\,\text{cal}$ or $1\,\text{cal} = 4.1868\,\text{W s}$.

The temperature rise in the experiment shown in Fig. 10.10 does not occur abruptly but continuously over the time interval Δt of the heating (Fig. 10.10b). During this time interval, a steady heat flux takes place between the hot water and its surrounding which decreases the temperature difference ΔT. In order to consider this, a temperature progression for a sudden change of ΔT is simulated, indicated by the vertical dashed line in Fig. 10.10b. The time t_1 is chosen such that the areas A_1 and A_2 are equal in order to maintain the same value for the integral $\int T \mathrm{d}t \sim \int \mathrm{d}Q = \Delta Q$.

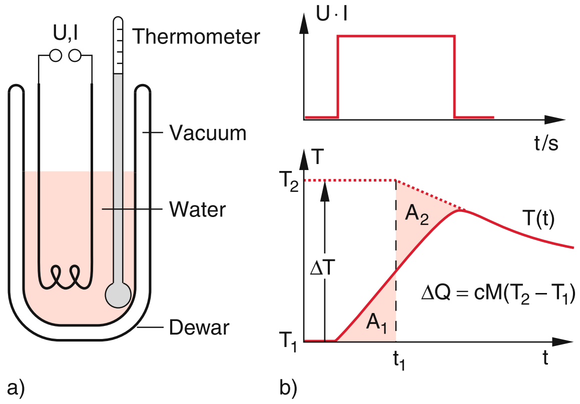


Figure 10.10 Measurement of the electric heat equivalent with immersion heater and Dewar flask. **a** Experimental setup; **b** time progression of electric power and temperature

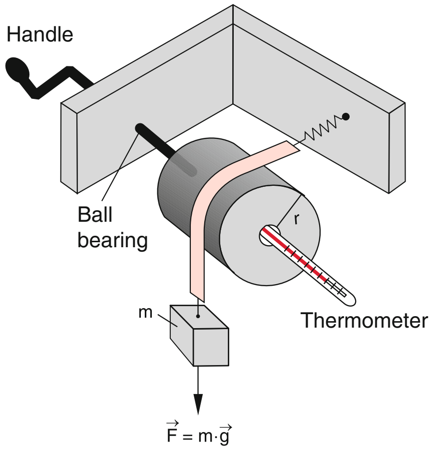


Figure 10.11 Measurement of mechanical heat equivalent

Instead of heat generation by electrical power, heat can be also produced by mechanical work due to friction. This is demonstrated by the arrangement in Fig. 10.11. Here a metal tape is wrapped around a copper cylinder, filled with water. A weight with mass m presses the tape tightly onto the cylinder. Now the cylinder with radius r is turned by a handle during a time interval Δt with such a frequency f that the weight $G = m \cdot g$ is just compensated by the friction force between tape and cylinder. The work performed against the friction force by turning the cylinder N-times during the time interval Δt is

$$\begin{aligned} \Delta W &= m \cdot g \cdot 2\pi r \cdot N \\ &= (c_{\text{W}} \cdot M_{\text{W}} + c_{\text{Co}} \cdot M_{\text{Co}})\Delta T_1 \,, \end{aligned} \tag{10.19a}$$

where M_{W} is the mass of the water and M_{Co} that of the copper cylinder. Repeating the experiment without water filling a larger temperature difference ΔT_2 is measured. From these two measurements we obtain from the relation

$$(c_{\text{W}} m_{\text{W}} + c_{\text{Co}} \cdot m_{\text{Co}})\Delta T_1 = c_{\text{Co}} \cdot m_{\text{Co}} \cdot \Delta T_2 = \Delta W$$

for the heat, put into the water the relation

$$\Delta Q = c_{\text{W}} M_{\text{W}} \Delta T_1 = \left(1 - \frac{\Delta T_1}{\Delta T_2}\right) \Delta W_{\text{mech}} \,. \tag{10.19b}$$

The **mechanical heat equivalent**, determined with such experiments is

$$\text{WE}_{\text{mech}} = \frac{\Delta Q/\text{cal}}{\Delta W_{\text{mech}}/\text{Nm}} = 4.186 \,, \tag{10.19c}$$

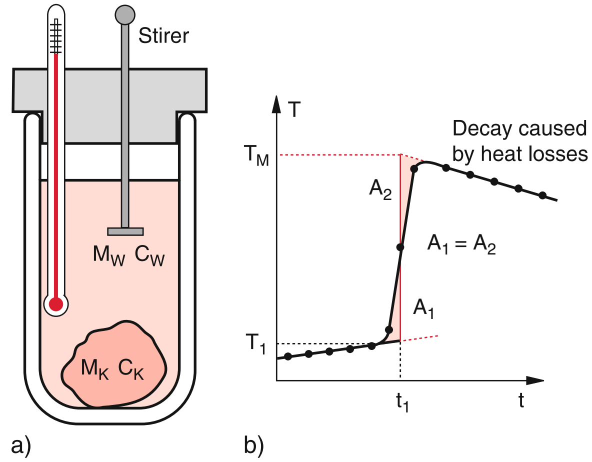


Figure 10.12 Measurement of specific heat c_K of a solid body using a mixture calorimeter. **a** Experimental setup; **b** measurement of time-dependent temperature (t_1 = immersion of solid body, T_1 = initial temperature, T_M = temperature of mixture)

should of course have the same mechanical value as the electrical heat equivalent, because of the definition $1\,\mathrm{W \cdot s} = 1\,\mathrm{N \cdot m}$ in the SI system.

The specific heat c_K of a body can be measured with the mixture calorimeter shown in Fig. 10.12. In a well-isolated Dewar container is water with the mass M_W at the temperature T_1. Now a solid body with the mass M_K that had been heated up to the temperature $T_2 > T_1$ is inserted into the water. The temperature $T_M(t)$ of the mixed system (body + Dewar + water) is measured as a function of time (Fig. 10.12b).

The heat $(c_K M_K (T_1 - T_M)$ transferred from the body to water plus Dewar is equal to the heat change $c_W \cdot M_W + c_D \cdot M_D$ of water plus Dewar. This gives the specific heat of the body

$$c_K = \frac{(M_W \cdot c_W + C_D)(T_M - T_1)}{M_K (T_2 - T_M)} , \tag{10.20}$$

where $C_D = c_D \cdot M_D$ is the heat capacity of the dewar. The temperature T_M of the mixture is determined in the same way as in Fig. 10.10. The measured curve $T(t)$ in Fig. 10.12b is replaced by the simulated red curve where the vertical line is placed at the time t_1 where the areas $A_1 = A_2$. This takes into account the heat loss during the heat transfer form body to water. The intersection points of the vertical line with the two horizontal red curves give the correct temperatures T_1 and T_M.

The heat capacity $C_D = c_D \cdot M_D$ of the Dewar can be measured when two portions of water with masses M_1 and M_2 at temperatures T_1 and T_2 are mixed in the Dewar and the mixing temperature T_M is measured [10.1].

10.1.6 Molar Volume and Avogadro Constant

One mole is according to the definition given in Sect. 1.6 the amount of a substance that contains as many atoms or molecules as 12 g carbon ^{12}C. The molar mass of a substance ^{y}X with the atomic mass number y is then equal to $(y/12) \cdot m(^{12}\mathrm{C})$g.

The molar volume V_M contains 1 mol of the gas.

Examples

1 mol helium gas He are 4 g He,
1 mol hydrogen gas H_2 are 2 g H_2,
1 mol nitrogen N_2 are 28 g N_2. ◄

The number of atoms or molecules per mole is the *Avogadro constant* N_A. This number is independent of the specific substance.

It can be measured with different methods (see Vol. 3, Chap. 2).

The average value of many measurements is

$$N_A = 6.022 \cdot 10^{23}/\mathrm{mol} .$$

One mole of atoms or molecules always fills the same volume under equal external conditions, independent of their specific kind. One finds under normal conditions

$$\begin{aligned} V_M(p = 1\,\mathrm{atm} = 101.3\,\mathrm{kPa}, T_C = 0\,°\mathrm{C}) &= 22.4\,\mathrm{dm}^3 \\ V_M(p = 1\,\mathrm{bar} = 100\,\mathrm{kPa}, T_C = 0\,°\mathrm{C}) &= 22.7\,\mathrm{dm}^3 . \end{aligned}$$

The general gas equation (10.14a) can be written for 1 mol with $V = V_M$ and $N = N_A$

$$p \cdot V_M = N_A \cdot kT = R \cdot T , \tag{10.21}$$

where the **general gas constant**

$$R = N_A \cdot k = 8.31\,\mathrm{J/(K \cdot mol)} \tag{10.22}$$

is the product of Avogadro number N_A and Boltzmann constant k. All gases that obey this equation are called **ideal gases**.

For an arbitrary volume $V = \nu \cdot V_M$ Eq. 10.14a can be written as

$$p \cdot V = \nu \cdot R \cdot T , \tag{10.21a}$$

where the number ν quotes how many moles are contained in V.

10.1.7 Internal Energy and Molar Heat Capacity of Ideal Gases

The amount of heat ΔQ supplied to one mole of a gas with molar mass M (kg/mol) leads to a temperature rise ΔT:

$$\Delta Q = c \cdot M_M \cdot \Delta T = C \cdot \Delta T .$$

The product $C = c \cdot M_{\mathrm{M}}$ of specific heat and molar mass is the **molar heat capacity** with the unit $[C] = [\mathrm{J}/(\mathrm{mol} \cdot \mathrm{K})]$. It is the heat energy that increases the temperature of 1 Mole by $\Delta T = 1\,\mathrm{K}$. For an arbitrary mass $M = \nu \cdot M_{\mathrm{M}}$ is

$$\Delta Q = \nu \cdot C \cdot \Delta T \,.$$

The quotient $\Delta Q/\Delta T = \nu \cdot C$ [J/K] is the **heat capacity** of the body with mass M.

The molar specific heat of a gas depends on whether the gas is heated at constant volume or at constant pressure. We will at first discuss the situation for a constant volume.

We define the internal energy of a gas with volume V as the total energy of its N molecules. It is composed of translational energy plus possible rotational and vibrational energy. For non-ideal gases also the potential energy of their mutual interaction has to be taken into account (Fig. 10.5). The internal energy of a gas depends on the number f of degrees of freedom of the molecules. In Sect. 7.3 it was shown that the mean energy of a molecule is $\langle E \rangle = f \cdot \frac{1}{2}kT$. The internal energy of a gas volume with N molecules is then

$$U = \tfrac{1}{2} f \cdot N \cdot kT$$

and for 1 mol with $N = N_{\mathrm{A}}$ it is

$$U(V_{\mathrm{M}}) = \tfrac{1}{2} f \cdot N_{\mathrm{A}} \cdot kT = \tfrac{1}{2} f \cdot R \cdot T \,. \qquad (10.23)$$

Under thermal equilibrium the energy U is uniformly distributed among all degrees of freedom.

This equipartition is accomplished by collisions between the molecules (see Sect. 4.2 and Vol. 3, Chap. 8).

When the heat ΔQ is supplied, the internal energy U increases by $\Delta U = \Delta Q$, if the volume V of the gas stays constant. We therefore obtain the equation

$$\Delta Q = \Delta U = \nu C_V \cdot \Delta T \,, \qquad (10.24)$$

and with $\Delta U = \frac{1}{2} f \cdot \nu \cdot R \cdot \Delta T$ **the molar heat capacity at constant volume**

$$C_V = \tfrac{1}{2} f \cdot R \,. \qquad (10.25)$$

10.1.8 Specific Heat of a Gas at Constant Pressure

When a gas is heated at constant volume the pressure increases according to the general gas equation (10.14a). In order to achieve a temperature increase at constant pressure, the gas volume must expand (Fig. 10.13b). Such an expansion can be realized when the piston with area A moves by the distance Δx against the external pressure p. This requires the work

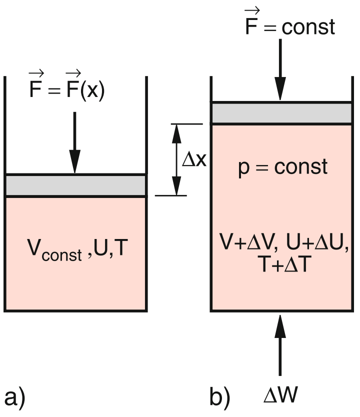


Figure 10.13 Determination of C_p. Heating of gas **a** at constant volume, **b** at constant pressure

$$\Delta W = F \cdot \Delta x = p \cdot A \cdot \Delta x = p \cdot \Delta V \,. \qquad (10.26)$$

This energy ΔW must be supplied additionally. The heat ΔQ is therefore

$$\Delta Q = C_V \cdot \Delta T + p \cdot \Delta V \,. \qquad (10.27)$$

The general gas equation for 1 mol of the gas before and after the expansion is

$$\begin{gathered} p \cdot V = R \cdot T, \\ p(V + \Delta V) = R \cdot (T + \Delta T) \,. \end{gathered}$$

Subtraction yields

$$p \cdot \Delta V = R \cdot \Delta T \,.$$

Inserting this into (10.27) we obtain

$$\Delta Q = (C_V + R)\Delta T = C_p \cdot \Delta T \,. \qquad (10.28)$$

The factor C_p is the molar specific heat at constant pressure

$$C_p = C_V + R \,. \qquad (10.29\text{a})$$

With

$$C_V = \tfrac{1}{2} f \cdot R \rightarrow C_p = \tfrac{1}{2}(f + 2)R \,, \qquad (10.29\text{b})$$

the quotient C_{p}/C_V is called **adiabatic index** or **specific heat ratio**

$$\kappa = \frac{C_p}{C_V} = \frac{f + 2}{f} \,. \qquad (10.29\text{c})$$

10.1.9 Molecular Explanation of the Specific Heat

Since atoms or molecules can move into three directions, they have three degrees of freedom of translation. Their mean translational energy is therefore

$$E_{\text{trans}} = 3 \cdot \tfrac{1}{2} kT\ ,$$

the molar specific heat of atomic gases is therefore

$$C_V = (3/2)R\ .$$

For molecules the supplied energy can be also converted into rotational or vibrational energy. Nonlinear molecules can rotate around three orthogonal axis. They have therefore three degrees of freedom for the rotation. Linear molecules have only 2 rotational degrees of freedom, because of the following reason:

The rotational energy

$$E_{\text{rot}} = L^2/2I$$

is determined by the angular momentum L and the moment of inertia I (see Sect. 5.5). As shown in Quantum physics (see Vol. 3 Chap. 4) the angular momentum has the amount $L = (l\cdot(l+1))^{(1/2)}\cdot\hbar$ with $l = 1; 2; 3; \ldots$. The smallest angular momentum is then $L_{\min} = \sqrt{2}\cdot\hbar$, where $\hbar = h/2\pi$ is Planck's quantum constant, divided by 2π. The moment of inertia for a rotation around the axis of a linear molecule is very small because the heavy nuclei are located on the axis and the light electrons do not contribute much to I. Therefore the rotational energy is very large, generally much larger than the translational energy at accessible temperatures. Collisions cannot excited this rotation and it therefore cannot contribute to the accessible energy.

The vibration of diatomic molecules is one-dimensional and has therefore only one degree of freedom. However, the vibrational energy has two contributions: The kinetic and the potential energy (see Sect. 11.6). The mean value of both contributions is equal to $\frac{1}{2}kT$ and the thermal energy of the vibration is kT. Therefore two degrees of freedom ($f = 2$) are formally attributed to the vibration. A diatomic molecule has then $f = 3 + 2 + 2 = 7$ degrees of freedom, if the temperature is sufficiently high to excite the vibrations.

Note: Quantum Theory shows (see Vol. 3) that the classical model of a vibrating oscillator with regard to the total energy $E = E_{\text{kin}} + E_{\text{pot}}$ is correct, but that the energy can be only absorbed in discrete quanta $h\cdot\nu$. This does, however, not influence our argumentation above.

For polyatomic molecules with j atoms each atom has three degrees of freedom. If we subtract 3 degrees of freedom for the translational motion of the whole molecule and 3 degrees of freedom for the rotation (2 degrees for a linear molecule) we end up with $f_{\text{vib}} = 3j - 6$ ($3j - 5$ for linear molecules) vibrational degrees of freedom.

The total internal energy U of a molecule with j atoms is then

$$U = \tfrac{1}{2}\cdot f \cdot N_{\text{A}} \cdot kT \quad \text{with} \quad f = f_{\text{trans}} + f_{\text{rot}} + f_{\text{vib}}\ . \tag{10.30}$$

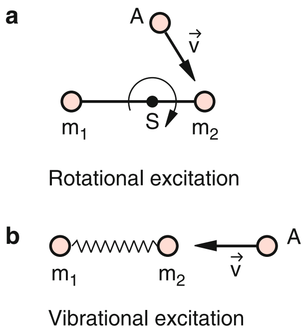


Figure 10.14 Excitation of rotational degrees of freedom of a diatomic molecule induced by collisions. The collision with an atom A causes a rotation of the molecule about an axis perpendicular to the drawing plane (**a**), or causes the excitation of a molecular vibration (**b**)

Since collisions can transfer translational energy to rotations or vibrations only if the thermal energy of the collision partners is sufficiently high, at low temperatures only translational degrees of freedom are available and $f_{\text{eff}} = 3$. With increasing temperature at first the rotation can be excited ($f_{\text{eff}} = 6$ resp. 5 for linear molecules) and at still higher temperature also the vibrations contribute to the specific heat, because their energy is higher than that of the rotations ($f_{\text{eff}} = 3 + 3 + 2\cdot(3j - 6)$ resp. $3 + 2 + 2(3j - 5)$ for linear molecules). This gives for diatomic molecules $f_{\text{eff}} = 3 + 2 + 2 = 7$.

The molar specific heat is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{2} f_{\text{eff}} \cdot R\ . \tag{10.31}$$

Here the partial derivative is used, because U can depend on several variables (p, V, T). The index V indicates that the energy supply occurs at constant volume.

Examples

1. For the atomic gas Helium is $f = 3$. Since the translational energy is not quantized all three degrees of freedom are excited even at low temperatures. Therefore the specific heat of Helium is independent of the temperature (Fig. 10.15).

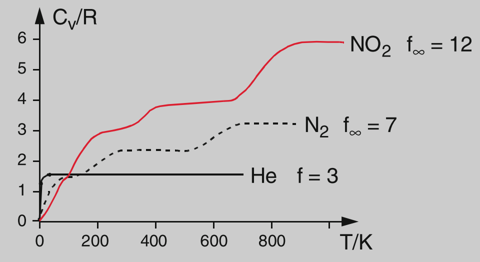


Figure 10.15 Temperature dependence of molar heat capacity of helium, nitrogen N_2 and nitrogen dioxyde NO_2 (see also Sect. 10.1.10)

2. For nitrogen gas consisting of the diatomic molecules N_2 kT is for very low temperatures smaller than the energy of the lowest rotational level (see Probl. 10.3). The rotational energy cannot be excited. Therefore $f_{\text{eff}} = 3$. With increasing temperature when $kT \approx E_{\text{rot}} f_{\text{eff}}$ approaches the value $f_{\text{eff}} = 5$. For still higher temperatures $kT \approx E_{\text{vib}} f_{\text{eff}}$ becomes $f_{\text{eff}} = 7$ because the vibrational degrees of freedom are counted twice (see Sect. 10.1.9). The specific heat of a molecular gas is therefore dependent on the temperature and reaches its maximum value only if kT is sufficiently high to excite all degrees of freedom.
3. Polyatomic gas (e. g. NO_2 at $T > 200\,\text{K}$ where NO_2 has a sufficiently high gas pressure). At this temperature already all three rotational modes can be excited. We then obtain $f = 3 + 3 = 6$.
   Above $T = 300\,\text{K}$ the bending vibration can be excited, rising f to $f = 8$. Only above $T = 800\,\text{K}$ all three vibrational mods can be excited and we have $f = 12$. The molar specific heat is then $C_V = 6R$. ◀

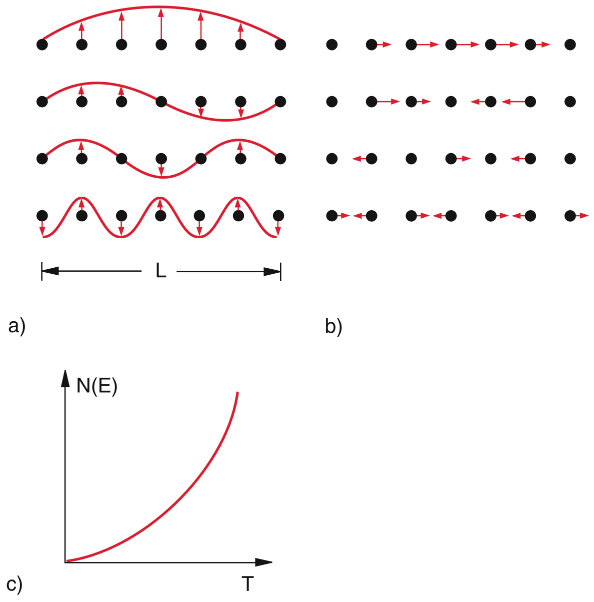


Figure 10.16 Stationary vibrational modes of a linear chain. **a** Transversal; **b** longitudinal standing waves. **c** Number of vibrational modes per energy interval dE of a solid body as function of temperature T

10.1.10 Specific Heat Capacity of Solids

With decreasing temperature all gases become liquids and pass finally into the solid state (except helium, which solidifies only under high pressures). Considerations about the specific heat of solids require a knowledge about the possible degrees of freedom for atoms and molecules in solids. Since the atoms in a solid can only oscillate in three directions around their fixed equilibrium positions but have no degrees of freedom for translation or rotation we would expect $f = 2 \cdot 3 = 6$. However, it turns out that the oscillation frequencies of all atoms are not the same but spread over a large frequency range. In order to get an idea about the frequency distribution, we regard a one-dimensional arrangement of atoms in an ideal crystal where all atoms are regularly placed at a distance d (Fig. 10.16a). When an atom oscillates around its equilibrium positions, the oscillation can be transferred to the neighbouring atoms, due to the coupling force between the atoms. This results in elastic waves travelling through the crystal (see Sect. 11.8). The waves are reflected at the end faces of the crystal, superimpose with the incoming waves and form stationary standing waves. Longitudinal as well as transversal standing waves can develop, depending on whether the oscillation occurs in the direction of wave propagation or perpendicular to it. The standing wave with the smallest possible wavelength λ (i. e. the highest frequency $\nu = c/\lambda$) is realized, when the neighbouring atoms oscillates against each other (Fig. 10.16a, b lowest line). The oscillation with the largest possible wavelength ($\lambda = L$ with $L =$ length of the crystal) has the lowest energy $h \cdot \nu$. At low temperatures only those vibrations with the lowest energy can be excited. With increasing temperature more and more vibrations can be excited. The number of possible vibrations $Z \sim N^3$ is proportional to the third power of the number N of atoms in the crystal. This means that the specific heat rises continuously with the temperature (Fig. 10.16c) until at $kT \geq E_{\text{vib}}^{\max}$ all vibrations are excited and the specific heat takes its maximum value. Since the interaction between neighbouring atoms depends on the specific kind of atoms the progression $C(T)$ differs for the different materials (Fig. 10.17). However, all curves $C(T)$ approach for high temperatures the same value of the molar specific heat

$$C_V = 6 \cdot \tfrac{1}{2} N_A \cdot k = 3R \qquad \text{(Dulong–Petit law)}\,. \tag{10.32}$$

Measurements of the temperature-dependent progression of $C_V(T)$ gives information about the distribution of the vibrational frequencies and therefore about the coupling forces between the atoms of the solid. They are furthermore a convincing experimental proof of quantum theory (see Vol. 3).

Table 10.5 gives numerical values of C_V for some materials.

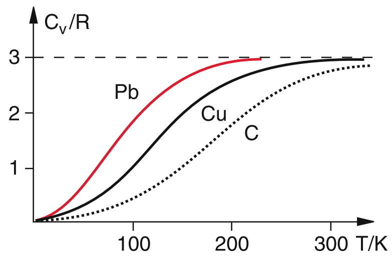


Figure 10.17 Qualitative temperature dependence of molar heat capacity of different solids

Table 10.5 Specific heat c of some materials at 20 °C and 1013.25 hPa, specific heat of fusion λ_f and heat of evaporation λ_e

Substance	c/kJ kg^{-1}K^{-1}	λ_f/kJ kg^{-1}	λ_e/kJ kg^{-1}
Water	4.182	333.5	2256
Ethanol	2.43	105	840
Mercury	0.14	12.4	285
Aluminium	0.896	397	10,900
Iron	0.45	277	6340
Gold	0.13	65	16,500
Copper	0.383	205	4790
Ice at 0 °C	2.1	332.8	–

10.1.11 Fusion Heat and Heat of Evaporation

When a constant heat power $\mathrm{d}Q/\mathrm{d}t$ is supplied to a container with 1 kg ice (specific heat c_i) at a temperature $T_C < 0\,°C$ the temperature

$$T(t) = T_i + a \cdot t \quad \text{with} \quad a = (\mathrm{d}Q/\mathrm{d}t)/c_i \tag{10.33}$$

rises linearly with the slope $a = (\mathrm{d}Q/\mathrm{d}t)\cdot c_i$, ($c_i$ = specific heat of ice) up to $T_m = 0\,°C$ at $t = t_1$. Here the temperature stays constant until t_2, when the ice is completely molten, in spite of a constant power supply $\mathrm{d}Q/\mathrm{d}t$ (Fig. 10.18). Then the temperature rises again but with a different slope $b = (\mathrm{d}Q/\mathrm{d}t)/c_W$ (c_W = specific heat of water) up to $T = 100\,°C$ at $t = t_3$, where the water starts to boil (at p = bar 1). Again the temperature remains constant until $t = t_4$ when the whole water is evaporated. Then the temperature rises further with the slope $(\mathrm{d}Q/\mathrm{d}t)/c_{\mathrm{vap}}$.

The energy $(\mathrm{d}Q/\mathrm{d}t)\cdot(t_2 - t_1)$ supplied during the melting process is called **fusion heat**, the energy $(\mathrm{d}Q/\mathrm{d}t)\cdot(t_4 - t_3)$ is the **heat of evaporation**.

The energy $\lambda_f = (\mathrm{d}Q/\mathrm{d}t)/m$ [J/kg] necessary to melt 1 kg of a substance is the **specific fusion heat** while the molar fusion heat is labelled by Λ_f [J/mol]. Analogue label λ_e and Λ_e the specific and the molar heat of evaporation.

Since the temperature has not changed during the melting process, also the kinetic energy must have stayed constant.

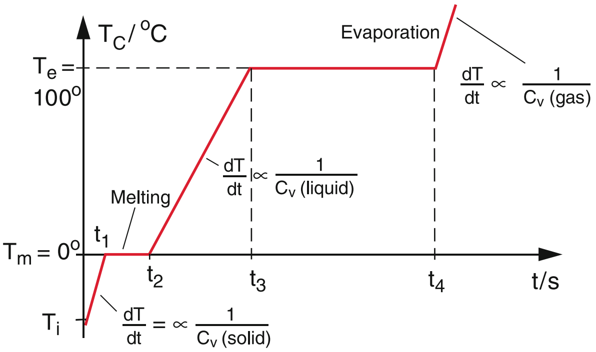


Figure 10.18 Temperature $T(t)$ of water under constant energy supply within the temperature range from below the melting temperature up to above the evaporation temperature (ice–water–water vapor)

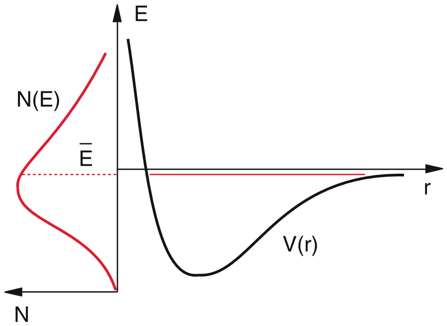


Figure 10.19 Energy distribution $N(E)$ and mean total energy E of molecules just below the melting temperature, illustrated by the interaction potential $V(r)$

Therefore the supplied energy $(\mathrm{d}Q/\mathrm{d}t)\cdot(t_2 - t_1)$ must have increased the potential energy of the atoms or molecules. This can be explained by the molecular model as follows:

The molecules in a solid body are bound to the equilibrium positions by attractive forces. This means that all molecules vibrate in a potential $V(r)$ that is determined by the vector sum $\boldsymbol{F} = \sum F_i = -\nabla V(r)$ of all forces. At the melting temperature the mean total energy $\overline{E} = \overline{E}_{\mathrm{kin}} + \overline{E}_{\mathrm{pot}}$ is illustrated in Fig. 10.19 by the horizontal line close to the dissociation energy E_D of the interaction potential between the atoms or molecules. The energy distribution $N(E)$ of the molecules follows a Maxwell–Boltzmann distribution, as depicted in Fig. 10.19. Those molecules with $E > E_D$ can leave their fixed equilibrium position without changing their kinetic energy.

Continuous energy supply increases the number of molecules that leave their fixed position until all molecules can freely move: The solid body has dissolved and has become a liquid.

The energy supplied during the melting process keeps the kinetic energy constant but increases the potential energy.

An analogous process occurs during the evaporation process. The molecules from the higher energy part of the Maxwell–Boltzmann-distribution have sufficient energy to leave the liquid against the attractive forces and enter the vapour phase. Since the density of the vapour at atmospheric pressure is about 3 orders of magnitude smaller than that of the liquid, the mean distance between the molecules if about 10 times larger. The negative potential energy of the mutual attraction is therefore in the gas phase negligible against their kinetic energy. Similar to the melting process the supplied energy increases the potential energy but not the kinetic energy because the temperature remains constant. The potential energy increases from a negative value (work function, surface tension, see Sect. 6.4) to nearly zero.

The numerical values of fusion energy and evaporation energy depend on the substance. In Tab. 10.5 the values for some materials are listed.

10.2 Heat Transport

Always when a temperature difference exists between two different locations, heat is transported from the warmer to the colder region (see Sect. 7.5.3) Such a heat transport is very important for many technical problems and also for different measuring methods. In many cases one tries to maximize heat transport (for example for cooling heat generating systems) in other cases it is minimized (for heat isolating devices such as Dewars or refrigerators).

There are essentially three mechanisms of heat transport: **Convection**, **heat conduction** and **thermal radiation**.

10.2.1 Convection

When the bottom of a container with water is heated, (Fig. 10.20) the lowest liquid layer is heated first. Its temperature increases and its density therefore decreases. This causes a rise of this lower layer through the layers across, which sink down. This process is called **convection**. It results in a heat transport from the warmer to the colder region. This convection of liquids can be demonstrated by colouring the lower layer and observing how this coloured layer moves upwards when the bottom of the container is heated.

Convection occurs also for gases. It plays an essential role in the earth atmosphere and is responsible for the generation and the equalization of pressure differences (Fig. 10.21). Heated air rises from the bottom just above the earth surface, creating a local low pressure region. Air from the surrounding with higher pressure streams into this region. The wind transports not only mass but also heat [10.2a, 10.2b]. This mass- and heat transport depends on the wind velocity and the temperature difference between high and low pressure region. The wind flow can be either laminar or turbulent, depending on the boundary conditions.

Although the total energy received by the earth is due to radiation from the sun, the local distribution of this energy is essentially determined by convection. This is illustrated by sudden local temperature changes when the wind direction changes, although the intensity of the sun radiation has not changed.

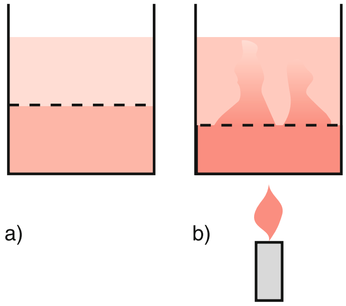


Figure 10.20 Convection in a liquid. **a** Lamination of dyed and pure water at equal temperatures; **b** mixing of the layers by convection due to heating at the bottom

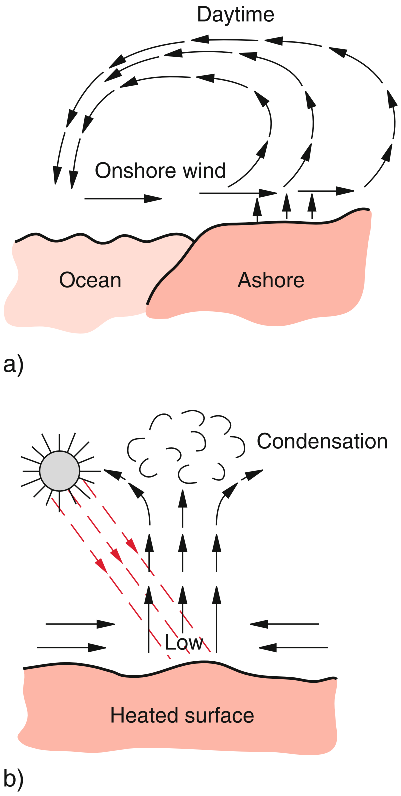


Figure 10.21 Convection in the earth atmosphere. **a** Onshore wind during the daytime, when the ocean surface is colder than the land surface; **b** wind flow into a low pressure region which is created by uprising air (thermal lift)

Also the temperature distribution in the oceans is mainly determined by convection. Examples are the gulf-stream, which influences the climate in the northern part of Europe, or the Humboldt current along the west coast of south America, causing the Atacama desert, because the cold water induces the moisture of the west wind to rain down before it reaches the dry areas.

When the temperature gradient of a liquid, heated at the bottom, exceeds a certain value that depends on the viscosity of the liquid, ordered macroscopic structures of the velocity field can develop. Current roles are created and the liquid moves along cylindrical stream lines (Fig. 10.22b). This sudden start of a

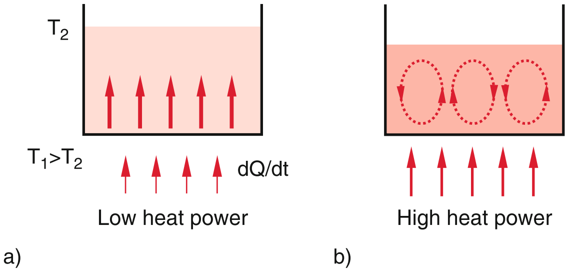


Figure 10.22 **a** Linear vertical temperature gradient; **b** Bénard instability

"self-organization" is called *Bénard-instability*. When the liquid is further heated, the rolls begin a wave-like motion along the cylinder axis. Such organized motions that develop from random conditions play an important role for the creation of organized structures from disordered systems. These processes are investigated in the rapidly developing field of *Synergetics*, which represents a frontier area between Physics, Chemistry, Biology and Computer Science [10.3, 10.4].

10.2.2 Heat Conduction

Contrary to the situation for convection, for heat conduction only energy transport takes place, but generally no mass transport. Heat conduction can only occur in matter, i. e. in vacuum no heat conduction is possible while thermal radiation also takes place in vacuum (otherwise we would not receive the sun radiation).

We will at first discuss heat conduction in solids, where the atoms or molecules are bound to fixed equilibrium positions and no convection can happen.

10.2.2.1 Heat Conduction in Solids

A rod with length L and cross section A is connected at both ends with thermal reservoirs that keep the two ends always at the fixed temperatures T_1 and T_2 with $T_1 < T_2$ (Fig. 10.23). After a sufficient long time a stationary state appears, where a temperature gradient $\mathrm{d}T/\mathrm{d}x$ is established that depends on the temperature difference $\Delta T = T_1 - T_2$, and on the length L. If we neglect heat losses through the side wall of the rod, a constant heat energy

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -\lambda \cdot A \cdot \frac{\mathrm{d}T}{\mathrm{d}x} \tag{10.34a}$$

flows per sec through the cross section A of the rod . The constant $\lambda([\lambda] = [\mathrm{W \cdot m^{-1} \cdot K^{-1}}])$ depends on the substance of the rod and is called **heat conductivity**. In Tab. 10.6 the heat conductivities of some substances are listed.

For a homogeneous rod with constant cross section A, the stationary temperature T(x) is a linear function of x, as can be seen by integrating (10.34a), which yields

$$T(x) = -\frac{\mathrm{d}Q/\mathrm{d}t}{\lambda \cdot A} x + C\,. \tag{10.34b}$$

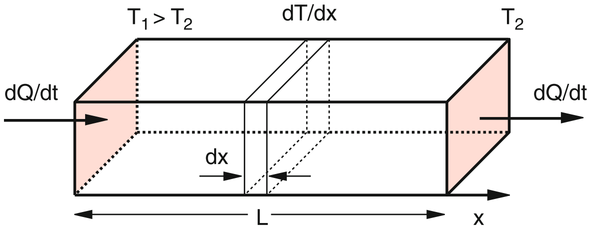


Figure 10.23 Heat conduction in a stab

Table 10.6 Heat conduction coefficient of some materials at 20 °C

Substance	$\lambda/(\mathrm{W\,m^{-1}K^{-1}})$
Aluminium	221
Iron	67
Gold	314
Copper	393
Zinc	112
Lead	35
Normal concrete	2.1
Foamed concrete	0.22
Glas	0.8
Glas wool	0.04
Wood	0.13
Ice	2.2
Water	0.6
Air ($p = 1$ atm)	0.026
CO_2 ($p = 1$ atm)	0.015
Helium ($p = 1$ atm)	0.14

The integration constant C is determined by the boundary condition $T(x = 0) = T_1 = C$. The energy supply necessary to maintain the given temperature gradient $\mathrm{d}T/\mathrm{d}x$, is obtained from

$$\mathrm{d}Q/\mathrm{d}t = \lambda \cdot A \cdot (T_1 - T_2)/L\,.$$

For the general nonstationary heat conduction through inhomogeneous bodies with variable cross section the temperature function $T(x, t)$ is more complicated. For its derivation we regard a volume element $\mathrm{d}V$ between the planes $x = x_1$ and x_2 (Fig. 10.24).

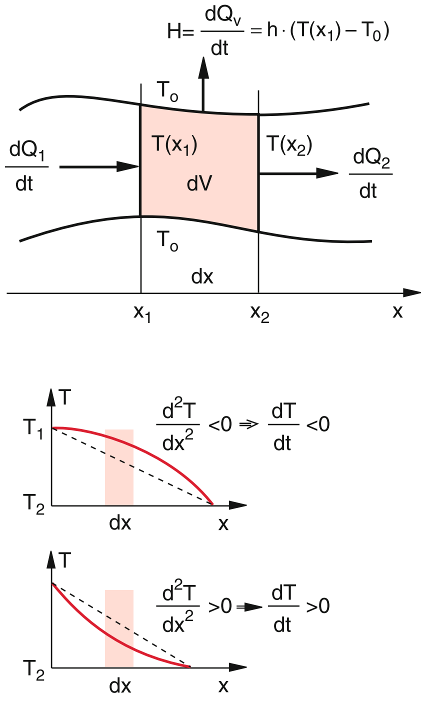


Figure 10.24 Derivation of the heat conduction equation

For the one-dimensional case (for instance a thin homogeneous rod) the temperature changes only in one direction and we obtain for the heat power, transported through the cross section A at the position x_1

$$\frac{\mathrm{d}Q_1}{\mathrm{d}t} = -\lambda \cdot A \cdot \frac{\partial T}{\partial x} . \tag{10.35}$$

The partial derivative is used here, because the temperature $T(x,t)$ depends on the two variables x and t. At the plane $x_2 = x_1 + \mathrm{d}x$ the temperature has changed to

$$T(x_2) = T(x_1) + (\partial T/\partial x) \cdot \mathrm{d}x .$$

The heat passing per sec through the plane at $x = x_2$ is

$$\frac{\mathrm{d}Q_2}{\mathrm{d}t} = -\lambda \cdot A \cdot \frac{\partial}{\partial x}\left(T + \frac{\partial T}{\partial x} \cdot \mathrm{d}x\right) . \tag{10.36}$$

When the temperature is higher at x_1 than at x_2, the heat $\mathrm{d}Q_1/\mathrm{d}t$ flows per sec from the left side in Fig. 10.24 into the volume $\mathrm{d}V = A \cdot \mathrm{d}x$, and the heat $\mathrm{d}Q_2/\mathrm{d}t$ leaves it per sec to the right side. The change $\mathrm{d}Q/\mathrm{d}t$ of the heat per second in the volume $\mathrm{d}V$ is then

$$\begin{aligned}\frac{\mathrm{d}Q}{\mathrm{d}t} &= \frac{\mathrm{d}Q_1}{\mathrm{d}t} - \frac{\mathrm{d}Q_2}{\mathrm{d}t} = \lambda \cdot \frac{\partial^2 T}{\partial x^2} \cdot A \cdot \mathrm{d}x \\ &= \lambda \cdot \frac{\partial^2 T}{\partial x^2} \cdot \mathrm{d}V .\end{aligned} \tag{10.37}$$

Because $\mathrm{d}Q = c \cdot m \cdot \mathrm{d}T$ and $m = \varrho \cdot \mathrm{d}V$ this net supply of heat power $\mathrm{d}Q$ changes the temperature T according to (10.37) by

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\varrho \cdot c} \cdot \frac{\partial^2 T}{\partial x^2} . \tag{10.38a}$$

If the rod has heat losses $H = \mathrm{d}Q_V/\mathrm{d}t$ through the side walls (for example through cooling by the surrounding air) a loss term $H = h \cdot (T - T_0)$ has to be added to (10.37) which is proportional to the temperature difference between the rod temperature at the position x and the surrounding temperature T_0. The factor h has the unit $[\mathrm{W} \cdot \mathrm{K}^{-1}]$. Equation 10.38a can then be generalized with $h* = h/(c \cdot m)$ as

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\varrho \cdot c} \cdot \frac{\partial^2 T}{\partial x^2} - h^* \cdot (T - T_0) . \tag{10.38b}$$

If T depends also on y and z all net heat power contributions supplied from all directions to the volume element $\mathrm{d}V$ add to the total energy increase of $\mathrm{d}V$. One obtains for this three-dimensional case the general equation for the heat conduction

$$\begin{aligned}\frac{\partial T}{\partial t} &= \frac{\lambda}{c \cdot \varrho}\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) \\ &= \frac{\lambda}{c \cdot \varrho} \cdot \Delta T = \lambda_{\mathrm{T}} \cdot \Delta T ,\end{aligned} \tag{10.39}$$

with the Laplace operator Δ (see Sect. 13.1.6). The factor $\lambda_{\mathrm{T}} = (\lambda/c \cdot \varrho)$ is the **thermal diffusivity**.

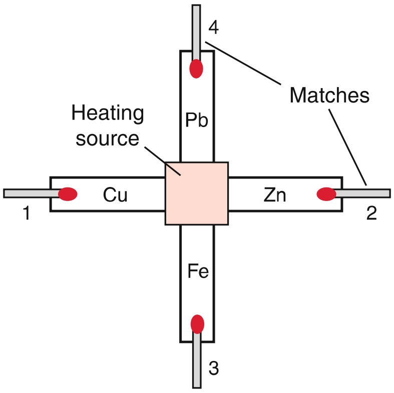


Figure 10.25 Demonstration of the different heat conduction of some metals

The heat conduction in solids is accomplished by the coupling between adjacent atoms, which causes the transport of the vibrational energy of atoms at the plane x to the neighbouring position $x + \mathrm{d}x$ without a transport of the atoms themselves.

In metals the freely moving electrons contribute essentially to heat conduction by collisions with each other and with the atoms. Because of their small mass, their thermal velocities and in particular their Fermi-velocities (which can be only explained by quantum theory, see Vol. 3) are very high. They can therefore transfer their large kinetic energy much faster by collisions. The heat conductivity in metals is therefore mainly due to the electrons. Experiments confirm in deed that for metals the thermal conductivity (λ) is proportional to the electrical conductivity (σ), which is solely caused by electron transport.

This is expressed by the *Wiedemann–Franz law*

$$\begin{aligned}\lambda/\sigma &= a \cdot T \quad \text{with } a = \pi^2 k^2/3e^2 \\ &= 2.45 \cdot 10^{-8}\mathrm{V}^2/\mathrm{K}^2 ,\end{aligned} \tag{10.40}$$

where the constant a is determined by the Boltzmann constant k and the elementary charge e.

This can be readily demonstrated by a simple experiment (Fig. 10.25). The red centre plate of a cross with four arms of different metals is heated by a small burner. At the ends of the arms four matches are placed. After the heating starts it takes different times t_i until the ends of the arms reach the ignition temperature. The matches are ignited at times $t_1 < t_2 < t_3 < t_4$. This time sequence reflects the electrical conductivity of the metals, where the arm 1 (Cu) has the highest electrical and thermal conductivities.

In solids (even in non-metals) the thermal conductivity is much larger than in gases, because of the much larger density and the resulting larger coupling strength between neighbouring atoms (see Tab. 10.6). However, the coefficient of heat conductivity $\lambda_T = \lambda(c \cdot \varrho)$, which gives the time constant of reaching a stationary temperature, is for solids and gases nearly the same because of the much smaller density ϱ of gases.

In gases temperature differences are equated in times comparable to those in solids.

One of the reasons is the much smaller heat energy to reach a temperature rise ΔT for a given volume of a gas than for the same volume of a solid.

For the measurement of heat conductivities stationary as well as time resolving techniques have been developed [10.5].

For the stationary methods a constant heat power $\mathrm{d}Q/\mathrm{d}t$ is supplied to one end of the body (for instance a rod), which is extracted on the other side by cooling. According to (10.35) this results for a rod with constant cross section A in a constant temperature gradient

$$\frac{\partial T}{\partial x} = \text{const} = \frac{T_1 - T_2}{L} = \frac{1}{\lambda \cdot A} \cdot \frac{\mathrm{d}Q}{\mathrm{d}t}\,, \tag{10.41}$$

which can be determined by measuring the temperatures T_1 and T_2 and the length L.

The dynamical methods for the measurement of the heat conduction under non-stationary conditions are based on a time-dependent supply of the heat power. The heat power $\mathrm{d}Q/\mathrm{d}t$ is either periodically modulated or supplied in short pulses. If for example the heat power supplied at $x = 0$ is

$$\mathrm{d}Q/\mathrm{d}t = \mathrm{d}Q_0/\mathrm{d}t + a \cdot \cos(\omega t)\,,$$

the temperature at $x = 0$ is

$$T(0,t) = T_1 + \Delta T \cdot \cos(\omega t)\,,$$

and one obtains from the heat conduction equation (10.38b) for a thin cylindrical rod with heat losses $h \cdot (T - T_0)$ through the side walls (Fig. 10.26) the solution

$$\begin{aligned} T(x,t) &= T_0 + (T_1 - T_0)\mathrm{e}^{-\alpha_1 x} \\ &\quad + \Delta T \mathrm{e}^{-\alpha_2 x} \cdot \cos(\omega t - kx)\,. \end{aligned} \tag{10.42}$$

Inserting this into (10.38b) yields for the coefficients

$$\begin{aligned} \alpha_1 &= \sqrt{\frac{\varrho c h^*}{\lambda}} = \sqrt{\frac{h^*}{\lambda_T}}\,, \\ \alpha_2 &= \left[\frac{(h^{*2} + \omega^2)^{1/2} + h^*}{2\lambda_T}\right]^{1/2}; \\ k &= \left[\frac{(h^{*2} + \omega^2)^{1/2} - h^*}{2\lambda_T}\right]^{1/2}. \end{aligned}$$

The temperature $T(x)$ along the rod is a superposition of a constant time-independent contribution that decays exponentially with x due to the heat losses through the sidewalls, and a damped temperature wave with an exponentially decreasing amplitude. The phase of this wave is determined by the loss coefficient h, the frequency ω and the wavelength λ_T of the temperature wave. The phase velocity of the wave

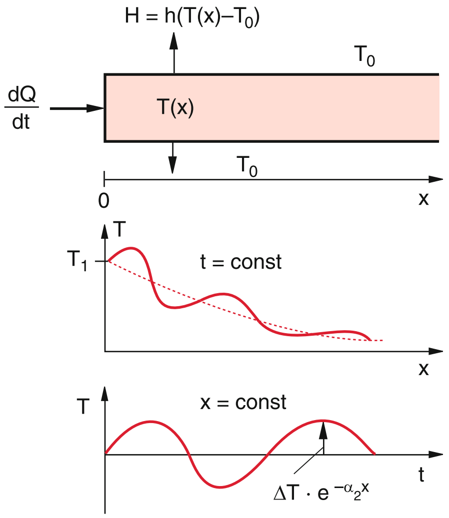


Figure 10.26 Damped temperature waves in a stab under periodic energy supply

$$v_{\text{Ph}} = \frac{\omega}{k} = \left[\frac{2\omega^2 \cdot \lambda_T}{(\omega^2 + h^{*2})^{1/2} + h^*}\right]^{1/2} \tag{10.42a}$$

depends on the frequency ω.

Temperature waves show dispersion!

When amplitude and phase of temperature waves are measured at selected points x for different frequencies ω, the quantities h and $\lambda_T = \lambda/\varrho \cdot c$ can be obtained.

Without heat losses ($h = 0$) (10.42) reduces to

$$\begin{aligned} T(x,t) &= T_1 + \Delta T \mathrm{e}^{-\alpha x} \cos(\omega t - kx) \\ \text{with} \quad \alpha &= k = (\omega/2\lambda_T)^{1/2}\,. \end{aligned} \tag{10.42b}$$

10.2.2.2 Heat Conduction in Liquids

In liquids, there are no shear forces (see Sect. 6.2). Therefore, the coupling between neighbouring atoms is much weaker than in solids and the heat transport is slower. The heat conduction in liquids that have no electrical conductivity, is therefore smaller than in solids (see Tab. 10.6). However, in liquids the freely moving molecules can transfer energy by collisions. The effective energy transfer depends on the mean velocity of the molecules, the time between two collisions and the cross section for energy transferring collisions.

In electrically conducting liquids (for example mercury or melted metals) the free electrons make the major contribute to

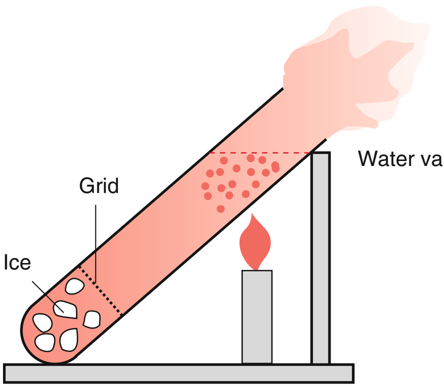


Figure 10.27 Demonstration of the small heat conductivity of water

the energy transfer, similar to the situation in solids. Their heat conductivity is therefore much larger than for non-conductive liquids, because of their much larger mass, the ions give only a minor contribution.

Because of the free mobility of the molecules in liquids, generally convection occurs besides heat conduction. This can be prevented when the liquid is heated from above, because then the hot liquid layer has a smaller density and therefore remains at the top.

The small heat conductivity of water can be demonstrated by the experiment shown in Fig. 10.27. At the bottom of a glass tube filled with water, are small ice cubes which are prevented from uprising by a mesh. One can heat the upper part of the water until it boils and emits water vapour. Nonetheless, the ice cubes do not melt in spite of the temperature difference of $\Delta T = 100\,^\circ\text{C}$ between the lower and upper part of the tube due to the poor heat conductivity of glass and water and the absence of convection.

10.2.2.3 Heat Conduction in Gases

In Sect. 7.5 it was shown, that heat conduction in gases is caused by collisional energy transfer between the molecules which move with thermal velocities. According to Eq. 7.49 the heat energy transferred per m^2 between two parallel walls at temperatures T_1 and T_2 is

$$J_w = \kappa \cdot (T_1 - T_2) \,.$$

According to (7.49a) the heat conduction coefficient is

$$\alpha = n \cdot v \cdot k \cdot f/8 \sim n \cdot \sqrt{T/m} \,.$$

Because of the much smaller density n of gases compared to liquids the heat conduction in gases is generally much smaller, except for ionized gases where the electrons contribute essentially to heat conduction. For neutral gases it is maximum for hydrogen because of the small mass m of hydrogen molecules.

When the mean free path Λ is larger than the dimensions of the gas container, the heat conduction becomes independent of the gas pressure.

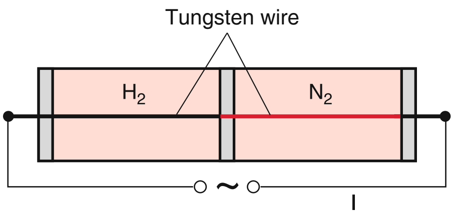


Figure 10.28 Demonstration of heat conduction in gases and its dependence on the molecular mass

The influence of the molecular mass m on the heat conduction can be demonstrated by the device shown in Fig. 10.28. A tungsten wire runs coaxially through two separated parts of a glass tube, which are filled with hydrogen gas in the left part and nitrogen gas in the right part. When the wire is heated by an electric current the right part has a higher temperature and is glowing red while the left part remains much colder due to the different heat conduction of the two gases. When removing the two gases both parts of the wire glow equally strong. This effect is intensified by two causes:

1. The electrical resistance R of tungsten decreases with decreasing temperature T. Therefore the electrical power $\mathrm{d}W/\mathrm{d}t = I^2 \cdot R$ supplied to the wire is smaller in the cold part.
2. The visible radiation power of the glowing wire is proportional to T^4. Even a small change of the temperature T results in a large change of the radiation power.

A modification of the demonstration experiment (Fig. 10.29) uses a vertical glass tube with the coaxial wire, which is filled with a gas mixture of H_2 and N_2. At first the heated wire glows equally bright along the whole tube. After some minutes, the lighter H_2-gas diffuses to the upper part while the heavier N_2-gas sinks to the bottom (see Sect. 7.6 and Fig. 7.34). This effect is even amplified by convection where the hot gas around the wire rises up while the colder gas close to the inner wall of the glass tube sinks down. Now the lower part of the wire is brighter than the upper part.

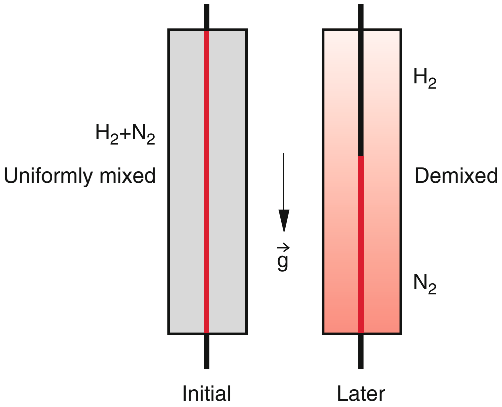


Figure 10.29 Demixing of a gas mixture by convection and diffusion in the gravitation field of the earth

For most situations the convection in gases at atmospheric pressure gives a larger contribution to the energy transport than heat conduction.

10.2.3 The Heat Pipe

Often the problem arises that heat produced in a volume V should be extracted as effectively as possible, in order to reach a sufficient cooling power. For the solution of this problem a special device was developed, which uses evaporation of a liquid on the hot side and condensation of the vapour on the cold side. The heat transport occurs by convection. This heat pipe allows a heat transport through the unit area that is larger by two orders of magnitude than can be achieved with metals. Its basic principle is illustrated in Fig. 10.30.

A tube of metal or another material is connected at the hot side (left) with the volume at the temperature T_1 that should be cooled and on the cold side with a cooling bath at $T = T_2 < T_1$. The evacuated tube is filled with a substance that has an evaporation temperature $T_e < T_1$ and a melting temperature $T_m < T_2$. For instance, if water is used, the temperatures should be $T_1 > 100\,°\text{C}$ and $T_2 > 0\,°\text{C}$.

At the hot side the substance boils which extracts the evaporation heat from the volume to be cooled. The vapour streams to the cold end where it condenses and delivers its heat of fusion to the cooling bath. Along the tube a gradient of the vapour density develops and an opposite gradient of the liquid density. An essential part of the heat pipe is a mesh that is wrapped around the inner part of the tube close to the wall. For the correct choice of the materials for tube and mesh the liquid substance wets both the mesh and the inner wall of the tube. Due to capillary action the liquid then flows between mesh and wall from the fusion zone back to the evaporation zone where it can be again evaporated and extract heat. The heat transport of this cyclic process depends on the vapour density and its flow velocity from the hot to the cold zone, but mainly on the magnitude of evaporation and fusion energy. For cooling media with a large evaporation energy (for example water) and a large convection velocity a very large heat transport per sec can be achieved.

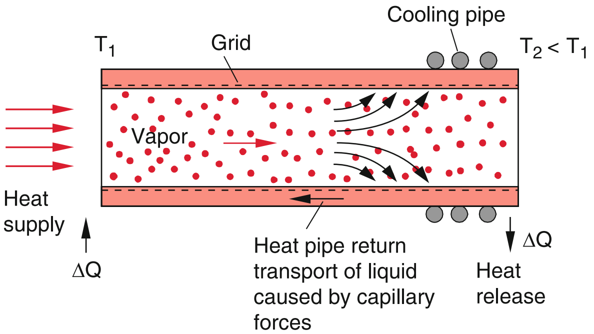


Figure 10.30 Heat pipe

With the mass $\mathrm{d}m/\mathrm{d}t$ evaporated per sec the energy extracted per sec from the hot volume is

$$\mathrm{d}W/\mathrm{d}t = \lambda_e \cdot \mathrm{d}m/\mathrm{d}t\,,$$

where λ_e is the specific evaporation energy. This is much larger than the heat $c_p(\mathrm{d}m/\mathrm{d}t)\Delta T$ transported through the heat pipe with a temperature difference $\Delta T = T_1 - T_2$ (see Tab. 10.5). At the cold end the heat

$$\mathrm{d}W_2/\mathrm{d}t = (\lambda_f \cdot + c_p \Delta T) \cdot \mathrm{d}m/\mathrm{d}t$$

has to be transferred to the cooling water.

More details about the technical design and the applications of heat pipes can be found in [10.6].

10.2.4 Methods of Thermal Insulation

While in Sect. 10.2.3 the realization of devices with a maximum heat transport was discussed, in this section we will treat methods to prevent heat transport out of a volume or to make it at least as small as possible. In order to reach this goal one has to take into account the contributions of all three heat transport mechanisms and minimize them. We will illustrate this by consider the thermal isolation of a residential house.

The heat transport between the inside and outside is mainly governed by heat conduction through walls and windows and to a minor part by air convection through leaky joints and during airing of a room. Depending on the size and the technical features of the windows also heat radiation can be important for heat exchange.

The heat flux through the area A of walls or windows with thickness d and a temperature difference $\Delta T = T_i - T_o$ between inside and outside is

$$\mathrm{d}Q/\mathrm{d}t = -(\lambda/d) \cdot A \cdot \Delta T\,, \qquad (10.43)$$

where λ $[\mathrm{W}/(\mathrm{m}\cdot\mathrm{K})]$ is the heat conductivity, which depends on the material. It is generally characterized by the constant $k = \lambda/d$, which gives the energy flux through the unit area $A = 1\,\mathrm{m}^2$ at a temperature difference $\Delta T = 1\,\mathrm{K}$. For most estimations of the heat isolation of houses the k value $[\mathrm{W}/(\mathrm{m}^2\cdot\mathrm{K})]$ of walls and windows is given. For good heat insulation it should be as small as possible. In Fig. 10.31 the k-values and the temperature rise from an outside temperature $T_0 = -15\,°\text{C}$ to the room temperature $T_i = +20\,°\text{C}$ are depicted for different wall compositions. These figures illustrate, that even a thin layer of Styrofoam considerably improves the thermal insulation. The largest heat losses are caused by the windows, where the heat transport process is more complex. We regard at first a single-layer window (Fig. 10.32). In spite of the small heat conductivity of glass ($\lambda = 0.9\,\mathrm{W}/(\mathrm{mK})$) the k-value $k = 200\,\mathrm{W}/(\mathrm{m}^2\cdot\mathrm{K})$ is much larger than that of the thick walls, due to the small thickness ($d = 4\,\mathrm{mm}$) of the window.

Because of the temperature gradient in the air layers close to the inside and outside of the glass a convective air current develops,

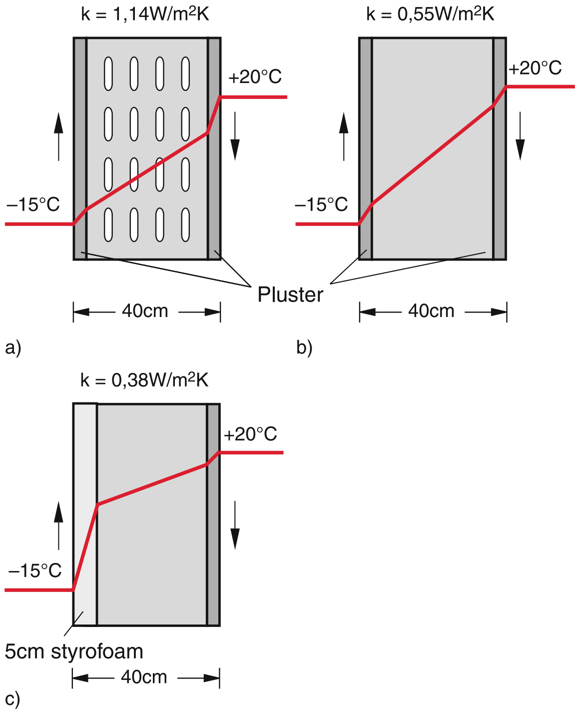


Figure 10.31 Thermal insulation. **a** Temperature behaviour across a plastered claybrick wall; **b** plastered wall of pumice stone; **c** pumice stone wall with styrofoam layer. The arrows give the direction of the convection current

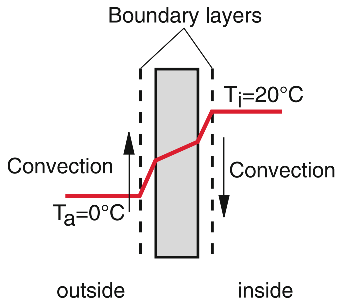


Figure 10.32 Heat transport across a single pane window

which is for $T_\text{o} < T_\text{i}$ downwards at the inside and upwards at the outside (Fig. 10.32). Due to friction between glass and air a thin boundary layer of air adheres on both sides of the glass (see Sect. 8.4). The heat passes through these layers to the convective air layers. Since the heat conduction is smaller for gas at atmospheric pressure than for glass, the k-value is smaller for these adhered air layers then for the pane of glass.

From Eq. 8.24 one obtains a thickness of 5 mm for the boundary air layer with a k-value $k = 3.4\,\text{W}/(\text{m}^2 \cdot \text{K})$ for heat conduction, compared to $k = 200\,\text{W}/(\text{m}^2 \cdot \text{K})$ for the pane of glass.

Another heat transport mechanism is heat radiation (see Sect. 10.2.5). The room temperature in the inner part of the house causes infrared radiation, which can escape through the windows. The heat loss can be estimated as $4.6\,\text{W}/(\text{m}^2 \cdot \text{K})$. This gives a total k-value of the inner air layer $k = 8\,\text{W}/(\text{m}^2 \cdot \text{K})$.

For the outer convective air layer the k-value is different because the air flows upwards against the gravitation. Detailed calculations give a value $k = 20\,\text{W}/(\text{m}^2 \cdot \text{K})$ including radiation losses. For successive layers the reciprocal k-values add (analogous to electrostatics where the reciprocal electric conductivities add) and we obtain from

$$\frac{1}{k} = \frac{1}{k_\text{i}} + \frac{1}{k_\text{g}} + \frac{1}{k_\text{o}} \tag{10.44}$$

the total k-value $k = 5.5\,\text{W}/(\text{m}^2 \cdot \text{K})$. The comparison with the k-value of the walls $k < 1\,\text{W}/(\text{m}^2 \cdot \text{K})$ shows that windows with a single pane of glass constitute a major heat loss.

A much better heat insulation can be achieved with windows of two panes of glass and an inert gas enclosed between the panes (Fig. 10.33a).

The k-value of the gas depends on the thickness d of the gas between the glass panes. For $d \leq 1$ cm the heat conduction is dominant, while for larger values of d convection undertakes the major part of heat transfer. Fig. 10.33b shows, that for $d = 1$ cm the minimum k-value is reached because the boundary layers that adhere to the glass walls, prevent convection.

For such a double glass window, the k-value for heat conduction is substantially smaller than for a single pane window. In order

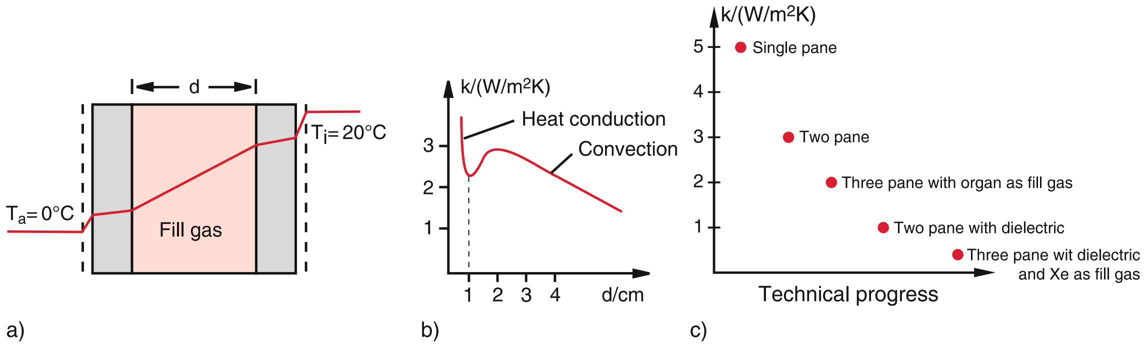


Figure 10.33 Double pane glas window. **a** Composition and temperature change across the window; **b** k-values as a function of the thickness d of the gas layer between the two glas panes; **c** decrease of k-values through technical progress

to minimize also the radiation losses, the glass panes are covered by a thin dielectric layer [10.8], which reflects the infrared radiation from the inside of the house (see Vol. 2, Sect. 10.4). Without a reflecting layer, k-values of $k \leq 3\,\mathrm{W/(m^2 \cdot K)}$ can be realized, while with reflecting layer the k-value decreases down to $k \leq 0.6\,\mathrm{W/(m^2 \cdot K)}$. The k-values are then comparable to those of the walls [10.8, 10.9].

The considerations above illustrate that all three heat-transfer processes as heat conduction, convection and radiation have to be taken into account in order to optimize the heat insulation of a house. In Fig. 10.33c the technical progress of minimizing the total k-value is illustrated.

A more quantitative representation of heat insulation can be found in [10.7] and the references gives there and also in many books on energy saving new house construction [10.9].

10.2.5 Thermal Radiation

Every body at a temperature T_K exchanges energy with its surrounding. If T_K is higher than the temperature T_S of the surrounding, the energy emitted by the body is larger than the energy received from the surrounding. If no energy is supplied to the system body +surrounding, the system approaches thermal equilibrium, where the temperature of the body is equal to that of the surrounding (Fig. 10.34). This energy balance can be reached by heat conduction, convection or radiation. If the body is kept in vacuum, (for instance our earth) radiation is the only way to exchange energy with the surrounding, because both heat conduction and convection need matter for the transport of energy.

Extensive experiments have proved, that radiation emitted by hot bodies represents electromagnetic waves, which can transport energy through matter and also through vacuum.

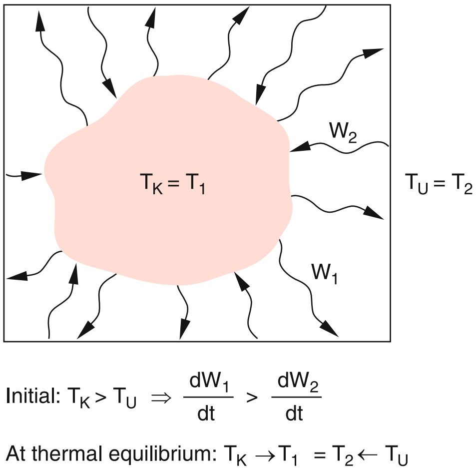


Figure 10.34 Energy exchange by thermal radiation between a body and its surroundings. At thermal equilibrium is $\mathrm{d}W_1/\mathrm{d}t = \mathrm{d}W_2/\mathrm{d}t$ and $T_\mathrm{K} = T_2$

Since the intensity and the spectral distribution of the radiation emitted by a body depends essentially on the temperature of the body, this radiation is called **heat radiation** or **thermal radiation**. In this section we will discuss the characteristics of thermal radiation.

10.2.5.1 Emissivity and Absorptivity of a Body

At first we will experimentally study, how the intensity of thermal radiation depends on the surface conditions of the body. We use a metal hollow cube filled with hot water, where the four side walls have a different surface structure (black, white, shiny and rough). All side walls have the same temperature. Four equal radiation detectors, which measure the total radiation (integrated over all wavelengths) are placed at the same distance d from the four walls (Fig. 10.35). They all show different radiation powers. When the cube is turned by $n \cdot 90°$ ($n = 1, 2, 3, \ldots$) about a vertical axis, it can be proved that the difference is not due to differences of the detectors but that the different sidewalls really emit different radiation powers. The experiment shows surprisingly that the black side wall emits the maximum power and the shiny white surface the minimum power. The radiation power emitted from the surface area $\mathrm{d}A$ into the solid angle $\mathrm{d}\Omega$ can be quantitatively described by

$$\frac{\mathrm{d}W}{\mathrm{d}t} = E^* \cdot \mathrm{d}A \cdot \mathrm{d}\Omega\,.$$

The constant E^* is the emissivity of the surface. It gives the radiation power $\mathrm{d}W/\mathrm{d}t$, integrated over all wavelengths that is emitted from a surface element $\mathrm{d}A = 1\,\mathrm{m}^2$ into the solid angle $\mathrm{d}\Omega = 1\,\mathrm{sr}$ around the surface normal (Fig. 10.36). According to the experiment the emissivity E^* of a black surface is larger than that of a white surface at the same temperature.

The integral absorptivity A^* is defined as the mean value of the quotient A^* = absorbed radiation power / incident radiation power, averaged over all wavelengths.

The ratio

$$K(T) = \frac{E^*(T)}{A^*(T)} \tag{10.45}$$

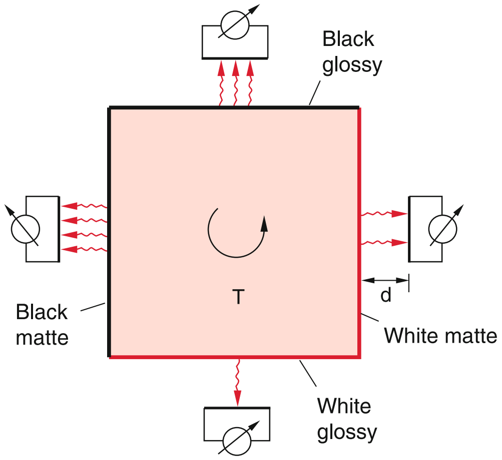


Figure 10.35 Experimental setup for the measurement of emission

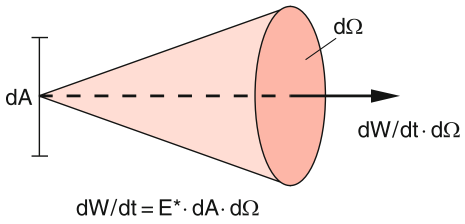


Figure 10.36 Illustration of the emissivity E^* of a surface element dA

depends solely on the temperature T and not on the material of the body, as can be demonstrated by the following experiment:

Experiment

We place in Fig. 10.37a in front of the black surface A_1 of the hot cube an equivalent surface A'_1 of the detector at a distance d and in front of the shiny surface A_2 a shiny detector surface A'_2 at the same distance d. Measuring the temperatures T_1 of A'_1 and T_2 of A'_2 one finds that $T_1 > T_2$.

Since the surface structure of A'_1 is equal to that of A_1, and that of A'_2 is equal to that of A_2, the absorptivity A_1^* must be equal to $A_1'^*$ and $A_2^* = A_2'^*$.

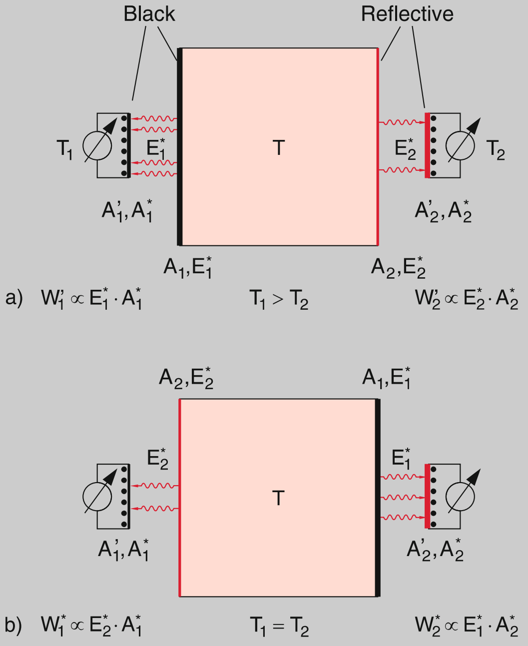


Figure 10.37 Derivation of (10.47)

The power absorbed by the two detector surfaces is

$$\mathrm{d}W'_1/\mathrm{d}t \sim E_1^* \cdot A_1'^* \quad \text{and} \quad \mathrm{d}W'_2/\mathrm{d}t \sim E_2^* \cdot A_2'^* \,.$$

Since $E_1^* > E_2^*$ (according to the foregoing experiment, a black surface emits a larger power than a shiny one) and $A_1'^* > A_2'^*$ (a black surface has a higher absorptivity than a shiny one) it follows that $\mathrm{d}W'_1/\mathrm{d}t > \mathrm{d}W'_2/\mathrm{d}t \to T_1 > T_2$.

Now the cube is turned about a vertical axis by 180° and the surface A_1 now faces A'_2 and A_2 faces A'_1 (Fig. 10.37b). The absorbed powers are

$$\mathrm{d}W_1/\mathrm{d}t \sim E_2^* \cdot A_1'^* \quad \text{and} \quad \mathrm{d}W_2/\mathrm{d}t \sim E_1^* \cdot A_2'^* \,.$$

The experimental result is now $T_1 = T_2 \to \mathrm{d}W_1/\mathrm{d}t = \mathrm{d}W_2/\mathrm{d}t$.

$$\Rightarrow \frac{E_1^*(T)}{A_1^*} = \frac{E_2^*(T)}{A_2^*} \,. \qquad (10.46)$$

◀

A separate experiment proves that the absorptivity of the surfaces does not depend on the temperature at least within the temperature range from 0–100 °C, which is covered in the experiment above. Therefore it follows from (10.46) for an arbitrary body

$$\frac{E_1^*(T)}{A_1^*} = \frac{E_2^*(T)}{A_2^*} = K(T) \,. \qquad (10.47)$$

The ratio of emissivity to absorptivity can be described for any body by a function $K(T)$ that depends solely on the temperature T.

A body with $A^* = 1$ is called a ***black body***.

It completely absorbs any incident radiation. According to (10.47) a black body must also have the maximum emissivity compared to all other bodies with equal temperature.

Note: Bodies with a large absorption coefficient α but a sudden increase of α at the glossy surface are not a black body, because their reflectivity also increases (Fig. 10.38a). Therefore the major part of the incident radiation is reflected and only the minor part, that penetrates into the body is absorbed (see Vol. 2, Chap. 8). In order to realize a black body, the absorption coefficient should not increase suddenly at the surface but must continuously increase over a distance $\Delta z > \lambda$ (λ = wavelength of the incident radiation) from zero to its maximum value (Fig. 10.38b). This can be for instance realized by a roughened surface (black velvet, soot or graphite with a rough surface) where the optical density rises slowly from the outside to the inner part of the body. The sun is an example of a nearly perfect black body, because the gas density and with it the absorptivity increases slowly from the diffuse outer edge of the photosphere to the interior.

Often the problem arises to keep a body at a constant temperature T_K, that differs from the temperature T_S of its surrounding by supporting ($T_\mathrm{K} > T_\mathrm{S}$) or extracting ($T_\mathrm{K} < T_\mathrm{S}$) energy. This energy can be minimized when heat conduction, convection and radiation are minimized. The experimental realization uses materials with low heat conductance and radiation shields.

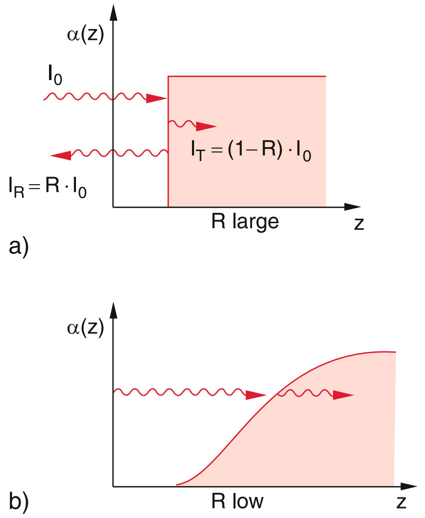


Figure 10.38 **a** For bodies with a large gradient $d\alpha/dz$ at the surface incident radiation is mainly reflected and only partly absorbed inspite of the large absorption coefficient α. **b** Most of the incident radiation is absoorbed, if $d\alpha/dz$ is small, i. e. $\alpha(z)$ rises slowly from $\alpha = 0$ to $\alpha = \alpha_{\max}$

Examples

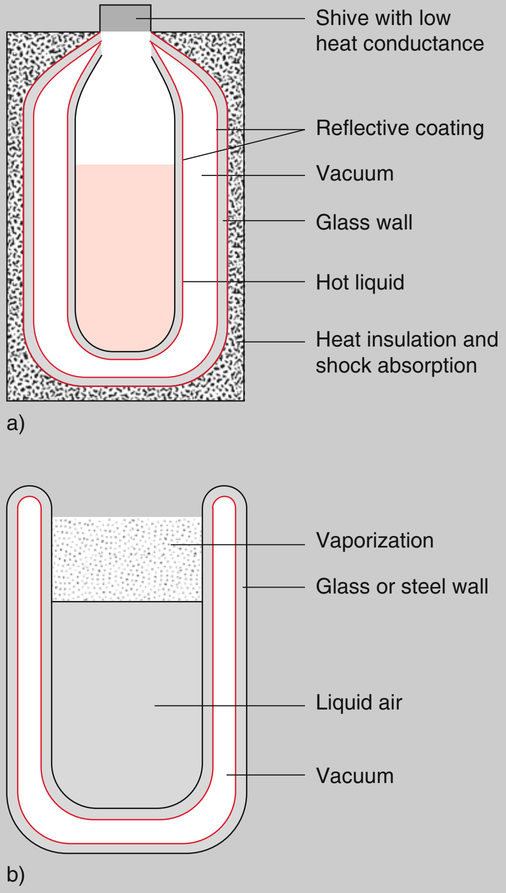


Figure 10.39 **a** Thermos bottle; **b** Dewar gasket

1. A *thermos bottle* (Fig. 10.39a) consists of a double wall glass flask. The space between the two walls is evacuated and the two inner sides of the walls are mirrored. The vacuum prevents heat conduction and convection. The reflective walls minimize the escape of thermal radiation to the outside. Therefore, the heat losses from the inner volume are very small and the coffee stays hot for a long time or cold drinks remain cold.
2. For the storage of liquid nitrogen a *Dewar* is used (Fig. 10.39b), which is based on the same principle as the thermos bottle. Here the heat transfer from the outside is minimized in order to keep the evaporation of the cold liquid nitrogen ($T = 77$ K) as low as possible. The small portion of evaporating nitrogen extracts the heat of evaporation and keeps the temperature in the Dewar low.
   If liquid air is used (78% N_2 and 21% O_2), the nitrogen evaporates faster because of its higher vapour pressure and the concentration of the reactive oxygen increases until an explosive concentration is reached. Therefore, generally liquid air is dangerous and is only used for special purposes. ◀

10.2.5.2 Characteristic Features of Thermal Radiation

The energy that is emitted by the surface element dA into the solid angle $d\Omega$ around the direction Θ against the surface normal can be measured with a radiation detector (for example a thermo-couple connected to a black surface). The detector area dA_2 at a distance r from the radiation source receives the radiation within the solid angel

$$d\Omega = \frac{dA_2}{r^2} .$$

Experiments prove that for many radiation sources the angular distribution of the measured radiation power is

$$dW(\Theta)/dt = S^* \cos\Theta \cdot dA \cdot d\Omega . \qquad (10.48)$$

The quantity S^* is the *emittance* or *radiation density* of the source. It describes the radiation power per m^2 of the radiation source, emitted into the solid angle $d\Omega = 1$ sr around the surface normal (Fig. 10.40a).

The radiant intensity

$$J(\Theta) = \int_F S^* \cos\theta dA , \quad [J] = 1\,\frac{W}{sr} \qquad (10.49)$$

is the total radiation power emitted by the radiation source into the solid angle $d\Omega = 1$ sr around the direction Θ against the surface normal.

Note: The relation between the *radiation density* S^* and the *emissivity* E^* is outlined in Sect. 10.2.5.3.

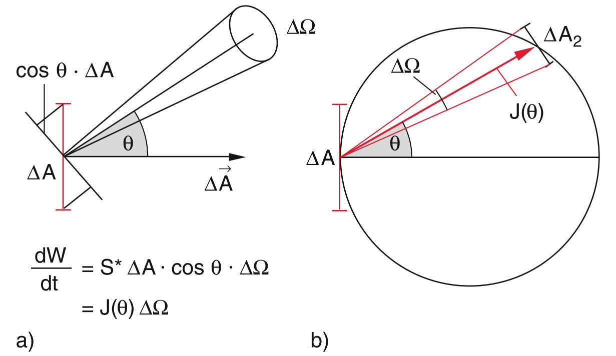


Figure 10.40 **a** Illustration of radiant intensity $J(\theta)$. **b** The length of the arrow is proportional to the radiant intensity $J(\theta)$

The emitted radiation power generally depends on the wavelength λ resp. the frequency $\nu = c/\lambda$ of the electromagnetic wave. The spectral radiation intensity S_ν^* is defined by the equation

$$S^* = \int_{\nu=0}^{\infty} S_\nu^* \mathrm{d}\nu \ . \tag{10.50}$$

The radiation of the source results in an electromagnetic field with the energy density w [J/m^3] and the intensity I [W/m^2]. The *spectral energy density* w_ν is the energy per m^3 within the spectral frequency interval $\Delta\nu = 1\,\mathrm{s}^{-1}$. It is related to the total energy density w by

$$w = \int w_\nu \cdot d\nu \ . \tag{10.51}$$

For a radiation source with isotropic radiation (for instance the sun) the relation between $I = |S|$ and w is

$$I = (c/4\pi) \cdot w \ , \tag{10.52a}$$

and similar for the spectral quantities

$$I_\nu = (c/4\pi) \cdot w_\nu \ , \tag{10.52b}$$

where c is the velocity of light. For plane waves the relations are $I = c \cdot w$ and $I_\nu = c \cdot w_\nu$.

The detector element ΔA_2 at a distance r from the isotropic source receives from the source element ΔA_1 the radiation power

$$\begin{aligned} \frac{\mathrm{d}W_1}{\mathrm{d}t} &= S_1^* \cos\theta_1 \, \Delta A_1 \, \Delta\Omega \\ &= \left(S_1^* \cos\theta_1 \, \Delta A_1 \, \Delta A_2 \cdot \cos\theta_2\right)/r^2 \ , \end{aligned} \tag{10.53}$$

where $\Delta\Omega = \Delta A_2 \cdot \cos\theta_2/r^2$ is the solid angle under which the tilted surface element ΔA_2 appears from the source (Fig. 10.41).

The Equation 10.53 is symmetric. Replacing S_1^* by the radiation intensity of the surface element ΔA_2 the equation describes the radiation power $\mathrm{d}W_2/\mathrm{d}t$ received by ΔA_1 from ΔA_2.

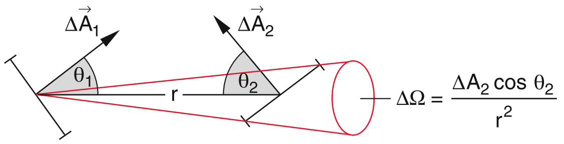


Figure 10.41 The surface element ΔA_2 receives from ΔA_1 the radiation power $\mathrm{d}W/\mathrm{d}t = (S^*\Delta A_1 \cdot \Delta A_2 \cdot \cos\theta_1 \cdot \cos\theta_2)/r^2$

The ratio

$$\frac{\mathrm{d}W_2/\mathrm{d}t}{\Delta A_2} = \int_{A_1} \left(\mathrm{d}A_1 S_1^* \cos\theta_1 \cos\theta_2\right)/r^2 \tag{10.54}$$

is the **irradiance** or **intensity** at the detector [W/m^2].

Note: The radiation power, absorbed by the detector with the normalized absorptivity A^*, the reflectivity R and the transmission T ($A^* + R + T = 1$) is

$$\frac{\mathrm{d}W_{\mathrm{abs}}}{\mathrm{d}t} = A^* \cdot \frac{\mathrm{d}W_1}{\mathrm{d}t} = (1 - R - T) \cdot \frac{\mathrm{d}W_1}{\mathrm{d}t} \ ,$$

because the fraction $(R + T)$ of the incident radiation is reflected and transmitted.

10.2.5.3 Black Body Radiation

A black body with the absorptivity A^* can be experimentally realized by a cavity with absorbing walls and a small hole with an area ΔA that is small compared to the total inner wall area A of the cavity (Fig. 10.42). Radiation that penetrates through the hole into the cavity, suffers many reflections at the absorbing walls before it can eventually escape with a very small probability through the hole. The absorptivity of the hole area ΔA is therefore $A^* \approx 1$.

When the cavity is heated up to a temperature T, the hole area ΔA acts as radiation source with an emissivity E^* that is, according to (10.47) larger than that of all other bodies with $A^* < 1$ at the same temperature T (the black body radiation is therefore also called *cavity radiation*). This can be demonstrated by the following experiment (Fig. 10.43):

The letter H is milled deeply into a graphite cube. At room temperature, the letter H appears darker than the surface of the cube (left picture of Fig. 10.43). When the cube is heated, up to

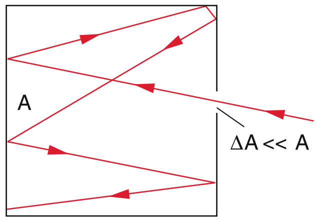


Figure 10.42 A cavity with a small hole ΔA absorbs nearly all of the radiation incident onto ΔA

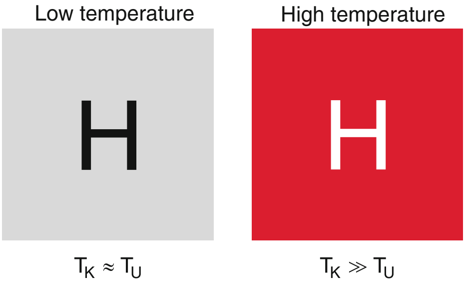


Figure 10.43 The letter H milled into a graphite block appears darker as its surrounding at low temperatures but brighter at high temperatures

$T = 1000\,\mathrm{K}$ the letter H appears much brighter than the other surface elements (right figure).

Some simple considerations allow one to postulate some basic laws of the black body radiation:

- Under stationary conditions ($T = \mathrm{const}$) emission and absorption of the cavity walls must be balanced. This implies for all frequencies ν of the radiation that the absorbed power of an arbitrary surface element ΔA of the walls must be equal to the emitted power:

  $$\mathrm{d}W_\mathrm{a}(\nu)/\mathrm{d}t = \mathrm{d}W_\mathrm{e}(\nu)/\mathrm{d}t\ .$$

  At this equilibrium we define the temperature T of the black body radiation as the temperature of the walls.
- The black body radiation is isotropic. The spectral irradiance I_ν $[\mathrm{W}/(\mathrm{m}^2 \cdot \mathrm{s}^{-1} \cdot \mathrm{sr}]$ is for any point in the cavity independent of the direction in the cavity and also of the material or structure of the walls. If the radiation were not isotropic, one could place a black disc into the cavity and orientate it in such a way, that its surface normal points into the direction of maximum radiation intensity S^*. The disc would then absorb more radiation power and would heat up to higher temperatures than the walls. This contradicts the second law of thermodynamics (see Sect. 10.3).
- The black body radiation is homogeneous, i. e. its energy density is independent of the specific location inside the cavity. Otherwise one could construct a perpetuum mobile of the second kind (see Sect. 10.3).

When we place a body in the radiation field of the cavity, the spectral radiation power $S_\nu^* \cdot d\nu \cdot \mathrm{d}A \cdot \mathrm{d}\Omega$, falls within the solid angle $\mathrm{d}\Omega$ onto the body. The spectral power absorbed by the surface element $\mathrm{d}A$ is

$$\frac{\mathrm{d}W_\mathrm{a}}{\mathrm{d}t} = A_\nu^* S_\nu^* \mathrm{d}A \cdot \mathrm{d}\Omega \cdot \mathrm{d}\nu\ , \qquad (10.55\mathrm{a})$$

while the emitted power is

$$\frac{\mathrm{d}W_\mathrm{e}}{\mathrm{d}t} = E_\nu^* \mathrm{d}A \cdot \mathrm{d}\Omega \cdot \mathrm{d}\nu\ . \qquad (10.55\mathrm{b})$$

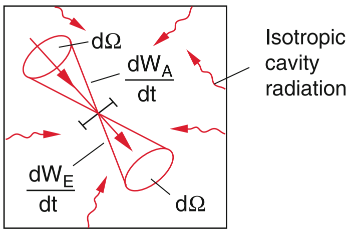


Figure 10.44 A body inside a closed cavity at thermal equilibrium with the radiation field

At thermal equilibrium the absorbed power must be equal to the emitted power. Since the cavity radiation is isotropic, this must be valid for all directions. Therefore it follows from (10.55a,b) the Kirchhoff-Law

$$E_\nu^* / A_\nu^* = S_\nu^*(T)\ . \qquad (10.56)$$

For all bodies in the radiation field of the cavity the ratio of spectral emissivity and absorptivity equals the spectral radiation density S_ν^* of the radiation field.

For a black body is $A^* = 1$ for all frequencies ν. We can therefore conclude:

> The spectral emissivity E_ν^* of a black body is equal to the spectral radiation density S_ν^* of the cavity radiation.

10.2.5.4 The Emitted Radiation Power of a Hot Body

The surface S of a black body at the temperature T emits, according to the **Stefan–Boltzmann Law**, (see Vol. 2, Sect. 12.3) the radiation power

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \sigma \cdot S \cdot T^4\ . \qquad (10.57)$$

For a black surface with $A^* = 1$ the Stefan–Boltzmann constant σ has the numerical value $\sigma = 5.67051 \cdot 10^{-8}\,\mathrm{W}/(\mathrm{m}^2 \cdot \mathrm{K})$. For bodies with $A^* < 1$ the emissivity is smaller and therefore also the emitted radiation power at the same temperature is smaller than for a black body. The Stefan–Boltzmann Law can be derived from Planck's radiation law (see Vol. 3, Chap. 3). The deviation of the experimental results for small wavelengths from those predicted by the Stefan–Boltzmann law,. gave the impetus for the development of quantum theory.

Note:

- The radiation power of a hot body is proportional to the fourth power of the surface temperature. With increasing temperature it therefore represents an increasing fraction of the total energy loss of a body.
- The thermal radiation is an electromagnetic wave and therefore propagates also through vacuum. The energy transport by radiation is not bound to matter. We own our existence to the heat radiation from the sun because this is the only energy transport mechanism from the sun to the earth (except the negligible contribution of particles such as electrons and protons emitted by the sun).

A more detailed and quantitative treatment of heat radiation will be postponed to Vol. 3, because it demands some basic knowledge of quantum theory.

10.2.5.5 Practical Use of Solar Energy

The radiation energy of the sun, received on earth, can be either directly converted to heat by solar energy collectors or transformed into electrical power by photovoltaic semiconductor elements. While the second technique is treated in Vol. 3, the first will be shortly discussed here [10.10, 10.11].

The radiation power of the sun, incident on $1\,\mathrm{m}^2$ of a surface black surface element outside of the earth atmosphere has an annual average $P_\odot = 1.4\,\mathrm{kW/m^2}$ (*solar spectral irradiance*). However, even at a clear day without clouds only a smaller power P_E reaches the earth surface because of absorption and light scattering in the atmosphere. For geographical latitudes $\varphi = 40°–50°$ one measures $P_\mathrm{E} \approx 0.5 P_\odot$. For an inclination angle α of the incident radiation to the surface normal the received power at a clear sky is $P_\mathrm{E} \approx 730 \cdot \cos\alpha\,\mathrm{W/m^2}$.

With the absorptivity A^* of the surface, the power absorbed within the time interval Δt by a plane surface with area ΔA is

$$P_\mathrm{a} = A^* \cdot \Delta A \cdot P_\mathrm{E} \cdot \cos\alpha \cdot \Delta t\,.$$

This results in a temperature increase ΔT of a sun collector with mass m and specific heat c

$$\Delta T = A^* \cdot \Delta A \cdot P_\mathrm{E} \cdot \cos\alpha \cdot \Delta t/(c \cdot m)\,, \qquad (10.58)$$

if no heat losses occur.

The temperature increases with irradiation time if the heat is not dissipated. This dissipation can be achieved, when on the backside of the sun collector tubes are welded with a good heat contact to the sun collector and a liquid is pumped through the tubes, which takes away the heat. In order to keep the temperature of the sun collector constant, the pumping speed is chosen such that the heat transport just balances the received radiation power.

With a mass flow $\mathrm{d}m_\mathrm{l}/\mathrm{d}t$ of the heat transporting liquid with the specific heat c_l and the temperature increase ΔT the energy balance is given by the equation

$$A^* \cdot P_\mathrm{E}\,\Delta A\,\cos\alpha = (\mathrm{d}m_\mathrm{l}/\mathrm{d}t)\,c_\mathrm{l}\,\Delta T + (\mathrm{d}W/\mathrm{d}t)_\mathrm{v}\,. \qquad (10.59)$$

The angle α depends on the inclination of the energy collecting plane, on the latitude φ and on the daytime. In Fig. 10.45 the daytime dependence of the sun energy received by a collector with $\alpha = 45°$ in Kaiserslautern ($\varphi = 49°$) is illustrated for three different dates. Two effects cause this variation with the daytime: 1) The variation of the angle α due to the apparent motion of the sun and 2) The variation of the path length of the sun radiation through the atmosphere during the day, where absorption and scattering attenuates the radiation energy.

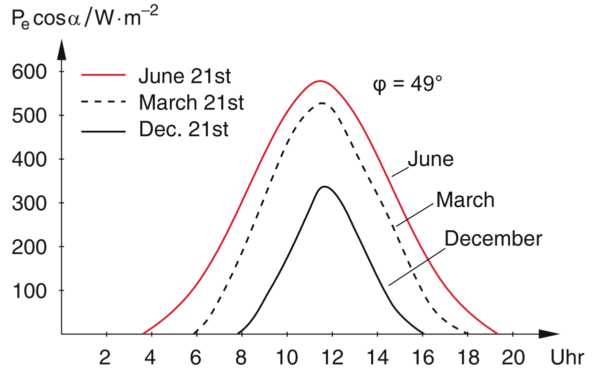


Figure 10.45 Variation of the sun radiation incident onto a sun radiation collector at the lattitude $\varphi = 49°$ as a function of daytime for three different times of the year

The area under the curves gives the integrated energy ($\mathrm{J/m^2}$· sun hours) received during a whole day between sunrise t_1 and sun set t_2.

$$W_\mathrm{E} = \int\limits_{t_1}^{t_2} P_\mathrm{E} \cos\alpha\,\mathrm{d}t \qquad (10.60)$$

The average radiation power per day is then $\langle P_\mathrm{E} \cdot \cos\alpha \rangle = W_\mathrm{E}/(t_2 - t_1)$.

Example

$A^* = 0.8$; $\langle P_\mathrm{E} \cdot \cos\alpha \rangle = 250\,\mathrm{W/m^2}$ during a clear day in August at $\varphi = 45°$; $\Delta A = 8\,\mathrm{m^2}$. With water as the heat transporting liquid ($c_\mathrm{W} = 4186\,\mathrm{Ws/(kg \cdot K)}$) which is heated from 20 to 60 °C. With a good heat insulation the heat losses $\mathrm{d}W_\mathrm{l}/\mathrm{d}t$ can be kept down to $50\,\mathrm{W/m^2}$ for a temperature difference of $\Delta T = 40\,°\mathrm{C}$. The amount of water heated per sec is then given by $\mathrm{d}m_\mathrm{W}/\mathrm{d}t = (A^* \cdot \langle P_\mathrm{E} \cdot \cos\alpha \rangle - \mathrm{d}W_\mathrm{l}/\mathrm{d}t) \cdot A/(c_\mathrm{W} \cdot \Delta T) = 0.0072\,\mathrm{kg/s}$. Within one hour 26 l water are heated from 20 to 60 °C.
◀

Figure 10.46 shows a possible realization of a sun power collector for the heating of houses. It consists of a blackened

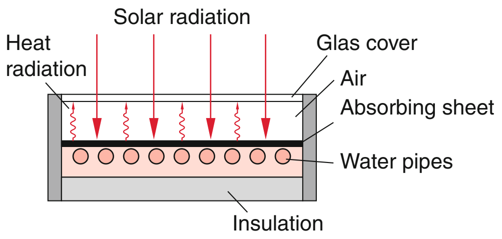


Figure 10.46 Cross section of a flat solar radiation collector which is mounted on house roofs

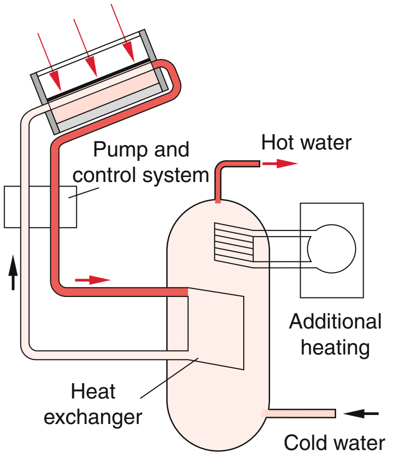


Figure 10.47 Thermal solar radiation collector for heating water with heat exchanger

absorber plate with pipes connected to the backside with good heat contact. Through the pipes a water-glycol mixture (to avoid freezing at low temperatures) is pumped. In cases where temperatures above 100 °C are reached, low viscosity oil is used. The absorber plate is placed inside a heat insulating housing with a glass plate in front. Heat losses are due to reflection of the sun radiation by the glass plate, by heat radiation of the black absorber plate and by heat conduction from the hot part of the sun radiation collector (including the pipes for the transport of the hot liquid) and convective cooling by the wind that blows along the device.

The heated liquid transfers its heat through a heat exchanger to a thermal storage system inside the house that generates hot service water (Fig. 10.47). A temperature sensor and a feedback system controls the temperature of the service water and takes care that it always has the wanted temperature. In case the sun energy is not sufficient, a conventional heating system is connected which only operates if the temperature sinks below the wanted value. When the hot water is used for room heating, a floor heating system is advantageous, because here the water temperature can be lower than that for radiator heating [10.9–10.11].

In large facilities for thermal solar energy conversion, it is more effective to heat the liquid above its boiling point. The generated vapour drives turbines which can produce electric current through electric generators. The technical realization uses large spherical mirrors that focus the sun radiation onto a black surface connected to a pipe system that transports the hot vapour. Temperatures above 1000 °C can be achieved and an electric output power of many kW has been demonstrated. The installation costs for such systems are up to now very high and therefore only a few pilot plants have been built. One example is the system in Almeria in Spain.

10.3 The Three Laws of Thermodynamics

We will define a thermodynamic system as a system of atoms or molecules that interacts with its surroundings by exchange of energy in form of heat or mechanical work. The system can be described by physical quantities such as temperature, pressure, volume, particle density etc. In this section we will discuss, how the state of such a system changes by the exchange of energy with its surroundings. The results of all investigations can be condensed in three laws of thermodynamics, which have a comparable importance for Physics as the conservation laws of mechanics for momentum, angular momentum and energy. These three laws are solely based on experimental data and cannot be derived mathematically from first principles contrary to a widespread false opinion.

At first we must discuss, which quantities are necessary to describe the state of a thermodynamic system.

10.3.1 Thermodynamic Variables

The state of a system is defined by all characteristic properties, which are determined by the external conditions. A thermodynamic system is completely determined if the chemical composition is known and the quantities pressure p, volume V and temperature T are given. If these quantities do not change with time, the system is in an equilibrium state and it is called a *stationary system*. Most of the thermodynamic considerations deal with stationary systems. Often a system changes so slowly, that it can be described by a succession of equilibrium states.

Systems far away from equilibrium play an important role for all chemical and biological reactions and they are intensively discussed in modern physics. They are therefore shortly treated at the end of this chapter. *In this section, we will restrict the discussion to ideal gases.* The thermodynamics of real bodies will be discussed later.

An equilibrium state of a system is unambiguously determined, if the three quantities pressure p, volume V and temperature T are fixed. These quantities are therefore called *thermodynamic variables*.

Definition

A thermodynamic variable is a variable in the equation of state of a thermodynamic system. It describes the momentary state of the system and is independent of the way on which the system has reached its momentary state. Besides V, p and T also the total energy, the entropy and the enthalpy are thermodynamic variables.

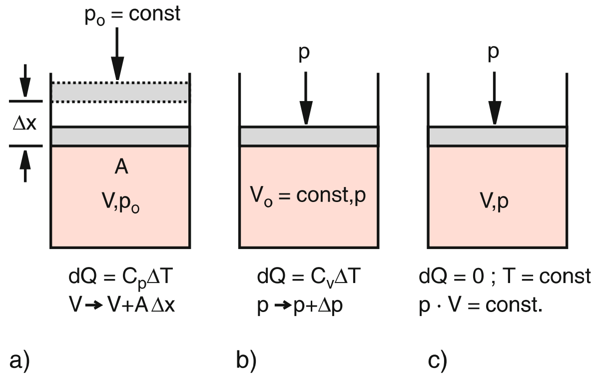


Figure 10.48 **a** Heating at constant pressure; **b** heating at constant volume; **c** no heat supply

The thermodynamic variables are related to each other by the equation of state for a gas volume V of an ideal gas with N molecules

$$p \cdot V = \nu \cdot R \cdot T\,, \tag{10.61}$$

where $\nu = N/N_A$ is the number of moles and N_A the Avogadro number. Also for real gases a corresponding equation can be derived (see Sect. 10.4). For a given volume V and a pressure p the temperature T determines the internal energy

$$U = \tfrac{1}{2} \cdot \nu \cdot f \cdot R \cdot T \tag{10.62}$$

of molecules with f degrees of freedom. For ideal gases (for instance helium) is $f = 3$. If the volume decreases ($\mathrm{d}V < 0$) at a constant pressure p the necessary work is

$$\mathrm{d}W = -p \cdot \mathrm{d}V\,. \tag{10.63}$$

The sign is chosen in such a way that the applied work is positive, if the energy of the system increases. Work performed by the system means a decrease of its internal energy and is therefore defined as negative.

When a gas is heated at constant pressure p its volume increases (Fig. 10.48a). The quantity

$$\gamma_p = \frac{1}{V} \cdot \left(\frac{\partial V}{\partial T}\right)_p\,, \tag{10.64}$$

that describes the relative volume change per Kelvin temperature rise, is the *isobaric expansion coefficient*.

In an analogous way the heating of a gas at a constant volume (Fig. 10.48b, where the pressure increases, is described by the isochoric pressure coefficient

$$\gamma_V = \frac{1}{p} \cdot \left(\frac{\partial p}{\partial T}\right)_V\,, \tag{10.65}$$

which describes the relative pressure increase $\Delta p/p$ for a temperature rise of 1 K.

The isothermal compressibility

$$\gamma_T = \kappa = -\frac{1}{V} \cdot \left(\frac{\partial V}{\partial p}\right)_T \tag{10.66}$$

gives the relative volume change $\Delta V/V$ for a pressure change Δp at a constant temperature T.

As recollection keep in mind:

isothermal: $T = \text{const}$
isobaric: $p = \text{const}$
isochoric: $V = \text{const}$.

The total change $\mathrm{d}V$ of the volume $V(p,T)$, when both quantities p and T are changing is

$$\begin{aligned} \mathrm{d}V &= \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T \\ &= -\kappa \cdot V \cdot \mathrm{d}p + \gamma_p \cdot V \cdot \mathrm{d}T\,. \end{aligned} \tag{10.67}$$

For isochoric processes the volume V stays constant, i. e. $\mathrm{d}V = 0$. Then (10.67) reduces to

$$\begin{aligned} 0 &= -\kappa \cdot V \cdot (\mathrm{d}p)_V + \gamma_p \cdot V \cdot (\mathrm{d}T)_V \\ &\Rightarrow \kappa \cdot \mathrm{d}p = \gamma_p \cdot \mathrm{d}T\,. \end{aligned} \tag{10.68}$$

Division by $\mathrm{d}T$ yields with $(dp/\mathrm{d}T)_V = \gamma_V \cdot p$ the relation

$$\gamma_p = \kappa \cdot \gamma_V \cdot p \tag{10.69}$$

between isobaric expansion coefficient γ_p, isothermic compressibility κ, isochoric expansion coefficient γ_V and pressure p.

10.3.2 The First Law of Thermodynamics

The heat ΔQ applied to a system can be either used for rising the temperature T at a constant volume V, or for the expansion of the volume V against the external pressure p where the system has to perform the work ΔW. Energy conservation demands

$$\Delta Q = \Delta U - \Delta W\,, \tag{10.70a}$$

where, as defined before, $\Delta W < 0$ if the system performs work (which decreases its own energy). This sign definition is in agreement with the definition (2.35) for the work. If the system, for instance, performs work against an external force $\boldsymbol{F} = -p \cdot \boldsymbol{A}$ when a piston with area A is moved along the distance Δx against the external pressure p, the work is

$$\Delta W = \boldsymbol{F} \cdot \boldsymbol{\Delta x} = -p \cdot A \cdot \Delta x = -p \cdot \Delta V \quad \text{with } \Delta V > 0\,.$$

Equation 10.70 is the **first law of thermodynamics**. It is a special case of the general law of energy conservation. It can be formulated as:

The sum of the external heat ΔQ, applied to a thermodynamic system, and the supplied mechanical energy ΔW is equal to the increase ΔU of the total internal energy U.

$$\Delta U = \Delta Q + \Delta W \tag{10.70b}$$

When the system performs work against an external force, is $\Delta W < 0$ and therefore $\Delta U < 0$. Many inventors have tried to construct machines that deliver more energy than they consume. Such a machine could use part of the delivered energy for its own operation. It could run continuously delivering energy without external energy input. Therefore this hypothetical machine is called a **perpetuum mobile**. Because it contradicts the first law of thermodynamics it is also called *perpetuum mobile of the first kind*.

Equation 10.70 can be also formulated in a more floppy way as:

A perpetuum mobile of the first kind is impossible.

Note: This statement cannot be proved mathematically. It is solely based on empirical knowledge.

For ideal gases the work performed during the expansion of the volume V by infinitesimal amount $\mathrm{d}V$ against the external pressure p is

$$\mathrm{d}W = p \cdot \mathrm{d}V \, .$$

The first law of thermodynamics for ideal gases can therefore be written in a differential form as

$$\mathrm{d}U = \mathrm{d}Q - p \cdot \mathrm{d}V \, . \tag{10.71}$$

For $\mathrm{d}V > 0$ the system releases energy and according to (10.71) $\mathrm{d}U < \mathrm{d}Q$, i. e. the loss of internal energy cannot be compensated by the supplied heat $\mathrm{d}Q$. For $\mathrm{d}V < 0$ the volume is compressed and the system gains the energy $p \cdot \mathrm{d}V$. Now $\mathrm{d}U > \mathrm{d}Q$, the gain of internal energy is larger than the supplied heat.

The relation between the thermodynamic variables p, V, T can be derived from (10.71) for special processes where in each case one of the variables p, V, T or the quantity Q is kept constant.

Note, that the quantity Q is not a thermodynamic variable! The state of a system does change with the supply of heat $\mathrm{d}Q$, but one cannot unambiguously determine the final state of the system, because either U or V or both variables can change. In a mathematical language this means: $\mathrm{d}Q$ is not a complete differential.

10.3.3 Special Processes as Examples of the First Law of Thermodynamics

Note: We will discuss the following processes for one mole of a gas where the number of moles is $\nu = V/V_\mathrm{M} = 1$.

10.3.3.1 Isochoric Processes (V = const)

With $\mathrm{d}V = 0$ it follows from (10.71)

$$\mathrm{d}Q = \mathrm{d}U = C_V \cdot \mathrm{d}T \, . \tag{10.72}$$

The heat supplied to the system is used solely for the increase of the internal energy U. We can therefore relate the specific heat to the internal energy U by

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \, . \tag{10.73}$$

10.3.3.2 Isobaric Processes (p = const)

The first law of thermodynamics has now the form

$$\mathrm{d}Q = \mathrm{d}U + p \cdot \mathrm{d}V = C_p \cdot \mathrm{d}T \, , \tag{10.74}$$

where we have used (10.28). When we introduce the *enthalpy*

$$H = U + p \cdot V \tag{10.75}$$

as new thermodynamic variable with

$$\mathrm{d}H = \mathrm{d}U + p \cdot \mathrm{d}V + V \cdot \mathrm{d}p = \mathrm{d}Q + V \cdot \mathrm{d}p \, , \tag{10.76}$$

we can write the first law of thermodynamics as

$$\mathrm{d}H = \mathrm{d}U + p \cdot \mathrm{d}V = \mathrm{d}Q \, . \tag{10.77}$$

For isobaric processes the increase $\mathrm{d}H$ of the enthalpy H is equal to the supplied heat $\mathrm{d}Q$.

The specific heat at constant pressure is then

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \, . \tag{10.78}$$

The variable H is often used for phase changes, chemical reactions or other processes that take place at constant pressure, but where the volume can change. A further example is the expansion of a gas from a reservoir with constant pressure into the vacuum where the pressure $p = 0$ is maintained by pumps.

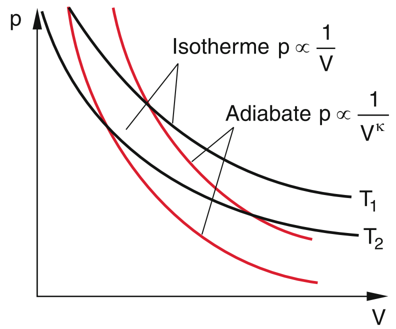


Figure 10.49 Isothermal and adiabatic curves in a p-V-diagram

10.3.3.3 Isothermal Processes (T = const)

Since the internal energy per mole of a gas depends solely on the temperature T but not on the pressure p or the volume V, for isothermal processes U must be constant, i. e. $\mathrm{d}U = 0$. From (10.71) it follows

$$\mathrm{d}Q = p \cdot \mathrm{d}V \ . \qquad (10.79)$$

The external heat energy $\mathrm{d}Q$ supplied to the system is completely transferred to the work $p \cdot \mathrm{d}V$ that the system releases to the outside. Its internal energy does not change.

The equation of state $p \cdot V = R \cdot T$ then reduces to the Boyle–Marriott law (see Sect. 7.1)

$$p \cdot V = \text{const} \ . \qquad (10.80)$$

The state $p(V)$ of the system can be plotted in a p-V-diagram (Fig. 10.49) for isothermal and adiabatic processes at different temperatures T. This gives for isothermal processes the hyperbolas

$$p = \frac{R \cdot T_{\mathrm{K}}}{V} = \frac{\text{const}}{V} \ ,$$

which are called *isotherms* (black curves in Fig. 10.49).

We will now discuss how large the work is that a system has to perform for an isothermal expansion from a volume V_1 to $V_2 > V_1$ at constant temperature T.

$$\begin{aligned} W &= -\int_{V_1}^{V_2} p \cdot \mathrm{d}V = -R \cdot T \cdot \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} \\ &= -R \cdot T \cdot \ln \frac{V_2}{V_1} = R \cdot T \cdot \ln \frac{V_1}{V_2} \ . \end{aligned} \qquad (10.81)$$

10.3.3.4 Adiabatic Processes

During adiabatic processes no heat is exchanged between the system and its surroundings. Adiabatic processes occur in nature, when changes of volume or pressure are so fast, that the energy exchange during this short time period can be neglected. An example is the propagation of acoustic waves at high frequencies ν through a medium (see Sect. 11.9). During one oscillation period $\Delta T = 1/\nu$ nearly no energy exchange between maxima and minima of the wave can occur.

The first law of thermodynamics (10.71) can be written with (10.73) for adiabatic processes

$$\mathrm{d}U = C_V \cdot \mathrm{d}T = -p \cdot \mathrm{d}V \ . \qquad (10.82)$$

From the equation of state (10.21) $p \cdot V = R \cdot T$ we obtain $p = R \cdot T/V$. Inserting this into (10.82) yields

$$C_V \cdot \mathrm{d}T/T = -R \cdot \mathrm{d}V/V \ .$$

Integration gives

$$\begin{aligned} C_V \cdot \ln T &= -R \cdot \ln V + \text{const} \\ \Rightarrow \ln\left(T^{C_V} \cdot V^R\right) &= \text{const} \ . \end{aligned}$$

With $R = C_p - C_V$ this can be written as

$$T^{C_V} \cdot V^{(C_p - C_V)} = \text{const} \ . \qquad (10.83a)$$

The $1/C_V$-th power of (10.83a) yields with the adiabatic index $\kappa = C_\mathrm{p}/C_V$ the equation

$$T \cdot V^{\kappa - 1} = \text{const} \ , \qquad (10.83b)$$

because $T = p \cdot V/R$, this can be also written as

$$p \cdot V^{\kappa} = \text{const} \ . \qquad (10.83c)$$

The Eq. 10.83a–c describe the relations between the thermodynamic variables T, p, V for adiabatic processes. They are called Poisson-adiabatic equations.

In a p–V-diagram (Fig. 10.49) the red adiabatic curves $p(V) \propto 1/V^{\kappa}$ ($\kappa > 1$) are steeper than the isothermal curves $p(V) \propto 1/V$.

For an ideal gas is $f = 3$ and $\kappa = (f + 2)/f = 5/3$. For molecular nitrogen N_2 is $f = 5 \rightarrow \kappa = 7/5$.

Example

In the pneumatic cigarette lighter, the volume V filled with an air–benzene-mixture is suddenly compressed to 0.1 V. According to (10.83b) the temperature T rises from room temperature ($T_1 = 293\,\mathrm{K}$) to $T_2 = T_1(V_1/V_2)^{\kappa-1}$. For air is $\kappa = 7/5$ which gives $T_2 = 736\,\mathrm{K} = 463\,°\mathrm{C}$. This is above the ignition temperature of the air–benzene-mixture. ◀

10.3.4 The Second Law of Thermodynamics

While the first law of thermodynamics represents the energy conservation when thermal energy is converted into mechanical energy, the second law of thermodynamics gives the maximum fraction of thermal energy that can be really transferred into mechanical energy.

As we will see, this is connected with the question, into which direction the transfer of one form of energy into another form proceeds by its own, i. e. without external action. All of our experience tells us, that heat flows by its own only from the hotter region into the colder one, not vice versa. Furthermore all experiments show, that mechanical energy can be completely converted into heat, but that for the opposite process only part of the heat can be converted into mechanical energy.

This fact, that is based solely on experimental experience, is formulated in the second law of thermodynamics:

> Heat flows *by its own* only from the warmer body to the colder one, never into the opposite direction.

We will now discuss more quantitatively the transformation of heat into mechanical work. This will be illustrated by considering thermodynamic cyclic processes, which leads us to a quantitative formulation of the second law of thermodynamics.

10.3.5 The Carnot Cycle

A thermodynamic cycle is a series of processes where a thermodynamic system passes through several different states until it finally reaches again its initial state. At the end of this cycle, the system shows again the same thermodynamic variables as in the initial state, although it has passed during the cycle through different states with different variables. A simple example is a system that is heated and then cooled again until it has reached the initial temperature.

If the cyclic process can traverse into both directions the cycle is called *reversible* (Fig. 10.50) otherwise it is called *irreversible*. Although such reversible processes can occur in micro-physics if only a few particles are involved, they represent in the real world of many-particle systems only idealized "*Gedanken-experiments*", which represent limiting cases of real processes that are always irreversible.

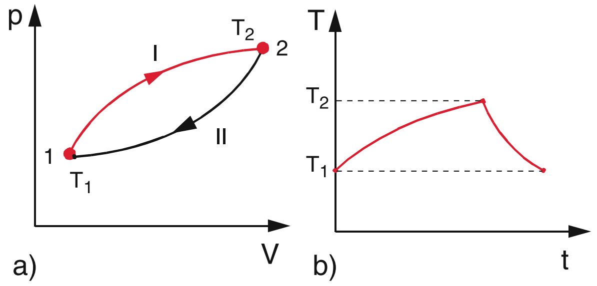


Figure 10.50 Thermodynamic cycle from the state 1 (T_1, p_1, V_1) via the state 2 (T_2, p_2, V_2) back to the state 1. **a** In a p–V-diagram; **b** in the temperature-time diagram. Note: The cycle shown here, can only proceed, if energy is fed into the system during the first step and energy is taken away from the system during the second step

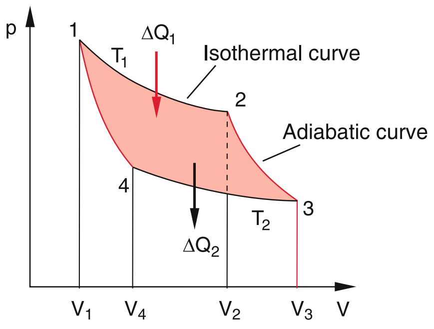


Figure 10.51 Carnot's cycle

All periodically operating machines, such as steam engines or car motors traverse irreversible cyclic processes. Although they arrive at the end of the cycle again at the initial state, if they are regarded as isolated systems, but they have lost energy during the cycle (for instance friction losses) which has to be replaced for each cycle.

The most famous reversible cyclic process is the Carnot-cycle that represents an idealized loss-free cycle. It was published in 1824 by *Nicolas Leonard Sadi Carnot*. This cyclic process will enable us to calculate the maximum fraction of heat that can be transformed into mechanical energy and therefore allows the quantitative formulation of the second law of thermodynamics. Furthermore, it illustrates nicely the difference between reversible and irreversible processes.

The Carnot Cycle is a "*Gedanken-Experiment*", where a thermodynamic system passes through two isothermal and two adiabatic processes during two expansion and compression events, until it finally reaches its initial state again (Fig. 10.51).

Note: The following considerations are valid for 1 mol of an ideal gas, where in Eq. 10.61 $V = V_M$ and $\nu = 1$.

The state of the system at the starting point 1 is defined by the thermodynamic variables (V_1, p_1, T_1). The isothermal expansion brings the system to the state $2 = (V_2, p_2, T_1)$. During this process, the heat ΔQ_1 has to be supplied to the system in order to keep the temperature constant. Now an adiabatic expansion follows and the system gets to the state $3 = (V_3, p_3, T_2 < T_1)$. In the next step the system is isothermally compressed and reaches the state 4 with the conditions $(V_4,\ p_4,\ T_2)$. Here the heat ΔQ_2 has to be removed from the system. Finally an adiabatic compression brings the system back to its initial state $1 = (V_1, p_1, T_1)$. Such a virtual thermodynamic system that passes through a Carnot cycle is called a *Carnot Machine*.

We will now calculate the heat energies ΔQ_1 and ΔQ_2 which are exchanged between the system and a heat reservoir during the isothermal processes.

1st process: Isothermal expansion from the state 1 to the state 2. According to the first law of thermodynamics we obtain for an isothermal expansion

$$dQ = p \cdot dV\ .$$

The heat supplied to the system is equal to the mechanical work the system performs during the expansion.

With (10.81) it follows:

$$\begin{aligned}\Delta Q_1 = -\Delta W_{12} &= \int_{V_1}^{V_2} p\, dV \\ &= R \cdot T_1 \cdot \ln(V_2/V_1)\ .\end{aligned} \tag{10.84a}$$

2nd process: Adiabatic expansion from state 2 to state 3. For adiabatic processes the heat exchange is zero. We therefore obtain:

$$dQ = 0 \rightarrow dU = -p \cdot dV = \Delta W_{23}\ . \tag{10.84b}$$

The work performed during the expansion is negative, because it is delivered from the system to the surrounding. This results in a decrease $\Delta U = U(T_2) - U(T_1)$ of the internal energy U because $T_2 < T_1$.

3rd process: Isothermal compression from state 3 to state 4. Similar to step 1 is the heat ΔQ_2 delivered at the lower temperature T_2 to the heat reservoir equal to the work ΔW_{34} necessary to compress the volume V

$$\Delta W_{34} = R \cdot T_2 \cdot \ln(V_3/V_4) = -\Delta Q_2 > 0\ . \tag{10.84c}$$

4th process: Adiabatic compression from state 4 to the starting conditions in state 1. Similar to step 2 is here no heat exchange with the surrounding and the work performed during the compression is converted to the increase ΔU of the internal energy

$$\Delta U = U(T_1) - U(T_2)\ . \tag{10.84d}$$

Total energy balance: The work delivered to the surrounding during the 2nd process is equal to the work supplied to the system during the 4th process. Therefore, only during the isothermal processes a net energy is transferred. The net mechanical work during the Carnot cycle (Fig. 10.52) is

$$\begin{aligned}\Delta W &= \Delta W_{12} + \Delta W_{34} \\ &= R \cdot T_1 \cdot \ln(V_1/V_2) + R \cdot T_2 \cdot \ln(V_3/V_4)\ .\end{aligned}$$

For the adiabatic processes 2 → 3 and 4 → 1 the relations hold

$$\begin{aligned}T_1 \cdot V_2^{\kappa-1} &= T_2 \cdot V_3^{\kappa-1} \quad \text{and} \\ T_1 \cdot V_1^{\kappa-1} &= T_2 \cdot V_4^{\kappa-1}\ .\end{aligned}$$

Division of the two equations yields

$$V_2/V_1 = V_3/V_4 \Rightarrow \ln(V_3/V_4) = -\ln(V_1/V_2)\ .$$

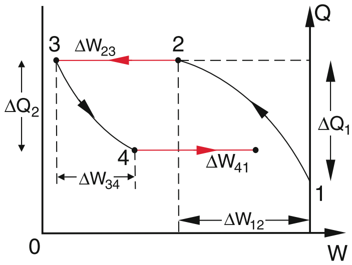


Figure 10.52 Heat exchange and net mechanical energy $\Delta W = \Delta W_{34} - \Delta W_{12}$ of Carnot's cycle

The net work is then

$$\Delta W = R \cdot (T_1 - T_2) \cdot \ln(V_1/V_2)\ . \tag{10.85}$$

The Carnot Engine has received the heat ΔQ_1 and has supplied the mechanical work $\Delta W < 0$ to the outside.

Such a machine that transfers heat into mechanical energy is called **heat engine**.

The heat ΔQ_2 supplied to the surrounding, is generally lost. Therefore the efficiency of the engine is defined as the mechanical work supplied by the engine divided by the heat ΔQ_1 put into the engine.

The efficiency of the Carnot Engine is then

$$\eta = \left|\frac{\Delta W}{\Delta Q_1}\right| = \frac{R(T_1 - T_2) \cdot \ln(V_2/V_1)}{R \cdot T_1 \cdot \ln(V_2/V_1)} = \frac{T_1 - T_2}{T_1}$$

$$\eta = \frac{T_1 - T_2}{T_1}\ . \tag{10.86}$$

This is a remarkable result: During the cycle the total received heat cannot be transformed into mechanical work, but only the fraction $\eta = (T_1 - T_2)/T_1 < 1$. This fraction is called *exergy*. The remaining part $(1 - \eta)$ of the input energy (*Anergy*) is exchanged as heat ΔQ_2 to the surrounding at the lower temperature T_2. The conservation of total energy can be written as

$$\text{Energy} = \text{Exergy} + \text{Anergy}\ .$$

The efficiency of the Carnot Engine increases with increasing temperature difference $T_1 - T_2$. It is therefore advantageous to choose T_1 as high as possible and T_2 as low as possible. We will see in Sect. 10.3.10 that it is impossible to reach $T_2 = 0\,\text{K}$.

This implies that η is always smaller than 1.

When the Carnot cycle is traversed into the opposite direction, heat is transported from the lower temperature T_2 to the higher temperature T_1. This requires the work

$$\Delta W = R \cdot (T_2 - T_1) \cdot \ln(V_1/V_2) \; .$$

This represents the ideal limiting case of a heat pump, which is also used as refrigerating machine (see Sect. 10.3.14). Its coefficient of performance (also called figure of merit) is defined as the ratio of delivered heat ΔQ to the input work ΔW.

$$\varepsilon_{\text{hp}} = \frac{\Delta Q_1}{\Delta W} = \frac{T_1}{T_1 - T_2} = \frac{1}{\eta} \; .$$

Note, that $\varepsilon_{\text{hp}} > 1$.

Example

$T_1 = 30\,°\text{C} = 303\,\text{K}$,
$T_2 = 10\,°\text{C} = 283\,\text{K} \Rightarrow \varepsilon_{\text{hp}} = 15.2$.

Note:

1. The heat pump does not contradict the second law of thermodynamics, because here the heat does not flow *by its own* from the colder to the hotter place but needs mechanical work to drive this heat transport.
2. The Carnot Engine works with an ideal gas and all energy losses are neglected. The Carnot Cycle is reversible. Real engines have always losses that cannot be avoided. They are due to friction of the moving pistons, friction in the non-ideal gas, heat conduction from the system to the surroundings etc. These losses decrease the efficiency of the engine. We will now indeed prove, that:

> There is no periodically working machine with a higher efficiency than that of the Carnot engine.

Proof

Assume, there is a machine M_x with a higher efficiency than the Carnot Engine. This "magic machine" needs for a given mechanical energy output a smaller heat input than the Carnot Engine, i. e. $\Delta Q_x < \Delta Q_1$. We now combine M_x with a Carnot engine that passes the cycle in opposite direction, i. e. it works as a heat pump (Fig. 10.53). We adapt the size of M_x in such a way that it delivers just the mechanical work ΔW, which the Carnot engine needs as heat pump. The Carnot engine then transports the heat

$$|\Delta Q_1| = |\Delta Q_2| + |\Delta W|$$

from the colder to the warmer reservoir. Since we have assumed that the magic machine M_x has a higher efficiency than the Carnot Engine, it needs less heat from the reservoir at the temperature T_1 for its operation than the Carnot Engine transports to this reservoir. It furthermore delivers less heat to the cold reservoir at T_2 than the Carnot engine needs for its operation as heat pump.

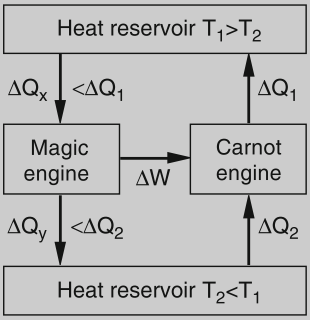


Figure 10.53 Proof of the impossibility of the perpetuum mobile of the second kind

The combined system therefore transports heat from the colder to the hotter reservoir without mechanical energy input. This contradicts the second law of thermodynamics which has been proved by numerous experiments. Therefore a heat engine with a higher efficiency than that of the Carnot engine is not possible!

Remark. These considerations can be also applied to a heat pump, where the cycle is traversed into the opposite direction. We replace the Carnot Engine in Fig. 10.53 by a "magic heat pump" and the magic machine M_x by the Carnot Engine (Fig. 10.54) and assume that the coefficient of performance ε_x is larger than that of a Carnot heat pump. An analogous consideration shows that $\varepsilon_x < \varepsilon_C = 1/\eta_C$. This can be seen as follows:

The Carnot engine in Fig. 10.54 now runs as heat engine that extracts the heat ΔQ_1 from the hot reservoir at the temperature T_1 and delivers the heat $\Delta Q_2 = \Delta Q_2 - \Delta W$ to the cold reservoir at $T_2 < T_1$. The output energy ΔW is transferred to the magic heat pump, which takes the heat ΔQ_4 from the cold reservoir

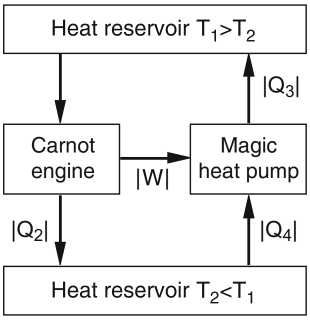


Figure 10.54 Proof, that the energy efficiency ratio of a heat pump is always smaller than that of a Carnot-engine that operates as a heat pump

and transports the heat $\Delta Q_3 = \Delta Q + \Delta W$ to the hot reservoir. Assume that the coefficient of performance $\varepsilon_x = \Delta Q_3/\Delta W$ of the magic heat pump is larger than $\varepsilon_C = 1/\eta_C = \Delta Q_1/\Delta W$ of the Carnot engine. Then $|\Delta Q_3| > |\Delta Q_1|$ and $|\Delta Q_4| = |\Delta Q_3| - W > |\Delta Q_2| = |\Delta Q_1|$ This implies that the combined system Carnot engine plus magic heat pump can pump heat from the cold to the hot reservoir without mechanical energy input. This again contradicts the second law of thermodynamics.

The coefficient of performance ε_x of an arbitrary heat pump cannot be larger than $\varepsilon_C = 1/\eta_C$ where η_C is the efficiency of the Carnot engine.

With other words: The coefficient of performance ε_x of any heat pump cannot be larger than that of a Carnot heat pump $\varepsilon_C = T_1/(T_1 - T_2)$.

From the considerations above it follows: All reversible cycles have the same efficiency

$$\eta = \Delta W/\Delta Q_1 = (T_1 - T_2)/T_1 ,$$

independent of the working material, which can be different from an ideal gas.

10.3.6 Equivalent Formulations of the Second Law

The considerations above allow the following statements:

- The efficiency $\eta = \Delta W/\Delta Q_1 < 1$ of any heat engine is always smaller than 100%. This means that heat cannot completely converted into mechanical work.
- The Carnot engine has the maximum possible efficiency: $\eta = (T_1 - T_2)/T_1$.

The value $\eta = 1$ would be only possible for $T_2 = 0$. However, we will see that this is excluded by the third law of thermodynamics (see Sect. 10.3.13)

The first and second laws of thermodynamics are purely rules of thumb, based on numerous experimental facts. They cannot be proved mathematically without additional assumptions.

The second law can be formulated in different ways:

- Heat flows by its own only from the hot to the cold region, never into the opposite direction.
- There is no periodically acting machine that can convert heat completely into mechanical work without additional energy supply.

Such a machine is called a *perpetuum mobile of the second kind*. The second law can then be formulated similar to the first law:

The realization of a perpetuum mobile of the second kind is impossible.

Example

A perpetuum mobile of the second kind could be a ship with engines that receive their energy solely from the heat of the sea. Such a ship could move without additional energy and would not need oil or coal. ◀

A perpetuum mobile of the second kind does not contradict the first law of thermodynamics, because it does not violate the energy conservation. Therefore numerous inventors have tried to construct such machines, however unsuccessful!

The Carnot cycle allows a method to measure the Kelvin temperature, which is independent of the thermometer substance and works down to very low temperatures where gas thermometers are no longer useful, because all gases condense at such low temperatures. From (10.84) we can deduce the ratio of the heat energies ΔQ_1 and ΔQ_2 supplied from and released to the heat reservoirs

$$\frac{\Delta Q_1}{\Delta Q_2} = \frac{T_1}{T_2} .$$

The temperatures of the two heat reservoirs can be compared, when the heat energies, exchanged between the system and the reservoirs, are measured. For instance, if one of the reservoirs is kept at the temperature $T_1 = 273.16\,\mathrm{K}$ of the triple point of water the temperature T_2 is obtained from

$$T_2 = 273.16 \cdot \frac{|\Delta Q_2|}{|\Delta Q_1|} = 273.16 \cdot (1 - \eta) .$$

The heat reservoir, kept at the temperature T_1, can be electrically heated, which allows the determination of ΔQ_1. The efficiency η can then be measured as the ratio of mechanical work $\Delta W = p \cdot \Delta A \cdot \Delta x$ when a piston with area A moves by the distance Δx against the external pressure p and the supplied heat ΔQ_1.

The temperature scale obtained by this way is called the *thermodynamic temperature scale*.

One Kelvin (1 K) is 1/273.16 times the temperature of the triple point of water.

10.3.7 Entropy

By introducing the entropy as new thermodynamic variable, the second law of thermodynamics can be mathematically formulated in an elegant way. When the heat $\mathrm{d}Q$ is supplied to a system at the temperature T we define as *reduced heat* the ratio $\mathrm{d}Q/T$.

For the Carnot cycle in Fig. 10.51 we can bring the system from the point 1 to the point 3 on two different ways: $1 \to 2 \to 3$ or $1 \to 4 \to 3$. Only during the isothermal processes, heat is exchanged with the surroundings. The absolute values of the reduced heat energies $|\Delta Q_1|/T_1$ and $|\Delta Q_2|/T_2$ on the two ways are equal, as can be seen from (10.84a–c). This means: The reduced energies do not depend on the way but only on starting and final state of the system. This is not only valid for the Carnot cycle but for all reversible processes.

We introduce the thermodynamic variable S called the *entropy* with the dimension $[S] = [\mathrm{J/K}]$, in the following way. We define the change $\mathrm{d}S$ of the entropy as the reduced heat exchanged on an infinitesimal part of a reversible process

$$\mathrm{d}S = \mathrm{d}Q/T\,.$$

Since the change ΔS for a system that is brought from a defined initial state into a defined final state is independent of the way between these two states, and depends solely on initial and final states of the system, the quantity S is a thermodynamic variable which describes together with pressure p, temperature T and volume V the state of a thermodynamic system.

In the Carnot Cycle the reduced heat energies change only during the isothermal processes. According to (10.84) the entropy then changes by

$$\Delta S = \frac{\Delta Q}{T} = \pm R \cdot \ln \frac{V_2}{V_1}\,. \tag{10.87}$$

For the complete reversible cycle we have

$$\frac{\Delta Q_1}{T_1} = -\frac{\Delta Q_2}{T_2}\,,$$

and therefore

$$\Delta S = 0\,.$$

For a reversible cycle the entropy S is constant.

Processes where $S = \text{const}$ are called **isentropic processes**. For these processes is $\Delta S = 0$ and therefore $\Delta Q = 0$ and $T = \text{const}$. During isentropic processes the system must be kept at a constant temperature. This distinguishes isentropic processes from adiabatic processes where also $\Delta Q = 0$ but where the temperature changes.

With the first law of thermodynamics (10.71) the entropy change $\mathrm{d}S$ during reversible processes of an ideal gas can be calculated as

$$\mathrm{d}S = \frac{\mathrm{d}Q_{\text{rev}}}{T} = \frac{\mathrm{d}U + p\,\mathrm{d}V}{T}\,. \tag{10.88}$$

For 1 mol of the gas is $\mathrm{d}U = C_V \cdot \mathrm{d}T$ and $p \cdot V_\mathrm{M} = R \cdot T$. This converts (10.88) to

$$\mathrm{d}S = C_V \frac{\mathrm{d}T}{T} + R \cdot \frac{\mathrm{d}V}{V}\,. \tag{10.89}$$

Integration over the temperature range from T_1 to T_2 where the molar heat capacity can be assumed as constant, yields for isobaric processes where V and T can change but $p = \text{const}$.

$$\Delta S_{\text{isobar}} = C_V \ln \frac{T_2}{T_1} + R \cdot \ln \frac{V_2}{V_1}\,. \tag{10.90}$$

In a similar way one obtains for isochoric processes ($V = \text{const}$) with $C_V = C_p - R$ and $p_1/T_1 = p_2/T_2$

$$\begin{aligned}\Delta S_{\text{isochor}} &= C_V \ln \frac{T_2}{T_1} = (C_p - R) \ln \frac{T_2}{T_1}\\ &= C_p \ln \frac{T_2}{T_1} - R \ln \frac{T_2}{T_1}\end{aligned}$$

$$\Delta S_{\text{isochor}} = C_p \ln \frac{T_2}{T_1} - R \cdot \ln \frac{p_2}{p_1}\,. \tag{10.91}$$

Since the entropy S is a thermodynamic variable, its change ΔS does not depend on the kind of process but only on initial and final state of the process. We can therefore determine ΔS also for irreversible processes. This can be seen as follows:

We consider a substance at the temperature T_1 (e. g. a solid body) in a gas volume V. The body should be in thermal contact with the gas. Now the gas is slowly expanded in an adiabatic process, which results in a slow decrease of the temperature. If this proceeds sufficiently slowly, the temperature of the body is always equal to that of the gas, because sufficient time is available for reaching temperature equilibrium. Finally the temperature has decreased to T_2. This process is reversible because the initial state can be retrieved by slow adiabatic compression.

When the solid body is regarded as isolated body without the gas, the cooling process is irreversible, because heat is transferred to the surrounding. The entropy change of the body is

$$\begin{aligned}\Delta S &= \frac{\Delta Q_{\text{irr}}}{T}\\ &= C_V \int\limits_{T_1}^{T_2} \frac{\mathrm{d}T}{T}\\ &= C_V \cdot \ln \frac{T_2}{T_1} < 0 \quad \text{for} \quad T_2 < T_1\,,\end{aligned} \tag{10.92}$$

as in the reversible process. However, since heat has been transferred to the surroundings the entropy of the surroundings increases. For the total change of the system body + surroundings $\Delta S_{\text{irrev}} > 0$, i. e. the entropy increases!

Example

1. We regard in Fig. 10.55 two equal bodies with mass m and specific heat c which have been brought by different energy supply to different temperatures T_1 and $T_2 < T_1$. Their heat energies are then $Q_1 = m \cdot c \cdot T_1$ and $Q_2 = m \cdot c \cdot T_2$. When they are brought into

thermal contact heat flows from the hot body 1 to the colder body 2 until the temperatures are equal to the average temperature T_m. If no heat is transferred to the surroundings the body 1 has lost the energy $\Delta Q_1 = m \cdot c(T_\mathrm{m} - T_1)$ and the body 2 has received the energy $\Delta Q_2 = -m \cdot c \cdot (T_2 - T_\mathrm{m})$. Because $\Delta Q_1 = \Delta Q_2$ we obtain the average temperature

$$T_\mathrm{m} = \frac{T_1 + T_2}{2} \,. \tag{10.93}$$

The entropy change ΔS of body 1 is

$$\begin{aligned}\Delta S_1 &= \int\limits_{T_1}^{T_\mathrm{m}} \frac{\mathrm{d}Q}{T} = mc \int\limits_{T_1}^{T_\mathrm{m}} \frac{\mathrm{d}T}{T} \\ &= mc\ln(T_\mathrm{m}/T_1) \,.\end{aligned}$$

Since $T_\mathrm{m} < T_1 \rightarrow \Delta S_1 < 0$.
The change of S_2 is accordingly

$$\Delta S_2 = mc\ln(T_\mathrm{m}/T_2) \,,$$

where $\Delta S_2 > 0$. The total change of the entropy of the system of bodies is therefore

$$\begin{aligned}\Delta S &= \Delta S_1 + \Delta S_2 \\ &= mc\ln\frac{T_\mathrm{m}^2}{T_1 \cdot T_2} \,.\end{aligned} \tag{10.94}$$

Since $T_\mathrm{m} = \frac{1}{2}(T_1 + T_2)$ we get $T_\mathrm{m}^2/(T_1 \cdot T_2) > 1$ because the arithmetic mean is always $\geq$ geometric mean. This gives $\Delta S > 0$. The entropy increases during the irreversible process. The combination of the two bodies at different temperatures to a combined system is an irreversible process, because the cooled body cannot heat up again by cooling the other body without the supply of energy from outside (second law).

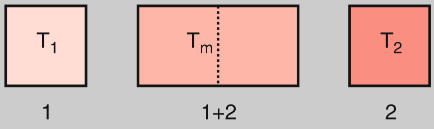


Figure 10.55 Increase of entropy during the equalization of temperatures at the contact of two bodies with different temperatures

2. The second example, which will give us a deeper insight into the meaning of entropy, is related to the diffusion of an ideal gas from a small volume V_1 through a hole into a larger volume V_2. Initially (for times $t \leq 0$) the gas is confined to the small volume V_1. At $t = 0$ the hole in the barrier separating V_1 from V_2 is opened and the gas molecules diffuse into the evacuated volume V_2 (Fig. 10.56). After a sufficiently long time $t > 0$ they are uniformly distributed over the whole volume $V = V_1 + V_2$. The gas temperature remains constant during this isothermal expansion (experiment of Gay-Lussac) because no work is needed for the expansion into the vacuum ($p \cdot \mathrm{d}V = 0$).

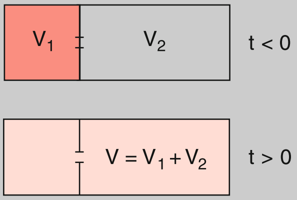


Figure 10.56 Diffusion of molecules from a small volume V_1 through a hole into the large volume V_2. After a sufficiently long time the molecules are uniformly distributed over the total volume $V_1 + V_2$

The diffusion is irreversible, because it is highly improbable that all gas molecules diffuse back through the hole into the small volume V_1 (see below). It is, however, nevertheless possible to calculate the entropy change by using as reversible substitute process the isothermal expansion (against an external pressure) with the same initial and final states as the diffusion. For this process, the supply of heat ΔQ is necessary in order to keep the temperature constant (Sect. 10.3.5). Since the reduced heat does not depend on the way during the expansion but solely on initial and final states the entropy change ΔS

$$\Delta S = R \cdot ln\frac{V}{V_1} \tag{10.95}$$

for the adiabatic expansions must be the same as for the diffusion.

This can be also understood, when we substitute the diffusion by a Gedanken-experiment, where the diffusion is separated into two steps (Fig. 10.57). The gas drives during the isothermal expansion a piston and extracts from a heat reservoir the heat ΔQ_1 as in the Carnot cycle. The work $\Delta W = \Delta Q_1$ performed during the expansion drives a stirrer that releases the heat ΔQ_1 again to the heat reservoir due to frictional losses. For this *Gedankenexperiment* initial and final states are identical to those of the diffusion. Therefore, the entropy change must be the same. Since in (10.95) $V \gg V_1 \rightarrow \Delta S > 0$.

Based on this diffusion process a statistical explanation of the entropy can be derived. We regard a molecule in volume V_1. Before the hole in the barrier is opened, the probability of finding the molecule in V_1 is $P_1 = 1$, because it must be for sure in V_1. After opening the hole the probability has decreased to $P_1 = V_1/(V_1 + V_2) = V_1/V$.

For two molecules the probability of finding both molecules in V_1 is equal to the product $P_2 = P_1 \cdot P_1 =$

P_1^2 of the probabilities for each molecule. For N molecules we therefore obtain

$$P_N = \left(\frac{V_1}{V}\right)^N . \qquad (10.96)$$

For 1 mol is $N = N_A = R/k$, where k is the Boltzmann constant and N_A the Avogadro number. We then get

$$P_{N_A} = \left(\frac{V_1}{V}\right)^{R/k} . \qquad (10.97)$$

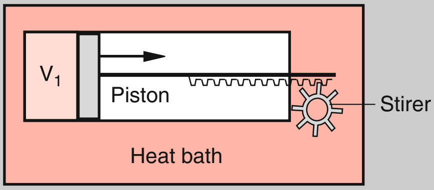


Figure 10.57 Separation of the diffusion process in Fig. 10.56 into two steps: Isothermal expansion and conversion of the mechanical work into heat at the heat reservoir

Example

For $V_1 = (1/2)V, N_A = 6 \cdot 10^{23}$ /mol the probability that all molecules are found in V_1 is

$$\begin{aligned} P_N &= 2^{-6 \cdot 10^{23}} \\ &= 10^{-1.8 \cdot 10^{23}} \\ &\approx 0 \quad \text{(Fig. 10.58)} . \end{aligned}$$

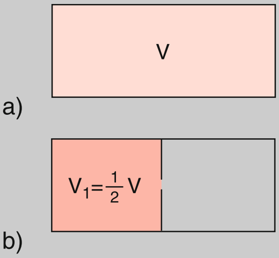


Figure 10.58 The probability P that all N molecules are simultaneously in the volume $V_1 = (1/2)V$ is $P = (1/2)^N$

Because of the large numbers in the exponent it is more convenient to use the logarithm of the probability P. From (10.97) we obtain

$$k \cdot \ln P = R \cdot \ln \frac{V_1}{V} = -R \ln \frac{V}{V_1} . \qquad (10.98)$$

According to (10.95) the right side of (10.98) is equal to the change ΔS of the entropy. We therefore obtain for the change ΔS during the transition from state 1 (all molecules are in volume V_1) to state 2 (all molecules are distributes over the volume $V = V_1 + V_2$ the result

$$\begin{aligned} \Delta S &= S(V) - S(V_1) = k \cdot (\ln P(V) - \ln P(V_1)) \\ &= k \cdot \ln \frac{P_{\text{final}}}{P_{\text{initial}}} . \end{aligned} \qquad (10.99a)$$

This illustrates that the entropy change ΔS during the diffusion from state 1 with the probability P_{initial} to the state 2 with the probability P_{final}

$$\Delta S = k \cdot \left(\ln \frac{P_{\text{final}}}{P_{\text{initial}}}\right) \qquad (10.99b)$$

is a measure for the probability that a system undergoes a transition from the initial to the final state. This can be formulated in a more general way:

The probability that a system occupies a state i is proportional to the number Z of possible ways that lead to this state.

Example

When N particles, each with the energy $n_i E_0$ that are integer multiples of a minimum energy E_0 occupy a state with the total energy $E = \sum n_i E_0$, the number Z of possible realizations of this state equals the number of possible combinations of the integers n_i that fulfil the condition $\sum n_i = E/E_0$.

The entropy S of a thermodynamic system state that can be realized by $Z = P$ possible ways is

$$S = k \cdot \ln P . \qquad (10.99c)$$

The entropy S of a thermodynamic state is proportional to the number of possible realizations for this state.

As a third example, we will discuss the increase of entropy for the mixing of two different kinds of molecules X and Y. Initially all N_X molecules X should be in volume V_1 and all N_Y molecules Y in volume V_2. We assume that pressure p and temperature T are equal in both volumes, which demands $N_X/V_1 = N_Y/V_2$. When we open a hole in the barrier between the two volumes the molecules will diffuse through the hole until a uniform distribution of both kinds of molecules is reached. This process is irreversible and the entropy increases because the molecules N_X as well as the molecules N_Y fill now a larger volume $V = V_1 + V_2$, and the number of possible realizations of this situation is larger than that of the initial state. The increase of entropy for the N_X molecules is

$$\Delta S_X = k \cdot \ln \left(\frac{V}{V_1} \right)^{N_X} = k \cdot N_X \ln \frac{V}{V_1}$$
$$= k \cdot N_X \ln \frac{N_X + N_Y}{N_X} \, ,$$

and for the N_Y molecules

$$\Delta S_Y = k \cdot N_Y \ln \frac{N_X + N_Y}{N_Y} \, .$$

The total change of entropy (called mixing entropy) is then

$$\Delta S_m = \Delta S_X + \Delta S_Y$$
$$= k \left[N_X \ln \frac{N_X + N_Y}{N_X} + N_Y \ln \frac{N_X + N_Y}{N_Y} \right] \, . \qquad (10.100)$$

These examples illustrate that only *changes* of entropy can be measured. The absolute value of the entropy $S(V, p, T)$ of a thermodynamic state

$$S = S_0 + \Delta S \qquad (10.101)$$

is only defined, if the constant term S_0 is known. We will show in Sect. 10.3.10, how S_0 can be determined.

10.3.8 Reversible and Irreversible Processes

For a completely elastic collision between two particles, energy and momentum of the two-body system are conserved (Sect. 4.2). A movie of such a collision process could run backwards and the observer would not notice this, because the reverse process is equally probable (Fig. 10.59). The collision process is reversible. One can also say that the process is time-invariant, i. e. one con exchange t with $-t$ without violating any physical law.

Contrary to this situation, the collision process in Fig. 10.60, where a bullet hits a glass ball that shatters in numerous pieces, is irreversible. The inverse process, where the pieces come again together to form a glass ball, which then emits the bullet, is highly improbable. The following question now arises: Since the glass ball consists of atoms and for each atom a reversible collision process should occur, why is the macroscopic process irreversible?

The answer to this question leads us again to the number of possible realizations of a macroscopic state that depends on a huge number of atoms or molecules. While before the collision the glass ball was at rest and the bullet had a well-defined energy and momentum the final state could have a very large number of possible realizations, because energy and momentum conservation still allows many different flight paths of the fragments as long as the sum of all individual pieces fulfils the conservation laws. The distribution of the fragments, observed for one experiment, represents only one of many possible distributions. At a second experiment under identical conditions, another distribution will be observed although both distributions obey energy and momentum conservation. The entropy increases during this collision process because the process starts from a state with a well-defined realization and ends at a large number of possible realizations. This is the signature of an irreversible process.

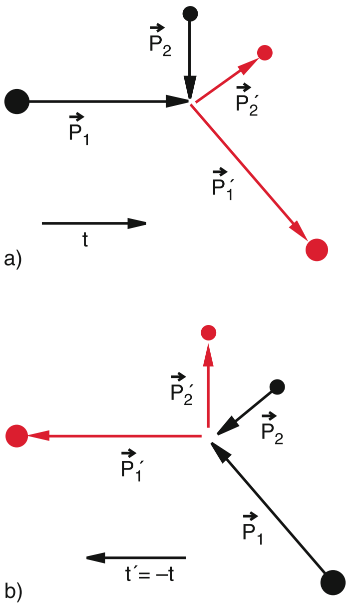


Figure 10.59 Reversible collision process. Reversing the time course of the process inverts the direction of all momentum vectors

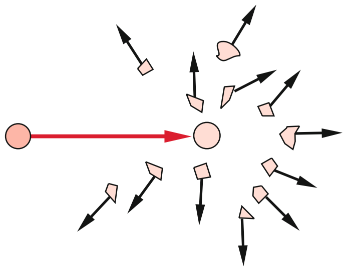


Figure 10.60 Collision of a steel ball with a glas hollow sphere, which bursts into many fragments, as example of an irreversible process

We can define an irreversible process as follows:

- The change of a thermodynamic state of a closed system is irreversible, if the reverse process that leads to the initial state, does not proceed by its own but only with additional energy supply from outside.
- The change of a thermodynamic state is irreversible, if the entropy increases during this process.
- The transition from an ordered state to a non-ordered state (for instance the melting of a crystal) always increases the entropy.

Note, that these statements are only valid for closed systems, which do not interact with their surroundings. For a macroscopic subsystem the entropy can indeed decrease if that of the other subsystems which, interact with the selected one, does increase.

Examples

1. When single crystals are formed out of the molten bath, a non-ordered state (the liquid) is transferred into an ordered state (the single crystal). The entropy S of the crystal is lower than that of the liquid, however, the decrease of S for a subsystem is over-compensated by the increase of S for the surroundings of the crystal.
2. All living beings (plants, animals, humans) decrease their entropy S by building up ordered structures, but at the expense of an increase of S of their surroundings (for example the digestion of food increases S). ◀

In all of these cases the entropy of the total system increases!

Ordered structures therefore cannot be formed in closed systems. Their formation needs open systems far away from thermal equilibrium. This nonequilibrium allows the exchange of energy between the open system and its surroundings, which can induce the decrease of the entropy of the open system.

For all macroscopic closed systems strictly speaking reversible processes cannot occur, because always part of the kinetic energy (even if it is very small) is converted into heat by the unavoidable friction. One of many examples is a swinging pendulum, where the amplitude continuously decreases due to friction by the air. The oscillation to the right will not be exactly reproduced by the following oscillation to the left, because of this amplitude decrease.

The interesting question, why the time has only one direction, can be related to the increase of entropy. The time-derivative $\mathrm{d}S/\mathrm{d}t$ can define a time arrow that allows us to distinguish between past and future [10.12]. For completely reversible processes time reversal would not change the validity of physical phenomena.

10.3.9 Free Energy and Enthalpy

The first and second law of thermodynamics contain the essential statements of thermodynamics. For their application to special problems it is useful to introduce as a new parameter the free energy

$$F = U - T \cdot S\,. \tag{10.102}$$

With the entropy S we can formulate the first law in a more specific form:

$$\mathrm{d}U = \mathrm{d}Q_{\text{rev}} + \mathrm{d}Q_{\text{irr}} + \mathrm{d}W\,. \tag{10.103a}$$

With $\mathrm{d}Q_{\text{rev}} = T \cdot \mathrm{d}S$ and inserting the free energy $F = U - T \cdot S \Rightarrow \mathrm{d}F = \mathrm{d}U - T \cdot \mathrm{d}S - S \cdot \mathrm{d}T$, this becomes

$$\mathrm{d}F = \mathrm{d}Q_{\text{irr}} + \mathrm{d}W - S\,\mathrm{d}T \le \mathrm{d}W - S\mathrm{d}T\,, \tag{10.103b}$$

where the equal sign holds for reversible and the $<$-sign for irreversible processes.

For isothermal processes is $\mathrm{d}T = 0$. This reduces (10.103) to

$$\mathrm{d}F \le \mathrm{d}W \Rightarrow -\mathrm{d}W \le -\mathrm{d}F\,. \tag{10.104a}$$

This means:

- For isothermal processes, the maximum increase of the free energy is equal to the mechanical work supplied to the system.
- The maximum work that a system can deliver during an isothermal process, is equal to the decrease of its free energy.

The difference

$$U - F = T \cdot S$$

is called bound energy. From the relations

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W \quad \text{and} \quad \mathrm{d}F \le \mathrm{d}W$$

follows by subtraction

$$d(U - F) \ge \mathrm{d}Q\,.$$

For isothermal processes the bound energy $U - F$ is completely converted into heat and is therefore not available for mechanical work. This explains the label "bound energy".

The second law of thermodynamics makes the following statement:

For isothermal processes, the change of the bound energy is at least equal to the supplied heat. The increase of the free energy is at most equal to the supplied mechanical energy.

If the isothermal process occurs at a constant volume ($\mathrm{d}V = 0$) no mechanical energy is exchanged, i. e. $\mathrm{d}W = 0$. Then

$$\mathrm{d}F \le \mathrm{d}W = 0\,, \tag{10.104b}$$

which means that the free energy decreases.

A spontaneous isothermal process without exchange of work always proceeds in the direction where the free energy decreases. The entropy S then increases because of

$$T \cdot S = U - F \quad \text{and} \quad U = \text{const}\,.$$

Since most of the processes occurring in nature are irreversible, the free energy of the universe decreases and therefore also the capability to perform mechanical work. All irreversible processes always tend to decrease existing temperature differences, because then the entropy increases (see the examples in the previous section).

Pessimists say: "The universe strives towards its *heat death*. This means, that all temperature differences approach zero, where no longer any chemical and biological processes are possible. However, it will take quite a while until this might happen and furthermore it is not clear, which fate the universe after many billion years will suffer, because it is still an open question, whether the universe represents a closed or an open system."

As the last thermodynamic parameter we will introduce besides the ethalpiy $H = U + p \cdot V$ the **free enthalpy** G (also called *Gibb's chemical potential*) defined by the relation

$$G = U + pV - TS = H - TS \,. \tag{10.105}$$

The total differential of G is

$$\mathrm{d}G = \mathrm{d}U + p \cdot \mathrm{d}V + V \cdot \mathrm{d}p - T \cdot \mathrm{d}S - S \cdot \mathrm{d}T \,. \tag{10.106a}$$

With the first law of thermodynamics

$$\mathrm{d}U + p \cdot \mathrm{d}V = T \cdot \mathrm{d}S \,, \tag{10.106b}$$

this converts to

$$\mathrm{d}G = V \cdot \mathrm{d}p - S \cdot \mathrm{d}T \,. \tag{10.106c}$$

10.3.10 Chemical Reactions

Chemical reactions represent the basis of all living processes. The utilization of food or the decomposition of waste products proceed by chemical reactions. It is therefore of essential interest, under which conditions chemical reactions proceed by themselves and when they need external energy supply for their start. For all reactions that proceed at constant pressure and constant temperature the Gibbs' potential is constant. That is the reason why G is called *chemical potential*. Often several components react with each other. If ν_i moles of the i-th component exist before the reaction, the total free enthalpy is $G = \sum \nu_i \mu_i$ (μ_i = Gibbs potential for one mole of the i-th component).

The mixing of the different components increases the entropy (see (10.100)) by the amount

$$\Delta S_\mathrm{m} = -R \cdot \sum_i \nu_i \ln x_i \,, \tag{10.107}$$

where $x_i = \nu_i / \sum \nu_i$ is the mole fraction of the i-th component.

A chemical reaction between the molecules A which results in the formation of molecules B is then described by

$$\sum_{i=1}^{k} \nu_i \mathrm{A}_i \rightarrow \sum_{j=k+1}^{p} \nu_j \mathrm{B}_j \,. \tag{10.108}$$

The number of moles can change by the reaction. For instance for the reaction

$$2\mathrm{H}_2 + \mathrm{O}_2 \rightarrow 2\mathrm{H}_2\mathrm{O}$$

is $\nu_1 = 2$; $\nu_2 = 1$ and $\nu_3 = 2 \rightarrow \sum \nu_i \neq \sum \nu_j$.

If the number ν_i of moles for the i-th component changes by $\Delta\nu_i$, the free enthalpy G changes for processes with $\Delta p = \Delta T = 0$ according to (10.106a) by

$$\begin{aligned} \Delta G &= \sum \Delta\nu_i \mu_i - T \cdot \Delta S_\mathrm{m} \\ &= \sum \Delta\nu_i \mu_i - RT \cdot \sum (\nu_i + \Delta\nu_i) \ln x_i' \,, \end{aligned} \tag{10.109a}$$

where $x_i' = (\nu_i + \Delta\nu_i) / \sum (\nu_i + \Delta\nu_i)$.

When a reaction proceeds by its own (without external energy supply), its free enthalpy must decrease; i. e. $\Delta G < 0$. Equilibrium is reached if G becomes minimal.

If the number of moles does not change during the reaction, one can define a chemical equilibrium constant K by

$$K = exp\left[\sum \nu_i G_i / RT\right] \,.$$

The change of the free enthalpy can then be written as

$$\Delta G = RT \left[\ln K + \sum \xi_i \ln \nu_i\right] \,, \tag{10.109b}$$

where ξ_i is the fraction of the component i that reacts.

When the quantity of all components is one mole ($\nu_i = 1$) Eq. 10.109b can be reduced to

$$\Delta G(1\,\mathrm{mol}) = RT \ln K \,. \tag{10.109c}$$

The equilibrium constant K is therefore directly related to the change ΔG of the chemical potential G.

10.3.11 Thermodynamic Potentials; Relations Between Thermodynamic Variables

The thermodynamic variables: internal energy U, free energy F, Gibbs' potential G and enthalpy H are also called **thermodynamic potentials**. The advantage of their introduction is based on the fact that all thermodynamic variables can be written as partial derivatives of these potentials. The total differentials of the potentials are

$$
\begin{aligned}
\mathrm{d}F &= \left(\frac{\partial F}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial F}{\partial T}\right)_V \mathrm{d}T \\
\mathrm{d}U &= \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V + \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S \\
\mathrm{d}G &= \left(\frac{\partial G}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial G}{\partial T}\right)_p \mathrm{d}T \\
\mathrm{d}H &= \left(\frac{\partial H}{\partial S}\right)_p \mathrm{d}S + \left(\frac{\partial H}{\partial p}\right)_S \mathrm{d}p \;,
\end{aligned}
$$

where the lower index at the brackets denotes the quantity that is kept constant. The comparison with the equations derived in the previous sections

$$
\begin{aligned}
\mathrm{d}F &= -p\mathrm{d}V - S\mathrm{d}T \;, && (10.103)\\
\mathrm{d}U &= -p\mathrm{d}V + T\mathrm{d}S \;, && (10.88)\\
\mathrm{d}G &= V\mathrm{d}p - S\mathrm{d}T \;, && (10.106c)\\
\mathrm{d}H &= \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p && (10.76)\\
&= \mathrm{d}Q + V\mathrm{d}p
\end{aligned}
$$

gives the following relations between the thermodynamic variables and the potentials.

For the entropy we obtain

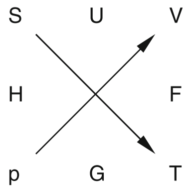
$$S = -\left(\frac{\partial G}{\partial T}\right)_p = -\left(\frac{\partial F}{\partial T}\right)_V \;, \tag{10.110a}$$

and for the pressure

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_S \;, \tag{10.110b}$$

while the relation for the volume V is

$$V = \left(\frac{\partial G}{\partial p}\right)_T = \left(\frac{\partial H}{\partial p}\right)_S \;. \tag{10.110c}$$



In the "Guggenheim Square", each thermodynamic potential can be placed in such a way, that the results of their derivatives can be immediately seen by the following procedure: One goes in the scheme from the potential symbol to the derivative variable and from there to the opposite corner on the diagonal. If this way on the diagonal is in the direction of the arrow, the result is positive, if it is opposite to the arrow, it is negative.

Examples

$$\left.\frac{\partial U}{\partial S}\right|_V = T \;; \qquad \left.\frac{\partial G}{\partial T}\right|_p = -S \;;$$

$$\left.\frac{\partial F}{\partial V}\right|_T = -p \;; \qquad \left.\frac{\partial H}{\partial p}\right|_V = V \;.$$

An example for the application of thermodynamic potentials is given in Sect. 10.4.2.

10.3.12 Equilibrium States

The thermodynamic potentials play a comparable role in thermodynamics as the mechanical potential E_p that determines the forces $\boldsymbol{F} = -\mathbf{grad}\, E_\mathrm{p}$ which governs the motion of particles. In a similar way the gradient of the thermodynamic potentials keeps the chemical processes running until the minimum of the potentials is reached.

A system is at equilibrium, if without the action of external influences the state of the system does not change. If the state of a system changes due to external action, but returns to its original conditions after the external action ends, the equilibrium is stable. If, however, the system further removes from equilibrium, even after the termination of the external influence, the equilibrium is unstable. A mechanical example is a mass m which is fixed to a rigid rod that can rotate around a horizontal axis. At the minimum of the potential energy, where the mass is just below the horizontal axis the mass is in a stable equilibrium. When the mass is at its maximum height vertically above the horizontal axis, the equilibrium is unstable. Every slight perturbation brings m downwards. In a thermodynamic system, the thermodynamic potentials take the role of the potential energy in our example. We will illustrate this for several specific processes.

We assume a thermodynamic system with the internal energy U and the volume V at the temperature T and the pressure p. An arbitrary change of the conditions of the system is described by the differentials $\mathrm{d}U$, $\mathrm{d}V$, $\mathrm{d}T$ and $\mathrm{d}p$. If the change is reversible, the work $\mathrm{d}W = -p \cdot \mathrm{d}V$ performed by the system during an adiabatic expansion, causes a decrease $\mathrm{d}U = \mathrm{d}W$ of the internal energy.

For irreversible processes, the system loses heat which causes a decrease of the total energy. Equilibrium is reached, if no further irreversible process is possible. Since for all irreversible processes with constant volume the entropy increases, the equilibrium condition can be formulated as

$$\mathrm{d}S \le 0 \;. \tag{10.111}$$

For all possible processes, which bring a thermodynamic system away from equilibrium the entropy must decrease.

With other words:

A closed system with constant volume is in an equilibrium state if its entropy is maximal.

The thermodynamic potentials of an equilibrium state have their minimum value. This can be seen as follows:

With the change of entropy $\mathrm{d}S = \mathrm{d}Q/T$ we obtain from the first law of thermodynamics (10.71)

$$\mathrm{d}U + p \cdot \mathrm{d}V - T \cdot \mathrm{d}S = 0\,. \tag{10.112}$$

For isothermal-isochoric processes is $\mathrm{d}V = 0$ and $T = \text{const.}$ From (10.111) it follows: $\mathrm{d}S \le 0$. Inserting this into (10.112) gives

$$\mathrm{d}(U - T\mathrm{d}S) \ge 0 \to \mathrm{d}F \ge 0\,. \tag{10.113}$$

Under isothermal and isochoric conditions a system has reached its equilibrium state, if the free energy F has its minimum value.

Under isothermal-isobaric conditions ($\mathrm{d}T = 0$ and $\mathrm{d}p = 0$) equilibrium is reached if

$$\mathrm{d}U + pdV - T\mathrm{d}S = d(U + p \cdot V - T \cdot S) = \mathrm{d}G = 0\,,$$

because for all processes that drive the system away from equilibrium $\mathrm{d}G > 0$, as can be seen in an analogous way as the arguments above for $\mathrm{d}F > 0$.

Under isothermal-isobaric conditions a system is in an equilibrium state, if the Gibbs' potential is minimal.

In a similar way it can be proved, that for adiabatic-isobaric processes ($\mathrm{d}Q = 0$ and $\mathrm{d}p = 0$) the system is in an equilibrium state if the enthalpy $H = U + p \cdot V$ is minimal.

For adiabatic-isochoric processes ($\mathrm{d}Q = 0$ and $\mathrm{d}V = 0$) the internal energy $< U$ must be minimal at equilibrium.

All reactions that are possible without external interaction must start from states far away from equilibrium.

Therefore the thermodynamic treatment of chemical reactions and biological processes is based on the description of systems that are not at thermodynamic equilibrium.

10.3.13 The Third Law of Thermodynamics

We have seen in Sect. 10.3.7 that the entropy S is only determined apart from an additive constant S_0. We will now show, that for $T \to 0$

$$\lim S(T) = 0\,.$$

This fixes the constant $S_0 = S(T = 0) = 0$.

For the proof we start with the free energy $F = U - T \cdot S$. Because of (10.110a) this can be also written as

$$F = U + T\left(\frac{\partial F}{\partial T}\right)_V\,. \tag{10.114a}$$

We regard an isothermal chemical reaction where the system starts with the free energy F_1 and ends at F_2. The change $\Delta F = F_1 - F_2$ is

$$\Delta F = \Delta U + T\left(\frac{\partial}{\partial T}\Delta F\right)_V\,. \tag{10.114b}$$

For $T > 0$ the changes ΔF and ΔU differ, but for $T \to 0$ the difference approaches zero

$$\lim(\Delta F - \Delta U) = 0\,. \tag{10.114c}$$

Nernst observed that with decreasing temperature the derivatives $\mathrm{d}(\Delta F)/\mathrm{d}T$ and $\mathrm{d}(\Delta U/\mathrm{d}T)$ decreased and that they approached zero for $T \to 0$. This means that the curves $\Delta F(T)$ and $\Delta U(T)$ come towards each other with horizontal slopes (Fig. 10.61).

Nernst therefore postulated that also for the general case

$$\lim_{T\to 0}\left(\frac{\partial \Delta F}{\partial T}\right)_V = 0 \quad \text{and} \tag{10.115a}$$

$$\lim_{T\to 0}\left(\frac{\partial \Delta U}{\partial T}\right)_V = 0\,. \tag{10.115b}$$

because of (10.114a) it follows then

$$\lim_{T\to 0}\left(\frac{\partial U}{\partial T} - \frac{\partial F}{\partial T}\right) = 0\,. \tag{10.115c}$$

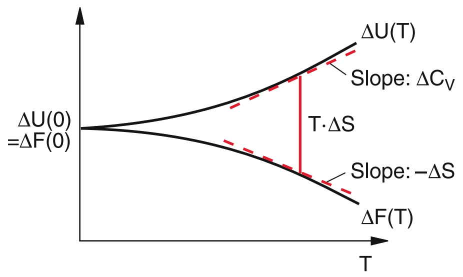


Figure 10.61 Nernst's theorem: Temperature course of $\Delta U(T)$, $\Delta F(T)$ near the absolute zero temperature

With

$$\left(\frac{\partial}{\partial T}\Delta F\right)_V = -\Delta S$$

$$\Rightarrow \lim_{T\to 0} \Delta S(T) = 0 \,.$$

This means that at sufficiently low temperatures reactions in pure condensed substances proceed always without changes of entropy i. e. $\Delta S = 0$. These reactions therefore proceed reversible.

Investigating the dependence $S(T)$ of condensed substances (liquified or solid gases) at very low temperatures, one finds indeed that the entropy does not depend on the crystal modification or on the specific substance as long as it is a pure substance, i. e. not a mixture of different substances. This suggests that the entropy of all pure substances approaches for $T \to 0$ the same value. Quantum theoretical considerations show (see Vol. 3) that for all pure substances the entropy S approaches zero for $T \to 0$.

$$\lim S(T) = 0 \,. \qquad (10.116)$$

The relations (10.115)–(10.116) are named the **3rd law of thermodynamics** or **Nernst's Theorem**.

Regarding the statistical interpretation of the entropy $S = k{\cdot}\ln W$ the 3rd law can be also formulated as:

> The thermodynamic equilibrium state at $T = 0$ is a state with maximum order, which has only one possible realization with $P = 1$. The entropy is then $S = 0$.

Note: The statement $S(T = 0) = 0$ is only valid for pure substances. Mixed substances (for example mixed crystals) have even for $T = 0$ an entropy $S > 0$, called the mixing entropy (see Sect. 10.3.7).

The definition $S_0 = 0$ for the zero point of the entropy allows the determination of the absolute value of $S(T > 0)$.

For one mole one obtains

$$S(T) = \int_0^T \frac{\mathrm{d}Q_{\text{rev}}}{T'} = \int_0^T \frac{C(T')}{T'}\mathrm{d}T' \,. \qquad (10.117)$$

In order to fulfil the condition $\lim S(T \to 0) = 0$ the specific heat $C(T)$ must converge sufficiently fast towards zero for $T \to 0$ This is indeed observed experimentally (see Sect. 10.1.10). More detailed measurements show that for solids at very low temperatures $C(T) \propto T^3$ (see Vol. 3). This is indeed observed experimentally. The entropy $S(T)$ is then, according to (10.117), also proportional to T^3.

Remark. The first and second law of thermodynamics could be formulated as the impossibility to realize a perpetuum mobile of the first resp. the second kind. Also the third law can be formulated as an impossibility statement:

> It is impossible to reach the absolute zero $T = 0$ of the thermodynamic = absolute temperature scale.

This can be seen as follows by an experimental argument.

If one tries to reach experimentally the absolute zero $T = 0$ this could be only realized by an adiabatic process, because every cooling process where heat is exchanged, requires a system that is colder than the system to be cooled.

During an adiabatic process no entropy change occurs because $\mathrm{d}Q = S \cdot \mathrm{d}T = 0$. For an adiabatic isobaric process is

$$\mathrm{d}S = \frac{\partial S}{\partial V}\mathrm{d}V + \frac{\partial S}{\partial T}\mathrm{d}T = 0 \,.$$

This gives

$$\mathrm{d}T = -\frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_p}\mathrm{d}V \,. \qquad (10.118a)$$

For the partial derivative applies

$$\frac{\partial S}{\partial T} = \lim_{\Delta T\to 0}\left(\frac{\Delta S}{\Delta T}\right)_p = \lim_{\Delta T\to 0}\left(\frac{1}{T}\,\frac{\Delta Q}{\Delta T}\right)_p = \frac{C_p}{T} \,,$$

and with (10.110a) and (10.114a) it follows

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right) .$$

For $T \to 0$ is with (10.115c)

$$\frac{\partial F}{\partial T} \to \frac{\partial U}{\partial T} = C_V \,,$$

and we obtain from (10.118a)

$$\mathrm{d}T = -T \cdot \frac{C_V}{C_p} = -T \cdot \frac{C_V}{C_V + R} \,. \qquad (10.118b)$$

This shows that for $T \to 0$ also $\mathrm{d}T \to 0$. The absolute zero $T = 0$ for the temperature can be therefore not reached.

10.3.14 Thermodynamic Engines

When the Carnot cycle in Fig. 10.51 is traversed into the opposite direction, i. e. counterclockwise, the corresponding engine uses mechanical work to transport heat from the cold to the warmer part of a system (Fig. 10.62). This has technical applications in refrigerators and heat pumps.

10.3.14.1 Refrigerators

In refrigerators the heat Q_2 is extracted at a temperature T_2 from the volume V_2 that should be cooled and a larger heat energy $Q_1 = Q_2 + W$ is transported to a warmer environment. This

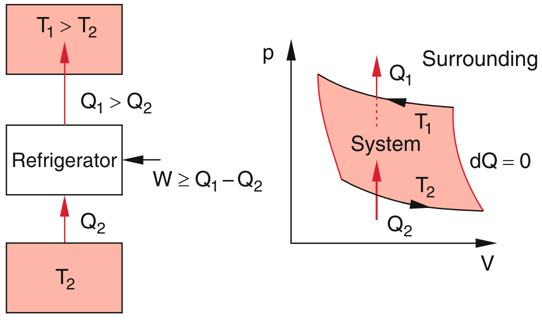


Figure 10.62 Principle of a refrigeration machine and heat pump based on the inverse Carnot's cycle

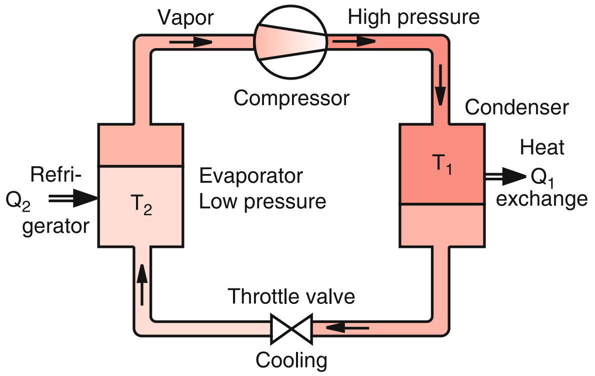


Figure 10.63 Technical realization of a refrigerator

demands the supply of mechanical or electrical work W to the system. We have neglected all energy losses by friction or heat conduction. The coefficient of performance

$$K_{\mathrm{ref}} = \frac{Q_2}{W} = \frac{\mathrm{d}Q_2/\mathrm{d}t}{\mathrm{d}W/\mathrm{d}t} \tag{10.119a}$$

gives the ratio of cooling rate $\mathrm{d}Q_2/\mathrm{d}t$ and power input $\mathrm{d}W/\mathrm{d}t$.

From the efficiency η of the Carnot engine we obtain for the inverse Carnot cycle the coefficient of performance for the refrigerator the relation

$$K_{\mathrm{ref}} = 1/\eta = \frac{T_2}{T_1 - T_2} \,. \tag{10.119b}$$

This shows that a refrigerator works more efficiently for small temperature differences $(T_1 - T_2)$ between the cooled volume and the warmer environment.

10.3.14.2 Heat Pumps

Heat pumps use the heat reservoir of the environment (air, ground) for heating water for floor heating of rooms or for swimming pools. The basic principle is the same as that of refrigerators. Heat is transported from a cold to a warmer volume. This demands the supply of mechanical or electrical energy. The useful energy is the heat transported to the warmer volume. Therefore the coefficient of performance is defined as in (10.119b)

$$K_{\mathrm{hp}} = \frac{Q_1}{W} = \frac{\mathrm{d}Q_1/\mathrm{d}t}{\mathrm{d}W/\mathrm{d}t} = \frac{T_1}{T_1 - T_2} \,. \tag{10.120}$$

Contrary to the efficiency $\eta < 1$ of the Carnot engine the coefficient $K_{\mathrm{hp}} = 1/\eta$ is larger than 1! It increases with decreasing temperature difference $\Delta T = T_1 - T_2$.

Example

A heat pump used for heating a swimming pool takes the heat from a river with a water temperature of 10 °C = 283 K and heats the swimming pool to a temperature of T = 27 °C = 300 K. The maximum coefficient of performance is then $K_{\mathrm{hp}} = 17.6$. One therefore saves a factor of 17.6 of heating costs compared with the direct heating of the swimming pool. In this idealized example all other losses of the heat pump system have been neglected. Realistic values, taking into account all losses, are $K_{\mathrm{hp}} = 5$–10. ◀

For practical applications heat pumps and refrigerators operate with special cooling liquids, which are not permanent gases but evaporate and condense during one cycle. This is illustrated schematically in Fig. 10.63. The heat Q_2 is transported from the room to be cooled to the liquid cooling agent at the low temperature T_2 in the evaporator. The resulting temperature increase of the cooling liquid results in the evaporation of the liquid . In the condenser the heat Q_1 is extracted by a heat exchanger from the vapour at high pressure. This causes the condensation of the vapour. The liquid under high pressure expands through a throttle valve, which decreases its temperature and is again used for heat extraction from the volume to be cooled.

10.3.14.3 Stirling Engine (Hot Air Engine)

The Stirling engine uses air as working agent, which is periodically expanded and compressed in a cycle of two isotherms and two isochors (Fig. 10.64a). The red arrows indicate the heat exchange between the environment (white) and the system (red). During the isothermal expansion 1 → 2 the heat Q_1 is supplied at the temperature T_1 to the system. During the isochoric cooling 2 → 3 the temperature drops to $T_2 < T_1$. Now isothermal compression 3 → 4 occurs where the heat Q_2 is transported to the environment. Finally the isochoric compression 4 → 1 with heat supply Q_4 brings the system back to its original state 1. The heat Q_4 is necessary to increase the temperature from T_2 to $T_1 > T_2$. Since no work is performed during the isochoric processes, the energy balance demands

$$Q_2 = -Q_4 = C_v \Delta T \,.$$

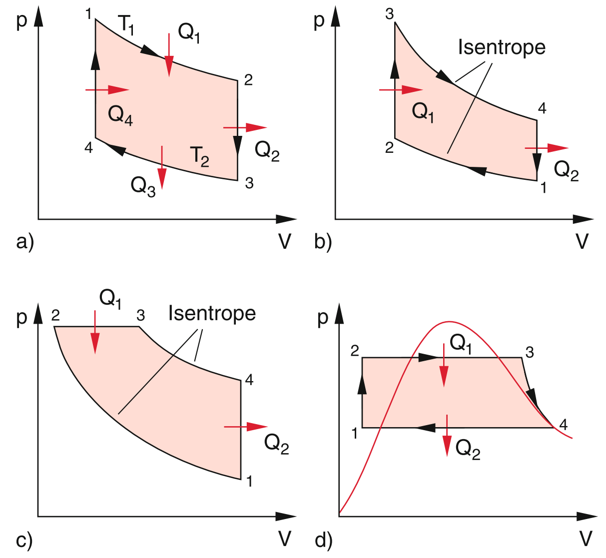


Figure 10.64 Cycle of **a** Stirling engine, **b** Otto engine (gasoline engine), **c** Diesel engine, **d** steam engine. The *red curve* gives the vapor pressure $p(V)$ of water vapor

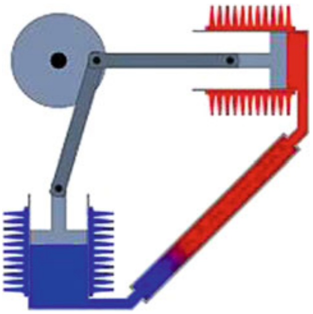


Figure 10.65 Stirling engine with two pistons and two cylinders

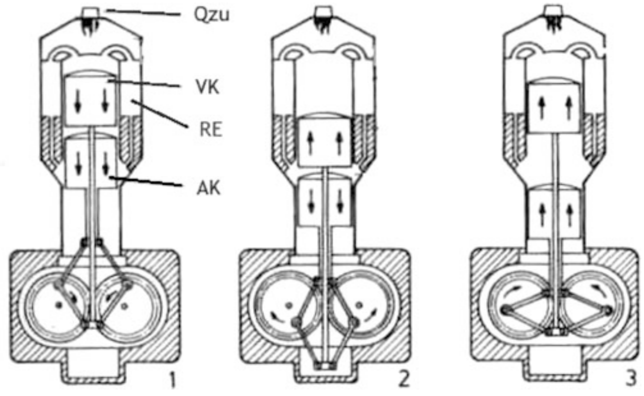


Figure 10.67 Stirling motor with two pistons in one cylinder

When the extracted heat Q_2 can be stored and resubmitted to the system during the process 4 → 1, the system does not loose energy during a cycle and the efficiency of the Stirling process would be comparable to that of the Carnot cycle.

This can be technically realized, at least approximately, by using two pistons, the working piston and the displacer piston in two different cylinders: a hot cylinder and a cold one (Fig. 10.65). The two pistons are driven by the same crankshaft with a 90° phase shift against each other. The two cylinders are connected by a pipe filled with an energy storage material (regenerator). When the piston compresses the gas in the hot cylinder the hot gas flows from the hot to the cold cylinder through the connecting pipe and heats up the storage material. In the next step the cold cylinder is compressed and the cold gas flowing through the pipe is heated by the storage material. About 80% of the energy exchanged during one cycle can be stored in the regenerator. In the diagrams of Fig. 10.66 the time sequence of the total volume, the hot and the cold volume are depicted for the Stirling engine, used as heat engine and as heat-pump.

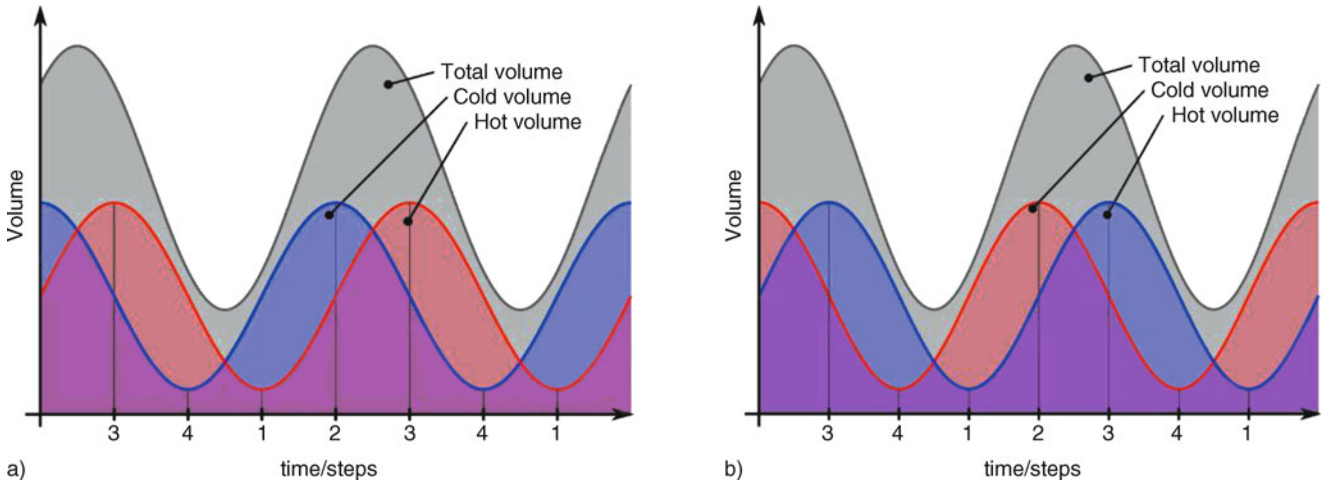


Figure 10.66 Volume-diagram $V(t)$ of a Stirling engine: *Left diagram:* used as heat engine, *right diagram:* used as heat pump

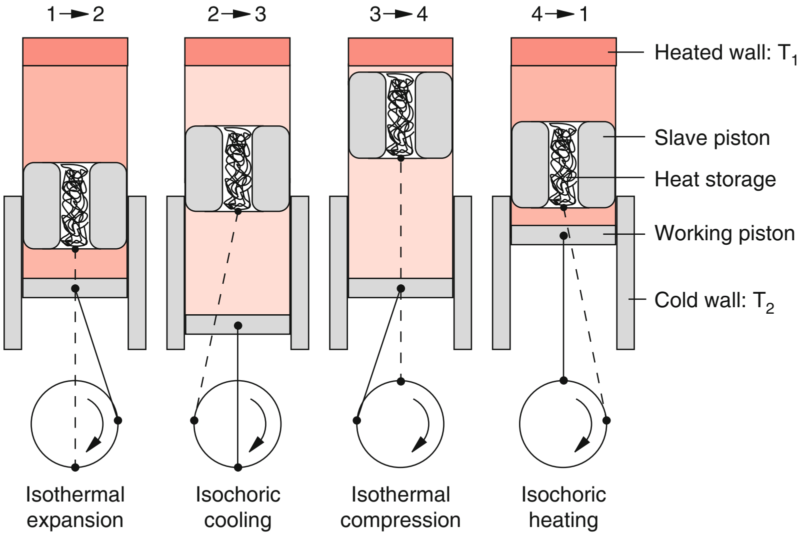


Figure 10.68 Positions of working piston and slave piston during the four sections of a Stirling cycle. The energy necessary for the operation of the engine is supplied by heating the upper wall

Another version of the Stirling engine uses only one cylinder but still two pistons. The displacer piston presses the air periodically into the upper hot volume and in the next step into the lower cold volume. During these processes the air streams through a hole in the piston which is filled with metal cuttings. They are heated during the passage 2 → 3 of the hot air and they transfer their heat during the passage 4 → 1 to the cold air.

In Fig. 10.67 and 10.68 the different steps durng a working cycle are illustrated for a Stirling engine with one cylinder and two pistons.

10.3.14.4 The Otto-Engine

The Otto-engine is used in many cars as effective drive. In the p-V-diagram it passes a cycle consisting of two isentropic and two isochoric processes (Fig. 10.64b). In the state 1 the gasoline-air mixture is sucked in and compressed. At point 2 the ignition oocurs where the mixture explodes so fast that the volume does not change essentially. The heat Q_1 released at the explosion is fed into the system and increases the pressure very fast up to point 3. Now an isentropic expansion (no further heat supply) follows until point 4 is reached. Here the exhaust valve is opened and the exhaust gas streams into the exhaust pipe. This causes a decrease of the pressure, a release of the heat Q_2 and the restitution of state 1.

The efficiency η depends on the compression ratio V_1/V_2. One obtains (see Probl. 10.12)

$$\eta = 1 - \frac{1}{(V_1/V_2)^{\kappa-1}}\,, \tag{10.121}$$

where $\kappa = C_p/C_v$ is the specific heat ratio.

Example

$V_1/V_2 = 9$ and $\kappa = 9/7 \rightarrow \eta = 0.44$. Note, that the real efficiency is only about 0.3–0.35 due to energy losses by friction and heat conduction. ◀

10.3.14.5 Diesel Engine

For the Diesel engine the cycle in the p-V-diagram (Fig. 10.64c) consists of two isentropic, one isobaric and one isochoric process. In the state 1 air is sucked in and the volume is compressed until point 2 is reached. The compression ratio is much larger (up to 1:20) as in the Otto-engine. During this compression the temperature rises to 700–900 °C, which is above the ignition termperature of Diesel-fuel. Now Diesel fuel is injected, which does not explode as in the Otto-engine but burns more slowly (there is no electrical ignition). This causes the air-fuel-mixture to expand isobaric until point 3 is reached, where the combustion stops. The volume now further expands isentropically to the point 4, where the exhaust valve opens and the pressure suddenly drops to the atmospheric pressure outside. Here the intial point 1 is reached again.

The efficiency of the Diesel engine is higher thatn that of the Otto-engine because of the higher compression ratio. Its theoretical value is about 0.55 but due to unavoidable losses the real enegines only reach about 0.45. The disadvantage of the Diesel engine is the higher output of NO_x gases and soot particles.

10.3.14.6 Steam Engine

In a Steam Engine the cyclic process (Clausius–Rankine Process) consists of two isentropic and two isobaric parts (Fig. 10.64d). In the initial state 1 the system contains water. A pump increases the pressure at a constant volume isentropic from p_1 to p_2. From point 2 to 3 heat is supplied at constant pressure, which causes the volume to expand and increases the temperature above the boiling point of water. The hot vapour drives a piston during the isentropic expansion and the system reaches point 4 where the temperature is cooled down, the vapour condenses and the heat Q_2 is transferred to the surrounding. Now the initial point 1 is reached again. Mechanical work is performed on the part 3 → 4.

The red curve in Fig. 10.64d gives part of the Van der Waals curve $p(V)$ for water vapour (see Sect. 10.4.1). Inside this curve water and vapour can exist simultaneously, in the region left of the curve only the liquid phase exists, to the right hand of the curve only the vapour phase.

10.3.14.7 Thermal Power Plants

In thermal power plants, heat is produced by burning fossil fuels, such as coal, oil, wood or gas, or by fission of atomic nuclei. For fossil fuels the heat comes from the reaction heat that is released during the oxidation of atoms or molecules and is due to the different chemical binding energies of reaction partners and reaction products. The essential part of this energy stems from the oxidation of carbon atoms C to CO_2. The produced heat is 8 kcal = 33 kJ for 1 g C. The fission of 1 g Uranium produces an energy of $2.5 \cdot 10^7$ kJ. This is $7.5 \cdot 10^5$ times more!

The heat produced in thermal power plants is converted into the generation of hot water vapour under high pressure, driving turbines that propel electric generators for the production of electric energy. The maximum efficiency depends, according to the second law, on the initial temperature T_1 and the final temperature T_2.

The initial temperature is limited by technical conditions (heat and pressure resistance of the hot vapour tank. Typical values are between 600 and 700 °C. Only for the high temperature reactors, temperatures above 800 °C are realized.

For the choice of the final temperature T_2 two options exist:

1. One chooses $T_2 = 100\,°\mathrm{C}$ (condensation temperature of water) and uses the rest energy of the hot water for heating of houses. The efficiency for the conversion of heat into mechanical (or electric) energy is then for an initial temperature of $T_1 = 600\,°\mathrm{C} = 873\,\mathrm{K}$: $\eta = 500/873 = 0.57$. In addition the heat ΔQ of the hot water can be delivered to houses nearby the power station.
2. The final temperature of the water vapour is chosen as $T_2 = 30\,°\mathrm{C}$. In order to avoid condensation one has to lower the pressure below the atmospheric pressure by pumping the expanding volume. This increases the efficiency to $\eta = 570/873 = 0.65$. The work needed for evacuating the expanding volume against the external pressure is smaller than the additional energy gain due to the lower final temperature.

In case 1 one does not win the total energy of the hot water ΔQ compared to case 2 because here one could use the extra energy due to the higher efficiency $\eta_2 = (600 - 30)/873$ to transport electric energy for heating. The increase of the efficiency for case 2 compared to case 1 is

$$\begin{aligned}\eta_2 - \eta_1 &= (70/873 - \varepsilon)\Delta Q\\ &= (0.19 - \varepsilon)\Delta Q\,,\end{aligned}$$

where $\varepsilon \cdot \Delta Q$ is the mechanical work of the pump, necessary to evacuate the volume down to a pressure that is equal to the vapour pressure of water at $T = 30\,°\mathrm{C}$.

10.4 Thermodynamics of Real Gases and Liquids

Up to now, we have discussed the thermodynamics of ideal gases, where the interaction between the atoms of the gas has been neglected.

We will now discuss, which rules have to be generalized and which are still valid without restrictions, when we treat the thermodynamics of real atoms and molecules including their size and their mutual interactions.

While ideal gases remain gaseous at any temperature, real gases condense below their boiling temperature and they can even become solids below the melting temperature. In this section, we will investigate what are the conditions for transitions between the different phases solid, liquid and gaseous and what are the equilibrium conditions of the different phases.

10.4.1 Van der Waals Equation of State

At very high pressures, the density of atoms or molecules becomes so high, that the internal volume of the molecules (also called covolume) cannot be neglected compared with the free volume V that is available for the molecules.

When we describe the atoms as rigid balls with radius r, two atoms cannot come closer to each other than at a minimum distance $d = 2r$. If one atom is in the volume V the other atoms cannot penetrate into the volume $V_{\mathrm{forbidden}} = (4/3)\pi d^3 = 8V_{\mathrm{a}}$, where V_{a} is the volume of one atom in the model of rigid balls (Fig. 10.69a). Furthermore the centres of all balls must have the minimum distance $d = r$ from the walls of the container.

Assume there were only two atoms in the cubic volume $V = l_3$. The volume available for the second atom is then

$$V_2 = (L - 2r)^3 - 8V_{\mathrm{a}} \quad \text{(Fig. 10.69b)}\,.$$

A third atom could only be found in the volume

$$V_3 = (L - 2r)^3 - 2 \cdot 8V_{\mathrm{a}}\,,$$

and the rest volume available for the n-th atom is then

$$V_n = (L - 2r)^3 - (n - 1) \cdot 8V_{\mathrm{a}}\,.$$

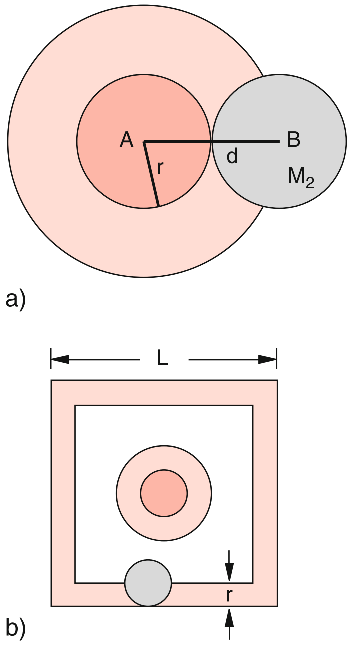


Figure 10.69 Illustration of the co-volume. **a** The center of B cannot be in the *bright red circle*. **b** Forbidden volume (*bright red*) of molecule B in the volume L^3 with one atom A

An estimation of the real sizes shows, however, that, for example, for $N = 10^{20}$ atoms in a volume with $L = 0.1\,\text{m}$ the forbidden volume at the wall is with $r \approx 10^{-10}\,\text{m}$ completely negligible compared to the internal volume $N \cdot V_a$ of the N atoms in the volume V. The average over all N atoms gives then for the mean volume available to each atom

$$\begin{aligned}V &= (L-2r)^3 - \frac{1}{N}\sum_{n=1}^{N}(n-1)\cdot 8V_a\\ &= L^3 - 6r\cdot L^2 - 6r^2\cdot L + 8r^3 - 4NV_a\\ &\approx L^3 - 4NV_a \quad \text{for} \quad N \gg 1\ .\end{aligned} \tag{10.122}$$

because the 2nd, 3rd and 4th term are neglible compared to the 1st and last term.

We therefore have to replace in the general gas-equation (10.21) the volume V by the reduced volume

$$V - b = L^3 - 4\cdot N\cdot V_a \quad \text{with} \quad b = 4\,\text{N}\cdot V_a\ .$$

For the situation $N \gg 1$ the volume $V_{\text{available}}$ available to the N atoms in a volume V is reduced by 4 times the total atomic volume $N \cdot V_a = N\cdot(4/3)\pi\cdot r^3$.

The next question concerns possible corrections for the pressure p due to the attractive or repulsive forces between the atoms. At low temperatures or for high densities the interaction between the atoms can be no longer neglected. The total force on a selected atom resulting from the interaction with all other atoms cancels for atoms inside a liquid or a gas volume, because the interaction forces are in the average uniformly distributed over all directions (Fig. 10.70a) (see the similar discussion about the surface tension in Sect. 6.4.1). At the boundaries between liquid and gas or between gas and wall, the interaction forces are no longer uniformly distributed but are directed only into the half space of the medium. They do not cancel and the total force F_a on one atom is not zero but is proportional to the number density n_a of atoms in the half-sphere shown in Fig. 10.70b, which means to the density $\varrho = M/V$, where M is the total mass of the gas in the volume V.

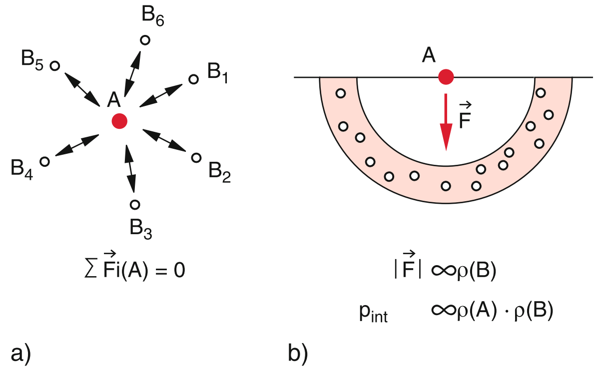


Figure 10.70 Illustration of the internal pressure. Forces on an atom A **a** inside a gas, **b** at the boundary between wall and gas

The amount of the total force $F = |\sum \boldsymbol{F}_i| \propto n_a \cdot F_a$ onto all n_a atoms is therefore proportional to $n_a^2 \propto \varrho^2$. The force is directed towards the interior of the gas and causes an intrinsic pressure

$$p_b = a\cdot\varrho^2 \propto a/V^2\ ,$$

which acts onto the atoms in addition to the external pressure p.

Taking into account this intrinsic pressure and the co-volume $b = 4N \cdot V_a$ the general gas equation for one mole of an ideal gas

$$p\cdot V_M = R\cdot T$$

has to be modified to the **van der Waals-equation** of real gases

$$\left(p + \frac{a}{V^2}\right)\cdot(V_M - b) = R\cdot T\ , \tag{10.123}$$

where the constant $b = 4\cdot N_a\cdot V_a$ gives 4-times the internal volume of the N_A atoms in the mole volume V_M.

The progression of the function $p(V)$ at constant T for a real gas, described by (10.123), depends on the constants a and b. In Fig. 10.71 the isotherms of CO_2 are shown for different temperatures. They confirm, that for high temperatures ($E_{\text{kin}} \gg |E_{\text{pot}}|$) the curves are similar to those of an ideal gas, but for low temperatures closely above the condensation temperature they deviate strongly.

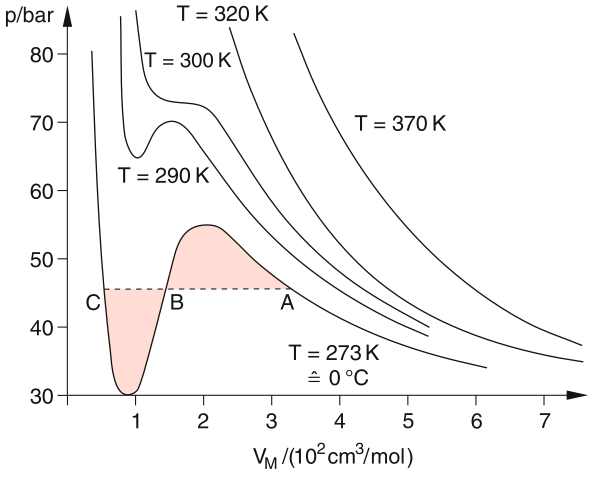


Figure 10.71 Van-der-Waals-isotherms of CO_2 for different temperatures

Solving (10.123) for p at constant T gives a polynomial $p(V)$ of third order, which shows for low temperatures a maximum and a minimum (Fig. 10.71). How looks the comparison of this theoretical curve with experimental results? Let's see this for the example of CO_2.

If one mole of CO_2 is compressed at the temperature $T = 0\,°\mathrm{C}$ starting at low pressures one finds in deed that the curve $p(V)$ follows quite nicely the theoretical curve until the point A in Fig. 10.71. Further compression does **not** increase the pressure p, which stays constant until the point C is reached where the pressure shows a steep increase and follows again the van der Waals curve.

The reason for this strange behaviour is the condensation of the CO_2 vapour that starts at the point A. On the way from A to C the fraction of the liquid phase continuously increases until in C the vapour is completely liquefied. On the way from C to smaller volumes, the pressure increases steeply because of the small compressibility of the liquid. Between A and C gas and liquid can both exist (co-existence range).

For a quantitative description of the condensation process we must discuss the different phases (aggregation states) in more detail.

10.4.2 Matter in Different Aggregation States

The different aggregation states of matter (solid, liquid gas) are called its phases. In this section we will discuss, under which conditions a phase transition solid → liquid, liquid → gas or solid → gas can occur and when two or three phases can exist side by side.

10.4.2.1 Vapour Pressure and Liquid–Gas Equilibrium

When a liquid is enclosed in a container which it fills only partly, one finds that part of the liquid is vaporized and in the volume above the liquid surface a vapour phase has established at a vapour pressure $p_s(T)$ that acts upon the walls and the liquid surface. The dependence of the vapour pressure $p_s(T)$ on the temperature can be measured with the pressure tank shown in Fig. 10.72 that is equipped with a thermometer and a manometer.

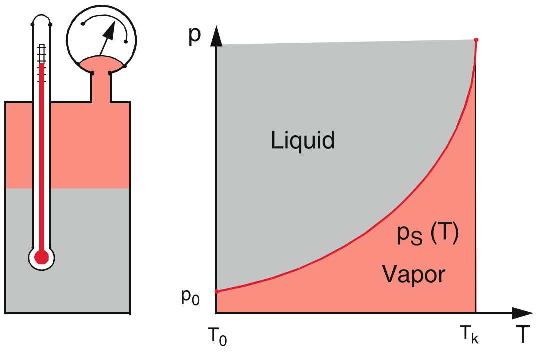


Figure 10.72 Measurement of vapor pressure curve $p_s(T)$

At a constant temperature T a constant saturation vapour pressure $p_s(T)$ is present where the liquid and the gaseous phase can exist simultaneously under stable conditions.

The explanation given by molecular physics is based on the kinetic gas theory (Sect. 7.4). Similar to the situation in a gas also the molecules in a liquid show a velocity distribution with kinetic energies that follow the Maxwell–Boltzmann distribution. The fastest molecules in the high energy tail of the velocity distribution can leave the liquid, if their energy is larger than the surface tension of the liquid (See Sect. 6.4). On the other hand, when molecules in the gas phase hit the liquid surface, they can enter into the liquid.

At the saturation vapour pressure $p_s(T)$ the liquid and the gas-phase are at equilibrium, which means that the rate of molecules leaving the liquid is equal to the rate of molecules that reenter the liquid from the gas phase.

The higher the temperature the more molecules have sufficient energy to leave the liquid, i. e. the vapour pressure rises with increasing temperature (Fig. 10.72). The quantitative form of the vapour pressure curve $p_s(T)$ can be calculated in the following way:

In Fig. 10.73 we regard for 1 mol of the evaporating liquid a cyclic process in the p, V-diagram of Fig. 10.71. In the state $C'(T + \mathrm{d}T, p_s + \mathrm{d}p_s)$ the vapour should be completely condensed and the liquid occupies the volume V_l. Now the volume is isothermally expanded at the temperature $T + \mathrm{d}T$, while the pressure is kept constant. Here the heat $\mathrm{d}Q_1 = \Lambda$, which is equal to the evaporation energy of 1 mol, has to be supplied in order to keep the temperature constant. At A' the total liquid is evaporated. During the next step, the adiabatic expansion $A' \to A$, pressure and temperature are lowered by an infinitesimal small amount. The system remains in the vapour phase and reaches the point $A(p_s, T)$. Now the vapour is isothermally compressed while the pressure remains constant, because condensation progresses during the path from A to the point C. The

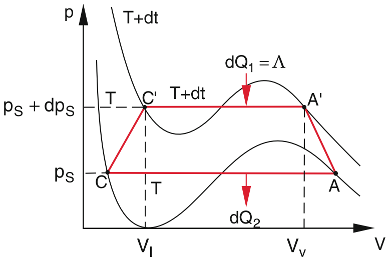


Figure 10.73 Carnot cycle C′A′ACC′ in a *p*-*V* diagram of Fig. 10.71 illustrating the derivation of the Clausius–Clapeyron-equation

condensation heat $\mathrm{d}Q_2$ is released to the surrounding. The step $A \to C$ corresponds to the curve ABC in Fig. 10.71. The liquid state in point C is then transferred by an infinitesimal step to the initial point $C'(p + \mathrm{d}p, T + \mathrm{d}T)$.

The temperature of the system changes only on the short paths $A' \to A$ and $C \to C'$. During the isothermal expansion $C' \to A'$ the system has delivered the work $\mathrm{d}W_1 = (p_s + \mathrm{d}p_s) \cdot (V_l - V_v)$, while during the compression $A \to C$ the work $\mathrm{d}W_2 = p_s \cdot (V_v - V_l)$ has to be supplied to the system. The net work is therefore $\mathrm{d}W = \mathrm{d}W_1 + \mathrm{d}W_2 = (V_l - V_v) \cdot \mathrm{d}p_s$.

In Sect. 10.3.5 it was shown that the efficiency η of the Carnot engine for an arbitrary working material is

$$\begin{aligned}\eta &= \frac{|\Delta W|}{\Delta Q_1} = \frac{(V_v - V_l)\mathrm{d}p_s}{\Lambda} \\ &= \frac{T + \mathrm{d}T - T}{T + \mathrm{d}T} \approx \frac{\mathrm{d}T}{T} ,\end{aligned}$$

because here is $\mathrm{d}T \ll T$. This gives for the evaporation energy for 1 mol evaporated liquid the **Clausius–Clapeyron equation**

$$\Lambda = T \frac{\mathrm{d}p_s}{\mathrm{d}T} (V_v - V_l) . \qquad (10.124)$$

The evaporation heat is proportional to the difference of the mole-volumes of the liquid and gaseous phases and to the slope $\mathrm{d}p_s/\mathrm{d}T$ of the vapour pressure curve.

Note: Often the specific evaporation energy λ [kJ/kg] is given instead of the molar evaporation energy [kJ/mol]. The conversion factor is

$$1\,\mathrm{kJ/mol} = (10^{-3} M)\,\mathrm{kJ/kg} ,$$

where M is the molar mass in g/mol.

The evaporation energy pro molecule is $w = \Lambda/N_A$ with N_A = Avogadro number.

The heat of evaporation has two causes: The first cause is the energy necessary to enlarge the volume V_l of the liquid to the larger volume V_v of the vapour against the external pressure p.

The second cause is the energy spend to enlarge the distance between the molecules against their mutual attraction. The second contribution is by far the largest one. It is therefore nearly equal to the heat of evaporation.

Example

The volume of 1 kg water expands during the evaporation from $V_l = 1\,\mathrm{dm}^3$ to $V_v = 1700\,\mathrm{dm}^3$. The work performed during the expansion against the external pressure of 1 bar is $W = p \cdot \mathrm{d}V = 10^5\,\mathrm{Nm} \cdot 1.7\,\mathrm{m}^3 = 170\,\mathrm{kJ}$. The measured specific evaporation heat is $\lambda = 2080\,\mathrm{kJ/kg}$. Therefore the first contribution only amounts to 8%. ◀

As one of many applications of the thermodynamic potentials we will derive the Clausius–Clapeyron equation (10.124) with the help of the thermodynamic potentials, where here the Gibbs'-potential $G(p, T)$ of (10.105) is used.

Differentiation of (10.105) gives

$$\mathrm{d}G = \left.\frac{\partial G}{\partial p}\right|_T \mathrm{d}p + \left.\frac{\partial G}{\partial T}\right|_p \mathrm{d}T .$$

The compilation scheme of the potentials in Sect. 10.3.11 shows

$$\left.\frac{\partial G}{\partial p}\right|_T = V \quad \text{and} \quad \left.\frac{\partial G}{\partial T}\right|_p = -S .$$

At the phase equilibrium is $\mathrm{d}G_1 = \mathrm{d}G_2$

$$\begin{aligned}&\to \mathrm{d}G_1 = V_1\mathrm{d}p - S_1\mathrm{d}T = V_2\mathrm{d}p - S_2\mathrm{d}T = \mathrm{d}G_2 \\ &(S_2 - S_1)\mathrm{d}T = (V_2 - V_1)\mathrm{d}p \\ &\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_2 - S_1}{V_2 - V_1} .\end{aligned}$$

From the definition of the entropy we conclude

$$S_2 - S_1 = \int_1^2 \frac{\mathrm{d}Q_{\mathrm{rev}}}{T} = \frac{\Lambda}{T} ,$$

which finally gives

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Lambda}{T(V_2 - V_1)} .$$

The heat supply does not increase the kinetic energy of the molecules, (because the temperature stays constant), but only the potential energy. Therefore in Fig. 10.18 the long horizontal line T(t) appears during the evaporation process.

Since in (10.124) $V_v \gg V_l$ we can neglect V_l in (10.124) and we can also approximate in the general gas equation $p \cdot V = RT$ the volume $V \approx V_v \to V_v = R \cdot T/p_s$. Inserting this into (10.124) we get

$$\frac{1}{p_s}\frac{\mathrm{d}p_s}{\mathrm{d}T} = \frac{\Lambda}{RT^2} .$$

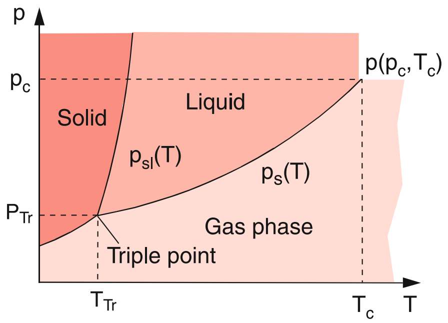


Figure 10.74 Phase diagram with vapor pressure curve $p_s(T)$ representing the separating line between liquid and vapor phase from the triple point up to the critical point $P(p_c, T_c)$ and melting curve $P_{sl}(T)$ as separation line betweeen solid and liquid phase

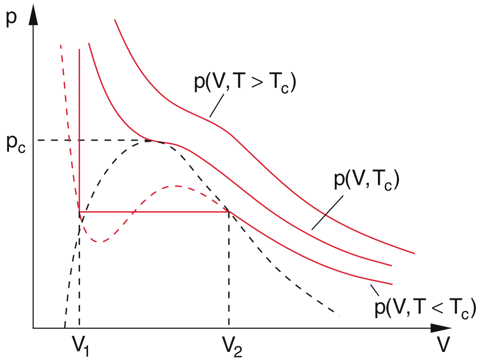


Figure 10.75 Behaviour of Van-der-Waals isotherms $p(V)$ around the critical point (p_c, T_c)

Integration yields

$$\ln p_s = -\frac{\Lambda}{RT} + C$$

with the integration constant C. This gives with the boundary condition $p_s(T_0) = p_0$

$$p_s = p_0 \cdot A \cdot e^{-\Lambda/(RT)} \quad \text{with} \quad A = e^{\Lambda/RT_0} \,. \tag{10.125}$$

This **van't-Hoff equation** shows that the vapour pressure rises proportional to $\exp(-1/T)$.

Along the vapour pressure curve $p_s(T)$ the vapour phase and the liquid phase are at equilibrium, i. e. at each temperature there exists a vapour pressure $p_s(T)$ where the two phases exist simultaneously and are both stable.

The vapour pressure curve divides the area in the p-T-diagram into two sections (Fig. 10.74). For $p(T) < p_s(T)$ only the vapour phase exists under equilibrium conditions, for $p(T) > p_s(T)$ only the liquid phase.

The vapour pressure curve terminates at the critical temperature $T = T_c$. The corresponding vapour pressure $p_c = p_s(T_c)$ is the critical pressure. Above the critical temperature T_c no distinction between liquid and vapour phase is possible. The densities of both phases become equal. The slope of the vapour pressure curve is there

$$\left(\frac{\mathrm{d}p_s}{\mathrm{d}T}\right)_{T_c} = \frac{p_c \cdot \Lambda}{RT_c^2} \,. \tag{10.126}$$

The evaporation heat decreases with increasing temperature and becomes zero at the critical temperature T_c. Just below T_c part of the liquid changes statistically into the vapour phase and back. This causes striations in the optical density which can be seen in the transmitted light.

The critical temperature is related to the interaction potential between the molecules. Above T_c the mean kinetic energy of the molecules is larger than the amount of the mean potential energy. In the p-V-diagram of Fig. 10.71 the isotherms have for T_c three intersection points with the horizontal line $p = \text{const} < p_c$.

When the volume V is compressed, the real pressure curve (Fig. 10.75) shows a kink at $V = V_2$ and follows until V_1 not the van der Waals curve but the horizontal line $p = \text{const}$ because here condensation takes place. The dashed black curve in Fig. 10.75 gives the volume V_2 where condensation starts and V_1 where the whole gas is liquefied. At the critical temperature T_c the curve $p(V)$ has no longer minima and maxima but only an inflection point, which indicates that there are no longer phase transitions but only a unique phase is present, which is called the supercritical phase. The tangent to the curve p(V) in the critical point $p(T_c, V_c)$ is horizontal. The critical point can be calculated from the van der Waals equation (10.123) with the conditions

$$\left(\frac{\partial p}{\partial V}\right)_{T_c, V_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_{T_c, V_c} = 0 \,.$$

This gives for p_c and T_c the results

$$p_c = \frac{1}{27}\frac{a}{b^2}\,; \quad V_c = 3b\,; \quad T_c = \frac{8}{27}\frac{a}{R\,b}\,, \tag{10.127a}$$

and for the van der Waals constants a and b

$$a = 3 p_c V_c^2\,; \quad b = \frac{1}{3} V_c \,. \tag{10.127b}$$

It is therefore possible to gain information about the attractive interaction between the molecules and their internal volume from measurements of the critical parameters p_c and T_c.

10.4.2.2 Boiling and Condensation

If the vapour pressure p_s becomes larger than the external pressure p acting on the liquid surface, vapour bubbles can form in the inside of a liquid. They rise, due to buoyancy, to the liquid surface: The liquid boils. The boiling temperature T_b depends on the external pressure p. From (10.125) one obtains

$$T_b(p) = T_b(p_0) \cdot \frac{1}{1 - \frac{RT_b(p_0)}{\Lambda} \ln(p/p_0)} \,. \tag{10.128}$$

Example

Water boils under a pressure $p = 1\,\mathrm{bar}$ at $T_b = 373\,\mathrm{K} = 100\,°\mathrm{C}$. For $p = 400\,\mathrm{mbar}$ $T_b = 77\,°\mathrm{C}$. Since the cooking time of food strongly depends on the temperature, cooking at high altitudes becomes tedious. Therefore one uses a pressure cooker, which operates at about 1.5–2 bar and reduces the cooking time considerably. ◀

If the vapour pressure becomes smaller than the external pressure the vapour starts to condensate.

In our atmosphere the air mixed with water vapour generally does not reach an equilibrium state (p, T), because the conditions in the atmosphere change faster than the time necessary to establish an equilibrium. The water vapour pressure is therefore in general lower than the saturation pressure.

The concentration of water vapour in our atmosphere, measured in $\mathrm{g/m^3}$, is called the *absolute humidity* φ_a. The maximum possible concentration of water vapour is reached, when the water vapour pressure p_w is equal to the saturation pressure p_s. The humidity φ at this pressure is the *saturation humidity* φ_s.

The relative humidity is the quotient

$$\varphi_{\mathrm{rel}} = \frac{\varphi_a}{\varphi_s} = \frac{p_w}{p_s} \,. \tag{10.129}$$

Example

A relative humidity of 40% is reached, when the vapour pressure of water is $p_w = 0.4 p_s$ (H_2O). ◀

For a given absolute humidity the relative humidity increases with decreasing temperature because the vapour pressure of water decreases with T. (Fig. 10.76). When $\varphi_{\mathrm{rel}} = 1$ it starts to rain. The temperature T_d where $\varphi_{\mathrm{rel}} = 1$ is the *dew point* or saturation temperature.

For the operation of air conditioning systems, this has to be taken into account. If the air is cooled below the dew point, the water vapour will condense and increase the humidity in the cooled room. The air has therefore to be dried before it is cooled down.

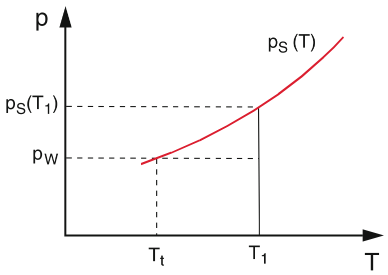


Figure 10.76 Illustration of relative and absolute humidity of air and of dew point

10.4.2.3 Liquefaction of Gases; Joule–Thomson Effect

In order to liquefy gases at the pressure p one has to lower their temperature below the pressure-dependent boiling temperature $T_s(p)$. There are several experimental realizations:

Adiabatic Cooling with Energy Output

Here the internal energy U of the gas at the pressure p_1 decreases because the expanding gas delivers the work $\mathrm{d}W = p{\cdot}\mathrm{d}V$ against the lower external pressure p, while no heat is exchanged ($\mathrm{d}Q = 0$). From the first law (10.82) we obtain for 1 mol

$$\mathrm{d}U = C_v \cdot \mathrm{d}T = -p \cdot \mathrm{d}V \,.$$

This yields the temperature decrease

$$\mathrm{d}T = -\frac{p_p}{C_v}\mathrm{d}V \,.$$

Example

10 mol of a gas at room temperature $T = 300\kappa$ are expanded against an external pressure of $10\,\mathrm{bar} = 10^6\,\mathrm{Pa}$ by $\Delta V = 10^{-2}\,\mathrm{m^3}$ (this corresponds to 5 mol volumes. With $C_v = 20.7\,\mathrm{J/(mol \cdot K)}$ we obtain $\Delta T = -4.8\,\mathrm{K}$. ◀

This adiabatic cooling can be realizes for ideal and also for real gases. It comes from the decrease ΔU of the internal energy due to the partial transfer into mechanical work.

Joule–Thomson Effect

For real gases cooling can be also achieved without the transfer into mechanical work. The expansion of the volume V increases the mean distance between the molecules. This requires work against the attractive forces between the molecules, which means that the potential energy of the system increases at the expense of the kinetic energy and the temperature decreases.

When a real gas expands adiabatically through a nozzle at a pressure p_1 that is kept constant, from the volume V_1 into the volume V_2 (Fig. 10.77) with the pressure $p_2 < p_1$ there is no heat exchange with the surrounding ($\mathrm{d}Q = 0$) and the enthalpy $H = U + p \cdot V$, is constant because the cooling is due to the work against the attractive forces between the molecules during the expansion.

The internal energy U of a real gas is the sum of the kinetic energy $E_{\mathrm{kin}} = (f/2) \cdot R \cdot T$ and a the potential energy

$$E_p = \int\limits_{\infty}^{V_1} \frac{a}{V^2}\mathrm{d}V = -\frac{a}{V_1} \,,$$

which is due to the attractive forces between the molecules and causes the internal pressure (cohesion pressure).

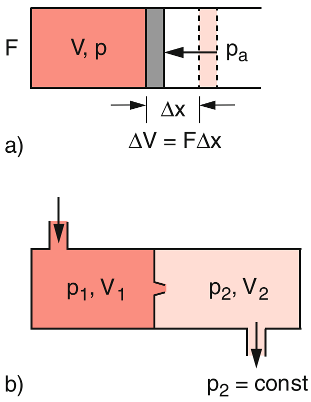


Figure 10.77 Comparison between adiabatic cooling and Joule–Thomson effect. **a** Adiabatic expansion with work delivery $\Delta W = p_a \cdot \Delta V$; **b** adiabatic expansion through a nozzle without work output

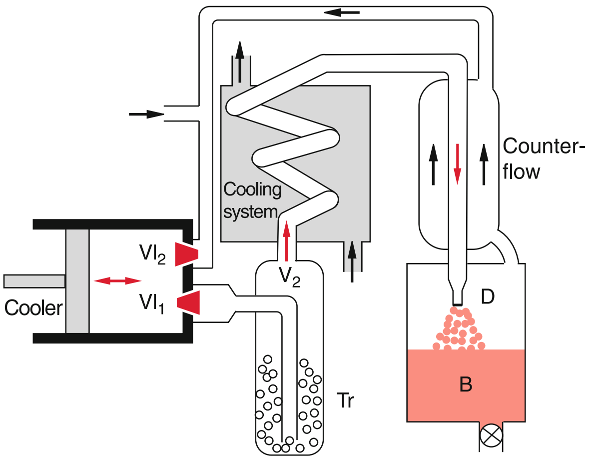


Figure 10.78 Schematic illustration of the Linde-process for liquefaction of air

Solving the van der Waals equation (10.123) for p, we obtain

$$p = \frac{R \cdot T}{V - b} - \frac{a}{V^2} \,.$$

The enthalpy then becomes

$$\begin{aligned} H = U + p \cdot V &= \frac{f}{2} RT - \frac{a}{V} + \left(\frac{RT}{V - b} - \frac{a}{V^2} \right) \cdot V \\ &= RT \left(\frac{f}{2} + \frac{V}{V - b} \right) - \frac{2a}{V} \,. \end{aligned} \tag{10.130}$$

Since H is constant during the adiabatic expansion through the nozzle, we get

$$\begin{aligned} \mathrm{d}H &= \frac{\partial H}{\partial V} \mathrm{d}V + \frac{\partial H}{\partial T} \mathrm{d}T = 0 \\ \Rightarrow \mathrm{d}T &= - \frac{\frac{\partial H}{\partial V} \mathrm{d}V}{\frac{\partial H}{\partial T}} = \frac{\frac{bT}{(V - b)^2} - \frac{2a}{RV^2}}{\frac{f}{2} + \frac{V}{V - b}} \mathrm{d}V \\ &\approx \frac{bRT - 2a}{(\frac{1}{2} f + 1) RV^2} \mathrm{d}V \,. \end{aligned} \tag{10.131}$$

For temperatures below the inversion temperature

$$T_\mathrm{i} = \frac{2a}{bR} \,, \tag{10.132}$$

we get $\mathrm{d}T < 0$. The gas cools down although no heat exchange with the surrounding takes place. The value of the inversion temperature depends on the ratio of the amount of the attractive forces (described by the constant a) and the covolume $b = 4N \cdot V_\mathrm{a}$ of the molecules. For ideal gases is $a = b = 0 \Rightarrow \mathrm{d}T = 0$ and no cooling occurs. The cooling of real gases through adiabatic expansion through a nozzle is the **Joule–Thomson effect**. It is only realized for real gases, not for ideal gases. This can be seen as follows: When the gas flows through the nozzle, driven by the pressure p_1, the energy $p_1 \cdot V_1$ is released. The gas, streaming into V_2, builds up the pressure p which requires the energy $p_2 \cdot V_2$. Energy conservation demands $U_1 + p_1 \cdot V_1 = U_2 + p_2 \cdot V_2 \Rightarrow H_1 = H_2$ (10.76). The expansion therefore proceeds at constant enthalpy.

For temperatures above the inversion temperature is $\mathrm{d}T > 0$, i. e. the gas heats up. In order to use the Joule–Thomson effect for cooling, the gas has at first to be precooled below the inversion temperature. For higher pressures the density of molecules increases and with it the relative share of the covolume $b = 4N \cdot V_\mathrm{a}$ and the inversion temperature T_i becomes pressure dependent. More detailed information on the curves $T_\mathrm{i}(p)$ can be found in [10.14].

In Tab. 10.7 the maximum values of T_i are compiled for some gases. The numbers show that for air the inversion temperature lies above room temperature. Therefore precooling is not necessary. The gases N_2 and O_2 can be cooled below their condensation temperatures solely with the Joule–Thomson effect. This is realized with the Linde-gas liquefying system, which uses the counter-current principle (Fig. 10.78). The gas is compressed by the piston K and streams through the valve Vl_1 into the volume V_2 where it is dehumidified. It then passes through a cooling system where it is precooled, before it streams through the counter current cooler and finally through a nozzle into the container D at low pressure. During this last step, it further cools down. The cooling rate is for air $\Delta T / \Delta p = 0.25\,\mathrm{K/bar}$. For a pressure difference $\Delta p = 100\,\mathrm{bar}$ one reaches a cooling rate of $25\,\mathrm{K}$ per step. The cold vapour is guided through the counter-current cooler and helps to precool the incoming gas. Finally, it is sucked in through the valve Vl_2 into the initial chamber during the expansion phase of the piston. The next step starts then already with a colder gas and reaches therefore a lower final temperature. After several steps the cooling during the expansion through the nozzle reaches the condensation temperature and the gas is liquefied.

During the cooling of air, which is composed of N_2 and O_2, at first the higher condensation temperature of oxygen is reached

Table 10.7 Critical temperatures T_c, critical pressure p_c, maximum inversion temperature T_i and boiling temperature for some gases

Gas	T_c/K	P_c/bar	$a/\mathrm{N\cdot m^4/mol^2}$	$b/10^6\,\mathrm{m^3/mol}$	T_i/K	T_s/K at $p_0 = 1.013$ bar
Helium	5.19	2.26	0.0033	24	30	4.2
Hydrogen	33.2	13	0.025	27	200	20.4
Nitrogen	126	35	0.136	38.5	620	77.4
Oxygen	154.6	50.8	0.137	31.6	765	90.2
Air	132.5	37.2	–	–	650	80.2
CO_2	304.2	72.9	0.365	42.5	>1000	194.7
NH_3	405.5	108.9	0.424	37.2	>1000	–
Water vapor	647.15	217.0	–	–	–	373.2

before N_2 liquefies. Therefore the two gases can be readily separated.

Nowadays liquid nitrogen rather than liquid air is used for many applications, because liquid oxygen contains the explosive ozone O_3. Liquid air that is kept in a Dewar increases its O_2 and O_3 concentration in the course of time since N_2 evaporates faster due to its higher vapour pressure and therefore after some time liquid air reaches a critical concentration of O_3 which explodes above a critical temperature.

The gases H_2, He of Ne can be liquefied by precooling them with liquid nitrogen below the inversion temperature before they can be further cooled by the Joule–Thomson effect.

10.4.2.4 Equilibrium Between Solid and Liquid Phase; Melting Curve

If the temperature of a solid material is increased above a certain temperature that depends on the material, the solid phase starts to convert into the liquid phase. Only at the melting temperature T_m, both phases can coexist under equilibrium conditions. The pressure dependence dT_m/dp of the melting temperature is much smaller than that of the evaporation temperature, i. e. the slope of the curve $p(T)$ in the p-T-diagram of Fig. 10.79 is much larger than that of the evaporation curve. One of the reasons is the much smaller change of the volume during the melting process, compared with the much larger change during the evaporation process. A similar consideration as that resulting in Eq. 10.124 for the heat of evaporation gives the heat of fusion

$$\Lambda_m = T\cdot\frac{dp}{dT}(V_{\text{liquid}} - V_{\text{solid}}) \,. \qquad (10.133)$$

For most materials the density decreases during the melting process, i. e. $V_{\text{liquid}} > V_{\text{solid}}$. This gives $dp/dT > 0$, because $\Lambda_m > 0$. There are some substances (e. g. water) where $V_{\text{liquid}} < V_{\text{solid}}$. For these substances is $dp/dT < 0$, the melting curve has a negative slope (anomaly of water) (Fig. 10.79b).

Note: The fact that for water $V_{\text{liquid}} < V_{\text{solid}} \to \varrho_{\text{liquid}} > \varrho_{\text{solid}}$ is essential for many processes in nature. Lakes freeze up from the top to the bottom. Since the heat conductivity of ice is small, this gives an isolating layer at the top, preventing the complete freezing of the water, thus protecting fishes and other sensitive creatures.

The fact, that water has its maximum density at $T = 4\,°\mathrm{C}$ is called its *anomaly*. It is due to the temperature dependent molecular structure of water. Liquid water does not solely consist of H_2O molecules but also contains multimers $(H_2O)_n$ in a concentration that depends on the temperature and on the distance from the surface of water. In the multimers the different H_2O molecules are connected by hydrogen bonds. At higher temperatures theses weak bonds break and a structural change results in a change of the mean distance and therefore also a change of the density. In the solid phase the H_2O-molecules form a regular lattice with empty space between the molecules. Therefore the density of the solid is smaller than that of the liquid phase.

Example

At $T = 0\,°\mathrm{C}$ the density of solid ice is $\varrho = 0.917\,\mathrm{kg/dm^3}$, that of sea water is $\varrho = 1.04\,\mathrm{kg/dm^3}$. Therefore, only about 12% of an iceberg are above the seawater surface, but 88% are below. ◀

Application of external pressure decreases the mean distance between the molecules and therefore the ice can melt, according to the principle of minimum constraint. This is utilized by skaters,

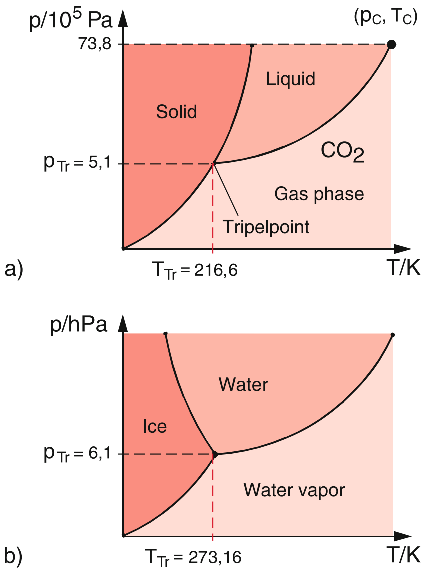


Figure 10.79 Melting curve, vapor pressure curve and triple point for **a** a positive, **b** a negative slope of the melting curve. **a** represents the phase diagram of CO_2, **b** that of water

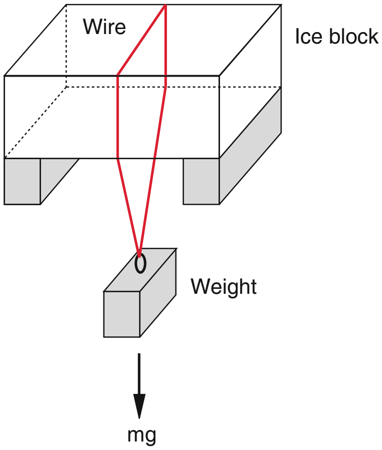


Figure 10.80 Apparently convincing demonstration of the lowering of the melting temperature by pressure

where the high pressure below the sharp ice skates forms a thin liquid layer with low friction (see, however, the remarks below).

The lowering of the melting temperature $\Delta T_\mathrm{m} = (\mathrm{d}T_\mathrm{m}/\mathrm{d}p) \cdot \Delta p$ is often demonstrated by a wire that is pulled through an ice block by a heavy weight (Fig. 10.80).

Remark. More detailed calculations show, however, that the major part of the necessary melting energy comes from heat conduction from the higher temperature of the wire to the ice surface (see Probl. 10.11).

Even without external pressure a thin liquid layer is formed at the surface of ice above $T = -33\,°\mathrm{C}$. The necessary energy for melting this layer is provided by the gain in surface energy. The boundary ice-air needs more energy for evaporating molecules than the boundary ice-liquid. A liquid layer therefore has a lower potential energy and the loss of potential energy is larger than the melting energy.

10.4.2.5 Coexistence of different phases; Triple Point

Since the melting curve in the p-V-diagram of Fig. 10.76 has a larger slope than the vapor curve the two curves must intersect in a point $(p_\mathrm{tr}, T_\mathrm{tr})$, called the **triple point**. Here the three phases solid, liquid and gase can coexist.

For $T < T_\mathrm{tr}$ there is one boundary curve (*sublimation curve*) that separates the solid and the gaseous phases. It has in the (p, V)-diagram generally a positive slope. Solid materials can directly pass into the gaseous phase without becoming liquid. This process is called **sublimation**. Because of the small vapor pressure of solids this process is, however, very slow.

If there are more than one phase of a material in a container, pressure p and temperature T are no longer independent of each other. For example, the coexistence of the liquid and the vapor phase is only possible on the vapor curve $p_\mathrm{S}(T)$. This implies that p and T are related by the evaporation coefficient Λ in (10.125). It is possible to change T but then $p_\mathrm{S}(T)$ is fixed. At the triple point $(p_\mathrm{tr}, T_\mathrm{tr})$ p and T are connected by two conditions: the vapor curve and the sublimation curve. This means that none of the two variables p and T can be changed without leaving the triple point.

This can be generalized by **Gibb's phase rule**, which relates the number f of the degrees of freedom in the choice of the variables p and T with the number q of coexisting phases. It states:

$$f = 3 - q \tag{10.134}$$

At the triple point is $q = 3 \rightarrow f = 0$, i.e. no degree of freedom in choosing the variables p and T. If only one phase is present ($q = 1$) we obtain $f = 2$. The pressure p as well as the temperature T can be chosen independently (within certain limits). On the vapor curve is $q = 2$ and therefore $f = 1$. We can choose one variable and the other is then fixed.

For a mixture of different chemical components, which can be present in different phases the generalized Gibbs phase rule states:

$$f = k + 2 - q \tag{10.135}$$

where k is the number of components.

10.4.3 Solutions and Mixed States

Up to now we have discussed only pure substances, which are composed of only one component and do not contain any impurities. We have explained the different phases of solid, liquid and gaseous states and possible transitions between these phases. In nature, however, often mixed substances are present where molecules of different species are mixed together. Examples are NaCl-molecules or sugar molecules, which are dissolved in water and dissociate into their atomic components. Other examples are metal alloys

For the complete characterization of such mixed states pressure and temperature are not sufficient, but also the concentration of the different components have to be defined.

The concentration of a substance dissolved in a liquid is generally given in g/litre or in mole/litre. Often not the complete substance has dissolved but a rest remains as solid sediment (if $\varrho_\mathrm{solid} > \varrho_\mathrm{liquid}$) or as layer on the liquid surface (if $\varrho_\mathrm{solid} < \varrho_\mathrm{liquid}$).

The solution of substances can alter the characteristic features of the liquid considerably. In this section we will shortly discuss the most important features of solutions.

10.4.3.1 Osmosis and Osmotic Pressure

Assume a container with a semipermeable membrane including a solution with the concentration c of the dissolved substance is submerged into a reservoir with the pure liquid (Fig. 10.81). One observes that the level of the solution in a standing pipe rises above the level of the pure solution, if the molecules of the solvent can penetrate through the semipermeable membrane but not the molecules of the dissolved substance. Such permeable

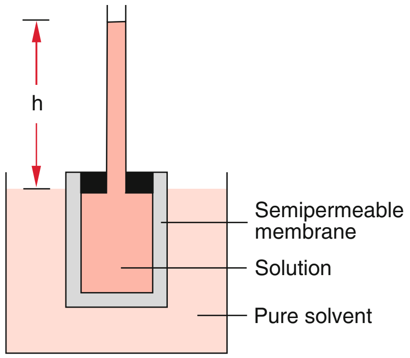


Figure 10.81 Demonstration of osmosis in a Pfeffer cell

membranes with substance-specific transmission play an important role in biological cells.

In the example of Fig. 10.81 the concentration difference of the dissolved substance between outside and inside of the container results in a diffusion of the solvent molecules into the solution through the permeable membrane. This builds up a pressure difference, indicated by the height h in the standing pipe.

$$\Delta p = \varrho \cdot g \cdot h \,,$$

which stops the net diffusion, because now an equal number of molecules diffuses into and out of the container.

The net diffusion caused by the concentration difference is called *Osmosis* and the pressure difference Δp is the *osmotic pressure*.

The osmotic pressure p_{osm} is proportional to the concentration of the dissolved molecules and to the temperature.

Experiments show that

$$p_{\text{osm}} \cdot V = \nu \cdot R \cdot T \,, \qquad (10.136)$$

where ν is the number of moles dissolved in the volume V of the solvent.

This **van't Hoff's Law** is the analogue to the general gas equation

$$p \cdot V = \nu \cdot R \cdot T \,.$$

> The osmotic pressure of a solution exerted onto the walls of the container equals the pressure that would be present, if the dissolved molecules were in the gas phase at the temperature T.

10.4.3.2 Reduction of Vapour Pressure

Due to the additional attractive forces between the dissolved molecules and the solvent molecules the work function of the solvent molecules increases. This means that at identical temperatures less molecules evaporate than in pure liquids. The vapour pressure is therefore lower than in a pure solvent.

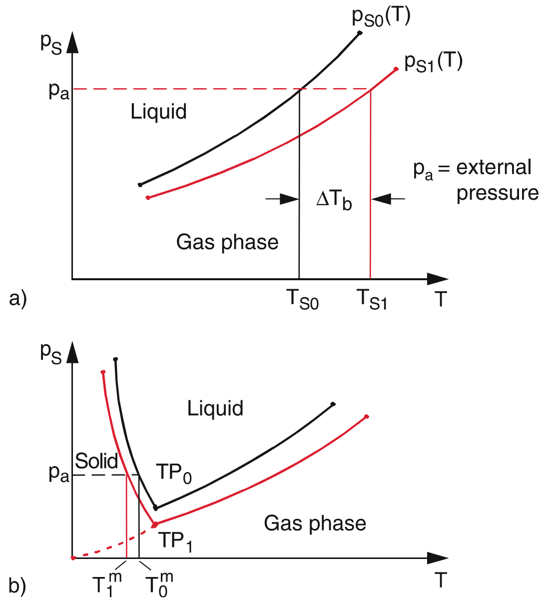


Figure 10.82 **a** Decrease of vapor pressure and increase of boiling temperature ΔT_b of a solution compared to that of a pure solvent; **b** decrease of melting temperature ΔT_m

The vapour pressure reduction Δp is proportional to the concentration of the dissolved molecules (if their vapour pressure is negligible).

Francois Marie Raoult formulated in 1882 the law

$$\frac{\Delta p_\text{s}}{p_{\text{s}0}} = -\frac{\nu_1}{\nu_0 + \nu_1} \,, \qquad (10.137\text{a})$$

here $p_{\text{s}0}$ is the vapour pressure of the pure solvent, ν_0 is the number of moles of the solvent and ν_1 that of the dissolved substance. For diluted solutions is $\nu_1 \ll \nu_0$ and (10.137a) reduces to

$$\Delta p_\text{s} = -p_{\text{s}0} \cdot \frac{\nu_1}{\nu_0} \,. \qquad (10.137\text{b})$$

The lowering of the vapour pressure causes an increase ΔT_b of the boiling temperature as shown in Fig. 10.82a. The vapour pressure has to rise by Δp_s to reach the external pressure p_a. From the vapour pressure curve $p_\text{s}(T)$ in Eq. 10.125 we can derive the relation between Δp_s and ΔT_b. Differentiation of (10.125) gives

$$\frac{\mathrm{d}p_\text{s}}{\mathrm{d}T} = \frac{\Lambda}{RT^2} p_\text{s} \Rightarrow \Delta T = \frac{RT^2}{\Lambda} \frac{\Delta p_\text{s}}{p_\text{s}} \,. \qquad (10.137\text{c})$$

Together with (10.137) this yields the Raoult' Law

$$\Delta T_\mathrm{b} = \frac{RT^2}{\Lambda}\frac{\nu_1}{\nu_0} \,. \tag{10.138a}$$

When several substances with the molar concentrations ν_i are dissolved, this generalizes to

$$\Delta T_\mathrm{b} = \frac{RT^2}{\Lambda\nu_0}\sum_i \nu_i \,. \tag{10.138b}$$

Since ΔT_b depends on the molar evaporation heat Λ, it is dependent not only on the dissolved substances but also on the specific solvent.

For dissolved substances that partly dissociate (for instance dissociates NaCl into $\mathrm{Na}^+ + \mathrm{Cl}^-$) the sum in (10.138b) extends over all dissociated and non-dissociated components dissolved in the solvent.

The lowering of the vapour pressure also results in a lowering of the melting temperature T_m (Fig. 10.82b). Similar to (10.138a) one gets

$$\Delta T_\mathrm{m} = -\frac{RT^2}{\Lambda_\mathrm{m}}\frac{\nu_1}{\nu_0} \,, \tag{10.139}$$

where Λ_m is the molar melting heat.

Example

For water with the concentration of ν_1 moles of a dissolved substance is the lowering of the melting temperature

$$\Delta T_\mathrm{m} = -1.85\,\mathrm{K}\cdot\nu_1 \,.$$

When 50 g NaCl are dissolved in 1 litre water, (1 mol NaCl are 58 g), the lowering of the melting temperature is with $\sum\nu_\mathrm{i} = 2\cdot 50/58 = 1.72\,\mathrm{mol}$: $\Delta T_\mathrm{m} = -3.2\,\mathrm{K}$.

Seawater has a melting temperature that lies several degrees below 0 °C depending on the salt concentration.

The lowering of the melting temperature is used to clear icy roads from ice and snow by salting the roads.

The zero point of the Fahrenheit temperature scale is defined by the melting temperature of a specific salt-water solution. From (10.2) and (10.139) the zero point can be obtained as

$$0\,^\circ\mathrm{F} = -17.8\,^\circ\mathrm{C} \,.$$

Solutions with dissolved substances have generally a larger temperature range of the liquid phase than pure solvents, because the boiling point rises and the melting point is lowered.

10.5 Comparison of the Different Changes of State

Here we will summarize all possible changes of thermodynamic states and the corresponding equations.

1. Isochoric processes: $V = \mathrm{const}$

$$\mathrm{d}Q = C_V\cdot\mathrm{d}T \tag{10.140a}$$

2. Isobaric processes: $p = \mathrm{const}$

$$\mathrm{d}Q = C_p\cdot\mathrm{d}T = \mathrm{d}U + p\cdot\mathrm{d}V \tag{10.140b}$$

3. Isothermal processes: $T = \mathrm{const}$

$$\mathrm{d}U = 0, \quad \mathrm{d}Q = p\cdot\mathrm{d}V, \quad p\cdot V = \mathrm{const} \tag{10.140c}$$

4. Adiabatic processes: $\mathrm{d}Q = 0$

$$p\cdot V^\kappa = \mathrm{const}; \quad \kappa = C_p/C_V \tag{10.140d}$$

5. Isentropic processes: $S = const$

$$\begin{aligned}&\mathrm{d}S = C_V\cdot\mathrm{d}T/T + R\cdot\mathrm{d}V/V = 0\\ &\Rightarrow T\cdot V^{\kappa-1} = \mathrm{const}\end{aligned} \tag{10.140e}$$

A reversible adiabatic process is always isentropic, but not every isentropic process is also adiabatic.

6. Isoenthalpic processes

$$\begin{aligned}&H = U + p\cdot V = \mathrm{const}\\ &\mathrm{d}H = (\partial H/\partial p)_{T=\mathrm{const}} + (\partial H/\partial T)_{p=\mathrm{const}}\end{aligned} \tag{10.140f}$$

10.6 Energy Sources and Energy Conversion

The supply of sufficient energy that can replace to a large extent manual work, has changed our life considerably. It is fair to say that only the provision of sufficient and affordable energy has essentially improved our standard of life. This is the reason why in developing countries the desire for more energy will cause a drastic increase of worldwide energy consumption.

The first law of thermodynamics teaches us, however, that energy can be neither generated nor annihilated. The phrase "energy generation" (for example in power stations) means correctly speaking the conversion of energy from a specific form into another (for instance from thermal energy into electric energy).

In fossil power stations the potential energy of CO- and $\mathrm{CO_2}$-molecules is transferred into heat (kinetic energy of the molecules and atoms), which is further converted via turbines into mechanic energy of the rotating turbine, which drives an electric generator that produces electric energy.

Figure 10.83 Cooling towers of the coal power plant Staudinger. The plant delivers 500 MW electric power and 300 MW heat power. It reaches an efficiency of 42.5% (With kind permission of Preußen Elektra AG, Hannover)

In car engines this molecular potential energy is converted into mechanical energy that drives the car. In nuclear power stations the potential energy of uranium nuclei (which exceeds that of molecular bindings by 6 orders of magnitude) is converted by nuclear fission into kinetic energy of the fission products and then into heat of circulating cooling water.

Wind energy converters convert the kinetic energy of airflow into rotation energy of the converter rotor blades, which drive an electric generator. The wind energy has its origin in the solar radiation energy, which in turn stems from nuclear fusion energy in the interior of the sun.

In order to realize an energy conversion efficiency as high as possible, one has to understand the basic physical processes of the different conversion processes. We have learned in Sect. 10.3.3 that the maximum possible conversion factor for the conversion of heat into mechanical energy is given by the efficiency of the Carnot engine which depends on initial and final temperature during the conversion. The maximum initial temperature is generally limited by the material of the container walls which enclose the working gas. The lowest final temperature is often limited by the temperature of the surrounding. By using the rest energy of the cooled gas for heating (combined heat and power) the energy efficiency can be improved. This reduces the waste of energy which would otherwise heat up the environment. The non-usable rest heat energy is taken away by cooling towers (Fig. 10.83).

The increasing concern about the warming of our atmosphere (global warming) by man-made emission of molecular gases such as CO_2, CH_4, NO_2 etc., which absorb the infrared emission of the earth surface thus heating up the atmosphere, has led to the proposal and partly realization of several different "energy sources", i. e. energy conversion processes. In particular regenerative energy sources, where the working material is available in unlimited quantities, or where the consumption of the working material is replaced by nature over time intervals of many centuries, are favourable candidates. Such energy conversion processes should not contribute to global warming. Examples are nuclear energy conversion, wind energy, solar energy and energy conversion based on the tides of the ocean. The most important renewable energy conversion processes include:

- Hydro-electric power plants (based on the potential or kinetic energy of water)
- Wind-energy converters
- Geothermic plants
- Solar-thermal power plants
- Solar-electric conversion (photo-voltaic devices)
- Bio-energy (burning of regrowing biological material such as wood, plants)

Some examples shall illustrate these different "energy sources".

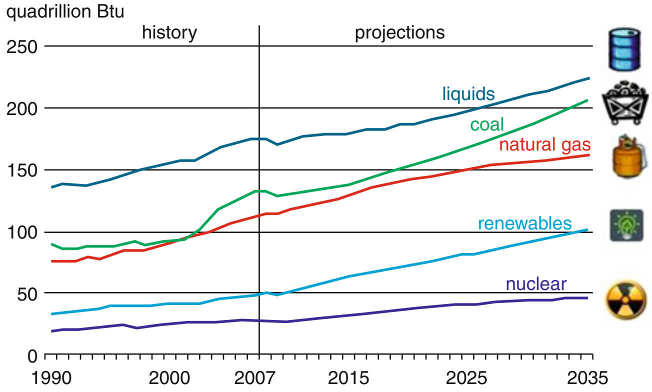
At first we will clarify some often used definitions.

The **primary energy** is the energy directly obtained from the different sources (coal, oil, gas, water, wind, sun radiation, nuclear fission) while the **secondary energy** is won by conversion of the primary energy into other energy forms (mechanical energy, electric energy, etc.). The conversion of primary into secondary energy has an efficiency $\eta < 1$. This means a fraction $(1 - \eta)$ is lost and is delivered as heat into the surrounding. If the consumption of primary energy in a country is larger than the production of energy sources, the country has to import coal, oil or gas.

In Tab. 10.8 the increase of the worldwide primary energy consumption is summarized from 1990 to 2012. Note the large increase of the electric power consumption. In Fig. 10.84 the contributions of the different energy sources to the total worldwide energy consumption are illustrated and Tab. 10.9 lists some countries with the highest energy consumption. It illustrates the enormous increase during the last 40 years.

Table 10.8 Worldwide total energy consumption (in 10^3 TWh) and electric energy

Year	Total energy	Electric energy
1990	71	6
2000	117	15
2012	155	23



Source: U.S. Energy Information Administration
(Report #.DOE/EIA-0484(2010))

Figure 10.84 Worldwide energy consumption of different energy sources in units of 10^{15} Btu $\approx 10^{18}$ J $\approx$ 300 TWh

The units for energy and their abbreviations are given below:

1 Kilojoule $= 1$ kJ $= 10^3$ J
1 Megajoule $= 1$ MJ $= 10^6$ J
1 Gigajoule $= 1$ GJ $= 10^9$ J
1 Terrajoule $= 1$ TJ $= 10^{12}$ J
1 Petajoule $= 1$ PJ $= 10^{15}$ J
1 Exajoule $= 1$ EJ $= 10^{18}$ J
1 Kilowatt hour $= 1$ kWh $= 3.6$ MJ

It is interesting to compare the total energy consumption of Germany (13 400 PJ per year) with the energy that it receives per year from the sun. The energy of solar radiation per sec and m^2 outside the atmosphere (solar constant) is $1.367\,\mathrm{kW/(m^2 \cdot s)}$. During its transit through the atmosphere, the radiation power decreases through backscattering (30%) and absorption (20%)

Table 10.9 The countries with the highest consumption of primary energy (in Megatons Oil-Units) [10.31]

Pos.	Country	1970	2000	2010	2013	%
1	China	202.1	980.3	2339.6	2852.4	22.4
2	USA	1627.7	2313.7	2284.9	2265.8	17.8
3	Russia	483.0	619.4	674.1	699.0	5.5
4	India	64.8	295.8	510.2	595.0	4.7
5	Japan	279.9	518.0	506.8	474.0	3.7
6	Canada	156.4	303.0	315.6	332.9	2.6
7	Germany	309.6	333.0	322.5	325.0	2.6
8	Brasilia	36.8	185.8	257.4	284.0	2.2
9	South Korea	14.3	193.9	254.6	271.3	2.1
10	France	155.8	258.7	253.3	248.4	2.0

and therefore only about 50% reach the earth surface. Since the sun radiation generally does not incide vertically onto a surface element but under an angle α that depends on the daytime, the latitude and the yearly season, the annual average $P = P_0 \cdot \cos\alpha$ of the incident radiation intensity is for a latitude of 45° about $300\,\mathrm{W/(m^2 \cdot s)}$. With an annual sunshine duration of 1000 h/year ($3.6 \cdot 10^6$ s/year) we receive the annual average of solar radiation energy of about 1 GJ per $\mathrm{m^2}$ and year. In order to match the energy consumption one needs in Germany an area of $3 \cdot 10^4\,\mathrm{km^2}$ for solar energy collectors with an efficiency of 50%.

For the whole earth (the hemi-sphere with the area of $2.55 \cdot 10^8\,\mathrm{km^2}$) the total incident sun radiation power is $10^{15} \cdot 2.55 \cdot 10^8 = 2.55 \cdot 10^{23}$ J/year. The total energy consumption in the year 2011 was, however, only $5 \cdot 10^{20}$ J/year which is about 0.2% of the incident sun energy.

10.6.1 Hydro-Electric Power Plants

Most of the hydro-electric power plants use water reservoirs where the water outlet streams through pipes and drives turbines that generate electric power. Here the potential energy of the damned up water is converted into kinetic energy of the water flowing through the pipe.

For a storage height h an area A of the reservoir and a density ϱ of the water the total potential energy is

$$E_{\mathrm{pot}} = \varrho \cdot g \cdot h \cdot A \cdot \Delta h\,,$$

when the storage height is lowered by $\Delta h \ll h$.

Example

$A = 1\,\mathrm{km^2} = 10^6\,\mathrm{m^2}$, $h = 30\,\mathrm{m}$, $\Delta h = 5\,\mathrm{m} \rightarrow E_{\mathrm{pot}} = 1.5 \cdot 10^{12}\,\mathrm{J} = 1.5\,\mathrm{TJ}$. ◀

Some hydro-electric power stations use the flow energy of rivers, where in most cases, however, the river has several barrages where again the potential energy of the dammed river is used to drive turbines. This method was often used in earlier times to drive corn mills and hammer mills which only need moderate powers.

Example

When a channel with a width of 5 m and a depth of 3 m is branched off a river the water with a velocity of $v = 6\,\mathrm{km/h} = 1.67\,\mathrm{m/s}$ drives a turbine, the maximum available power is

$$P = \tfrac{1}{2} M v^2 = \varrho \cdot B \cdot h \cdot v^2/2\,.$$

With the numerical values given above this yields $P = 21\,\mathrm{kW}$. ◀

10.6.2 Tidal Power Stations

Tidal power stations use the tidal range between low and high tide for power generation. This range is in particular large in the mouth of rivers, where it can reach up to 16 m. The water passes through turbines built into logs in the river. At low tides, the water streams seawards and at high tides against the river. This streaming water drives the turbines at low tides as well as at high tides (Fig. 10.85), which activates generators for producing electric energy. At a water level difference Δh between the dammed river and the sea level the energy that can be converted is

$$W = \int (\mathrm{d}M/\mathrm{d}t) \cdot g \cdot \Delta h(t)\mathrm{d}t\,,$$

where $\mathrm{d}M/\mathrm{d}t$ is the mass of water passing pro second through the turbines, Δh is the time dependent level difference and T (about 5 h) the time duration of low resp. high tide.

Here the gravitational energy of earth-moon attraction and the decrease of the rotation energy of the earth (due to friction by the tides) are the primary energy sources. During the time intervals where $\Delta h = 0$ the tidal power station cannot deliver energy.

The first tidal power station was built in France in the mouth of the river *Rance* (Fig. 10.86) where a tidal range of 16 m is obtained. The river dam is 750 m long and has 24 passages where the turbines are located. The total power station delivers an electric power of 240 MW and per year an electric energy of 600 GWh. This equals the energy delivered by 240 wind converters with 1 MW power each and 3000 hours of full operation per year.

The disadvantage of such tidal power stations is the separation of the bay at the mouth of the river. This can change the biological conditions for plants and fishes and it can furthermore influence the tidal range in neighbouring bays with the danger of flooding.

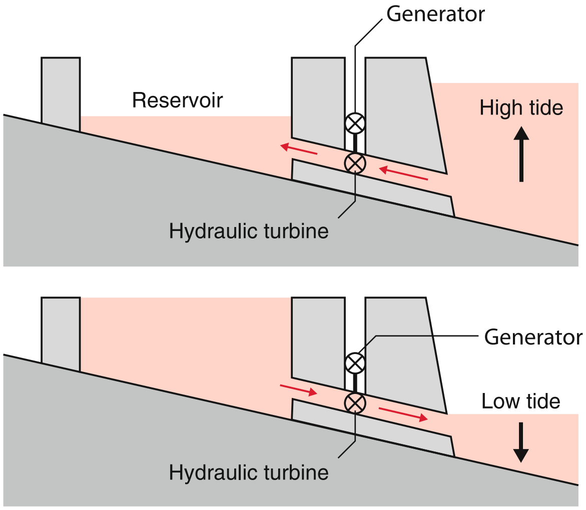


Figure 10.85 Schematic illustration of a tidal power station

Figure 10.86 Tidal Power Station St.Malo. Aerial view of the power station in the estuary of the river Rance in France. Here the tidal amplitude is about 8 m (see Sect. 6.6). With kind permission © Foto dpa

10.6.3 Wave Power Stations

Wave power stations use the kinetic and potential energy of sea waves for the generation of electric energy. Their basic principle is illustrated in Fig. 10.87. A pneumatic chamber is filled with air in its upper part while the lower part has a connection to the sea. The incoming waves induce a periodic change of the water level in the lower part of the chamber. This causes a periodic change of the air pressure in the upper part and an air flow through the pipe at the top of the chamber that periodically changes its direction. In the upper part of the pipe a *Wells-turbine* is installed, that always rotates in the same direction independent of the direction of the air flow. This turbine has symmetric blade profiles in contrast to normal turbines that have asymmetric blade profiles, optimized for one direction of the airflow. The efficiency of the Wells-turbine is smaller than that of normal turbines. It has, however, the advantage that it rotates continuously for both directions of the air flow.

Wave power stations do not use the tide difference between high and low tide but the wave energy, which is in turn driven mainly by the wind energy and only to a minor part by the tides [10.32, 10.33].

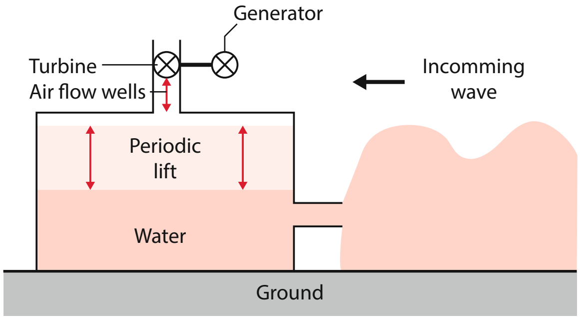


Figure 10.87 Concept of a wave-power station

10.6.4 Geothermal Power Plants

The temperature of the earth's interior increases with increasing depth by about 3–5 °C/100 m, because heat flows from the hot kernel to the outer parts of the earth. The heat in the kernel was mainly generated in the formation period of the earth (about 4 billion years ago) where heavier elements dropped down to the kernel due to gravitational forces. This increased the temperature of the kernel. Another cause for the production of heat is the radioactive decay of elements such as Uranium, Thorium and Potassium that are contained in the kernel as well as in the earth mantle.

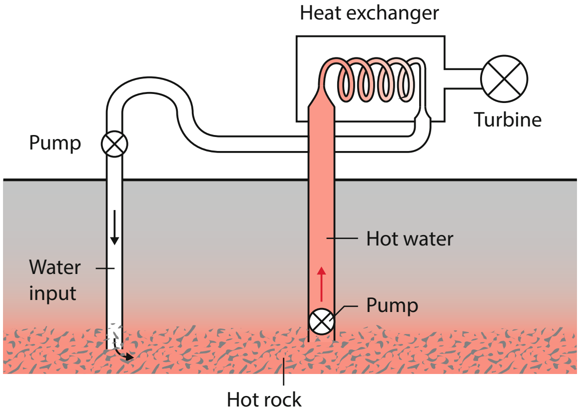


Figure 10.88 Schematic illustration of a geothermic power station

In regions with volcanic activities, water rising from the interior to the surface of the earth has a sufficiently high temperature to be useful as energy source. For example in *Iceland* residences, green houses and swimming pools are heated by hot water from the earth interior. This energy streaming out of the earth interior is called **geo-thermal energy**.

Iceland can cover about 80% of its primary energy consumption (40 PJ $= 40 \cdot 10^{15}$ J) by this geothermal sources.

In regions without such active volcanism, one can drill deep bore holes (3000–5000 m) in order to utilize geothermal energy. The temperature at a depth of 5000 m is about 200–300 °C. For energy production water is pumped into the bore holes which interacts with the hot rock and is heated up. The hot water is pumped back to the surface and can be used for heating purposes or, if its temperature is above 100 °C it can produce through heat exchangers hot steam that drives turbines (Fig. 10.88).

The limitations of the geothermal energy usage in non-volcanic regions is the slow transport of heat from the surrounding of a bore hole, which is mainly due to heat conduction. When the heat extraction becomes larger than the supply of energy from the surroundings the temperature drops and the efficiency of the plant decreases accordingly [10.24]. A much more serious problem are possible geological dislocations. The water pumped under high pressure into the bore hole can modify the rock in the surroundings of the bore hole and can increase the volume of such chemically altered porous rocks. This will cause local uplifts at the earth surface which can damage buildings. Such geothermal plants should be therefore operated far away from inhabited areas.

10.6.5 Solar-Thermal Power Stations

These power stations use the heating of material that absorbs the sun radiation and transfers the heat to a liquid transport medium, such as water or oil. In order to reach sufficiently high temperatures the sun radiation is focused by parabolic or spherical mirrors onto the heated devices.

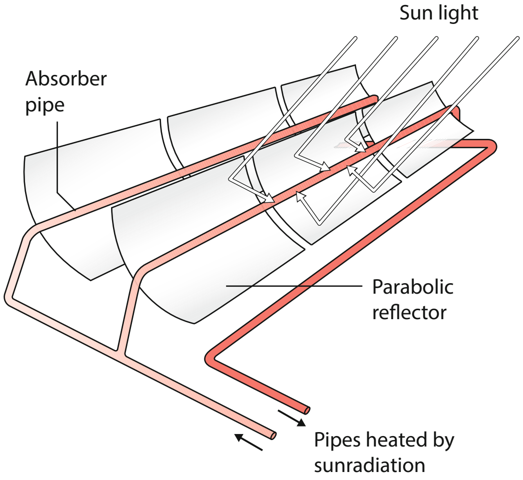


Figure 10.89 Thermal solar power station using parabolic reflectors

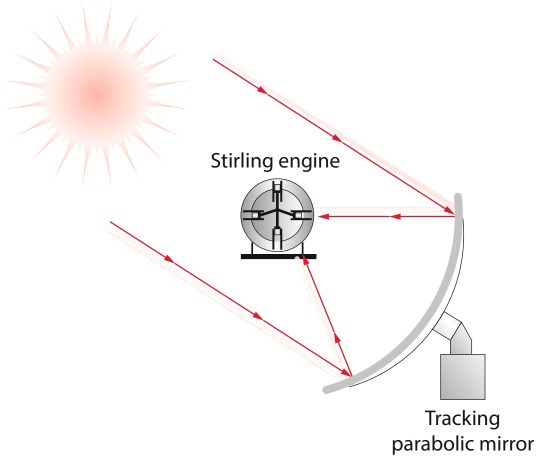


Figure 10.90 Solar power station with parabolic mirrors, that follow up the sun position and focus the sun radiation onto a Stirling motor [10.26]

In the *parabolic gullies construction* the water or oil is pumped through pipes that are located in the focal line of cylindrical mirrors with parabolic profile (Fig. 10.89), which concentrates the sun radiation onto the pipes [10.25].

Another modification consists of several hundred parabolic mirrors (heliostats) that follow up the changing sun position during the day (Fig. 10.90) and concentrate the sun radiation, nearly independent of the position of the sun, onto a small volume at the top of a high tower (Fig. 10.91).

The achievable radiation density of this device is much higher than in the parabolic gully construction and temperatures of about 1000 °C can be reached. This increases the efficiency for the conversion into electric energy. The generated hot steam drives turbines as in fossil power stations.

An example of such a solar-thermal power station is the plant “Plataforma solar de Almeria” in Spain (Fig. 10.92). Here 300 heliostats with 40 m^2 parabolic mirror surface each concentrate the sun radiation onto the radiation collector at the top of an

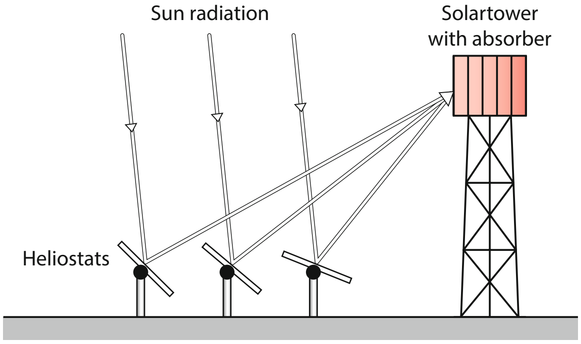


Figure 10.91 Solar tower power station

80 m high tower. This plant produces an average electric power of 40 MW.

The solar-thermal power plants discussed so far only work efficiently for direct sun radiation, i. e. under a clear sky, because the concentration by the heliostats onto a small volume does not work efficiently for the diffuse radiation at cloudy days.

Here another type of solar power stations, the upwind plant, is favourable (Fig. 10.93). The air above a large area under a sloped glass roof that is formed like a cone, is heated by direct or diffuse sun radiation. The hot air streams to the centre of the area where it rises up into a chimney, driving a turbine. Although the efficiency of such a plant is only about 5% it still pays off because of the low construction and operation costs.

An example is the plant “Fuente el Fresno” in Spain, where an area of 2.5 km^2 is covered by the glass roof. The chimney is 750 m high and the delivered electric power amounts to 40 MW. The large area is not lost for agriculture but can be used for growing plants and fruits even during colder periods, since it operates like a green house.

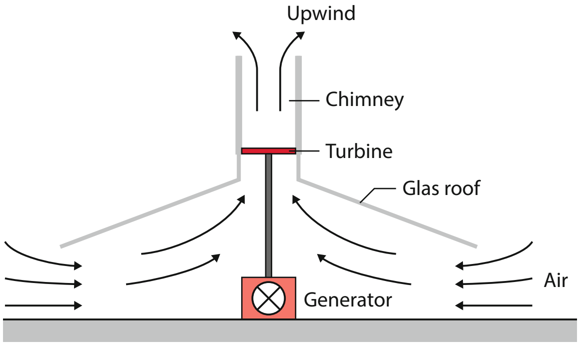


Figure 10.93 Upwind solar power station

10.6.6 Photovoltaic Power Stations

Here the sun radiation energy is directly converted into electric energy by photovoltaic semiconductors. The efficiency amounts to 5–20% depending on the semiconductor material. The basic physics of these devices is explained in Vol. 3.

The price per kWh was very high in the beginning but decreases now rapidly due to mass production of solar cells or thin film photovoltaic devices. In view of the rising prices for fossil energy sources it will soon be able to compete with conventional power plants.

The large disadvantage of all solar power plants is the dependence on the unreliable sunshine duration. It is therefore necessary to realize energy storage devices which can bridge the time periods where the sun does not shine.

Figure 10.92 Gemasolar power station close to Sevilla. 2650 mirrors reflect the sun light onto a tower where a salt solution is heated. It will deliver electric energy of 110 GWh per year. (Torresol Energy Investment S.A.)

10.6.7 Bio-Energy

The burning of farming refuse, such as waste wood, stray, garbage or biogas, which remains in agriculture can produce useful energy, named **bio-energy**, because the burned material is of biological origin. The advantage of this energy source is that it is renewable as long as the consumption does not exceed the natural production. Its disadvantage is the emission of CO_2 which generally exceeds the consumption of CO_2 by the growing plants, although the net emission balance is more favourable than for conventional fossil power plants. Furthermore other species such as SO_2, phosphor and heavy metal compounds are emitted. If only substances as burning material are used, which cannot be utilized for other purposes, the bio-energy can be judged positively. However, if food is used for the production of gasoline, this is contra-productive and should be rejected. Also the burning of wood pellets only makes sense, if they are produced from wood waste, but this technique is nonsense if the pellets are pressed from trees that could have been used elsewhere.

10.6.8 Energy Storage

The increasing production of energy from renewable resources that are not continuously available, demands the realization of sufficient energy storage systems in order to bridge time periods where these sources cannot deliver sufficient energy. There are several proposals for such storage systems, where some of them have been already realized.

The oldest energy storage systems are pumped hydro storage plants. Here water is pumped from a lower storage reservoir into a higher one during times, where sufficient energy is available. During periods where more energy is needed, the water runs back from the higher into the lower reservoir and drives turbines, which activate electric generators. The generators are used during the up-pumping period as electric motors that drive the pumps. This method is up to now the most efficient, but it needs sufficient space on the top of mountains for the upper reservoir. One of many examples is the *Walchensee plant* in Bavaria, Germany, where the water is pumped from the lower Kochelsee into the 200 m higher Walchensee.

For bridging the night periods, where solar plants cannot work, salt storage systems have been developed. Here the surplus energy produced during daytime is used to heat up and melt a salt solution. During night time the heat of the hot solution and the heat of fusion that is released when the solution solidifies, can be used to bridge the energy gap. With multi-component salt solutions, there are several melting temperatures and the heat of fusion is more uniformly delivered during the cooling of the solution. Examples of such salt solutions are $Mg(NO_3)_2 \cdot 6H_2O$, or $CaCl_2 \cdot 6H_2O$.

For small energy demands during night-time compact lithium batteries have been developed which have a storage capacity of 0.2 kWh per kilogram mass. For a volume of 0.5 m^3 of the battery system one can reach a storage energy of 20 kWh. This is sufficient for most private households, which may have solar collectors on the roof and can provide with such a combined system their energy demands during day and night.

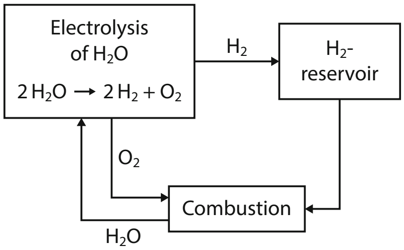


Figure 10.94 Hydrogen gas as energy reservior

A promising storage medium is hydrogen gas H_2, which can be produced by electrolysis during times where surplus solar or wind energy is available. According to the endothermic reaction

$$2H_2O \rightarrow 2H_2 + O_2 \ , \qquad \text{(a)}$$

(Fig. 10.94) hydrogen gas is produced by electrolysis of water. In the reverse exothermic reaction

$$2H_2 + O_2 \rightarrow 2H_2O \qquad \text{(b)}$$

energy is released. The advantage is, that no environmentally dangerous gases such as CO_2 or NH_3 are emitted. The electrolytic systems can be placed directly inside the tower of wind converters and the produced hydrogen gas can be stored in high pressure bottles. The systems can be controlled in such a way, that reaction (a) operates during the time period of wind energy surplus and reaction (b) during times of wind energy shortage. For large plants the hydrogen gas is stored in huge underground caverns, for instance in no longer used salt mines and is transported by underground pipes to special power stations which can burn hydrogen gas. Meanwhile long-time experience is present for the storage of hydrogen gas in caverns.

Example

The cavern *Clemens Dome*, close to Lake Jackson USA, has a volume of 580 000 m^3. The stored gas at a pressure of 10 MPa can deliver an energy of 90 GWh. It is operated since 1986.

While for H_2 storage the reaction energy of the reaction (b) is used, for air storage at high pressures the potential energy $p \cdot V$ of the gas volume is utilized. When the gas flows from the storage tank through a pipe, the potential energy is converted into kinetic energy, which is used to drive a turbine (Fig. 10.95).

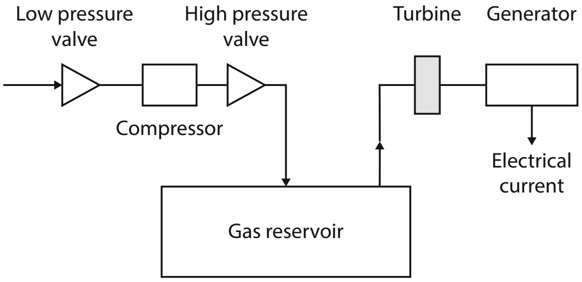


Figure 10.95 Scheme of a high pressure gas reservior

Example

$p = 100\,\text{atm} = 10\,\text{MPa},\ V = 500\,000\,\text{m}^3 \rightarrow E_{\text{pot}} = p \cdot V = 5 \cdot 10^{12}\,\text{N} \cdot \text{m} = 5 \cdot 10^{12}\,\text{Ws} = 1.39\,\text{GWh}.$ ◀

Summary

- The temperature of a body is given either as absolute temperature T in Kelvin or as Celsius temperature $T_C/\,^\circ\text{C}$ or in the US as Fahrenheit temperature. The relations are

$$\begin{aligned} T/\text{K} &= T_C/\,^\circ\text{C} + 273.15, \\ T/\text{F} &= (9/5)T_C\,^\circ\text{C} + 32 \\ &= (9/5)[T/\text{K} - 273.15) + 32 \\ &= (9/5)T/\text{K} - 459.67\ . \end{aligned}$$

  For temperature measurements all quantities can be used, that depend on the temperature (expansion of a liquid volume, electric resistance, thermo-voltage, conductivity of semiconductors).
- The thermal expansion of bodies is caused by the nonharmonic interaction potential between neighbouring atoms.
- The absolute temperature is determined with the gas thermometer, where the increase of the gas pressure with temperature in a constant volume is proportional to the temperature increase.
- The thermal energy of a body is determined by the kinetic and potential energy of the atoms or molecules. The temperature increase ΔT of the system is proportional to the supplied heat energy $\Delta Q = C \cdot \Delta T$.
- The molar heat capacity for a constant volume of a gas $C_V = R \cdot f/2$, is equal to the product of gas constant $R = k \cdot N_A$ times one half of the number f of degrees of freedom of the atoms or molecules in the gas.
- The molar heat capacity at constant pressure is $C_p = C_V + R$
- The transition from the solid to the liquid phase requires the molar melting energy $W = \Lambda_m$ per mole. During the melting the potential energy of the atoms or molecules increases while the kinetic energy stays constant. Similar the transition from the liquid to the gaseous phase needs the energy per mole $W = \Lambda_e$ (heat of evaporation).
- Thermal energy can be transported from one area to another
  - by heat conduction
  - by convection
  - by thermal radiation
- The amount of heat transported per second by heat conduction in the direction $\boldsymbol{r}$ through the area A is $\text{d}Q/\text{d}t = -\lambda \cdot A \cdot (\text{grad}\,T)_{\boldsymbol{r}}$, i.e. the product of heat conductivity λ, area A and temperature gradient in the direction of $\boldsymbol{r}$.
- For metals the heat conductivity is proportional to the electrical conductivity, which indicates that the electrons are mainly responsible for both conductivities.
- The thermodynamic state of a system is unambiguously determined by the state variables pressure p, volume V and temperature T. For ν moles of an ideal gas in the volume V the general gas equation is

$$p \cdot V = \nu \cdot R \cdot T\ .$$

  The number of internal state variables in real gases is given by Gibbs' phase rule (10.134).
- The entropy S of a system is a measure for the number of possible ways the state of the system can be realized. The change of the entropy is $\text{d}S = \text{d}Q/T$ where $\text{d}Q$ is the heat energy supplied to or by the system.
- The first law of thermodynamics $\Delta U = \Delta Q + \Delta W$ describes the energy conservation. The change ΔU of internal energy $U = N \cdot (f/2)kT$ of a system with N atoms or molecules equals the sum of supplied heat ΔQ and mechanical work ΔW performed on or by the system. For real gases is $U = E_{\text{kin}} + E_{\text{pot}}$, because the interaction energy between the atoms has to be taken into account.
- Special processes in a system of an ideal gas are:
  isochoric processes ($V = \text{const}$) $\Rightarrow \text{d}U = C_V \cdot \text{d}T$,
  isobaric processes ($p = \text{const}$) $\Rightarrow \text{d}U = \text{d}Q - p\text{d}V$,
  isothermal processes ($T = \text{const}$) $\Rightarrow p \cdot V = \text{constant}$,
  adiabatic processes ($\text{d}Q = 0$) $\Rightarrow \text{d}U = \text{d}W$ and $p \cdot V^\kappa = \text{constant}$ with $\kappa = C_p/C_V =$ adiabatic index.
- The second law of thermodynamics states that at the conversion of heat into mechanical energy at most the fraction $\eta = (T_1 - T_2)/T_1$ can be converted when the heat reservoir is cooled from the temperature T_1 to T_2.
- The entropy $S = k \cdot \ln P$ is a measure for the number P of realization possibilities for a system with a given temperature T and total energy E.

- Reversible processes are ideal processes where a system passes a cycle of processes and reaches its initial state without any losses. An example is the Carnot Cycle where the system passes through two isothermal and two adiabatic processes.
- For reversible processes the entropy remains constant. For all irreversible processes the entropy increases and the free energy $F = U - T \cdot S$ decreases.
- The entropy S approaches zero for $T \to 0$ (third law of thermodynamics).
- For real gases the Eigen-volume of the atoms and the interaction between the atoms cannot be neglected as for ideal gases. The equation of state $p \cdot V = \nu \cdot R \cdot T$ of ideal gases is modified to the van der Waals equation $(p + a/V^2) \cdot (V - b) = R \cdot T$, where a/V^2 denotes the internal pressure and $b/4$ the Eigen-volume of the N_A molecules per mole.
- The heat of evaporation of a liquid $\Lambda = T \cdot \mathrm{d}p_s/\mathrm{d}T \cdot (V_v - V_l)$ is due to the mechanical work necessary to enlarge the volume V_l of the liquid to the much larger volume V_v of the vapour against the external pressure and against the internal attractive forces between the molecules. The second contribution is much larger than the first one.
- In a $p(T)$ phase diagram the liquid and gaseous phases are separated by the vapour phase curve and the liquid and solid phase by the melting curve. The two curves intersect in the triple point (T_{tr}, p_{tr}) where all three phases can coexist.
- The vapour pressure of a liquid is lowered by addition of solvable substances, which increases the evaporation temperature. Also the melting temperature can be lowered.

Problems

10.1 Give a physically intuitive explanation, why the thermal expansion coefficient for liquids is larger than that of solids.

10.2 Prove example 2 in Sect. 10.1.2.

10.3 A container with 1 mol helium and a container of equal size with 1 mol nitrogen are heated with the same heat power of 10 W. Calculate after which time the temperature of the gas in the containers has risen from 20 to 100 °C. The heat capacity of the containers is 10 Ws/K. How long does it take, until $T = 1000\,°\mathrm{C}$ is reached, when we assume that the vibrational degrees of freedom of N_2 can be excited already at $T = 500\,°\mathrm{C}$? All heat losses should be neglected.

10.4 Give a vivid and a mathematical justification for the time dependent temperature function $T(t)$ during the mixing experiment of Fig. 10.12.

10.5 A container ($m = 0.1$ kg) with 10 mol air at room temperature rests on the ground. What is the probability that it lifts by itself 10 cm above ground? Such an event would cause a cooling (conversion of thermal into potential energy). How large is the decrease of the temperature? (Specific heat of the gas is $(5/2)R$, that of the container is $1\,\mathrm{kJ/(kg \cdot K)}$.)

10.6 A volume of $1\,\mathrm{dm}^3$ of helium under standard conditions ($p_0 = 1$ bar, $T_0 = 0\,°\mathrm{C}$) is heated up to the temperature $T = 500$ K. What is the entropy increase for isochoric and for isobaric heating?

10.7 The critical temperature for CO_2 ($M = 44$ g/mol) is $T_c = 304.2$ K and the critical pressure $p_c = 7.6 \cdot 10^6$ Pa, its density at the critical point is $\varrho = 46\,\mathrm{kg/m^3}$. What are the van der Waals constants a and b?

10.8 What is the entropy increase ΔS_1 when 1 kg water is heated from 0 to 50 °C? Compare ΔS_1 with the entropy increase ΔS_2 when 0.5 kg water of 0 °C is mixed with 0.5 kg of 100 °C.

10.9 A power station delivers the mechanical work W_1 when water vapour of 600 °C drives a turbine and cools down to 100 °C.

a) What is the Carnot efficiency?
b) How many % of the output energy can one win, when the water of 100 °C is used for heating and cools down to 30 °C?

10.10 A hot solid body ($m = 1$ kg, $c = 470\,\mathrm{J/(kg \cdot K)}$, $T = 300\,°\mathrm{C}$) is immersed into 10 kg of water at 20 °C.

a) What is the final temperature?
b) What is the entropy increase?

10.11 Calculate the pressure that a wire with 1 mm diameter exerts onto an ice block with a width of 10 cm (according to Fig. 10.80) when both ends are connected with a mass $m = 5$ kg. What is the increase of the melting temperature? What is the heat supplied to the ice block by the wire, if the outside temperature and the wire temperature are 300 K? How much ice can be melted per second by the wire?

10.12 Calculate from the diagram of Fig. 10.64b the theoretical efficiency of the Otto-motor.

10.13 Show that for a periodically supplied heat at $x = 0$ Eq. 10.42 is a solution of the Eq. 10.38b for one-dimensional heat conduction.

10.14 What is the maximum power an upwind power plant can deliver (area $5\,\mathrm{km}^2$, temperature below the glass roof $T = 50\,°\mathrm{C}$, height of the tower 100 m, outside temperature 20 °C at the top of the chimney).

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