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The Karlsruhe physics course

Lecture notes

# **Thermodynamics**

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## The Karlsruhe physics course

*Lecture notes*

- Mechanics
- **Thermodynamics**
- Electromagnetism
- Optics

**Der Karlsruher Physikkurs**

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# 1

## **Substance-like quantities and the structure of physics**

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## 1.1 Balance equations

We start by positioning thermodynamics in the rest of physics. We'll first have to take a little run-up.

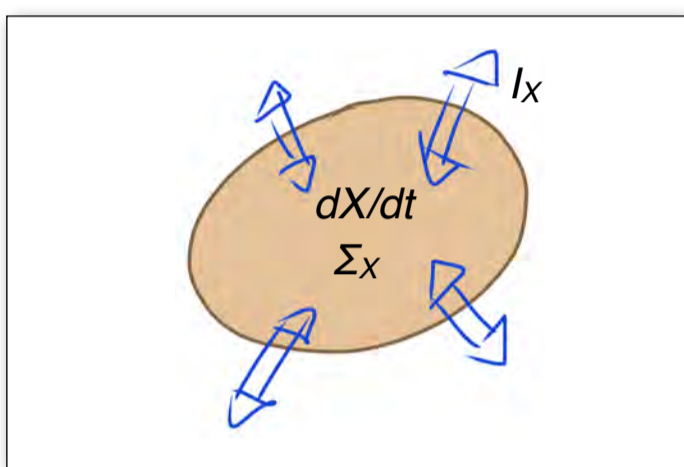
The values of a physical quantity usually refer to a certain geometric structure. Thus electric field strength, temperature and velocity refer to a point. The quantity voltage refers to a line. The force or momentum current, the power or energy current and the electric current refer to surface areas. The quantities we are interested in at the moment refer to a region of space. They include energy, momentum, electric charge, entropy, amount of substance and some others.

Substance-like quantities play a special role in physics. Let us look at some of their properties.

For each substance-like quantity  $X$ , an equation of the form

$$\frac{dX}{dt} = I_X + \Sigma_X \quad (1.1)$$

holds. Also this equation refers to a region of space. It allows the following interpretation, Fig. 1.1:  $X$  is imagined to be the amount of "something": the amount of energy, the amount of movement (in the case of momentum), the amount of electricity, the amount of heat (in the case of entropy) or the amount of a substance.



**Fig. 1.1**

The rate of change  $dX/dt$  has two causes: in- or outflow and creation or destruction.

The term  $dX/dt$  represents the temporal change of the amount of  $X$  in the interior of the region of space. The quantity  $I_X$  refers to the surface of the region. It can therefore be interpreted as a current strength: the strength of the current of the quantity  $X$  through the surface of the region of space under consideration. The quantity  $\Sigma_X$  finally refers again to the interior of the space region and can be interpreted as the production rate of  $X$  (where negative production means annihilation).

In this interpretation, equation (1.1) appears as a balance equation. It tells us that the quantity  $X$  can change in two ways: 1. by a current of  $X$  flowing through the surface into or out of the region, and 2. by production or annihilation of  $X$  taking place inside the region.

For some substance-like quantities, the term  $\Sigma_X$  is always equal to zero. These quantities can only change their value by an inflow or outflow. They are called *conserved quantities*. These include energy, momentum and electric charge. Examples of substance-like quantities which are not conserved are entropy  $S$  and amount of substance  $n$ . Entropy can be created, but not destroyed, while amount of substance can be both generated and annihilated.

The interpretation we present here is justified solely by the form of equation (1.1). In fact, this interpretation is common for some quantities, for others less. Everyone is accustomed to imagine the quantity  $Q$  as an amount of electricity or an amount of charge, and accordingly the quantity  $I$  as the strength of a current, the electric current. The balance equation for the electric charge reads

$$\frac{dQ}{dt} = I_Q$$

The balance equation for the energy is

$$\frac{dE}{dt} = P$$

and that for momentum

$$\frac{d\vec{p}}{dt} = \vec{F}$$

It is customary to interpret the last equation differently: It is said that a force acts on the area of space, or a body within it, and thereby the momentum inside the area changes. However, it is advisable to read this equation in the same way as the other balance equations: The change of the momentum is caused by a momentum current of current strength  $\vec{F}$ .

Each of the major areas of classical physics is characterized by a substance-like quantity. Mechanics is that part of physics which deals with momentum and its currents. Electricity deals with electric charge and electric currents. Accordingly, pure thermodynamics can be defined as that part of physics which deals with entropy and entropy currents. The amount of substances and its currents belong to chemistry.

Energy is a quantity that is not characteristic of any of these areas. It is equally important in all areas of physics.

## 1.2 Energy currents

It is an experience that an energy flow is always linked to the flow of another substance-like quantity  $X$ . The strength of the energy current is proportional to the current strength  $I_X$  of the other quantity. As a general rule we have:

$$P \sim I_X$$

Concrete examples of this relation are

$$P \sim F,$$

which describes the transport of energy through a bicycle chain, for example, or

$$P \sim I,$$

which applies to the transport of electrical energy. These proportionalities are used to define the so-called energy-conjugated intensive quantities.

The electrical potential difference  $U$  is defined by

$$P = U \cdot I \tag{1.2}$$

and the velocity can be defined by

$$P = \vec{v} \cdot \vec{F}. \tag{1.3}$$

We will see that for thermal energy transports the relationship

$$P \sim I_S$$

holds and that the temperature  $T$  is defined by

$$P = T \cdot I_S. \tag{1.4}$$

Accordingly, for chemical energy transports

$$P \sim I_n,$$

and the chemical potential  $\mu$  is defined by

$$P = \mu \cdot I_n. \tag{1.5}$$

The uniform structure of equations (1.2) to (1.5) shows that we are dealing with an analogy. The areas of physics mentioned before have a common structure. The analogy consists in the fact that certain physical quantities are mapped on each other. From a relation valid in one of the subareas, one obtains a relation in another sub-area by simply replacing the corresponding quantities. Energy, energy current, position and time are not translated, or in other words, they transform into themselves. The second and third columns of Table 1.1 show the substance-like and intensive quantities which are replaced by each other. The fifth column shows an example of an equation in its various analog variants.

	Extensive quantity	Intensive quantity	Currentstrength	$P = \xi \cdot I_X$
<b>Mechanics</b>	momentum $p$	velocity $v$	force $F$	$P = v \cdot F$
<b>Electricity</b>	electric charge $Q$	elektric potential $\phi$	electric current $I$	$P = U \cdot I$
<b>Heat</b>	entropy $S$	temperature $T$	entropy current $I_S$	$P = T \cdot I_S$
<b>Chemistry</b>	amount of substance $n$	chemical potential $\mu$	substance current $I_n$	$P = \mu \cdot I_n$

**Table 1.1**

Assignment of physical quantities to sub-areas of physics and chemistry

The intensive quantities defined by equations (1.2) to (1.5) play an important role in flows associated with “friction” in a more general sense, or dissipation. Such processes are

- mechanical friction;
- “electric friction”, i.e. the process that occurs when an electrical current flows through a resistor;
- the process by which entropy flows through a thermal resistor;
- diffusion and chemical reactions that occur spontaneously.

For all these “flows”, the substance-like quantity flows from the high to the low value of the corresponding intensive quantity.

Thus, during mechanical friction processes, momentum always flows from the body of the higher velocity to the body of the lower velocity.

In electrical resistors, the electric charge flows from high to low electric potential.

Entropy flows from places of high to places of low temperature.

Finally, substances always diffuse from places with high to places with low chemical potential. In addition, chemical reactions always run spontaneously in the direction of decreasing chemical potential.

If one wants to run any of these processes in the opposite direction, one has to supply energy.

To transfer momentum from a body of lower to a body of higher velocity, a motor can be used. Electricity is transferred from low to high electric potential with the help of a battery or a generator. Entropy is pumped with a heat pump from low to high temperature. And a chemical reaction is driven in the opposite direction to the spontaneous drive, for example in an electrolysis cell.

We are now able to say what thermodynamics is all about. Thermodynamics is more than just the physics of heat. It is more than just the relationship between entropy and temperature. Thermodynamics deals with the interplay of thermal, chemical and mechanical processes. In addition to the ubiquitous energy, the variables we will be dealing with are therefore the thermal variables entropy and temperature and the chemical variables amount of substance and chemical potential. In thermodynamics, mechanics usually does not enter with its variables momentum and velocity, but with the substitutes volume and pressure.

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# 2

## Entropy und temperature

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### 2.1 Entropy as a measure of heat

The entropy  $S$  is a quantity for which non-physicists have a good intuitive understanding and with which they intuitively operate correctly. There is probably no other quantity for which the physical term matches a colloquial term so well: Most colloquial statements in which the word “heat” or “quantity of heat” appears remain correct in the sense of physics if these words are replaced by the word “entropy”.

However, in physics the word “heat” is used with a different meaning, namely as the name of the “differential form”  $TdS$ , and this does not match the colloquial meaning of the word. We therefore will not use the word heat in this sense.

Below are some statements in which the word heat is used in its colloquial meaning. These sentences remain correct if the word heat is replaced by the word entropy. In this way we get a qualitative understanding of the concept of entropy:

If one holds an object, e.g. a piece of iron, over a gas flame, it becomes warmer, its temperature increases. Heat (entropy) flows into the object. The more heat flows into the object, the higher its temperature. If the object is removed from the flame and wrapped in polystyrene, the heat (entropy) remains in it. If it is divided into two equal parts, each part contains half the heat (entropy) contained in the entire object. The heat (entropy) is thus substance-like. A heat density (entropy density) can be defined.

When a warm object is brought into contact with a cold one, heat (= entropy) flows from the warm to the cold, i.e. from the object of higher to that of lower temperature. The greater the temperature difference, the easier the heat (entropy) flows. Whether it flows quickly from a warm to a cold body also depends on the type of contact or connection. If the objects are connected by a piece of wood, the heat (entropy) flows more slowly than if they are connected by a piece of copper. So there are good and bad heat conductors (entropy conductors).

If one holds first a container with air and second a container of the same size with water over a flame, one notices that the air heats up faster, i.e. reaches a certain temperature faster than the water. So one has to put more heat (entropy) into the water to reach this temperature. Water has a greater heat capacity (entropy capacity) than air.

One can also add heat (entropy) to a “system” without heating it up. If boiling water is left on the flame, heat (entropy) flows continuously into the water. But its temperature no longer increases. Instead water is constantly evaporated. The steam must therefore carry away the heat (entropy). One gram of steam therefore contains (much) more heat (entropy) than one gram of liquid water.

If one leaves an object, which one has previously heated, for a while (without a further heating), the heat (entropy) flows out of it; it spreads in the environment. In the process, it becomes so diluted that at the end it is not easy to tell exactly where it has gone. Nevertheless, it is somewhere, it has not disappeared in the sense of “destroyed”, but only disappeared in the sense of “hidden” or “dispersed”.

Heat (entropy) cannot be destroyed, but it can be produced, e.g. in a flame, in an electrical resistor or by mechanical friction.

Energy is needed to produce heat (entropy). Since we believe in the conservation of energy, we conclude that with the heat (entropy) that flows away from an electrical resistance, energy also flows away.

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### 2.2 Definition of the entropy scale

When introducing a new physical quantity, a scale of the quantity must be defined. The scale allows to attribute values to the quantity. The definition of a scale includes 1. the specification of the unit and 2. a rule for constructing multiples of the unit.

The definition of the unit is essentially a technical problem.

The specification of multiples, on the other hand, affects the essential of the quantity. In fact, the definition of multiples is a delicate problem in certain cases. There are quantities where this definition has changed throughout the history of physics. In the course of time the scale has been distorted, or better: rectified. An example is the temperature scale.

Let us first consider how to define the unit and the scale of entropy. We'll start with the unit.

The unit of entropy is the Carnot, abbreviated Ct. We know that entropy is needed to melt ice. With 1 Ct at normal pressure 0.893 cm<sup>3</sup> ice is melted. It could therefore have been decided by law:

„1 Carnot is that amount of entropy with which 0.893 cm<sup>3</sup> of ice is melted at normal pressure.“

In fact, a different procedure has been preferred as the legal definition. This procedure is somewhat more complicated in concept, but allows a more precise definition of the unit. We'll come back to this later.

Now to the construction of multiples of entropy values. For substance-like quantities, the construction of multiples is always trivial. If a system contains one unit of a quantity, two units are obtained by simply placing an identical system next to the first.

Practical measurement procedures must be distinguished from the procedure for defining the unit and the multiples of the values of the quantity. In order to determine the values of a quantity practically, one needs a procedure, which is not too cumbersome. In principle, an amount of entropy could be measured by melting ice and measuring the corresponding change of the volume of the ice. However, this procedure is impractical. Why? The entropy to be measured is located in any system: a container or a body. From there it must be transferred to the ice to be melted. Now it is very difficult to transfer entropy from one body to another without creating new entropy. It is particularly difficult if the body from which the entropy is taken is at a different temperature than the ice. The entropy must then be carefully pumped up or flow down (with the help of a heat pump or a heat engine, respectively). There is a more practical way to measure entropy. This makes use of the producibility of entropy. We will get to know this procedure later.

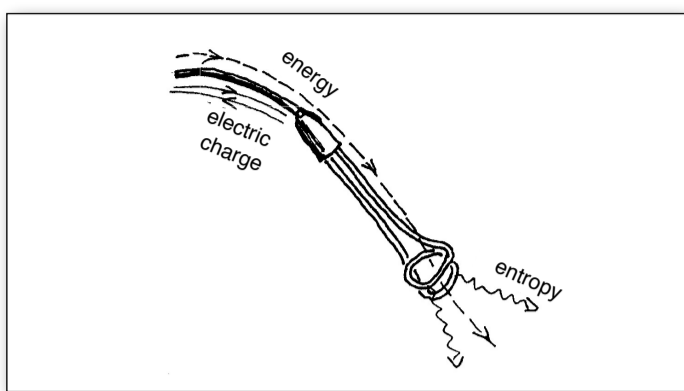
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## 2.3 Entropy and energy – the temperature scale

Before we turn to the definition of the temperature scale, we must examine the energy and entropy balances of some simple devices.

Fig. 2.1 shows an immersion heater. First the entropy balance: Entropy comes out of the immersion heater, but no entropy flows into it. The entropy is generated in the immersion heater.



**Fig. 2.1**  
Energy and entropy balance of an immersion heater

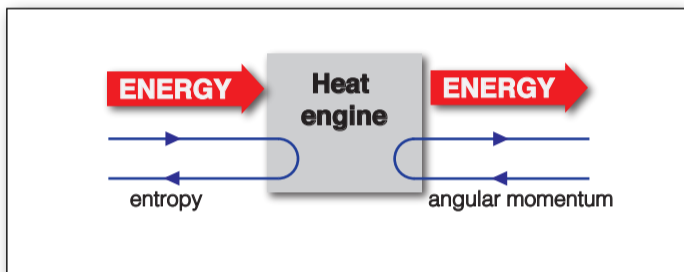
And the energy balance: Energy flows into the immersion heater via the cable, and it must come out again. The only possibility for this is that it comes out across the outer surface together with the entropy. It is also said that the energy enters the immersion heater with the *energy carrier* “electric charge”, and it comes out with the energy carrier “entropy”. We conclude that an entropy current is accompanied by an energy current.

We are now looking for the relationship between the entropy current  $I_S$  and the energy current  $P$ . Since both quantities are currents of substance-like quantities, the relationship must be:

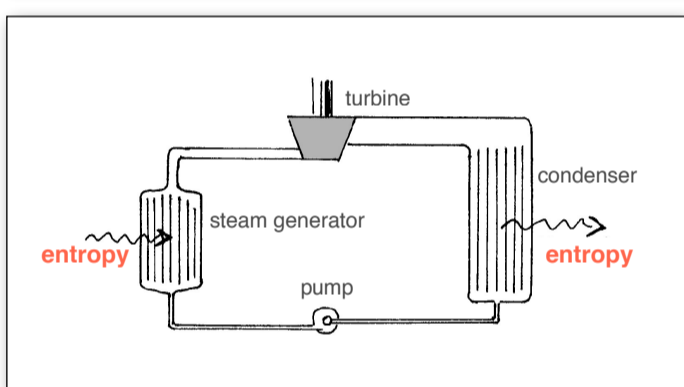
$$P \sim I_S \quad (2.1)$$

(One can imagine, for example, operating two immersion heaters next to each other. Then both the energy and the entropy current for both together are twice as large as for a single one.)

The next system we look at is the entropy and energy balance of a thermal engine. Fig. 2.2 shows the corresponding flow diagram, Fig. 2.3 shows the thermal engine in more detail.



**Fig. 2.2**  
Flow diagram of a heat engine



**Fig. 2.3**  
The heat engine of a power plant consists of the steam generator, the turbine, the condenser and the pump.

Thermal engines are used in coal-fired and nuclear power plants, among others. Entropy flows into the system at high temperature. This entropy is obtained by production: by burning coal or by fission of uranium and plutonium. The entropy enters the system in the steam generator. The steam expands in a turbine. Thereby it becomes colder. In the condenser, the steam condenses, releasing the entropy that was previously (in the steam generator) absorbed. This entropy is transferred to the water of a river or (in a cooling tower) to the ambient air.

The entropy current at the inlet of the heat engine system is equal to that at the outlet. If in a real machine, the entropy current at the output is somewhat greater than at the input, this is due to imperfections of the machine, which in principle can be made as small as desired.

As the entropy flows through the system, the turbine delivers energy via the shaft. This energy must have entered into the machine. The only possibility is that the entropy flowing out carries less energy than the entropy flowing in. The difference between the energy current flowing in with the entropy and that coming out again with the entropy leaves the machine via the shaft. There must be a difference between the entry and the exit of the entropy. More precisely: The proportionality factor that makes the relationship (2.1) an equation must have different values for input and output. It must depend on a variable that has different values at input and output. Now we know that the output of the machine is colder than the input, that the temperature of the output is lower than that of the input, whichever is the temperature scale used.

Since we have not yet defined the temperature scale, we can do it now: The proportionality factor that makes (2.1) an equation is called temperature. The temperature  $T$  is therefore defined as:

$$T := \frac{P}{I_S} \quad (2.2)$$

To distinguish  $T$  from the temperature measured in °C, this variable is also called absolute temperature.

The definition (2.2) is analogous to that of the electrical voltage. In fact, the electrical voltage is defined as the quotient of energy current and electric current. (This fact is often formulated differently, for example: Voltage equals energy per charge. However, this formulation is equivalent to our version.)

We write equation (2.2) in the form in which it is usually remembered:

$$P = T \cdot I_S \quad (2.3)$$

### 2.4 The units of temperature and entropy

Since the scales, and thus the multiples of energy and entropy are defined, equation (2.2) also specifies the multiples of the temperature. However, we had initially postponed the definition of the unit of the entropy. We can now make up for what is still missing. If one were to define the entropy unit, the temperature unit would also be defined with equation (2.2) (because the energy unit is already known from mechanics). In reality, however, we proceed the other way round: we define a temperature unit by law and deduce the entropy unit, the Carnot, using equation (2.2). Thus, the temperature unit is defined as follows:

The temperature of water at the “triple point” is 273.16 Kelvin.

The triple point is the temperature at which solid, liquid and gaseous water coexist. It is particularly suitable for defining the temperature unit, because no additional information about the values of other variables has to be given. So it does not have to be specified: “at a pressure of...”. When water is at the triple point, the pressure is inevitably fixed.

We summarize the somewhat complicated process of defining the scales of entropy and temperature.

The multiples of entropy result simply from the substance-likeness of the quantity. The multiples of temperature values are defined by equation (2.2). The unit of the temperature is defined by the triple point of the water. From this follows the entropy unit via equation (2.2):

$$1 \text{ Ct} = 1 \text{ J/K.}$$

One more remark about the “crooked” value in the definition of the temperature unit. It was chosen because a temperature difference of 1 Kelvin should be equal to the previously introduced °C (degrees Celsius).

The temperature of the phase transition between solid and liquid water at normal pressure (the temperature of melting ice) is 273.15 K. For the relationship between Celsius temperature  $\vartheta$  and absolute temperature  $T$ , the following applies

$$\frac{T}{\text{K}} = \frac{\vartheta}{\text{°C}} + 273.15$$

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## 2.5 Heat engine and heat pump

We can now establish the energy balance of the heat engine. (The entropy balance is trivial: just as much flows in as flows out.)

With the entropy (current  $I_S$ ) flowing into the machine at the high temperature  $T_2$ , an energy current

$$P_2 = T_2 \cdot I_S$$

enters into the machine, and with the entropy flowing out at the low temperature  $T_1$ , an energy current

$$P_1 = T_1 \cdot I_S$$

comes out.

Thus, a net energy current

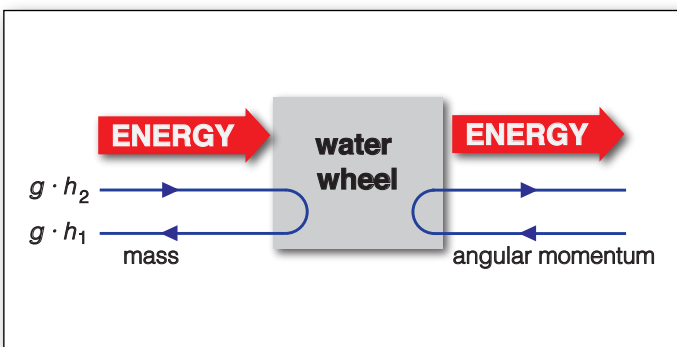
$$P = P_2 - P_1 = T_2 \cdot I_S - T_1 \cdot I_S$$

or

$$P = (T_2 - T_1) I_S \quad (2.4)$$

enters the machine.

It can be seen that the working principle of the heat engine is similar to that of a water wheel, compare Fig. 2.4 with Fig. 2.2.



**Fig. 2.4**

Flow diagram of a water wheel

The entropy corresponds to the water in the water wheel, or more precisely, to the mass  $m$  of the water, and what is the temperature in the thermal engine is the gravitational potential  $g \cdot h$  ( $g$  = gravitational field strength,  $h$  = height) in the water wheel. A mass current flows at a great height towards the water wheel, a mass current of the same strength flows away from it at a lower height. At the water wheel, the mass moves down from a great height to a small height, thereby releasing energy. The corresponding energy current is

$$P = P_2 - P_1 = g \cdot h_2 \cdot I_m - g \cdot h_1 \cdot I_m = g (h_2 - h_1) I_m$$

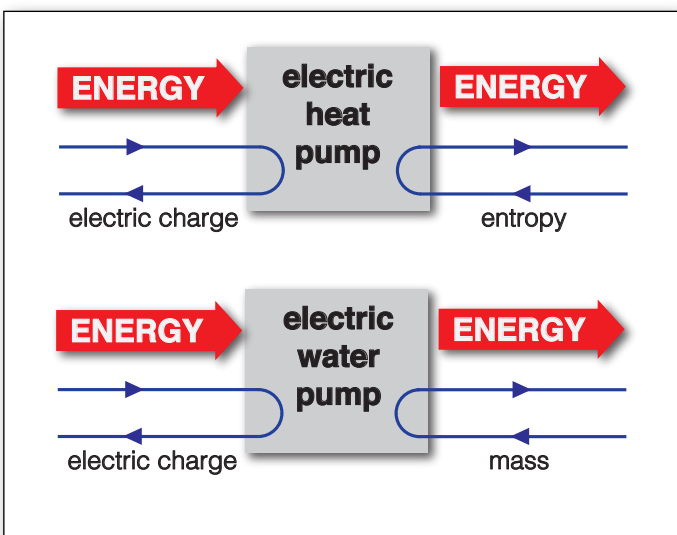
Now to the heat pump. The heat pump does just the opposite of what a heat engine does: it conveys entropy from low temperature to high temperature. Since the entropy flowing away at the high temperature carries more energy than that entering at the low temperature, the heat pump needs an energy supply. The energy it needs to pump is again given by the equation

$$P = (T_2 - T_1) I_S .$$

In analogy to this, there is also an inversion to the water wheel: the water pump. Its energy demand is given by the equation

$$P = g (h_2 - h_1) I_m$$

Fig. 2.5 shows the flow diagrams of an electric heat pump and an electric water pump.

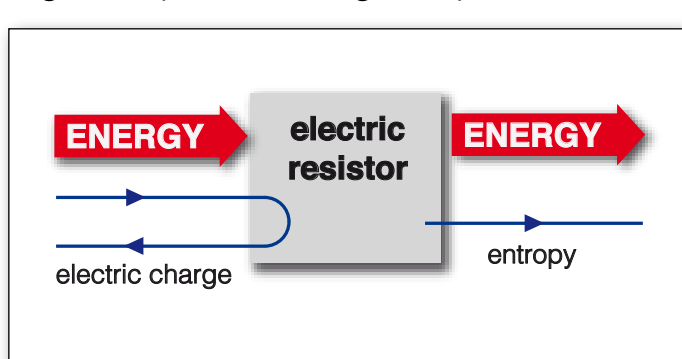


**Fig. 2.5**

Flow diagrams of an electric heat pump and an electric water pump.

## 2.6 Entropy production – reversible and irreversible processes

If electricity flows through an electrical resistor – from high to low electric potential –, the resistor becomes warm, entropy is produced, Fig. 2.6. (See also Fig. 2.1.)



**Fig. 2.6**  
Flow diagram of an electric resistor

The energy flowing to the resistor must be equal to the energy flowing away. It must therefore apply:

$$(\phi_2 - \phi_1) \cdot I = T \cdot I_{S \text{ prod}} \quad (2.5)$$

Here is  $\phi$  the electric potential,  $I$  the electric current and  $I_{S \text{ prod}}$  the time rate of entropy production. We read the equation as follows: Towards the resistor, energy flows with the energy carrier electric charge and away from the resistor with the carrier entropy. The entropy with which the energy leaves the resistor was produced within the resistor. If  $U = \phi_2 - \phi_1$ ,  $I$  and  $T$  are known, the produced entropy can easily be calculated:

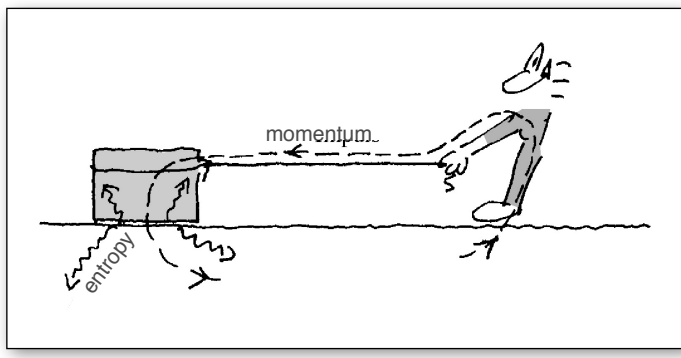
$$I_{S \text{ prod}} = U \cdot I / T$$

It is an important experience that entropy cannot be destroyed. As a result, processes in which entropy is produced cannot run backwards, they are *irreversible*.

Equation (2.3) tells us that energy is needed to carry the produced entropy away. We say that this energy is *dissipated*. Processes in which entropy is produced are called dissipative processes.

There are some standard dissipative processes that have certain characteristics in common. One of these is the process just discussed, in which an electric current flows through an electric resistor.

Another such standard process is mechanical friction, Fig. 2.7: entropy is produced while momentum flows from one body to another through a “momentum resistor”, i.e. through the contact surface between the two bodies.



**Fig. 2.7**  
Momentum and entropy balance for a friction process

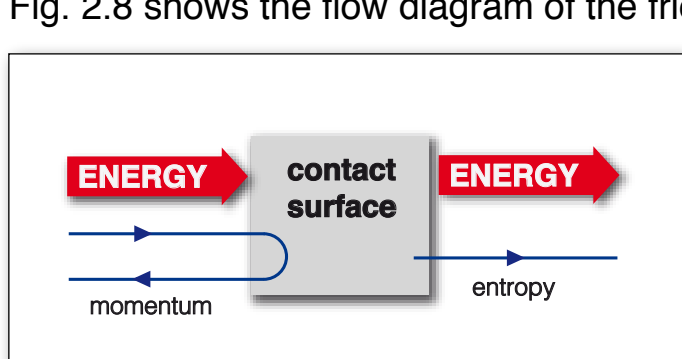
The momentum flows from the body with higher velocity  $v_2$  to the body with lower velocity  $v_1$ . The energy flow required to maintain the process has the strength

$$P = (v_2 - v_1) \cdot F.$$

Thus, the energy balance is:

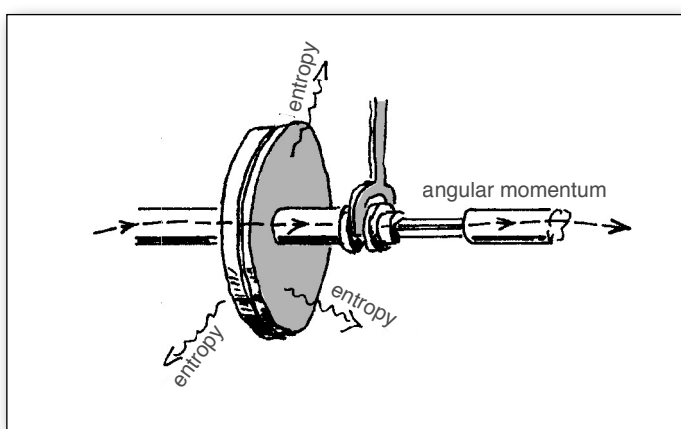
$$\Delta v \cdot F = T \cdot I_{S \text{ prod}}.$$

Fig. 2.8 shows the flow diagram of the friction process.



**Fig. 2.8**  
Flow diagram of a friction process

Fig. 2.9 shows a third dissipative process. Here, angular momentum flows from the shaft with the higher angular velocity to the shaft with the lower angular velocity in a slipping clutch.

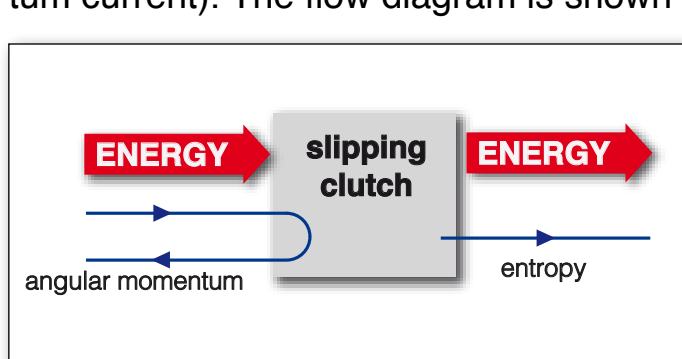


**Fig. 2.9**  
Angular momentum and entropy balance for a slipping clutch

The energy balance reads:

$$\Delta \omega \cdot M = T \cdot I_{S \text{ prod}},$$

( $\omega$  is the angular velocity and  $M$  is the torque or the angular momentum current). The flow diagram is shown in Fig. 2.10.



**Fig. 2.10**  
Flow diagram of a slipping clutch

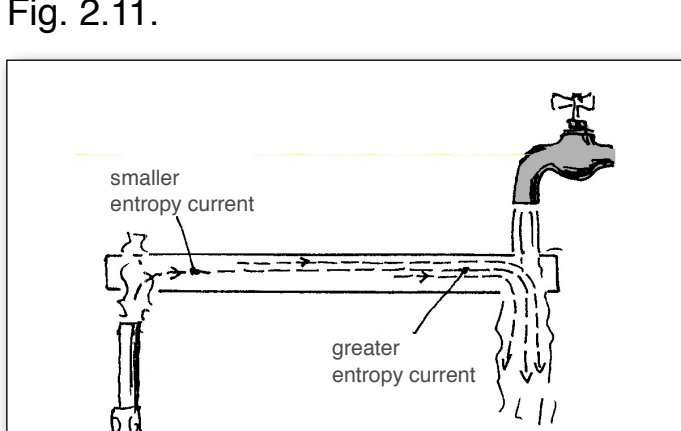
One type of process, which we will not consider until the next chapter, is a free-running chemical reaction. Also here entropy is generated, and also here an energy balance equation can be formulated, which has the same structure as that of the electric resistance:

$$\Delta \mu \cdot I_n = T \cdot I_{S \text{ prod}}.$$

Here  $\mu$  is the chemical potential and  $I_n$  the substance conversion (measured in mol/s).  $\Delta \mu$  is the difference between the chemical potentials of reactants and products.

All the processes we have discussed here have in common that a substance-like quantity flows from one point to another or goes from one state to another via a kind of resistor. The corresponding intensive quantity – electric potential, velocity, angular velocity, chemical potential – has a higher value at the first position, or in the first state, than at the second position, or in the second state. The substance-like quantity flows “from the high value of the intensive quantity to the low value”.

Finally, we consider a dissipative process that has a peculiarity. Through a thermal conductor (= resistor), whose ends are at the different temperatures  $T_2$  and  $T_1$ , an entropy current flows from the end with the high temperature  $T_2$  to the end with the low temperature  $T_1$ , Fig. 2.11.



**Fig. 2.11**  
Entropy balance of a heat conductor

Also in this case entropy is produced. This means that more entropy arrives at the cold end than has flowed into the thermal resistor at the hot end. The energy balance can be formulated as follows:

$$T_2 \cdot I_{S2} = T_1 \cdot I_{S1}, \quad (2.6)$$

because the incoming and outgoing energy currents must be equal.

This equation shows that the entropy current  $I_{S1}$  must be greater than  $I_{S2}$ . Since the entropy current flowing out is composed of the current flowing in and the entropy produced in the resistor per time,  $I_{S1}$  can be written.

$$I_{S1} = I_{S2} + I_{S \text{ prod}},$$

Together with (2.6) this results in

$$(T_2 - T_1) \cdot I_{S2} = T_1 \cdot I_{S \text{ prod}}.$$

If we omit the index 2 for the entropy current flowing in, we get

$$(T_2 - T_1) \cdot I_S = T_1 \cdot I_{S \text{ prod}}, \quad (2.7)$$

i.e. again an equation of the type of equation (2.5).

The process described in equation (2.7) could be called thermal friction. The peculiarity of the process is that the flowing quantity is of the same nature as the produced one.

## 2.7 Efficiency

Many devices and machines serve the purpose of transferring energy from one energy carrier to another. The electric motor receives energy with the carrier electric charge and releases it with angular momentum. Energy flows into an electric heat pump with electric charge, and it leaves it with entropy. Such devices or machines are often called energy converters. This way of speaking is not very appropriate. In fact, nothing is converted. The energy only changes its companion. We therefore prefer the name *energy transloader*. We say the energy is loaded from one carrier to another.

Every energy transloader has losses. The cause of energy losses is always the production of entropy. Part of the incoming energy is used or consumed to carry the produced entropy away, according to equation (2.3).

The transport of a substance-like quantity is also associated with more or less entropy production. Again, energy is needed, and this is also to be recorded as a loss.

Energy is always lost when entropy is produced. Thus, the motto “save energy” should better be replaced by “avoid entropy production”.

In fact, any activity that produces entropy can also be realized by a process that runs without entropy production. There is no physical reason why we consume energy at all. In principle, all production and transport services could be managed without energy expenditure. It is technically important to assess whether an appliance, a machine, a transport device is wasting energy. We therefore define an *efficiency*  $\eta$  for the equipment in question.

To define the efficiency, the system to be evaluated is compared with another system that provides the same service, but does not produce entropy, i.e. with a perfect, ideal system. Let the energy consumption of the real machine be  $P_{\text{real}}$  and that of an ideal machine with the same achievement (whatever it may be)  $P_{\text{ideal}}$ . We define the efficiency as

$$\eta = \frac{P_{\text{ideal}}}{P_{\text{real}}} \quad (2.8)$$

The definition is such that for a device in which no entropy is produced, the efficiency  $\eta = 1$  results.

We now want to calculate the efficiency of a notorious energy waster: an electric heater. The service that we expect from the heater is to provide a certain entropy current  $I_S$  at a certain temperature  $T_2$ . If the heater is used to heat a house,  $I_S$  is also the entropy current that leaves the house through the heat leaks.  $T_2$  is the temperature inside the house.

The real electric heater needs an energy current of

$$P_{\text{real}} = T_2 \cdot I_S$$

A reversibly working machine for heating the house would be a heat pump that pumps the required entropy into the house from outside the house. The energy consumption of the heat pump is (see section 2.5)

$$P_{\text{ideal}} = (T_2 - T_1) I_S.$$

This results in the efficiency (2.8):

$$\eta = \frac{P_{\text{ideal}}}{P_{\text{real}}} = \frac{(T_2 - T_1) I_S}{T_2 I_S} = \frac{T_2 - T_1}{T_2}$$

It is interesting that the efficiency can be expressed by only two temperatures. The fact that it is a resistance heater is not reflected in the equation. In fact, the same equation results for any other heater, where all the required entropy is obtained by production. Because of its universal meaning, this expression has its own name. The expression

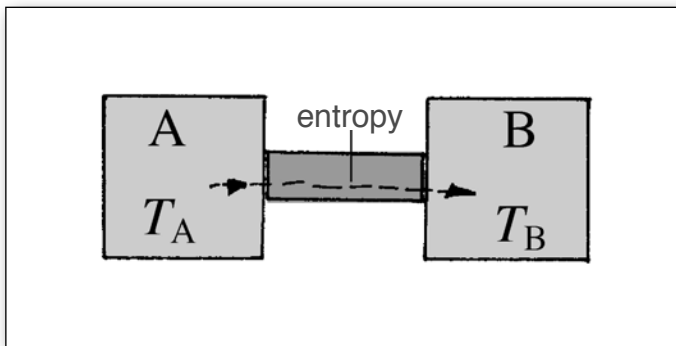
$$\eta = \frac{T_2 - T_1}{T_2} \quad (2.9)$$

is called *Carnot factor*.

## 2.8 Thermal equilibrium

When entropy flows via a heat conductor from a body A of higher temperature into a body B of lower temperature, the temperature  $T_A$  decreases and the temperature  $T_B$  increases, Fig. 2.12: The two temperatures equalize. Finally

$$T_A = T_B.$$



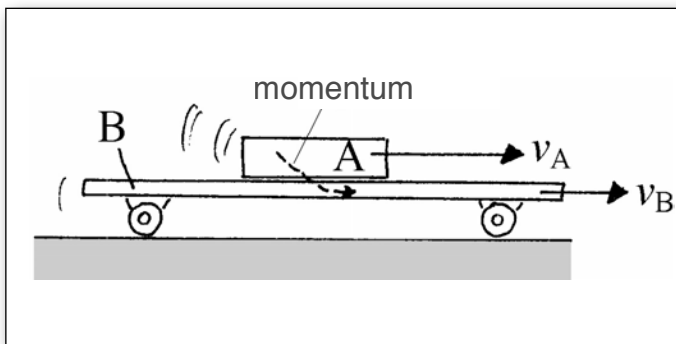
**Fig. 2.12**

Thermal equilibrium establishes between the two bodies.

When this state is reached, there is no longer any “drive” for the entropy current, the entropy ceases to flow. This state is called *thermal equilibrium*.

It is analogous to other equilibrium states. Momentum equilibrium occurs when two bodies A and B rubbing against each other reach the same velocity, Fig. 2.13, i.e. when

$$v_A = v_B.$$

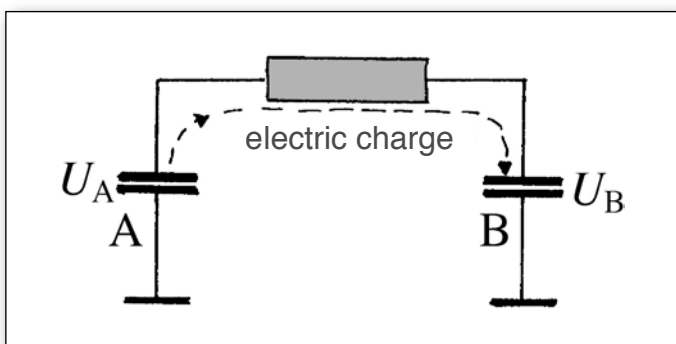


**Fig. 2.13**

Momentum equilibrium establishes between the two bodies.

Electric equilibrium is reached between two capacitors connected to each other by a resistor, Fig. 2.14. In the electric equilibrium is

$$U_A = U_B.$$



**Fig. 2.14**

Electric equilibrium establishes between the two capacitors.

## 2.9 Measuring temperature and entropy

### Measuring temperature

For measuring the temperature, those effects are suitable where mechanical, electrical or optical variables depend on the temperature, e.g.

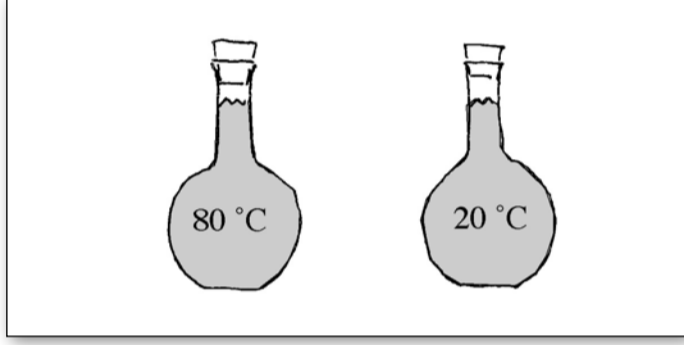
- thermal expansion of a solid: bimetallic strip (used in thermostats);
- thermal expansion of a liquid: mercury thermometers;
- thermal expansion of gases: gas thermometer;
- thermoelectric effect: an entropy current is coupled to a current of charged particles; with an open circuit the particle current cannot flow, and a temperature difference causes a difference in the electrochemical potential;
- the electric resistance of a material depends on temperature: for metals the resistance increases with  $T$ , for semiconductors it decreases;
- every body emits electromagnetic radiation; the spectrum of the radiation depends on temperature: radiation pyrometer;
- some substances change their color when a certain temperature is exceeded.

In most temperature measurement procedures, the measuring instrument is brought into thermal equilibrium with the system  $Y$ , whose temperature is to be determined: an entropy conducting connection allows for an entropy flow from  $Y$  to the measuring instrument. The entropy flows until the measuring instrument and system  $Y$  have the same temperature. The entropy capacity of the instrument must be small compared to that of  $Y$ . Furthermore, the measuring instrument should not have a thermal leak, otherwise the entropy flow between  $Y$  and the measuring instrument never comes to a standstill. Analogous remarks apply to the measurement of other intensive quantities.

### Measuring entropy

The fact that entropy can be produced makes its measurement more difficult if a method is applied that is analogous to the methods used to measure conserved quantities, such as electric charge. Actually, however, it facilitates the measurement, since a method can be employed that is not possible with conserved quantities.

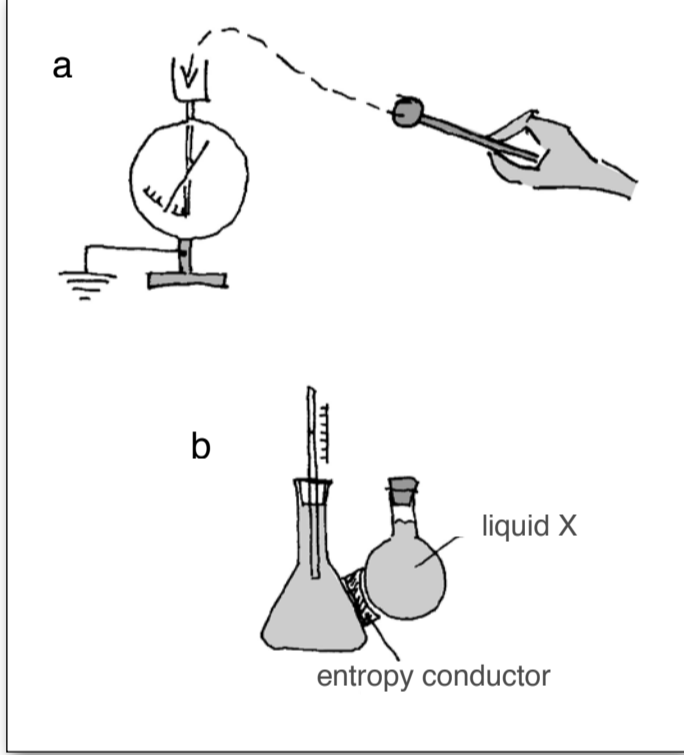
In the following we assume that we do not want to measure the total entropy contained in a system, but only the amount by which the entropy content of the system differs in two given states. The measuring task is e.g.: How much more entropy is contained in a certain amount of liquid  $X$  at  $80^\circ\text{C}$  than at  $20^\circ\text{C}$ , Fig. 2.15?



**Fig. 2.15**  
By how many Carnots do the entropy contents differ?

### Method without entropy production

We orientate ourselves on the measurement of electric charge. One transfers the amount of charge to be measured to an electrometer, Fig. 2.16a. The electrometer is calibrated, i.e. the relation between deflection and charge is known.



**Fig. 2.16**  
(a) Measuring electric charge. The charge to be measured is transferred to the calibrated electrometer.  
(b) Measuring entropy. The entropy to be measured is transferred to the calibrated entropy measuring instrument.

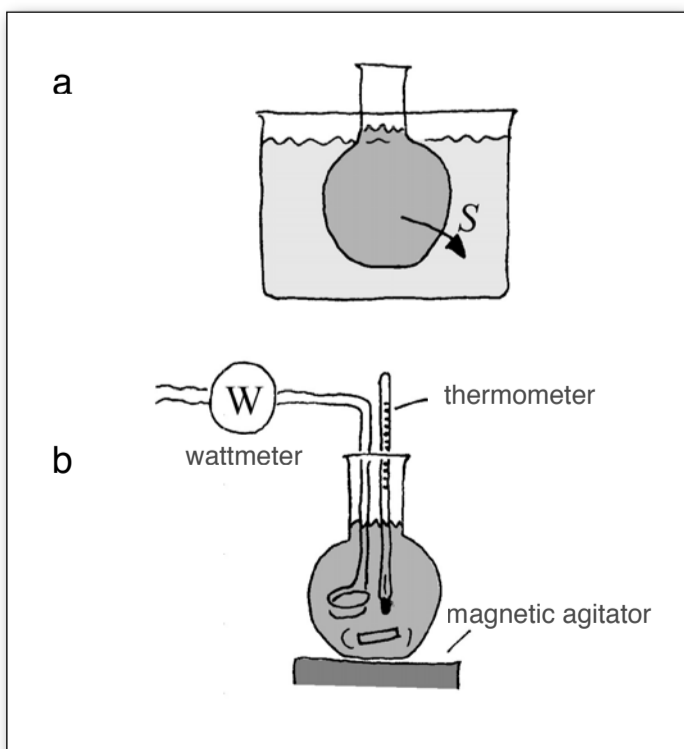
Accordingly, the entropy to be measured can be transferred into a container filled with water, Fig. 2.16b. The water expands. The vertical pipe is calibrated, i.e. the relation between vertical rise and entropy content of the water is known. However, the procedure is very impractical, because in general the entropy to be measured is located in a system whose temperature is different from that of the calibrated water tank. If the system is at a higher temperature than the measuring instrument, the entropy to be measured can be transferred with a heat conductor. But this produces additional entropy and the meter displays too much. If the system is at a lower temperature than the instrument, the entropy does not flow into the instrument at all. This means that a heat pump or a heat engine must always be installed between the system and the measuring device so that the entropy is brought to the temperature of the measuring device. This procedure is so impractical and inaccurate that it is not used.

### Method with entropy production

With this method it is not possible to determine the amount of entropy already in the system. Instead, the entropy whose value one wants to determine is first transferred to the environment and the same amount is then produced anew.

In our case, we will first allow the entire entropy to be measured to flow out of our liquid  $X$ , which is at  $80^\circ\text{C}$ : We cool the liquid to  $20^\circ\text{C}$ , Fig. 2.17a. Then we produce the entropy anew and measure the incoming energy flow as well as the temperature, Fig. 2.17b. The energy current  $P$  and the entropy current  $I_S$ , which flow out of the heating device, are related by

$$P = T \cdot I_S.$$



**Fig. 2.17**  
One lets the entropy to be measured flow out of the system (a) and then produces the same amount anew (b).

The temperature is the same throughout the liquid (thanks to the agitator). Energy is supplied until the temperature has risen from  $(273.15 + 20)$  K to  $(273.15 + 80)$  K. The entropy produced in the heating resistor is

$$S = \int_{t(20^\circ\text{C})}^{t(80^\circ\text{C})} I_S(t) dt = \int_{t(20^\circ\text{C})}^{t(80^\circ\text{C})} \frac{P(t)}{T(t)} dt$$

## 2. Entropy and temperature

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### 2.10 The first and the second law

Statements about whether or not a substance-like physical quantity is conserved have historically often been regarded as important, if not the most important, physical laws at all. This can be seen by the fact that these statements often have their own, sometimes quite pretentious name.

*Newton's second law:*

Momentum can neither be produced nor destroyed.

*The first law of thermodynamics:*

Energy can neither be produced nor destroyed.

*The second law of thermodynamics:*

Entropy can be produced, but not destroyed.

These names indicate that the discovery of the respective theorem was laborious. The reason for this difficulty is probably that the “substance-likeness” of these quantities was initially not recognized. The theorem of the conservation of the electric charge does not bear its own name, since the substance-likeness of the charge (= electricity) was recognized first, and shortly afterwards the conservation was discovered (Franklin 1747). The situation is similar with the amount of substance. Its substance-likeness was clear from the beginning, and its non-conservation was so obvious that one felt no need to express it in as a new theorem.

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## 2. Entropy and temperature

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### 2.11 Entropy content at absolute zero

If one tries to extract more and more entropy from a body with a very good heat pump, one realizes two things:

- The temperature can be as close as desired to 0 K, but cannot be lower.
- At this temperature, the pump does no longer pump entropy.

We conclude that, as we approach the temperature of 0 K, the entropy content is approaching zero. So we have:

$$T \rightarrow 0 \text{ exactly when } S \rightarrow 0.$$

In words: Absolutely cold bodies contain no entropy.

But there are cases in which this statement seems to be violated. When liquid glasses are cooled down quickly, they release less entropy than when they are cooled slowly. During rapid cooling entropy seems to be frozen or trapped.

We will explain this process later as follows: the glass can be broken down into subsystems, and one of these subsystems is not in thermal equilibrium with the rest if it cools too quickly. Although a thermometer indicates that  $T$  approaches zero Kelvin, both  $S$  and  $T$  of this subsystem do no longer decrease. The total system has two different temperatures.

One can also describe the phenomenon like this: Entropy has become immobile, similar to immobile electrical charge.

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## 2.12 Entropy capacitance

Whether a system contains much or little entropy can be seen from various properties, more precisely, from the values of various other physical quantities. In particular, the entropy content increases with increasing temperature. We call the entropy increase per temperature increase the entropy capacitance  $C_S$  of the system:

$$C_S = \frac{\Delta S}{\Delta T}$$

This quantity is defined in analogy to the electrical capacitance

$$C_Q = \frac{Q}{U}$$

and to the mass, which can be interpreted as the momentum capacitance

$$C_p \equiv m = \frac{p}{v}$$

In contrast to  $C_Q$  and  $C_p$ ,  $C_S$  is not defined as a quotient, but as a differential quotient of an extensive and an intense quantity.

We are now addressing a problem that is normally only encountered with the entropy capacitance. The entropy of a system depends not only on  $T$ , but also on other variables, e.g. on the volume  $V$  and on the amount of substance  $n$ . So it is:

$$S = S(T, V, n).$$

However, it is also possible to choose other independent variables for the same system, e.g.  $T$ ,  $p$  and  $n$ .  $S$  is another function of the variables  $T$ ,  $p$  and  $n$ . If one wants to determine the entropy capacitance – mathematically or experimentally – i.e. one asks for the change of the entropy content for a given temperature increase, one has to decide what should happen with the other variables in this process. The most natural thing to do is to leave the volume and the amount of substance unchanged during the temperature increase.

The entropy capacitance, that is determined in this way, is

$$\frac{\partial S(T, V, n)}{\partial T}.$$

To indicate that the volume is constant, we denominate this quantity  $C_S^V$ . The fact that  $n$  is also kept constant is an implicit convention and is not expressed in the symbol.

So it is

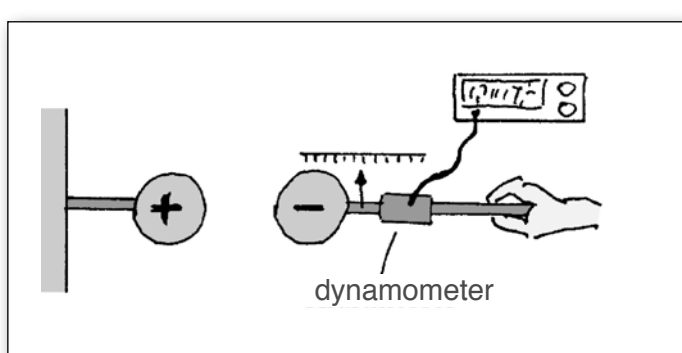
$$C_S^V = \frac{\partial S(T, V, n)}{\partial T}.$$

Sometimes an entropy capacitance is also useful, which is determined by a temperature change at constant pressure:

$$C_S^p = \frac{\partial S(T, p, n)}{\partial T}.$$

We emphasize that  $S(T, V, n)$  and  $S(T, p, n)$  are different functions.

With the electrical capacitance one could make quite analog distinctions. Fig. 2.18 shows a “capacitor” consisting of two spheres. We can write the charge  $Q$  either as a function of the variables  $U$  and  $x$  (distance between spheres):  $Q = Q(U, x)$  or as a function of  $U$  and  $F$  (momentum current from one sphere to the other):  $Q = Q(U, F)$ .



**Fig. 2.18**

When charging the capacitor, either the distance or the force can be kept constant.

Accordingly, two capacitances can be defined

$$C_Q^x = \frac{\partial Q(U, x)}{\partial U} \quad \text{and} \quad C_Q^F = \frac{\partial Q(U, F)}{\partial U}$$

To measure  $C_Q^F$ , when charging the capacitor, the distance  $x$  must be increased so that  $F$  remains constant. However, this case has no practical interest. When we talk about the (electric) capacitance of an arrangement, we always think that the geometry of the arrangement is not modified when the voltage is changed.

In thermodynamics, molar quantities are often used. We mark them with a “roof” above the symbol of the quantity. For homogeneous systems, a molar variable depends only on intensive and other molar variables. Therefore, the molar entropy, i.e. the entropy per amount of substance is:

$$\hat{S} = \hat{S}(T, \hat{V}) \quad \text{or} \quad \hat{S} = \hat{S}(T, p)$$

A third variable no longer appears, because the amount of substance per amount of substance is equal to 1.

We therefore define molar entropy capacitances

$$c_S^V = \frac{C_S^V}{n} = \frac{1}{n} \frac{\partial S(T, V, n)}{\partial T} = \frac{\partial \hat{S}(T, \hat{V})}{\partial T} \quad (2.10)$$

$$c_S^p = \frac{C_S^p}{n} = \frac{1}{n} \frac{\partial S(T, p, n)}{\partial T} = \frac{\partial \hat{S}(T, p)}{\partial T} \quad (2.11)$$

The values of  $c_S^p$  and  $c_S^V$  for some substances are listed in Table 2.1. These molar entropy capacitances do not depend on the size of the section from a system that is considered, but only on local variables: intensive and molar variables. We will discuss their temperature dependence later.

Substance	$c_S^p$ (Ct · mol <sup>-1</sup> · K <sup>-1</sup> )	$c_S^V$ (Ct · mol <sup>-1</sup> · K <sup>-1</sup> )
Potassium	99	
Iron	87	
Silver	86	
Lead	91	
Water	256	
Benzene	0.45	
Helium	77	46
Air	107	76
Hydrogen	104	74
CO <sub>2</sub>	101	92

} at 20 °C

} at 0 °C

**Table 2.1**

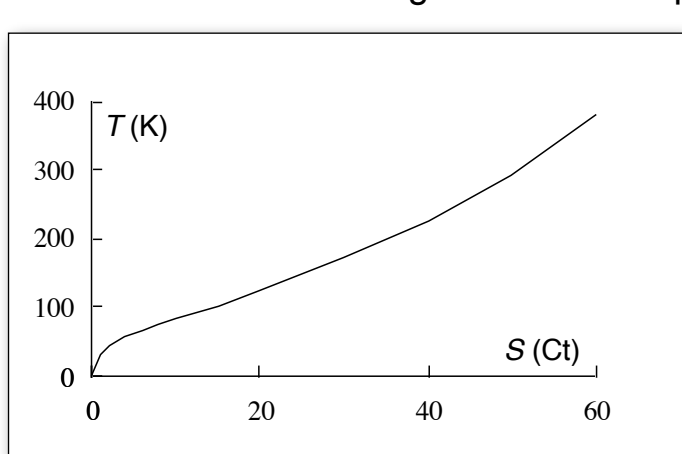
Molar entropy capacitances

Instead of entropy capacitances, tables usually show the product  $c_S \cdot T$ , which has the dimension of an energy capacitance. This expression is called molar *heat capacitance*. Its symbol is  $c_V$  or  $c_p$ , respectively:

$$c_V = c_S^V \cdot T \quad \text{and} \quad c_p = c_S^p \cdot T$$

Caution: It is not correct to say that a system contains heat when the word heat is used in the sense of physics, because  $TdS$  is not a substance-like quantity. Therefore, the term heat capacitance is somewhat misleading.

Fig. 2.19 shows the temperature over entropy for copper. It is typical for all substances as long as there is no phase transition.



**Fig. 2.19**

Temperature over entropy for 100 g Copper

## 2.13 Entropy conductivity

If entropy flows through a material medium, energy is dissipated, (additional) entropy is produced, Fig. 2.11. For the entropy to flow, a temperature gradient is necessary.

The temperature gradient can be interpreted as a driving force for the entropy current. We consider a section of a heat conductor that is so short that the entropy produced in this section is sufficiently small compared to the entropy flowing through it.

Experience shows that

$$I_S \sim \frac{T_2 - T_1}{\Delta x}$$

Written in differential form the relation reads

$$I_S \sim \text{grad } T.$$

$I_S$  depends on the cross-sectional area  $A$  of the heat conductor and on the material. We thus can write

$$I_S = \sigma_S \cdot A \cdot |\text{grad } T|$$

and call  $\sigma_S$  the *entropy conductivity*. For the entropy current density we thus obtain

$$\vec{j}_S = -\sigma_S \cdot \text{grad } T \quad (2.12)$$

Tables usually show the *thermal conductivity*

$$\lambda = \sigma_S \cdot T$$

If equation (2.12) is multiplied by  $T$ , we obtain

$$T \cdot \vec{j}_S = -T \sigma_S \cdot \text{grad } T = -\lambda \cdot \text{grad } T$$

With

$$T \cdot \vec{j}_S = \vec{j}_E$$

we get the energy current density

$$\vec{j}_E = -\lambda \cdot \text{grad } T \quad (2.13)$$

$\sigma_S$  (like  $\lambda$ , but also like the electric conductivity and the momentum conductivity) depends on temperature.

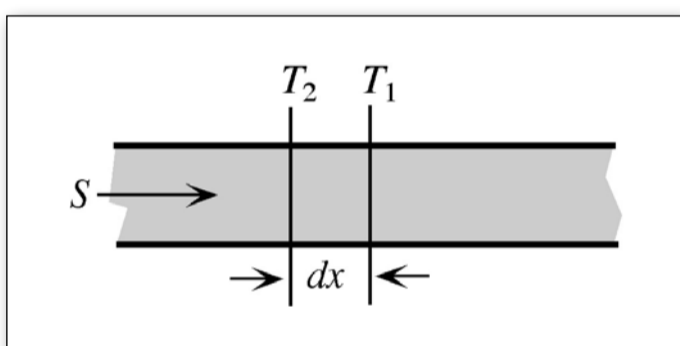
Table 2.2 shows the values of  $\sigma_S$  and  $\lambda$  for some substances.

Substance	$\sigma_S$ (Ct · K <sup>-1</sup> · s <sup>-1</sup> · m <sup>-1</sup> )	$\lambda$ (J · K <sup>-1</sup> · s <sup>-1</sup> · m <sup>-1</sup> )
silver	1.54	420
copper	1.43	390
iron	0.29	79
lead	132	36
glass	0.003 7	1.0
water	0.000 9	0.25
ethanol	0.000 66	0.18
styrofoam	0.000 13	35
air	0.000 088	25

**Table 2.2**

Entropy conductivity and heat conductivity

We now want to find a differential equation that allows us to calculate temperature distributions. To derive it, we consider a one-dimensional problem: a heat conductor whose temperature changes only in the  $x$ -direction, Fig. 2.20.



**Fig. 2.20**

Entropy is flowing from left to right.

We cut a slice out of the heat conductor perpendicularly to the  $x$ -direction and make the energy balance for this slice. The time rate of change  $dE/dt$  inside the slice is equal to the difference of the energy currents flowing in on the left and out on the right:

$$\frac{dE}{dt} = -[P(x+dx) - P(x)] \quad (2.14)$$

With the help of  $dE = c \cdot n \cdot dT$  we express the left side by the time rate of change of the temperature:

$$\frac{dE}{dt} = c \cdot n \cdot \frac{\partial T}{\partial t} = c \cdot \rho_n \cdot A dx \cdot \frac{\partial T}{\partial t}$$

Here  $c$  is the molar heat capacity,  $n$  the amount of substance and  $\rho_n$  the density of  $n$ . The right side of equation (2.14) can be written

$$-\frac{dP}{dx} dx = -A dx \cdot \frac{dj_E}{dx} = A dx \cdot \lambda \cdot \frac{\partial}{\partial x} \left( \frac{\partial T}{\partial x} \right) = A dx \cdot \lambda \cdot \frac{\partial^2 T}{\partial x^2}$$

Here, first  $P = j_E \cdot A$  and then  $j_E = -\lambda \cdot \partial T / \partial x$  was used. We thus get from equation (2.14):

$$c \cdot \rho_n \cdot A dx \cdot \frac{\partial T}{\partial t} = A dx \cdot \lambda \cdot \frac{\partial^2 T}{\partial x^2}$$

or

$$\frac{\partial^2 T}{\partial x^2} - \frac{c \cdot \rho_n}{\lambda} \cdot \frac{\partial T}{\partial t} = 0$$

The three-dimensional calculation would have resulted in:

$$\Delta T - \frac{c \cdot \rho_n}{\lambda} \cdot \dot{T} = 0$$

With  $c = T \cdot c_S$  and  $\lambda = T \cdot \sigma_S$  we can also write:

$$\Delta T - \frac{c_S \cdot \rho_n}{\sigma_S} \cdot \dot{T} = 0$$

The structure of this differential equation is the same as that of the Schrödinger equation for a free particle

$$-\frac{\hbar^2}{2m} \Delta \psi = i \hbar \frac{\partial \psi}{\partial t}$$

In the steady state we have  $\partial T / \partial t = 0$ , thus

$$\Delta T = 0.$$

*Example:* The temperatures  $T_1$  and  $T_2$  of the ends of a metal rod are kept constant over time. Since  $\partial T / \partial t = 0$  and the arrangement is one-dimensional, we obtain

$$\frac{\partial^2 T}{\partial x^2} = 0$$

From this follows

$$\frac{\partial T}{\partial x} = \text{const.}$$

The temperature profile is therefore a straight line.

The entropy currents investigated so far were driven by a temperature gradient. We call them *conductive currents*.

There are also currents in which a current  $I_X$  is entrained by a current  $I_Y$ . The entire flow is driven solely by the gradient of the intensive variable belonging to  $Y$ . We call the current  $I_X$  a *convective current*. The entropy current in the pipe of a central heating system, for example, is a convective entropy current. Conductive entropy currents are unsuitable for the transmission of large amounts of entropy. How thick would the lines of a central heating system have to be if the heat was to be sent conductively through copper rods? The earth's heat balance is also essentially realized with convective currents. Another type of current, a kind of supercurrent, will be discussed later: entropy transmission with electromagnetic radiation.

### 2.14 Remarks on the history of the concept of heat

Until about 1840, heat was the name of what physicists today call entropy, and what non-physicists still today call heat. This concept of heat was established in physics in the course of the 18th century. We owe the first important contributions to the chemist and physician Joseph Black (1728-1799). He recognized heat as a substance-like quantity and distinguished it from temperature which was already known at that time. Black also introduced the heat capacitance, namely  $dS/dT$ , which we now call entropy capacitance.

The next decisive step was taken by Sadi Carnot (1796-1832). In his *Réflexions sur la puissance motrice du feu* (1824) he compares a heat engine with a water wheel. Just as water does work when it goes down over a water wheel from a greater to a lower height, so heat (“calorique” or “chaleur”) does work when it goes from higher to a lower temperature in a thermal engine. Expressed in modern language we can say that Carnot combines entropy and energy. For him, just as for Black, heat, i.e. what we call entropy today, was a substance-like quantity. A corresponding idea about what we call energy today, did not yet exist. In fact, energy as a substance-like, conserved quantity was introduced only 20 years later.

When around the middle of the 19th century energy was introduced, it was concluded that Carnot’s work was wrong and that heat was a so-called “form” of the energy. Thus “heat” was no longer the name of a physical quantity but of a structure of the form  $\xi dX$ , a so-called differential form, just like “work”. A short time later, entropy was reinvented by Rudolf Clausius (1822-1888). Clausius’ construction of entropy is witty, but unfortunately also very unintuitive. This construction, together with the interchange of names, is the reason why entropy still today appears as one of the most abstract physical quantities.

Two important names remain to be mentioned. Gibbs (1839-1903) has given thermodynamics a form in which it allows to describe much more than pure thermal phenomena. The analogies we keep coming across here are based on Gibbs’ work.

Boltzmann (1844-1906) tried to trace thermodynamics back to mechanics by explaining thermal phenomena through the movement of small particles. Temperature and entropy were interpreted mechanically. He invented statistical physics. Its significance goes far beyond the mechanical models used to derive it.

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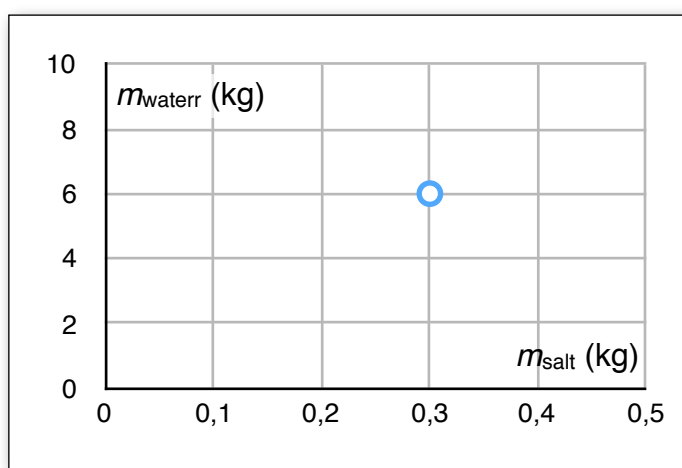
# 3

**Amount of substance  
and chemical potential**

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### 3.1 Substances and basic substances

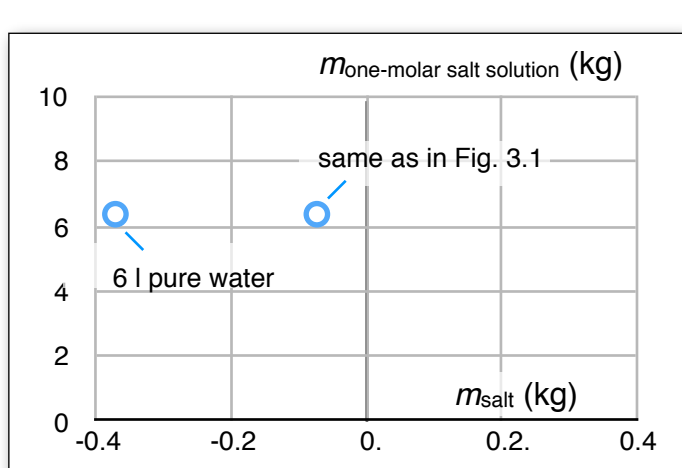
As one describes the location of a point in space by three coordinates in a spatial reference system, so one can characterize a material by its coordinates in a reference system of substances. To the coordinate axes we assign *basic substances*. The value of a coordinate  $X_i$  of substance S indicates the amount of basic substance  $i$  contained in S. In Fig. 3.1, a specific solution of common salt in water is represented by a point in an  $m_{\text{water}} - m_{\text{salt}}$  coordinate system. (Here we use mass as a measure of the amount of the substances.) The values of all other coordinates, e.g.  $m_{\text{iron}}$  or  $m_{\text{alcohol}}$  are zero. All mixtures of water and salt can be displayed in this coordinate system, from pure water to pure common salt.



**Fig. 3.1**

A given saline solution as a point in a  $m_{\text{water}} - m_{\text{salt}}$  coordinate system

The same substance manifold “saline solution” can also be described in a different coordinate system obtained from the first by linear combination, Fig. 3.2. However, in this case negative quantities of the substances must also be permitted. Pure water, for example, then “consists” of one-molar salt solution and a negative amount of common salt.



**Fig. 3.2**

The same saline solution as in Fig. 3.1 in another coordinate system

Which and how many substances are chosen as basic substances is largely a question of expediency. There must not be too many – otherwise the coordinates of a substance are no longer unambiguous. With our saline solution, for example, we must not take water, common salt and a one-molar saline solution. If there are too few, two things can happen.

- A substance cannot be represented in these coordinates. For example, a quantity of gasoline cannot be described by the coordinates “amount of common salt” and “amount of water”.
- Different substances have the same coordinates. If we take “electrons”, “protons” and “neutrons” as basic materials, for example, many substances that the chemist wants to distinguish have the same coordinates.

When speaking of a substance, one usually abstracts from the total amount. Instead of the amounts of the basic substances, it is therefore customary to indicate numerical proportions of the substances. If A, B, C... are the basic substances, a substance is represented by the “molecular formula”

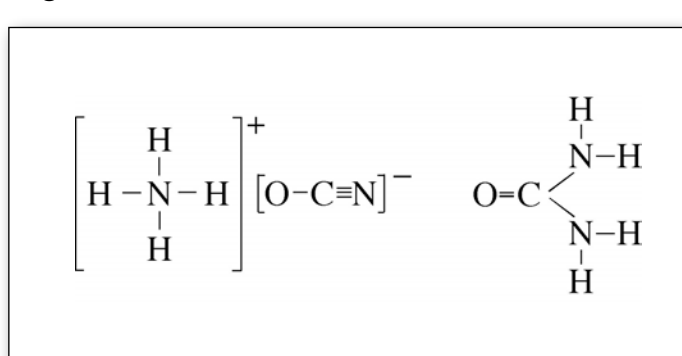
$$A_{v1} B_{v2} C_{v3} \dots$$

where we have

$$n_A : n_B : n_C : \dots = v_1 : v_2 : v_3 : \dots$$

The chemist’s basic substances are the approximately 100 chemical elements. They have the special feature that their quantities in pure substances behave like small integers.

Here, too, it is often not sufficient to specify the coordinates in a substance coordinate system to characterize a substance. Two different substances can have the same molecular formula, e.g. ammonium cyanate and urea:  $\text{CH}_4\text{ON}_2$ . This proves that the substances are not microscopically homogeneous. In order to distinguish them, the chemist indicates the spatial linkage of the atoms, Fig. 3.3.



**Fig. 3.3**

Ammonium cyanate and urea have the same molecular formula, but the molecules have different structures.

Some “pure” substances do not exist at all, e.g. carbonic acid  $\text{H}_2\text{CO}_3$  exists only in aqueous  $\text{CO}_2$  solution, or  $\text{FeO}$  exists only together with  $\text{Fe}_2\text{O}_3$ .

What for chemists appears to be a uniform substance proves to be a mixture of even “purer” substances: there are different isotopes for each basic chemical substance. If one wants to consider the different isotopes in the characterization of a substance, one has to deal with about 2000 nuclides of these elements instead of 100 chemical elements.

The nuclides, on the other hand, can be described by only three basic substances e, p and n, which, however, have no substance names. Their elementary proportions are called *electron*, *proton* and *neutron*. In order to break down the nuclides into these basic substances, higher energies have to be applied than those that the chemist uses to break down his substances into basic substances. The substances e, p and n do not exist in pure form in large quantities on earth, but small quantities can easily be produced. The filament of an incandescent lamp is surrounded by a thin layer of pure e. A p-gas is obtained by an electric gas discharge in hydrogen. Pure n also exists on Earth, but in much larger quantities in certain celestial bodies, the neutron stars.

Using very high energies, however, substances can be produced that are outside the e-p-n coordinate system. New basic materials have to be added: Antiprotons, antineutrons and many different mesons... But also these substances can again be described by fewer, even more elementary basic substances: Quarks and leptons, and at this level of the hierarchy the same thing happens as before: By using higher energies, the number of new basic substances increases again and ... of course, one is looking for even more elementary basic substances.

A material coordinate system is used to bring order to the variety of substances. One chooses the coordinate system in such a way that the amount of each basic substance remains constant during the reactions that one examines. Thus, chemists limit themselves to reactions in which the quantity of each chemical element is conserved. By selecting the coordinate system, the description of the chemical reactions becomes very simple: The amounts of the chemical elements are conserved quantities in all chemical processes.

In the following we will mostly use the coordinate system of the chemists. In fact, this coordinate system contains one more coordinate than just the chemical elements. The chemists also operate with substances called ions. They speak of the amount of  $[\text{Na}]^+$  ions or  $[\text{CO}_3]^{2-}$  ions. To describe these substances, it is sufficient to introduce one more basic substance in addition to the chemical elements. Which one is to be taken is again largely a question of expediency. One possibility would be the electrons e. Thus, we would obtain

$$[\text{Na}]^+ = \text{Na}_1 e_{-1} \quad [\text{CO}_3]^{2-} = \text{C}_1 \text{O}_3 e_2.$$

But one could just as well take the protons  $p = [\text{H}]^+$  as new basic substance, then we would have

$$[\text{Na}]^+ = \text{Na}_1 \text{H}_{-1} p_1 \quad [\text{CO}_3]^{2-} = \text{C}_1 \text{O}_3 \text{H}_2 p_{-2}.$$

In both cases there are negative coordinates.

### 3.2 The amount of substance

A measure of the amount of a substance should provide information on how much of one substance is equivalent to a given amount of another. Since different substances are to be compared, equivalence will only refer to certain properties, depending on the choice of the quantity. If the mass is used as a measure for the amount, equal amounts are equivalent with respect to their inertia and their weight. Certain physical laws are substance-independent when the mass is used as a measure of the amount, for example

$$\vec{F} = m \cdot \vec{g}$$

or

$$\vec{p} = m \cdot \vec{v}$$

There is another quantity which in certain cases is a more convenient measure of the amount of a material than the mass: the *amount of substance*  $n$ . There are physical laws that become substance-independent if they are formulated with  $n$  instead of  $m$ . An example of this is the ideal gas law

$$pV = nRT.$$

If one would use  $m$  instead of  $n$ , the universal gas constant  $R$  would have to be replaced by a substance-dependent constant.

Another substance-independent statement is

$$\text{Two portions of different substances with the same amount of substance } n \text{ contain the same number of particles.} \quad (3.1)$$

However, the statement that a relationship is substance-independent is only interesting, i.e. a statement that can be tested in an experiment, if the quantity  $n$  was not defined by the relationship. If we use the ideal gas law to define  $n$ , the proposition (3.1) is a statement that can be tested in an experiment, it is a law of nature. If, on the other hand, the quantity  $n$  is defined as a certain number of particles, the fact that the ideal gas law is substance-independent is an interesting, verifiable fact.

The proposition (3.1) tells us that one can obtain a simple idea of  $n$ :  $n$  is a measure of a number of items. It describes what ten molecules, ten photons, ten apples, ten cars and ten stars have in common.

The unit of measurement for the quantity  $n$  is the mol. It is defined as follows:

1 mol is the amount substance of a portion of the carbon isotope  $^{12}_6\text{C}$  whose mass is 12.000 g.

Since we know how many atoms are contained in 12 g of carbon, proposition (3.1) can be formulated as follows:

$$\text{A portion of a substance has the amount of substance } n = 1 \text{ mol if it consists of } 6.022 \cdot 10^{23} \text{ particles.} \quad (3.2)$$

$N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$  is called the *Avogadro constant*.

The propositions (3.1) and (3.2) express an important property of the quantity  $n$ :  $n$  is quantized, just like the electric charge  $Q$  and the angular momentum  $L$ . Its value is an integer multiple of its natural unit. The elementary quantum of the amount of substance is:

$$\tau = 1.66 \cdot 10^{-24} \text{ mol}$$

$\tau$  corresponds to the elementary charge  $e$ , the elementary quantum of angular momentum  $\hbar$  and the elementary quantum of the entropy  $k$ :

$$\begin{aligned} e &= 1.6022 \cdot 10^{-19} \text{ C} \\ \hbar &= 1.0546 \cdot 10^{-34} \text{ Js} \\ k &= 1.380 \cdot 10^{-23} \text{ Ct} \end{aligned}$$

Products or quotients of these elementary quanta are again natural constants. So,

$$\Phi_0 = \pi \cdot \hbar / e = 2.06 \cdot 10^{-15} \text{ Vs}$$

is the elementary quantum of the magnetic flux, or half of the elementary quantum of the magnetic charge.

$$F = e/\tau = 0.965 \cdot 10^5 \text{ C/mol}$$

is the *Faraday constant*, and

$$R = k/\tau = 8.324 \text{ Ct/mol}$$

is the *gas constant*.

Since substances can be produced and destroyed,  $n$  is not a conserved quantity. In 3.1, however, it had already been said that basic substances are selected in such a way that their quantities are conserved in the processes of interest.

If different substances A, B,... are present simultaneously, several amount-of-substance variables  $n_A, n_B, \dots$  are used. However, one should not conclude from this that  $n_A$  and  $n_B$  are different physical quantities. They are no more so than the masses  $m_A$  and  $m_B$  or the entropies  $S_A$  and  $S_B$  of the substances.

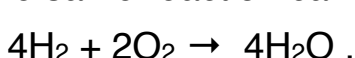
In a chemical reaction, the quantities of the reactants are in certain integer ratios. If, for example, hydrogen combines with oxygen to form water, the three quantities of substances  $n[\text{H}_2]$ ,  $n[\text{O}_2]$  and  $n[\text{H}_2\text{O}]$  behave like this:

$$n[\text{H}_2] : n[\text{O}_2] : n[\text{H}_2\text{O}] = 2 : 1 : 2$$

This is also expressed in the reaction equation:



The same reaction can also be described as follows



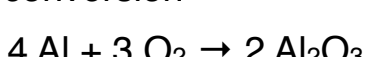
If the reaction equation is written with the smallest integers, as equation (3.3), it is in the *standard form*.

To describe how far a reaction has progressed, it is not necessary to specify the amounts of all substances involved. It is sufficient to specify a single molar number, the *conversion*  $n(\text{R})$  of the reaction. The conversion is defined as follows:

Multiplying the standard form of the reaction equation by  $x$  mol gives a reaction equation describing the conversion of  $n(\text{R}) = x$  mol.

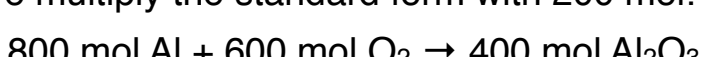
*Example:*

A conversion



of 200 mol is to be realized.

We multiply the standard form with 200 mol:



Thus, 800 mol Aluminum must react with 600 mol Oxygen whereby 400 mol Aluminium oxide is produced.

### 3.3 The chemical potential

Just as there is an associated intensive variable  $\Phi$  to the substance-like quantity  $Q$  and an intensive variable  $T$  to the substance-like quantity  $S$ , there is also an intensive variable  $\mu$  which corresponds to the substance-like quantity  $n$ : the chemical potential.

Before we discuss the construction of the  $\mu$  scale, we want to get a qualitative idea of the quantity. (For the temperature this was not necessary, as everyone already has such an idea of the temperature.)

Just as a temperature difference can be seen as a driving force for an entropy current, a difference in the chemical potential represents a drive for an  $n$ -current. Entropy flows from high to low “thermal potential”  $T$ , amount of substance flows from high to low potential  $\mu$ . If a substance flows through a kind of resistor from a place A to a place B and no other driving force is present, i.e. no electrical voltage  $\Delta\Phi$  and no thermal drive  $\Delta T$ , we can conclude that the chemical potential of the substance at A is higher than at B; between A and B there is a chemical potential difference  $\Delta\mu$ .

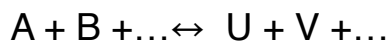
If one pours a few drops of ether at one point of the room, it evaporates and spreads evenly throughout the room. This propagation process is called diffusion. It is driven by differences in the chemical potential.

The value of the chemical potential usually refers to a certain substance, in our case to ether. The chemical potential of the air in the room has a different value. However, this does not imply that  $\mu[\text{ether}]$  and  $\mu[\text{air}]$  are different physical quantities: They are the values of the same quantity on two different systems. (Compare the corresponding remarks about  $n$ ).

Since substances can be produced and destroyed,  $\Delta\mu$  plays yet another role than that of the drive for a current from one point A to one point B. If a substance A can transform into substance B, and vice versa, i.e. if the reaction  $A \leftrightarrow B$  can take place, the chemical potentials of the two substances  $\mu_A$  and  $\mu_B$  tell us in which direction the reaction will proceed. If  $\mu_A > \mu_B$ , then A transforms into B, if  $\mu_B > \mu_A$ , B changes into A. If  $\mu_A = \mu_B$ , there is no reaction. It is said that there is a *chemical equilibrium*. For example, if the relative humidity is less than 100%, the chemical potential of liquid water is greater than that of gaseous water. The liquid water evaporates.

In fact, these two examples – diffusion and evaporation – are not as different as they look at first. The case of diffusion can also be seen as a reaction: “Ether at location A is transformed into ether at location B”. Thus  $\mu_A$  can be understood in general as the drive of a substance A to disappear. However, since certain conservation laws have to be satisfied, substance A cannot disappear without a trace: Its disappearance is accompanied by the formation of a substance B with a lower chemical potential. Substance B can either be the “same” substance as A, but at a lower pressure, in a lower concentration, in another physical state, in another phase, or it can be what is called another substance.

However, these are far from all the possibilities for how a substance can disappear: A substance can also disintegrate into two or more other substances, or it can react with other substances. In general:



Whether such a reaction runs from left to right or from right to left depends on the values of the chemical potentials of all substances involved. If

$$\mu_A + \mu_B + \dots > \mu_U + \mu_V + \dots,$$

the reaction runs from left to right: the substances A, B, ... disappear, and the substances U, V, ... are formed. If

$$\mu_A + \mu_B + \dots < \mu_U + \mu_V + \dots,$$

the reaction runs from right to left. If finally

$$\mu_A + \mu_B + \dots = \mu_U + \mu_V + \dots,$$

there is no drive to the reaction. It won't run at all. There is chemical equilibrium.

It is remarkable that so many different processes are described by the values of a single physical quantity. The chemical potential is therefore a very useful quantity.



### 3.4 The scale of the chemical potential

We define the  $\mu$  scale in a similar way as the  $T$  scale. Like an entropy current, a substance current flow is accompanied by an energy current, and the following must apply

$$P \sim I_n$$

We define the  $\mu$  scale by

$$P = \mu \cdot I_n$$

Thus, the unit of measurement of the chemical potential is J/mol, and we abbreviate

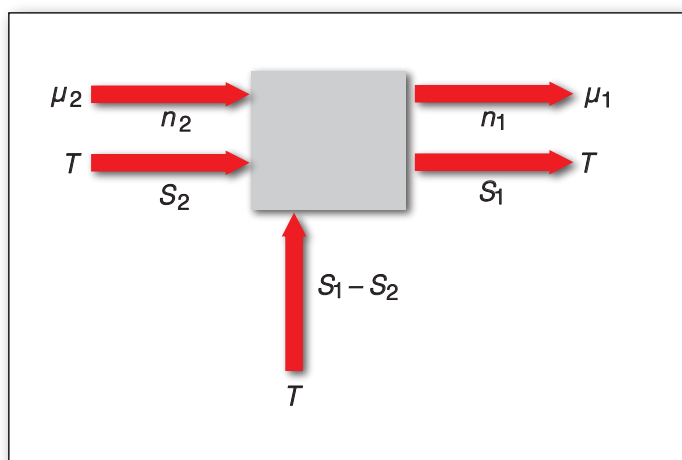
$$1 \text{ J/mol} = 1 \text{ Gibbs (G)}.$$

When a substance flow is realized, not only the quantity  $n$  flows, but also other substance-like quantities, i.e.  $S$ ,  $Q$ ,... Accordingly, the energy current is

$$P = \mu \cdot I_n + T \cdot I_S + \dots$$

If one wants to determine  $\mu$  via  $P/I_n$ , the terms  $T \cdot I_S$  etc. must be subtracted from the total energy flow before. In order to avoid this difficulty, we first consider a procedure that specifies  $\mu$  differences directly: We consider an energy transloader, into which energy enters together with amount of substance and which it leaves with another carrier, e.g. with angular momentum  $P = \omega \cdot M$  or with electric charge  $P = U \cdot I$ . The machine should be well constructed, i.e. no entropy should be produced in it.

We also limit ourselves to those energy transloaders in which reactions of the type  $A \rightarrow B$  take place, i.e. not  $A \rightarrow B + C$  or  $A + B \rightarrow C + D$ .... Such devices may not be of great practical importance, but that is not the point here. An example of such an energy transloader is a compressed air engine, Fig. 3.4: The air flows in at high chemical potential  $\mu_2$  (and thus at high pressure) and out at low potential  $\mu_1$  (and at low pressure).



**Fig. 3.4**

Compressed air engine, schematically

Thus the net energy current that flows into the machine is

$$P_2 - P_1 = (\mu_2 - \mu_1) \cdot I_n$$

This energy current can be measured as it leaves the machine mechanically through the shaft. So it is

$$P_{\text{mech}} = \omega \cdot M = (\mu_2 - \mu_1) \cdot I_n$$

However, this balance equation is only correct if no further energy flows are involved. Since a substance flow is always linked to an entropy flow, it is important that the substance flowing in has the same temperature as the substance flowing out, the machine must operate isothermally. It must also be taken into account that the entropy capacity of the substance flowing in and out is different. Such a machine must generally have another input or output for the entropy.

Another example of such an energy transloader is the galvanic cell described elsewhere. Hydrogen flows into the cell at high chemical potential and out of it at a lower potential. Therefore, the cell releases energy electrically. So the following applies

$$U \cdot I = (\mu_2 - \mu_1) \cdot I_n$$

Of course, one can also consider a machine or galvanic cell in which a more complicated reaction takes place, e.g. a combustion. It would allow to determine the chemical potential difference of the combustion reaction.

### 3.5 The zero point of the chemical potential

Like temperature, the chemical potential has an absolute zero point. The value follows from the equation  $P = \mu \cdot I_n$ . We consider a substance flow. We have

$$P_{\text{total}} = \mu \cdot I_n + v \cdot F + T \cdot I_S + \dots$$

If the substance in question has a rest mass different from zero, i.e. if it is not electromagnetic radiation,  $P$  is, except in extreme cases, very large compared to the terms  $v \cdot F$ ,  $T \cdot I_S$  etc., i.e.  $\mu \cdot I_n$  in these cases is almost identical with  $P_{\text{total}}$ , and we have

$$\mu = \frac{P}{I_n} = \frac{E}{n} = \frac{m}{n} c^2 = \hat{m} c^2$$

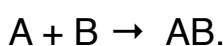
The absolute value of  $\mu$  is therefore very high for substances with a rest mass different from zero, Table 3.1.

Substance	$\mu$ (kG)
hydrogen H <sup>1</sup>	90.5791 · 10 <sup>9</sup>
helium He <sup>4</sup>	359.737 · 10 <sup>9</sup>
oxygen O <sup>16</sup>	1437.555 · 10 <sup>9</sup>

**Table 3.1**

Absolute values of  $\mu$  for three substances

Now chemical potential differences  $\Delta\mu$  in chemical reactions, i.e. in the processes of interest to us, are of the order of 100 kG, i.e. much smaller than the uncertainty with which the absolute values of  $\mu$  are known. Therefore, in normal chemistry (but not in nuclear chemistry) and in the physics of low energies one operates only with differences of the chemical potential. As long as one considers only those processes in which the atomic numbers of all chemical elements are conserved, i.e. as long as no nuclear reactions take place, one can define a zero point of the chemical potential for each of the chemical elements separately. This can be seen in the example of the simple reaction



We decompose the chemical potentials

$$\mu_A = \mu_{A0} + \mu_A'$$

$$\mu_B = \mu_{B0} + \mu_B'$$

$$\mu_{AB} = \mu_{A0} + \mu_{B0} + \mu_{AB}'$$

The chemical potential difference of the reaction

$$\mu_A + \mu_B - \mu_{AB} = \mu_A' + \mu_B' - \mu_{AB}'$$

results from the absolute values  $\mu_A$ ,  $\mu_B$  and  $\mu_{AB}$  of the chemical potentials, as well as from the primed values  $\mu_A'$ ,  $\mu_B'$  und  $\mu_{AB}'$ . We now are free to choose  $\mu_{X0}$  arbitrarily for each chemical element. One chooses  $\mu_{X0}$  so that  $\mu_X'$  becomes zero for a standard state that can easily be reproduced. Usually the chemical potential  $\mu_X'$  of substance X will be set to zero if the substance is in its most stable modification at 298 K and 1.01 bar. For dissolved substances (also ions) a one-molar solution (1 mol dissolved in 1 l solution) is chosen as the reference state. From now on we will omit the prime.

### 3.6 Values of the chemical potential

For a given substance, the chemical potential does not have a fixed value that remains constant in all states of the substance; rather, it depends on

- whether the substance is solid, liquid or gaseous, which is its crystal modification and whether it is dissolved in another substance;
- the temperature  $T$ ;
- the pressure  $p$ ;
- the density  $\rho_n$  of the amount of substance.

We will look more closely at these dependencies in Chapter 5. In the vicinity of the standard state  $p_0$ ,  $T_0$  however, the  $T$ - and  $p$ -dependence can be approximated linearly:

$$\mu(T, p_0) = \mu(T_0, p_0) + \alpha \cdot (T - T_0)$$

$$\mu(T_0, p) = \mu(T_0, p_0) + \beta \cdot (p - p_0)$$

For the solution of many problems it is therefore useful and sufficient to know the temperature coefficient  $\alpha$  and the pressure coefficient  $\beta$  in addition to the value of the chemical potential in the standard state  $\mu(T_0, p_0)$ .

The pressure coefficients  $\beta$  are always positive. This is easy to understand when one remembers that a chemical potential difference represents “driving force” for a substance flow. As is well known, substances flow from places of high to places of low pressure.

However, it is not so easy to understand that the temperature coefficient is negative. This seems to contradict the experience that water vapor diffuses in a heated room from warm places to cold, for example to the cold windows. However, the drive for this substance flow is not the difference of the chemical potential but that of the temperature: The temperature difference “pulls” at the entropy of the water vapor.

Table 3.2 lists the chemical potentials, and the pressure and temperature coefficients for some substances.

By definition, the chemical elements have the chemical potential zero at standard conditions in their most stable form. So  $\mu[\text{H}_2] = 0$  and not  $\mu[\text{H}] = 0$ . Furthermore one defines  $\mu[\text{H}^+] = 0$ .

Substances with a negative chemical potential do not spontaneously disintegrate into the elements they are made of.

Substance	$\mu$ (kJ/mol)	$\alpha$ (kJ/K)	$\beta$ (G/bar)
iron	0	-27	0.71
limestone	-1129	-93	3.69
sugar	-1544	-0.360	21.70
water	-237	-0.070	1.81
ethyne	209	-0.201	2446
CO <sub>2</sub>	-394	-0.214	2446
NO <sub>2</sub>	51	-0.240	2446
ClO <sub>2</sub>	122	-0.257	2446
Al <sub>2</sub> O <sub>3</sub>	-1582	-0.051	2.56
Fe <sub>2</sub> O <sub>3</sub>	-744	-0.087	3.04
Au <sub>2</sub> O <sub>3</sub>	164		
H <sub>2</sub>	0	-0.131	2446
H	203	-0.115	2446
graphite	0	-0.0057	0.541
diamond	2.9	-0.0024	0.342
Ca(OH) <sub>2</sub>	-897	-0.076	3.32
CaO	-604	-0.040	1.65
H <sup>+</sup>	0	0	0.02
NaCl	-384	-0.072	2.70
Na <sup>+</sup>	-262	-0.059	-0.16
Cl <sup>-</sup>	-131	-0.056	1.80
AgCl solid	-110	-0.096	2.58
AgCl dissolved	-73	-0.154	
Ag <sup>+</sup>	77	-0.073	0.17
HCl gas	-95	-0.187	2446
HCl dissolved	-131	-0.056	1.82
NH <sub>3</sub> gas	-16	-0.193	2446
NH <sub>3</sub> dissolved	-27	-0.111	2.41
Ca <sup>++</sup>	-553	0.055	
Pb <sup>++</sup>	-24	-0.010	-1.78
Zn <sup>++</sup>	-147	0.11	-2.6
Ba <sup>++</sup>	-561	-0.013	-1.24
CO <sub>3</sub> <sup>--</sup>	-528	-0.057	0.35
S <sup>--</sup>	86	-0.015	
J <sup>-</sup>	-52	-0.111	3.66
PbCO <sub>3</sub>	-626	-0.131	4.05
ZnCO <sub>3</sub>	-732	-0.082	2.82
CaCO <sub>3</sub>	-1129	-0.093	
BaCO <sub>3</sub>	-1139	-0.112	4.46
CaC <sub>2</sub>	-68	-0.07	
PbS	-99	-0.091	3.19
ZnS	-201	-0.058	2.39
BaS	-461		3.99
PbJ <sub>2</sub>	-173	-0.175	7.61
ZnJ <sub>2</sub>	-209	-0.161	6.74
BaJ <sub>2</sub>	-598		7.60
H <sub>2</sub> O solid	-236.59	-0.0448	1.973
H <sub>2</sub> O liquid	-237.18	-0.0699	1.807
H <sub>2</sub> O gas	-228.59	-0.1887	2446

**Table 3.2**

Chemical potential  $\mu$ , temperature coefficient  $\alpha$  and pressure coefficient  $\beta$  for some substances

### 3.7 Examples of dealing with the chemical potential

#### 1. Stability of oxides:

The table shows directly that under normal conditions the oxides  $\text{CO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  are stable, whereas  $\text{ClO}_2$ ,  $\text{Au}_2\text{O}_3$  and  $\text{NO}_2$  are not. ( $\text{ClO}_2$  gas even decays explosively, whereas  $\text{NO}_2$  decays very slowly; it is said to be *metastable*.)

#### 2. Setting of mortar: $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$

	$\mu(\text{kG})$
$\text{Ca}(\text{OH})_2$	-897
$\text{CO}_2$	-394
} -1291	
$\text{CaCO}_3$	-1129
$\text{H}_2\text{O}$	-237
} -1366	

The chemical potential of the reactants (-1291 kG) is greater than that of the products (-1366 kG).

#### 3. Production of ethyne: $\text{CaC}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$

When calculating the chemical potential difference of this reaction, it is important to note that water occurs in twice the amount of the other substances. So the chemical potential difference is

$$(\mu[\text{CaC}_2] + 2\mu[\text{H}_2\text{O}]) - (\mu[\text{Ca}(\text{OH})_2] + \mu[\text{C}_2\text{H}_2])$$

	$\mu(\text{kG})$
$\text{CaC}_2$	-68
$\text{H}_2\text{O}$	-237 · 2
} -542	
$\text{Ca}(\text{OH})_2$	-897
$\text{C}_2\text{H}_2$	+209
} -688	

The chemical potential difference is 146 kG. Notice that the reaction takes place although the chemical potential of the ethyne is  $> 0$ . All the same the reaction takes place because  $\mu[\text{Ca}(\text{OH})_2]$  is strongly negative.

#### 4. Making Diamond: $\text{C}_{\text{graphite}} \rightarrow \text{C}_{\text{diamond}}$

Under normal conditions, the chemical potential of diamond is greater than that of graphite, so diamond is metastable. However, since

$$\beta_{\text{graphite}} > \beta_{\text{diamond}}$$

by increasing the pressure it is possible to cause the chemical potential of graphite to be greater than that of diamond. We calculate the pressure at which the chemical potentials are equal (G = graphite, D = diamond):

$$\mu_{0G} + \beta_G \cdot \Delta p = \mu_{0D} + \beta_D \cdot \Delta p$$

$$\Rightarrow \Delta p = \frac{\mu_{0G} - \mu_{0D}}{\beta_D - \beta_G}$$

With

$$\mu_{0G} = 0$$

$$\mu_{0D} = 2.9 \text{ kG}$$

$$\beta_G = 0.541 \text{ kG/kbar}$$

$$\beta_D = 0.342 \text{ kG/kbar}$$

we obtain

$$\Delta p = \frac{0 - 2.9}{0.342 - 0.541} \text{ kbar} \approx 15 \text{ kbar}$$

#### 5. Melting of ice: Ice (E) $\rightarrow$ liquid water (W)

The table shows that under normal conditions, i.e. at 25 °C and 1 bar, the chemical potential of liquid water  $\mu_W$  is smaller than that of ice  $\mu_E$  – in accordance with the fact that ice does not exist under these conditions. Since  $\alpha_E > \alpha_W$ , however, at low temperatures ice must be the stable and liquid water the unstable state. We calculate the temperature at which  $\mu_E = \mu_W$ , i.e. for which there is chemical equilibrium between the solid and liquid phase. This is the melting temperature.

$$\mu_{0E} + \alpha_E \cdot \Delta T = \mu_{0W} + \alpha_W \cdot \Delta T$$

$$\Rightarrow \Delta T = -\frac{\mu_{0E} - \mu_{0W}}{\alpha_E - \alpha_W} = -\frac{236.59 - 237.18}{0.0448 - 0.0699} \text{ K} = -23.5 \text{ K}$$

The melting temperature should therefore be 25 °C – 23.5 °C = 1.5 °C. Despite the linear approximation, we got quite a good result.

#### 6. Freezing-point depression of water by changing the pressure

If the pressure is increased, the freezing point of water decreases. We calculate  $\Delta p/\Delta T$ . (W = liquid water, E = ice). At the freezing point there is always  $\mu_E = \mu_W$ . Therefore:

$$\mu_{0E} + \beta_E \cdot \Delta p + \alpha_E \cdot \Delta T = \mu_{0W} + \beta_W \cdot \Delta p + \alpha_W \cdot \Delta T$$

Since  $\mu_{0E} = \mu_{0W}$  we obtain

$$\Delta T = -\frac{\beta_W - \beta_E}{\alpha_W - \alpha_E} \Delta p$$

With the values of the table we get

$$\Delta T/\Delta p = -0.0066 \text{ K/bar.}$$

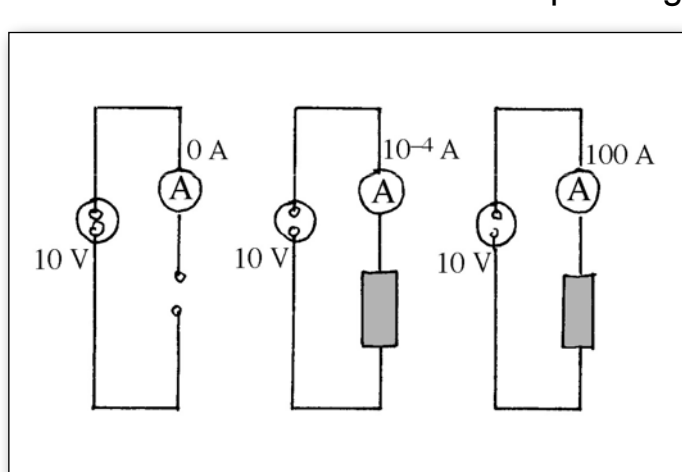
#### 7. Freezing-point depression by dissolving a foreign substance

At the freezing point of the water, the chemical potentials of ice and liquid water are equal. If some salt is added to an ice-water mixture, the salt dissolves and thereby the chemical potential of the liquid water decreases. Therefore, ice melts and the temperature decreases. Finally, a temperature is reached at which the chemical potential of the ice is equal to that of the saline solution.

### 3.8 Reaction resistance

In the previous section we asked for the values of the chemical potential of the reactants and the products of a reaction, i.e. for the chemical potential difference. If the chemical potential difference is different from zero, the reaction can take place; if it is zero, it does not take place. However, a non-zero chemical potential difference is a necessary but not yet sufficient condition for a reaction to take place, for a phase transition to take place or for a substance to flow or diffuse from one location to another — just as a non-zero electric potential difference is necessary for the flow of an electrical current, but not sufficient.

If an electric current is to flow, the resistance must not be too high, Fig. 3.5. If the resistance is infinitely high, then we say the electric current is inhibited. (“The electricity wants to flow, but it cannot.”) There is also a resistance to chemical reactions, and chemical reactions can also be completely inhibited, i.e. they do not take place despite a non-zero chemical potential difference. The verbal description of these inhibitions varies depending on the type of reaction.



**Fig. 3.5**  
An electric potential difference is necessary, but not sufficient for the flow of an electric current.

#### Conductors and nonconductors

Just as conductors and non-conductors are required as the most important components for the realization of electrical circuits, substance conductors and non-conductors are required for the realization of substance transports. However, since there are many different substances, it is desirable to have *selective conductors* and non-conductors: A component should allow substance A to pass through, but not substance B.

A simple but not very selective substance conductor is a pipe: It “conducts” uncharged liquids and gases.

Water is a conductor for many ions, but also for other substances that dissolve in water, e.g. sugar. It is a non-conductor for electrons.

Metals conduct electrons well, but virtually no other substances. (An exception is platinum that conducts  $H^+$  ions quite well.)

Glass lets pass visible light, but not air (or other gases and liquids).

Gases are permeable for other gases, although not very good.

A liquid A is permeable to a liquid B if A and B are “miscible”. For example, water is permeable to alcohol.

A solid wall that is permeable to certain types of ions but not to others is called a *diaphragm*.

#### Diffusion

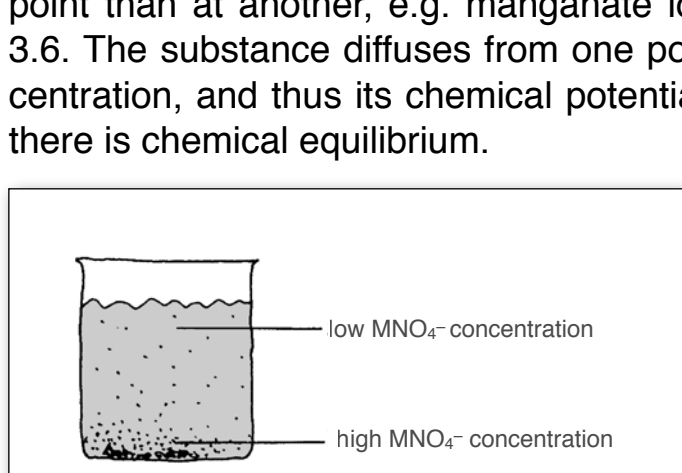
A substance transport is called diffusion if

- a substance A flows through substance B, where A is a gas, whereas B can be gaseous, liquid or solid;
- the drive for the current is a gradient of the chemical potential.

Diffusion is a dissipative process, entropy is produced.

The substance diffuses from one point to the other until the concentration, and thus its chemical potential, is the same everywhere; until there is chemical equilibrium.

Suppose a substance is present in a higher concentration at one point than at another, e.g. manganate ions dissolved in water, Fig. 3.6. The substance diffuses from one point to another until the concentration, and thus its chemical potential, is the same everywhere: there is chemical equilibrium.



**Fig. 3.6**  
The manganate ions go from places of higher to places of lower chemical potential.

The substance flow density is proportional to the gradient of the chemical potential:

$$\vec{j}_n = -\sigma_n \cdot \text{grad } \mu$$

The “substance conductivity” is related to the diffusion constant  $D$ :

$$\sigma_n = \frac{D \cdot \rho_n}{R \cdot T}$$

Thus the substance current depends

- on the cross-sectional area of the flow channel
- on its length (the longer it is, the smaller  $\text{grad } \mu$  will become for a given chemical potential difference)
- on  $\sigma_n$ .

Diffusion can be inhibited, for example, by making the distance between the two sites of different chemical potentials very large.

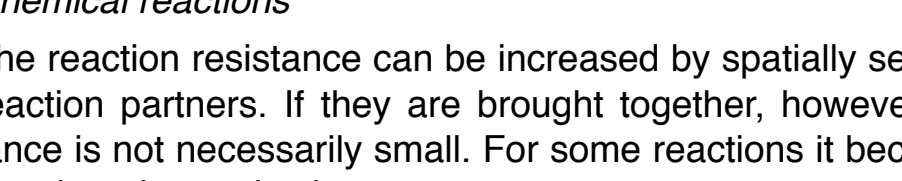
#### Phase transitions solid $\leftrightarrow$ liquid $\leftrightarrow$ gaseous

The phase transitions solid  $\leftrightarrow$  liquid and liquid  $\leftrightarrow$  gaseous usually proceed completely uninhibited, i.e. no chemical potential difference builds up between the phases. The phases are almost in equilibrium. It is only with difficulty that chemical potential differences can build up. Doubly distilled water can be heated up to  $140^\circ\text{C}$  without evaporating (boiling delay). The chemical potential of the liquid water is then greater than that of the gaseous water. Conversely, steam can also be supercooled (supersaturated steam); the chemical potential of the steam is then greater than that of the liquid. Accordingly, liquids can be supercooled. A small amount of dust-free water can be cooled down to  $-30^\circ\text{C}$  without solidifying.

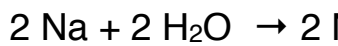
#### Chemical reactions

The reaction resistance can be increased by spatially separating the reaction partners. If they are brought together, however, the resistance is not necessarily small. For some reactions it becomes small, for others it remains large.

A reaction that runs spontaneously and very quickly is



For most reactions, the resistance is high; the reactions are inhibited. So the reaction



does not run by itself despite a high chemical potential difference.

The reaction resistance can be reduced in various ways

- by increasing the temperature
- with catalysts.

A catalyst acts like a “chemical switch”. If a suitable catalyst is available, an otherwise inhibited reaction can take place. The catalyst is not altered in the reaction.

In biological systems thousands of reactions take place. Most of them are normally inhibited. Their onset and progression is controlled by catalysts, the *enzymes*.

In order to synthesize a substance according to a given reaction equation, two conditions have to be met:

- The chemical potential difference must drive the reaction in the desired direction. This can be achieved by a suitable selection of temperature and pressure.
- The reaction resistance of the desired reaction must be small, that of competing reactions large. This can be achieved with catalysts.

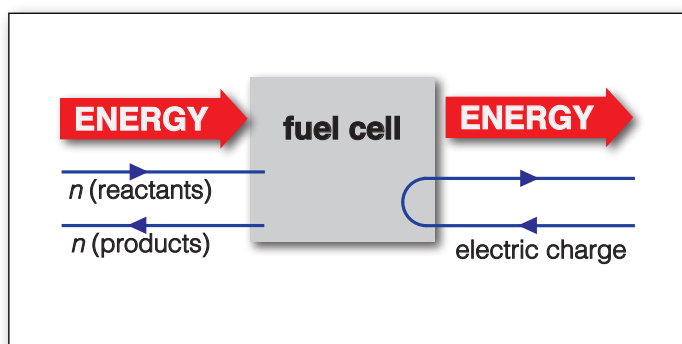
#### Nuclear reactions

When considering nuclear reactions, the zero point of the chemical potential may no longer be freely chosen for each chemical element. The  $\mu$  values of the chemical elements are coupled to each other by the nuclear reactions. Most chemical elements — more precisely: those with large and those with small atomic numbers — are metastable. The reaction, i.e. the decay of the heavy and the fusion of the light, is strongly inhibited. The nuclear reactor and fusion reactor serve to reduce the reaction resistance.

### 3.9 Reversibly running reactions – electrochemical reactions

Fuel cells, accumulators, monocells and various other types of batteries are energy transloaders. The energy is delivered with the carrier amount of substance and leaves the cell with the energy carrier electricity. In most of these cells, the reactants are located inside the cell from the outset. They are introduced into the cell during the production process. Only in the fuel cell the reactants are constantly supplied from the outside.

Fig. 3.7 shows the flow diagram of a fuel cell.



**Fig. 3.7**  
Flow diagram of the fuel cell

The energy balance equation is

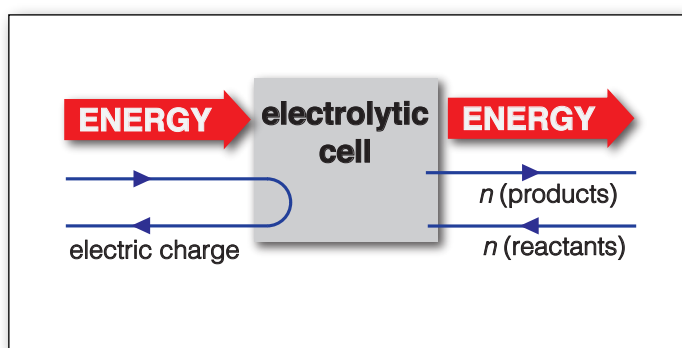
$$\Delta\mu \cdot I_{n(R)} = U \cdot I. \quad (3.4)$$

Here

$$I_{n(R)} = \frac{n(R)}{t}$$

is the *conversion rate* of the reaction.

There is also the counterpart to the fuel cell: a cell that receives energy with the carrier electricity and releases it with the amount of substance, Fig. 3.8. Examples of this are electrolytic cells and the accumulator while it is being charged.

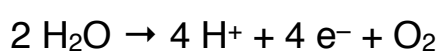


**Fig. 3.8**  
Flow diagram of the electrolytic cell

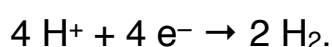
The reactions that take place in such cells, whether forward or backward, are called electrochemical reactions.

In an electrochemical reaction, the conversion rate  $I_{n(R)}$  is firmly coupled to the electric current  $I$ . We look at the electrolysis of water as an example.

The reaction



takes place at the anode of the electrolytic cell and



at the cathode.

With each mole converted, 4 moles of electrons flow through the outer circuit. Now, for electrons, the charge per amount of substance is equal to the negative Faraday constant:

$$\frac{Q_{\text{electron}}}{n_{\text{electron}}} = \frac{-e}{\tau} = -F = -9.6 \cdot 10^4 \text{ C/mol}$$

This means that  $4 \cdot 9.6 \cdot 10^4 \text{ C}$  flow through the circuit per mole of reaction conversion, i.e.

$$I = 4 \cdot F \cdot I_{n(R)}$$

For other reactions, another small integer  $z$  stands instead of the “4”:

$$I = z \cdot F \cdot I_{n(R)} \quad (3.5)$$

We insert (3.5) into the energy balance equation (3.4) and obtain:

$$\Delta\mu = z \cdot F \cdot U. \quad (3.6)$$

This equation tells us that the *chemical* potential difference can be determined by measuring an *electric* potential difference. If, on the other hand, the chemical potential difference is known, the electric potential difference of the corresponding electrochemical cell can be calculated using equation (3.6). For a hydrogen-oxygen fuel cell one obtains:

$$U = \frac{\Delta\mu}{4F} = \frac{474.36 \cdot 10^3 \text{ G}}{4 \cdot 9.6 \cdot 10^4 \text{ C/mol}} = 1.24 \text{ V}$$

## 3.10 Irreversibly running reactions – entropy balance of chemical reactions

Most chemical reactions are free-running: All the energy released during the reaction is used to produce entropy. This is the case, for example, when coal, heating oil, petrol or natural gas is burned in power stations or domestic heating systems.

The energy balance equation is:

$$\Delta\mu \cdot I_{n(R)} = T \cdot I_{S \text{ prod}} .$$

The entropy produced can be calculated according to

$$I_{S \text{ prod}} = \frac{\Delta\mu \cdot I_{n(R)}}{T}$$

One might expect that every free-running reaction “warms up”, i.e. the temperature of the products is higher than that of the reactants, or entropy is released from the reaction products. But this is not always the case.

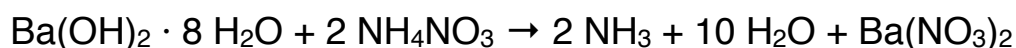
First, we consider a reaction that is not free-running, i.e. no entropy is produced (as is the case in an ideal electrochemical cell). During the reaction, the reactants disappear and the products are formed.

The reactants contain a certain amount of entropy, and this must be taken over by the products. However, this amount of entropy does not correspond to the same temperature for the reactants and the products. Thus, in some reactions the temperature of the products will be lower, in others it will be higher than that of the reactants. If the reaction is free-running, i.e. completely irreversible, new entropy is created. This contribution to the entropy balance increases the temperature of the reaction products. However, there are reactions whose reaction products have such a low temperature if they run reversibly, that the entropy generated in the irreversible process is not sufficient to bring the reaction products back to the initial temperature.

If such a reaction is to be carried out at constant temperature, entropy must be added. These reactions are called *endothermic*. Reactions in which entropy is released are called *exothermic*.

This means that entropy is also produced in endothermic reactions. However, the reaction products have such a large entropy capacitance that the produced entropy causes only a relatively small temperature increase.

An example of an endothermic reaction is



$\text{Ba(OH)}_2 \cdot 8 \text{H}_2\text{O}$  and  $\text{NH}_4\text{NO}_3$  are crystalline solids. The reaction products form an aqueous solution. The low temperature of the products is easy to understand: The water of crystallization of the barium hydroxide transforms into ordinary liquid water. This is a kind of melting process, and entropy is known to be needed for melting.

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# 4

**Energy differential, characteristic function, equilibria**

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### 4.1 Physical system and state

Physics describes real objects in an abstract way: by the relationship between the physical quantities of the object. To describe a desired class of processes, one must therefore first select the variables that do what is required. To describe a capacitor, for example, the variables  $Q$ ,  $U$ ,  $E$  (energy),  $\vec{E}$  (electric field strength), etc. are chosen. Normally one does not choose  $S$ ,  $T$ ,  $p$  or  $\vec{H}$  (magnetic field strength), because one gets along without them. There can be several reasons why certain variables are not needed: either because these variables are constant during the processes of interest, or because their values have no influence on the values of the variables of interest. In future, when we speak of “the” variables of a system, we mean only the variables of interest.

We say that a system is in a certain state when all variables have certain values. By “system” in a strict sense we no longer understand the object, but the set of all its states. The choice of variables already contained arbitrariness. What we call a system contains even more arbitrariness, because we can restrict the set of states under consideration as we wish. One often pretends to mean with the system “capacitor” all the states that are defined by the relationship

$$Q = C \cdot U$$

Realistically, however, one will restrict oneself to a tiny part of this diversity of states, because even the best capacitor does not tolerate arbitrarily high voltages.

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## 4.2 The energy differential

We had seen that a flow of energy can always be described by an expression of the form

$$P = \xi I_X$$

In general, several substance-like quantities are involved in an energy flow. At first we only look at energy flows with a single “energy carrier”.

We make energy flow into a system, so that the energy accumulates within the system. We want to describe the energy change of the system.

Two things can happen with the quantity  $X$ , which accompanies the energy current. Either it accumulates in the system (like the energy), or it passes through the system and only discharges the energy within the system. We consider successively different realizations of the relation  $P = \xi I_X$ , i.e. energy transports with different energy carriers  $X$ .

### 1. Energy supply with the carrier entropy

A body is warmed up, Fig. 4.1. An energy current

$$P = T \cdot I_S$$

flows into the body:

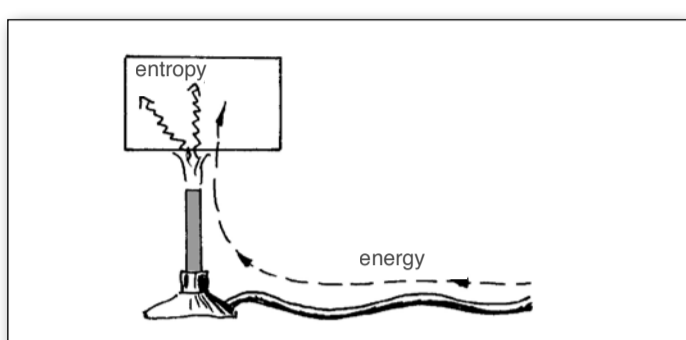
With the balance equations  $P = dE/dt$  und  $I_S = dS/dt$  we get

$$\frac{dE}{dt} = T \frac{dS}{dt}$$

and from that the energy differential

$$dE = T dS. \quad (4.1)$$

This differential tells us by how much the energy of a body changes when an amount of entropy  $dS$  is supplied to it.



**Fig. 4.1**  
The energy and entropy content of the body increase.

### 2. Energy supply with the carrier momentum

#### a) With accumulation of momentum

A vehicle is accelerated, Fig. 4.2. An energy current

$$P = \vec{v} \cdot \vec{F}$$

flows into the vehicle.

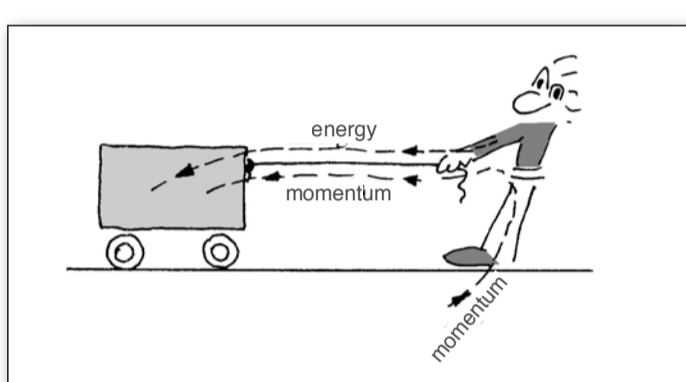
With the balance equations  $P = dE/dt$  and  $\vec{F} = d\vec{p}/dt$  follows

$$\frac{dE}{dt} = \vec{v} \frac{d\vec{p}}{dt}$$

and from this the energy differential

$$dE = \vec{v} d\vec{p} \quad (4.2)$$

The equation tells us by how much the energy of a body changes when the amount of momentum  $d\vec{p}$  is supplied to it.



**Fig. 4.2**  
The energy and momentum content of the vehicle increase.

#### b) Without accumulation of momentum

A spring is stretched, Fig. 4.3. An energy current

$$P = \vec{v} \cdot \vec{F}$$

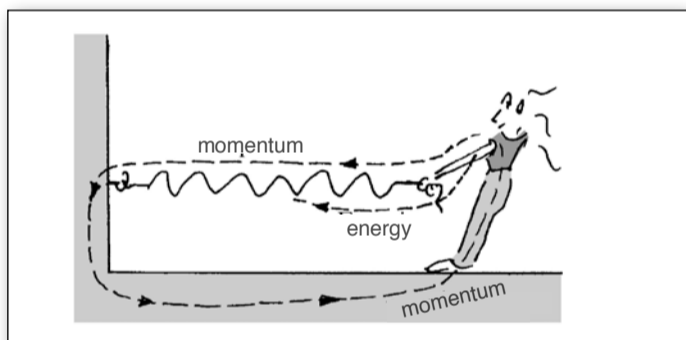
flows into the spring.

The momentum does not accumulate within the spring, it just flows through. With  $P = dE/dt$  and  $\vec{v} = d\vec{s}/dt$  we get

$$\frac{dE}{dt} = \vec{F} \frac{d\vec{s}}{dt}$$

and from this

$$dE = \vec{F} d\vec{s} \quad (4.3)$$



**Fig. 4.3**  
The energy content of the spring increases, the spring becomes longer.

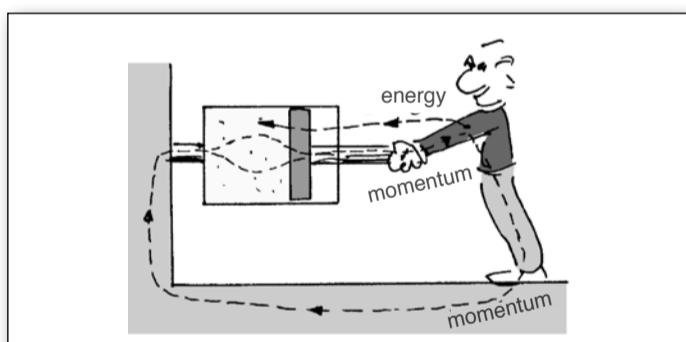
A variant of this is shown in Fig. 4.4, where the energy is stored in a gas in the cylinder. We express the force  $\vec{F}$  and the displacement  $d\vec{s}$  by the pressure  $p$  and the volume change  $dV$ :

$$F = -A \cdot p \text{ and } ds = (1/A) \cdot dV,$$

and obtain the energy differential

$$dE = -p dV. \quad (4.4)$$

The minus sign indicates that the energy increases with decreasing volume.



**Fig. 4.4**  
The energy content of the gas increases, the volume decreases.

### 3. Energy supply with the carrier amount of substance

Energy flows into a container with a substance current, Fig. 4.5. Since each substance also carries entropy, the energy current is

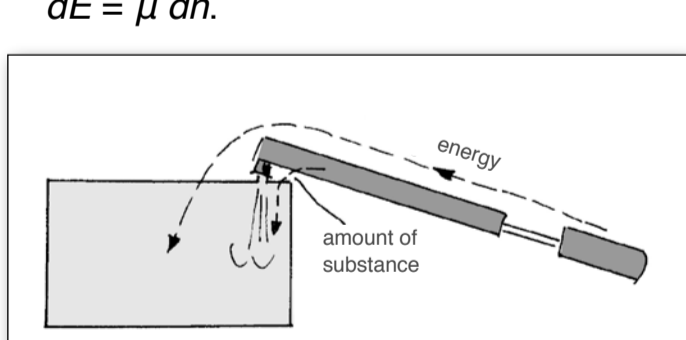
$$P = \mu \cdot I_n + T \cdot I_S.$$

If one ensures that the entropy flows off again simultaneously, then with the help of the balance equations  $P = dE/dt$  and  $I_n = dn/dt$  one gets

$$\frac{dE}{dt} = \mu \frac{dn}{dt}$$

and from this

$$dE = \mu dn. \quad (4.5)$$



**Fig. 4.5**  
The energy and amount of substance in the container increase.

### 4. Energy supply with the carrier electric charge

A capacitor is charged, Fig. 4.6. An energy current

$$P = U \cdot I.$$

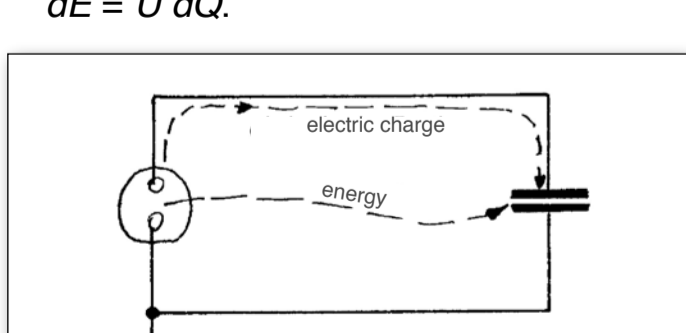
flows into the capacitor.

The net amount of the electric charge  $Q$  of the capacitor does not increase. For the charging of a single plate, however,  $I = dQ/dt$  applies. Together with the balance equation for the energy follows

$$\frac{dE}{dt} = U \frac{dQ}{dt}$$

and from this

$$dE = U dQ. \quad (4.6)$$



**Fig. 4.6**  
The energy within the capacitor and the electric charge on one of its plates increase.

All the differentials (4.1) to (4.6) have the same structure.

$$dE = \xi dX.$$

We call the quantities  $X$  extensive quantities and the quantities  $\xi$  intensive quantities. To a given extensive quantity always belongs a well-defined intensive quantity.

In the processes considered so far, only one extensive quantity changed at a time. In general, one must expect several extensive quantities to change their value simultaneously. Then the energy differential reads

$$dE = TdS - pdV + \mu dn + \vec{v}d\vec{p} + \vec{F}d\vec{s} \dots \quad (4.7)$$

Of course, the system can also have several independent variables  $S_1, S_2, \dots$  or  $V_1, V_2, \dots$  etc.. Then the expression has even more terms. It has as many terms as the system has independent variables.

### 4.3 Characteristic functions

Suppose the energy differential (4.7) for a system is

$$dE = TdS - pdV + \mu dn + \dots$$

If each of the extensive variables  $S$ ,  $V$ ,  $n, \dots$  is given a value,  $E$  also has a well-defined value.  $E$  is therefore a function of the extensive variables

$$E = E(S, V, n, \dots)$$

This function characterizes the system completely. Two systems for which these functions are the same are identical systems in the sense of physics. We call such a function a *characteristic function*. Table 4.1 lists the characteristic functions of some simple physical systems.

System	extensive variable	energy differential	characteristic function
capacitor	$Q$	$dE = UdQ$	$E(Q) = \frac{Q^2}{2C} + E_0$
capacitor with a variable plate distance	$Q, x$	$dE = UdQ - Fdx$	$E(Q, x) = \frac{Q^2 x}{2\epsilon\epsilon_0 A} + E_0$
spring	$x$	$dE = -Fdx$	$E(x) = \frac{D}{2}x^2 + E_0$
mass point	$p$	$dE = \vec{v} d\vec{p}$	$E(\vec{p}) = \frac{\vec{p}^2}{2m} + E_0$

**Table 4.1**  
Some characteristic functions

Only for few systems a characteristic function is known as an analytic expression.

For any system, in addition to

$$E = E(S, V, n, \dots).$$

there are also other characteristic functions.

They are all equivalent and can be derived from one another (by “Legendre transformation”), Table 4.2.

Name	Definition of the quantity	characteristic function
energy	$E$	$E = E(S, V, n)$
enthalpy	$H = E + p \cdot V$	$H = H(S, p, n)$
free energy	$F = E - T \cdot S$	$F = F(T, V, n)$
free enthalpy	$G = E + p \cdot V - T \cdot S$	$G = G(T, p, n)$
Hamilton function	$E$	$E = E(\vec{p} \cdot \vec{q})$
Lagrange function	$L = -E + \vec{p} \cdot \vec{v}$	$E = E(\vec{v} \cdot \vec{q})$

**Table 4.2**  
Several types of characteristic functions

Apart from the above-mentioned relation, in which the independent variable is the energy, the quantities on the left hand side of the other characteristic functions are rather unintuitive: the enthalpy, the free energy and the free enthalpy. Fortunately, we will get along with the first one alone, where the independent variable is the energy.

The characteristic functions are also called thermodynamic potentials. By the way, such functions are also used in mechanics. These are the Hamilton function and the equivalent Lagrange function.

### 4.4 The decomposition of a system

In general, the characteristic function  $E = E(X_1, X_2, \dots, X_n)$  is a complicated function of the variables  $X_1, X_2, \dots, X_n$  of the system. Sometimes, however, there is a simple structure, at least in certain ranges of values of the variables: Some characteristic functions break down into terms which have no variables in common:

$$E = E_A(X_1, X_2, \dots, X_k) + E_B(X_{k+1}, \dots, X_n)$$

In this case, not only  $dE$  is a complete differential, but also  $dE_A$  and  $dE_B$  taken separately. The system described by  $E = E(X_1, X_2, \dots, X_n)$  behaves like two independent systems. It can be *decomposed*. The individual terms  $E_A$  and  $E_B$  often have names of their own.

As an example, we consider a capacitor that can be moved, heated, and of course charged. Its variables are  $\bar{p}$ ,  $S$ , and  $Q_S$ . Thus, its energy differential is

$$dE = \bar{v}d\bar{p} + TdS + UdQ$$

The characteristic function of this system is

$$E(\bar{p}, S, Q) = \frac{\bar{p}^2}{2m} + \frac{Q^2}{2C} + E_0(S) \\ = E_1(\bar{p}) + E_2(Q) + E_0(S)$$

Each of the three terms depends on only one variable.

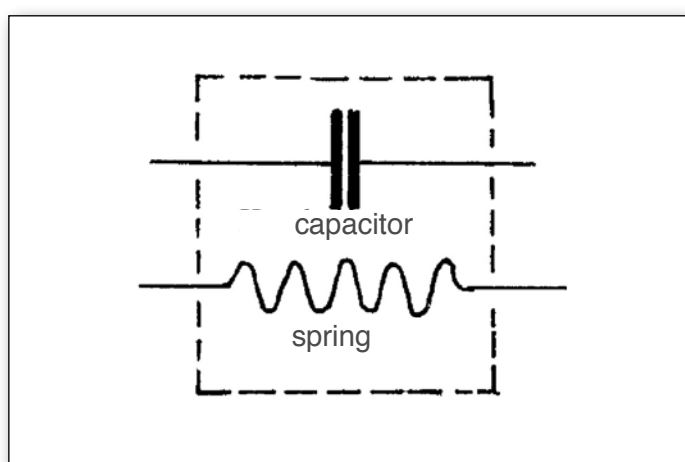
The terms are called

$$E_1 = \text{kinetic energy}$$

$$E_2 = \text{electric field energy}$$

$$E_0 = \text{internal energy}$$

Sometimes a system can be decomposed simply because it consists of spatially separated subsystems, Fig. 4.7.



**Fig. 4.7**  
The system within the dashed box can be decomposed for trivial reasons: It consists of two sub-systems that are spatially separated.

The characteristic function of the system in the dashed box is

$$E(Q, x) = \frac{Q^2}{2C} + \frac{D}{2}x^2 + E_0$$

Often the decomposition is only an approximation. For example the decomposition into kinetic and internal energy is only possible in non-relativistic approximation. The relativistic characteristic function of a body is:

$$E(|\bar{p}|, S) = \sqrt{c^2 \bar{p}^2 + E_0^2(S)}$$

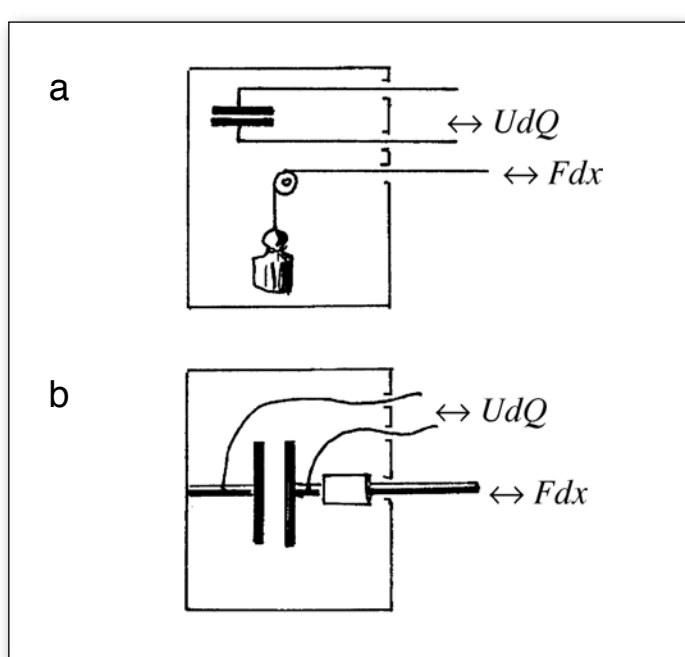
Only for  $c|\bar{p}| \ll E$  it decomposes into

$$E(|\bar{p}|, S) = \frac{\bar{p}^2}{2m} + E_0(S)$$

Let us compare two more systems, Fig. 4.8, which have the same variables and thus the same energy differential, namely

$$dE = U dQ - F dx, \tag{4.8}$$

one of which can be decomposed (Fig. 4.8a) and the other one cannot (Fig. 4.8b).



**Fig. 4.8**  
Two systems with the same energy differential. One (a) can be decomposed, the other (b) not.

We start with the uncoupled system. The characteristic function is

$$E(Q, x) = \frac{Q^2}{2C} + m \cdot g \cdot x + E_0$$

We calculate the differential  $dE$ :

$$dE = \frac{Q}{C}dQ + m \cdot g \cdot dx$$

Comparison with (4.8) provides

$$U = \frac{Q}{C} \quad \text{and} \quad F = -m \cdot g.$$

And now the coupled system. Its characteristic function is

$$E(Q, x) = \frac{Q^2 x}{2\epsilon_0 A} + E_0$$

It follows

$$dE = \frac{Qx}{\epsilon_0 A}dQ + \frac{Q^2}{2\epsilon_0 A}dx$$

and by comparison with (4.8):

$$U = \frac{Qx}{\epsilon_0 A} \quad \text{and} \quad F = -\frac{Q^2}{2\epsilon_0 A}$$

While in the first case each intensive variable depends only on its own conjugated extensive variable

$$U = U(Q) \quad F = \text{even constant}$$

we have in the second a coupling between the variables of the two terms of the energy differential:

$$U = U(Q, x) \quad F = F(Q)$$

## 4.5 Energy forms

To the name energy often attributes are added. There is kinetic, potential, electric, chemical, free, nuclear, thermal, rest and radiant energy and many more. However, the classification of energy into different “forms of energy” is not based on a uniform principle, but on different criteria. Some of the attributes are simply intended to identify the system or object that contains the energy. So by radiation energy we mean nothing more than the (total) energy of the radiation in question – just as the electron charge means the charge of an electron and solar mass means the mass of the sun. In most cases, however, there is a more far-reaching intention when indicating a form of the energy.

The need to classify energy into forms arose around the middle of the 19th century, immediately after the introduction of the concept of energy. At that time it was found that a new physical quantity could be introduced, although there was no general characteristic of this quantity, and there was no general rule for obtaining its values. The energy manifested itself in different systems and processes in very different ways. The fact that in the various cases one had to deal with the same quantity was only deduced from the observation that certain combinations of other physical quantities changed in a certain ratio during certain processes. There were, so to speak, fixed exchange rates between these combinations of quantities, the so-called equivalents. The best known of these exchange rates was the “mechanical heat equivalent”. It was a great scientific achievement to recognize these combinations of quantities as manifestations of a single, new physical quantity.

On the one hand, the new quantity had the beautiful characteristic of being very general in nature. It played a role in various sub-fields of physics. It created a link between the various physical sub-disciplines. On the other hand it had a flaw: it did not always show up in the same way as one would have expected from a well-behaving physical quantity. There was no characteristic by which one could always recognize it, by which one could determine its value in every case. For this reason, some physicists also considered it as nothing more than a mathematical aid. In any case, it seemed reasonable to call the various combinations of quantities that represented the different appearances of energy the *forms of energy*. The energy did not always show up in the same way, but in one form or another.

This was the state of the art until around the turn of the 19th and 20th centuries. We will see later that the concept of energy form is superfluous in the light of 20th century physics, just as superfluous as the concept of momentum or entropy forms would be. However, since the concept of the energy form has survived to this day, we would first like to make a few comments on the physical principles of the classification.

It is important to note that a distinction must be made between two classification procedures.

- One method is used to classify *energy changes and energy flows*. We have seen that every flow of energy is accompanied by a flow of another extensive quantity. Depending on which quantity this is, we speak of an energy transport or exchange in one form or another, Table 4.3.
- The other method is to assign a name to *stored energy*, i.e. the energy contained in a system or subsystem. We had mentioned the procedure in the previous section. If the characteristic function of a system breaks down into terms without common variables, the terms are often given their own names like kinetic energy, potential energy, tensional energy (of a spring) or internal energy.

energy exchange	
$P = \vec{v} \cdot \vec{F}$	work
$P = T \cdot I_S$	heat
$P = U \cdot I$	electric energy
$P = \mu \cdot I_n$	chemical energy

**Table 4.3**  
Forms of energy exchanges

It is unfortunate to call the results of both classification procedures by the same name, namely “energy form”. In fact, the two types of energy forms are often confused in the literature.

The clearest way to deal with the problem is to avoid the names altogether. In fact, from today’s perspective, the concept of the energy form is not only superfluous, but also misleading. To speak of forms of energy suggests that these are different physical quantities, with the strange property that one can convert one into the other. It also suggests that energy in different forms has different properties. Of course, this is not the case.

Since we know the special theory of relativity, we know that energy is a physical quantity in its own right, and not just a derived quantity. Talking about forms of energy is therefore just as unfounded today as talking about different forms of electric charge, depending on whether the charge is carried by electrons, protons or muons. The theory of relativity tells us what general characteristics energy has. From the energy-mass equivalence it follows that the energy has exactly those properties that we know from the mass: Gravity and inertia.

In order to distinguish between the different energy transports in Table 4.3, it is not necessary to speak of different forms of energy; it is sufficient to specify which quantity is transmitted together with the energy. Instead of e.g. talking about energy in form of heat, one simply says that beside the energy current there is also an entropy current. Or, as we have often done here, the accompanying quantity is referred to as the energy carrier.

Similar arguments hold for the terms of the characteristic function. Also here the name energy form is misleading. After all, these terms always represent subsystems. If one wants to refer to such a term, it is almost always clearer to name the subsystem to which the it belongs, instead of adding an adjective to the energy. So it is more correct to speak of the energy of the field of a capacitor instead of the potential energy of one capacitor plate in the field of the other.

## 4.6 Equations of state

We calculate the differential of the energy  $E(S, V, n, \dots)$ :

$$dE = \frac{\partial E(S, V, n)}{\partial S} dS + \frac{\partial E(S, V, n)}{\partial V} dV + \frac{\partial E(S, V, n)}{\partial n} dn$$

Comparing with

$$dE = TdS - pdV + \mu dn$$

we obtain

$$\frac{\partial E(S, V, n)}{\partial S} = T(S, V, n) \quad (4.9)$$

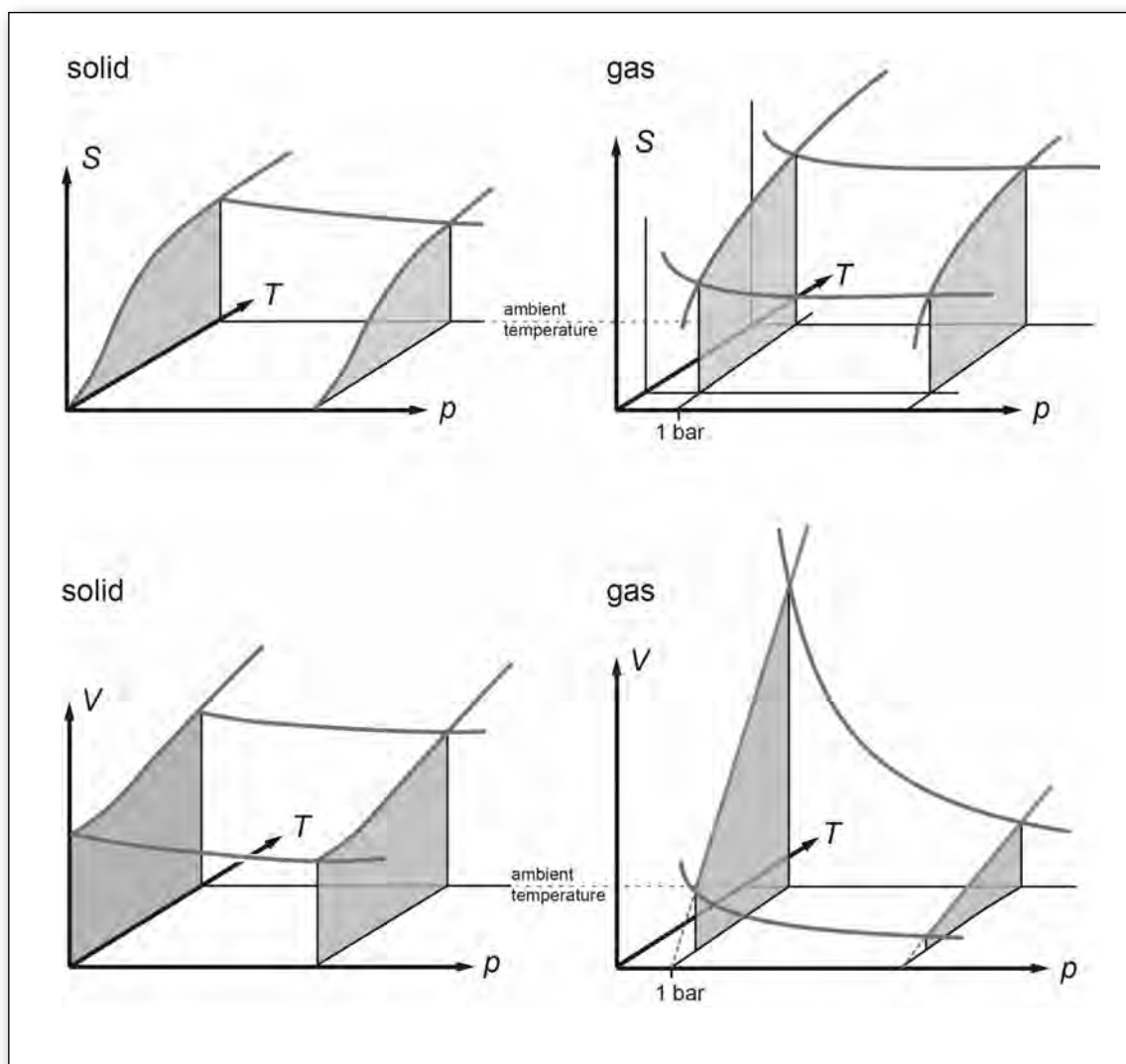
$$\frac{\partial E(S, V, n)}{\partial V} = -p(S, V, n) \quad (4.10)$$

$$\frac{\partial E(S, V, n)}{\partial n} = \mu(S, V, n)$$

Knowing the functions  $T = T(S, V, n)$ ,  $p = p(S, V, n)$  and  $\mu(S, V, n)$  is equivalent (apart from a constant term) to knowing the characteristic function. These three functions are called *equations of state*. They play an important role in thermodynamics, because often not all equations of state of a system are known, and therefore its characteristic function is not known either. For many purposes, however, knowledge of a single equation of state is sufficient.

*Example: Solid materials and gases*

Figure 4.9 shows the state functions  $S(p, T)$  and  $V(p, T)$  for solids and for gases for fixed  $n$ .



**Fig. 4.9**

The state functions  $S(p, T)$  (above) and  $V(p, T)$  (below) for a solid (left) and a gas (right)

## 4.7 Maxwell relations and flip rule

The equations of state are not independent of each other. Here is how one can see it. With equations (4.9) and (4.10) we obtain

$$\frac{\partial}{\partial V} \left( \frac{\partial E(S, V, n)}{\partial S} \right) = \frac{\partial T(S, V, n)}{\partial V}$$

and

$$\frac{\partial}{\partial S} \left( \frac{\partial E(S, V, n)}{\partial V} \right) = - \frac{\partial p(S, V, n)}{\partial S}$$

Since the left sides are equal, it must be:

$$\frac{\partial T(S, V, n)}{\partial V} = - \frac{\partial p(S, V, n)}{\partial S} \quad (4.11a)$$

This is a condition which the two equations of state  $T(S, V, n)$  and  $p(S, V, n)$  must fulfill.

The following two relationships are obtained in a similar way:

$$\frac{\partial T(S, V, n)}{\partial n} = \frac{\partial \mu(S, V, n)}{\partial S} \quad (4.11b)$$

$$\frac{\partial p(S, V, n)}{\partial n} = - \frac{\partial \mu(S, V, n)}{\partial V} \quad (4.11c)$$

Equations of this type are called *Maxwell relations*. There are more of them. We will derive three more. We proceed in a similar way as above, however we do not start from the differential of the energy, but of

$$G = E + pV - TS$$

We have

$$dG = \frac{\partial G(T, p, n)}{\partial T} dT + \frac{\partial G(T, p, n)}{\partial p} dp + \frac{\partial G(T, p, n)}{\partial n} dn \quad (4.12)$$

Moreover,

$$\begin{aligned} dG &= d(E + pV - TS) \\ &= TdS - pdV + \mu dn + pdV + Vdp - TdS - SdT \\ &= Vdp - SdT + \mu dn \end{aligned}$$

Comparison with equation (4.12) results in:

$$\frac{\partial G(T, p, n)}{\partial T} = -S(T, p, n)$$

$$\frac{\partial G(T, p, n)}{\partial p} = V(T, p, n)$$

$$\frac{\partial G(T, p, n)}{\partial n} = \mu(T, p, n)$$

We thus have obtained the state equations

$$S = S(T, p, n)$$

$$V = V(T, p, n)$$

$$\mu = \mu(T, p, n)$$

Also these are equivalent to the knowledge of any of the characteristic functions. These three functions are particularly popular because the variables  $T$ ,  $p$  and  $n$  can easily be measured.

$S = S(T, p, n)$  is obtained directly from the entropy capacity at constant pressure  $C_p^S$ , which can be measured. The relationship  $V = V(T, p, n)$ , the so-called *ideal gas law*, can also be easily obtained by measurement. This function has the special feature that it has a very simple, universal form for diluted systems, namely:

$$V(T, p, n) = R \frac{n \cdot T}{p}$$

Here  $R$  is the *gas constant* (see also section 3.2):

$$R = 8.31441 \text{ Ct/mol.}$$

Also these state functions are not independent of one another. The following Maxwell relations apply:

$$- \frac{\partial S(T, p, n)}{\partial p} = \frac{\partial V(T, p, n)}{\partial T} \quad (4.13a)$$

$$- \frac{\partial S(T, p, n)}{\partial n} = \frac{\partial \mu(T, p, n)}{\partial T} \quad (4.13b)$$

$$\frac{\partial V(T, p, n)}{\partial n} = \frac{\partial \mu(T, p, n)}{\partial p} \quad (4.13c)$$

The auxiliary quantity  $G$ , which we used for the derivation, is no longer included in these relations. The Maxwell relations are very simple, but sometimes surprising. For example, equation (4.13b) says that the change of the chemical potential with temperature is equal to the change of the entropy with the amount of substance, i.e. equal to the molar entropy, except for the sign.

If we look more closely at the structure of equations 4.11 and 4.13, we notice that they are “knitted” according to a simple principle; there is a simple procedure that allows one to express any given differential quotient through another one. We will give the rules without proving them, but we will check their validity on the relationships 4.11 and 4.13 calculated above.

We start from the energy differential of the system under consideration. Since we do not want to restrict ourselves to a specific system, we write it in the general form

$$dE = \xi_1 dX_1 + \xi_2 dX_2 + \xi_3 dX_3 + \dots \quad (4.14)$$

We are interested in a differential quotient that can be formed from any two of the variables on the right, for example

$$d\xi_1/dX_3$$

or

$$d\xi_1/d\xi_3$$

or

$$dX_1/dX_3.$$

We only exclude quotients where both variables come from the same term in equation (4.14), for example  $d\xi_1/dX_1$ .

Now a new differential quotient is obtained as follows:

1. The numerator and denominator are interchanged, and each of the two variables is simultaneously replaced by its “conjugate”, i.e. intensive by extensive, and extensive by intensive. Here are our three examples:

$$\frac{d\xi_1}{dX_3} \Rightarrow \frac{d\xi_3}{dX_1}$$

$$\frac{d\xi_1}{d\xi_3} \Rightarrow \frac{dX_3}{dX_1}$$

$$\frac{dX_1}{dX_3} \Rightarrow \frac{d\xi_3}{d\xi_1}$$

2. If the quantities in the numerator in the denominator are both intensive or both extensive, a minus sign must be added:

$$\frac{d\xi_1}{dX_3} \Rightarrow + \frac{d\xi_3}{dX_1}$$

$$\frac{d\xi_1}{d\xi_3} \Rightarrow - \frac{dX_3}{dX_1}$$

$$\frac{dX_1}{dX_3} \Rightarrow - \frac{d\xi_3}{d\xi_1}$$

Thus we obtain

$$\frac{d\xi_1}{dX_3} = \frac{d\xi_3}{dX_1}, \quad \frac{d\xi_1}{d\xi_3} = - \frac{dX_3}{dX_1}, \quad \frac{dX_1}{dX_3} = - \frac{d\xi_3}{d\xi_1}$$

Make sure that the term  $pdV$  contains a minus sign from the outset, which must be taken into account. One can imagine that this minus sign is a part of the variable “volume”.

This rule is called the *flip rule*.

Verify that the 6 equations 4.11 and 4.13 can be obtained by using the flip rule.

*Example: Capacitor with variable plate spacing*

The system cannot be decomposed. We call the plate spacing  $x$ .

One characteristic function is:

$$E(x, Q) = \frac{Q^2 x}{2\epsilon\epsilon_0 A} + E_0$$

$$dE = \frac{\partial E(Q, x)}{\partial Q} dQ + \frac{\partial E(Q, x)}{\partial x} dx$$

Comparing with the energy differential

$$dE = UdQ - Fdx$$

we find

$$U(Q, x) = \frac{\partial E(Q, x)}{\partial Q} = \frac{Q \cdot x}{\epsilon\epsilon_0 A} \quad F(Q, x) = - \frac{\partial E(Q, x)}{\partial x} = - \frac{Q^2}{2\epsilon\epsilon_0 A}$$

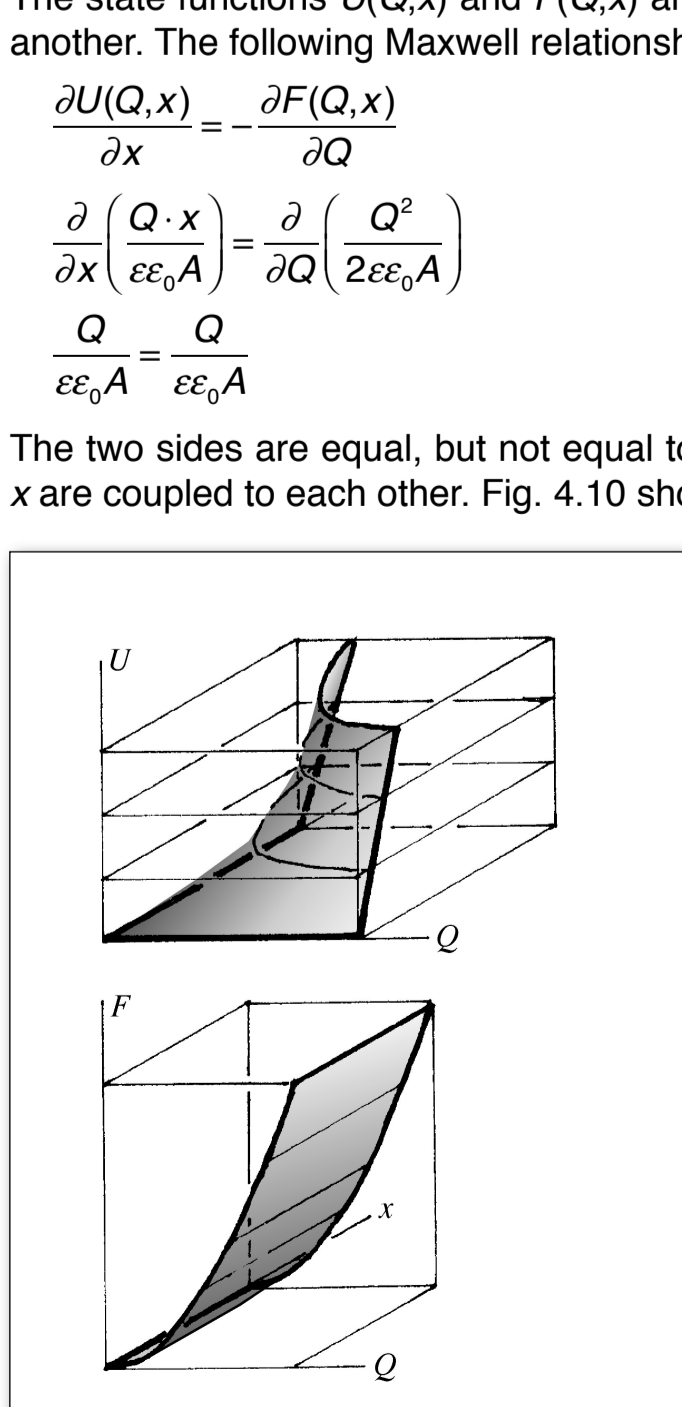
The state functions  $U(Q, x)$  and  $F(Q, x)$  are not independent from one another. The following Maxwell relationship applies:

$$\frac{\partial U(Q, x)}{\partial x} = - \frac{\partial F(Q, x)}{\partial Q}$$

$$\frac{\partial}{\partial x} \left( \frac{Q \cdot x}{\epsilon\epsilon_0 A} \right) = \frac{\partial}{\partial Q} \left( - \frac{Q^2}{2\epsilon\epsilon_0 A} \right)$$

$$\frac{Q}{\epsilon\epsilon_0 A} = \frac{Q}{\epsilon\epsilon_0 A}$$

The two sides are equal, but not equal to zero. The variables  $Q$  and  $x$  are coupled to each other. Fig. 4.10 shows  $U(Q, x)$  and  $F(Q, x)$ .



**Fig. 4.10**  
The state equations  $U(Q, x)$  and  $F(Q, x)$  of a capacitor with variable plate spacing

## 4.8 Linear approximation of the characteristic function

The knowledge of the characteristic function  $Y(X_1, X_2, \dots, X_n)$  is equivalent to the knowledge of  $n$  equations of state. Here, “knowledge” does not necessarily mean that an analytical expression must be known. The knowledge can also be expressed in a table of values or in a diagram.

Of course, a characteristic function or the corresponding state functions of an object are only known within a limited range of values of the variables.

For many purposes it is sufficient to know the state functions in a small interval, so that all relations between the variables of the state functions can be approximated by linear functions.

We suppose the equations of state to be  $V(T, p)$  and  $S(T, p)$ . If  $S$  and  $V$  are given for a pair of values  $\{T_0, p_0\}$ , i.e.  $V(T_0, p_0)$  and  $S(T_0, p_0)$ , then the volume and the entropy can be calculated in the vicinity of this independent coordinate point if the derivatives

$$\frac{\partial V(T, p)}{\partial T}, \quad \frac{\partial V(T, p)}{\partial p}, \quad \frac{\partial S(T, p)}{\partial T} \quad \text{and} \quad \frac{\partial S(T, p)}{\partial p}$$

at the point  $\{T_0, p_0\}$  are known.

Now the first and the last of these differential quotients are the same because of the Maxwell relation (4.13a) (except for the sign).

Therefore in a small vicinity of the point  $\{T_0, p_0\}$  the knowledge of two values ( $V(T_0, p_0)$  and  $S(T_0, p_0)$ ) and three derivatives, i.e. five numbers, is equivalent to the knowledge of the characteristic function. It is advisable to eliminate the size or extension of the system by dividing the derivatives by extensive quantities. The coefficients thus obtained have special names and are listed in tables:

$$\kappa = -\frac{1}{V} \frac{\partial V(T, p)}{\partial p} = \text{compressibility}$$

$$\alpha = \frac{1}{V} \frac{\partial V(T, p)}{\partial T} = \text{volumetric thermal expansion coefficient}$$

$$c_S^p = \frac{1}{n} \frac{\partial S(T, p)}{\partial T} = \text{molar entropy capacity}$$

Instead of the last of these three coefficients, more frequently one uses

$$c_p = \frac{T}{n} \frac{\partial S(T, p)}{\partial T} = \text{molar heat capacity}$$

Of course, other derivatives can be given. Altogether, however, only three are independent of each other (as long as we remain with two independent variables). Thus, for example, the pressure coefficient

$$\beta = \frac{\partial p(T, V)}{\partial T}$$

can be expressed by the compressibility and the volumetric thermal expansion coefficient:

$$\beta = \frac{\alpha}{\kappa}$$

Moreover, it can be shown that

$$C_S^p - C_S^V = V \frac{\alpha^2}{\kappa}$$

In section (3.6) we had already made use of the linear approximation of the state function  $\mu(T, p)$ .



### 4.9 Cyclic processes

The task we are confronting is to “transload” energy arriving with one carrier  $X_1$  to another carrier  $X_2$ . For this we need a system whose energy differential has two terms:

$$dE = \xi_1 dX_1 + \xi_2 dX_2$$

However, this condition is not yet sufficient for the system to be an energy transloader. In addition, the variables 1 must be coupled to the variables 2.

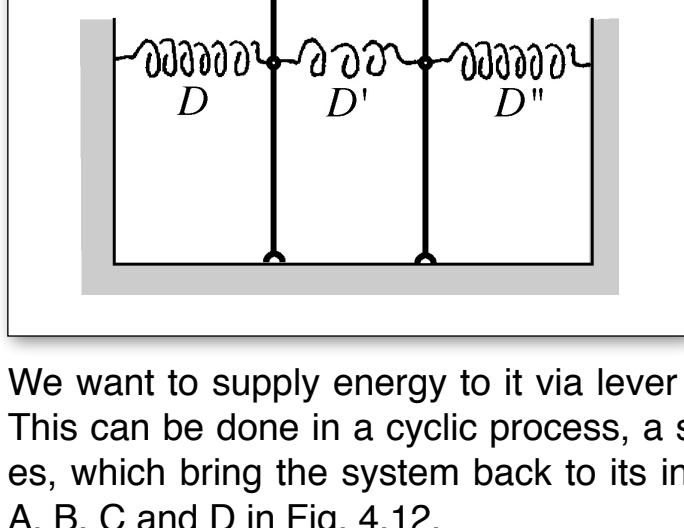
Let's start with a simple example from mechanics. The system consists of 2 levers and 3 springs, Fig. 4.11. Its energy differential is:

$$dE = F_1 dx_1 + F_2 dx_2$$

and its characteristic function is:

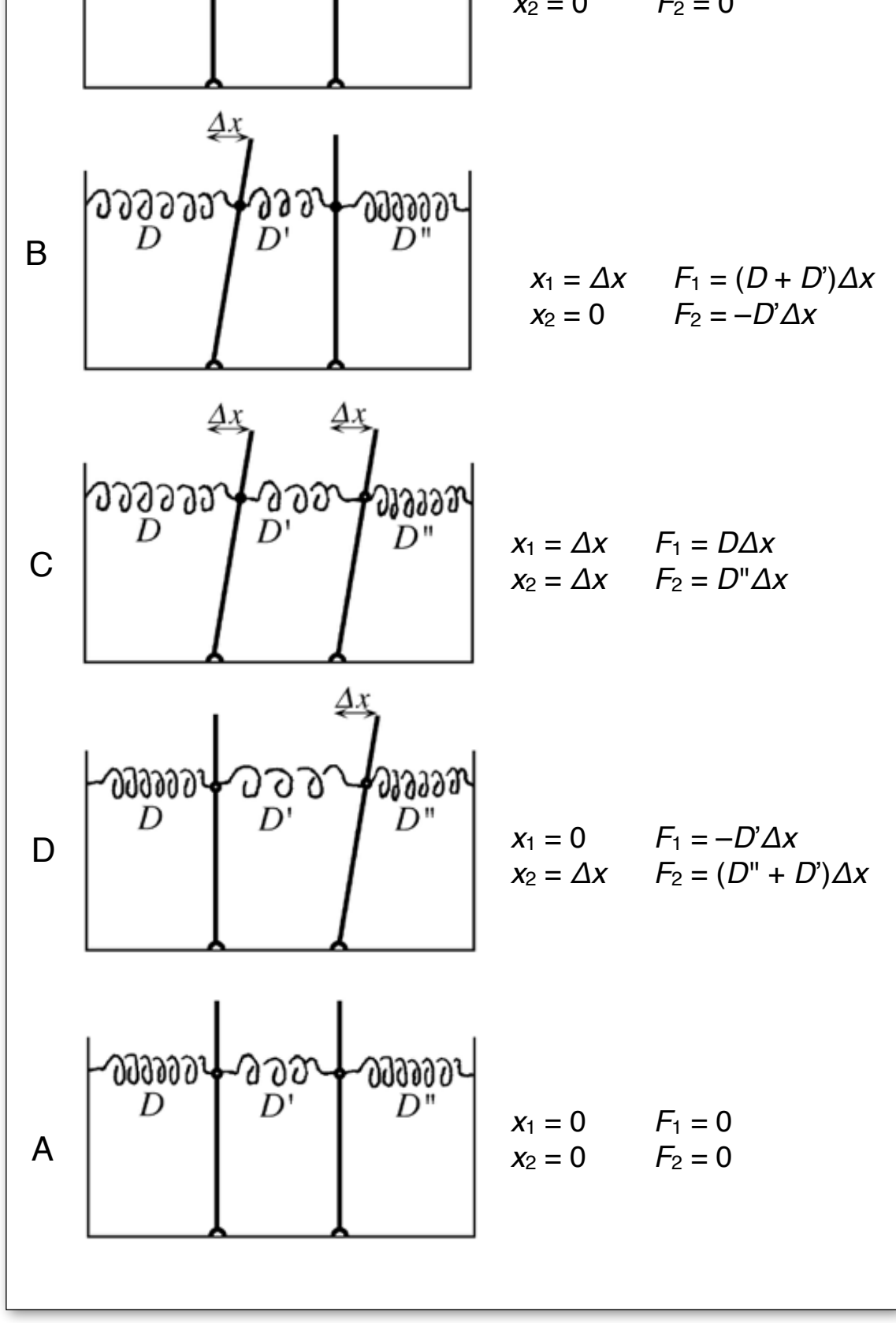
$$E(x_1, x_2) = \frac{D}{2} x_1^2 + \frac{D'}{2} (x_1 - x_2)^2 + \frac{D''}{2} x_2^2$$

It can be seen that the system cannot be decomposed.



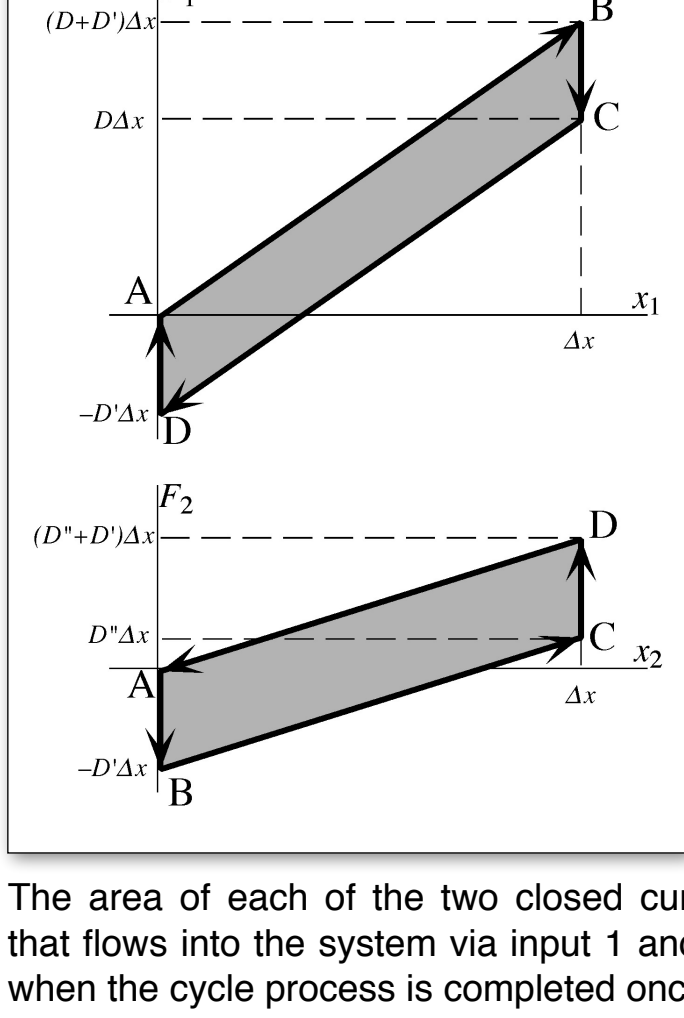
**Fig. 4.11**  
Simple mechanical “energy transloader”. Input 1 and output 2 are coupled by the spring  $D'$ .

We want to supply energy to it via lever 1 and extract it via lever 2. This can be done in a cyclic process, a sequence of 4 sub-processes, which bring the system back to its initial state. The 4 states are A, B, C and D in Fig. 4.12.



**Fig. 4.12**  
Cyclic process. After four steps, the system returns to its initial state. It absorbs energy via lever 1 and releases energy via lever 2.

It is appropriate to represent circular processes in two  $\xi$ - $X$  diagrams, Fig. 4.13.

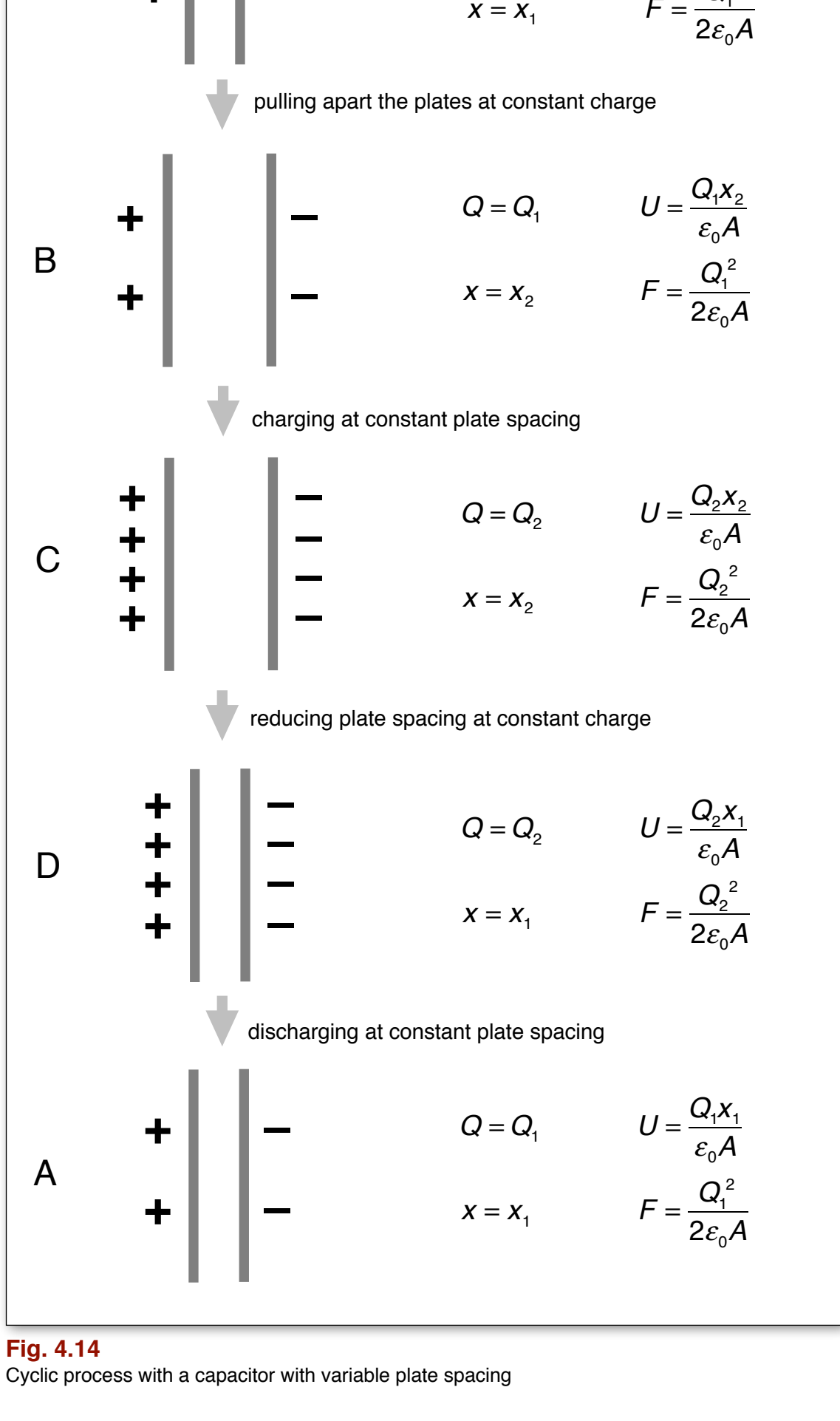


**Fig. 4.13**  
The cyclic process of Fig. 4.12 in a  $F_1$ - $x_1$  and a  $F_2$ - $x_2$  diagram

The area of each of the two closed curves represents the energy that flows into the system via input 1 and leaves it through output 2 when the cycle process is completed once.

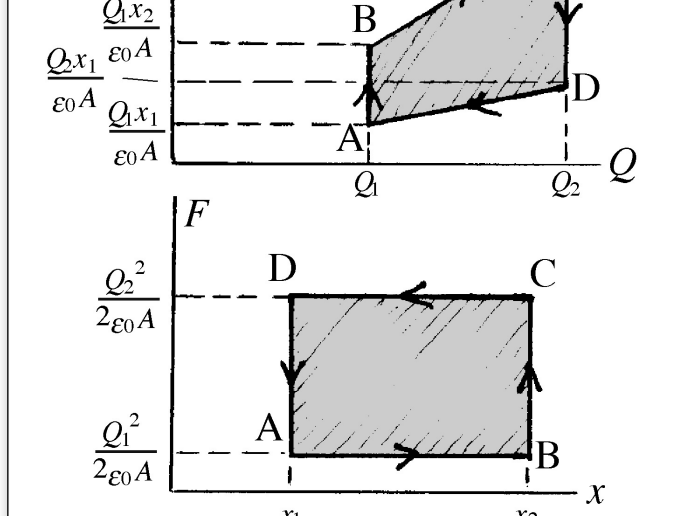
In this mechanical structure, the middle spring  $D'$  is responsible for the coupling. Without it, the characteristic function could be decomposed and the system could not work as an “energy transloader”. The energy that enters at input 1 could only be taken out again at input 1. The device would represent two independent energy stores.

As a second example of a cyclic process we consider a capacitor with variable plate spacing. It represents an electromechanical energy transloader, Fig. 4.14.



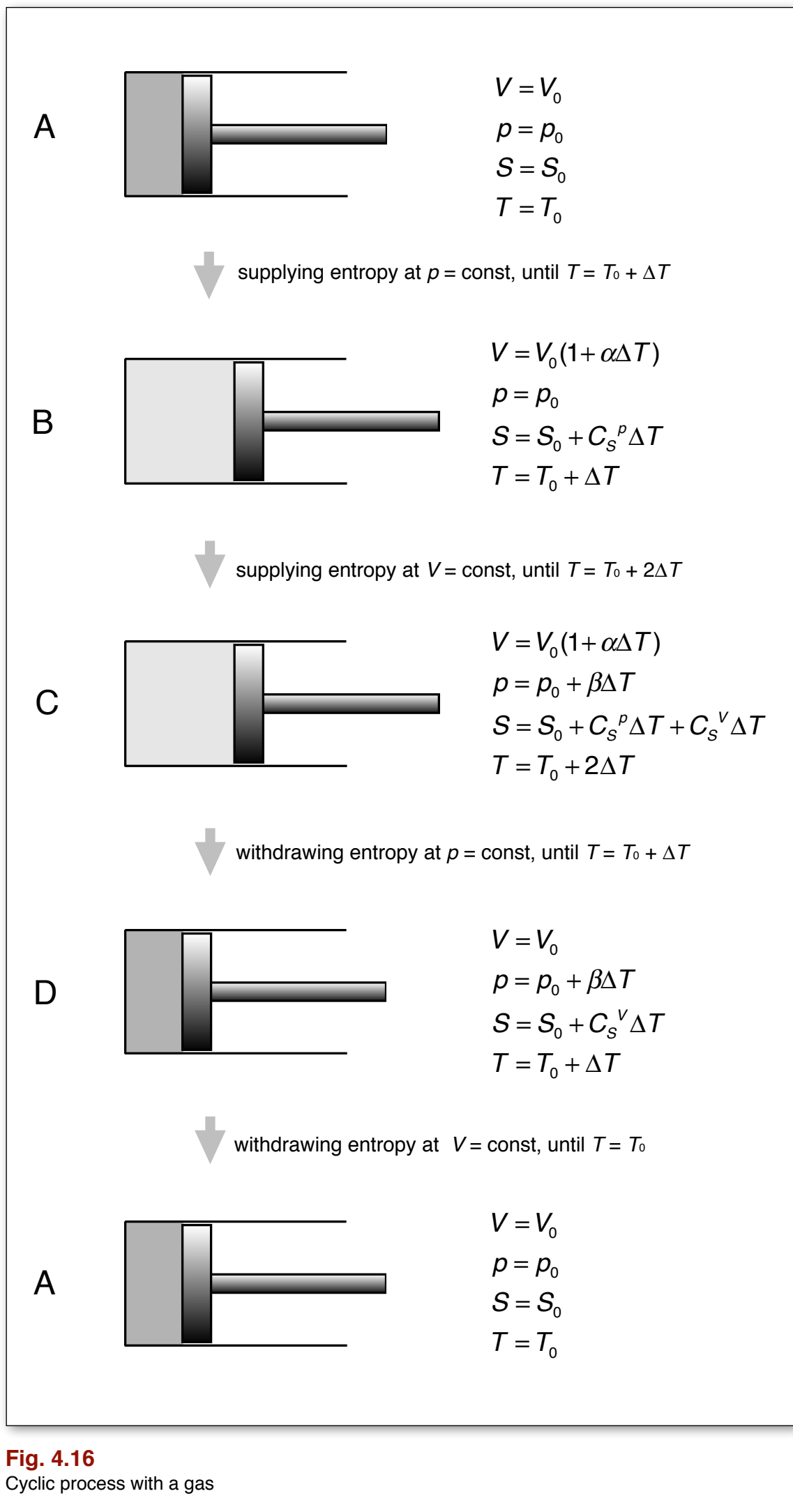
**Fig. 4.14**  
Cyclic process with a capacitor with variable plate spacing

Fig. 4.15 shows the process in the  $U$ - $Q$  and in the  $F$ - $x$  diagram.



**Fig. 4.15**  
The cyclic process of Fig. 4.14 in a  $U$ - $Q$  and in a  $F$ - $x$  diagram

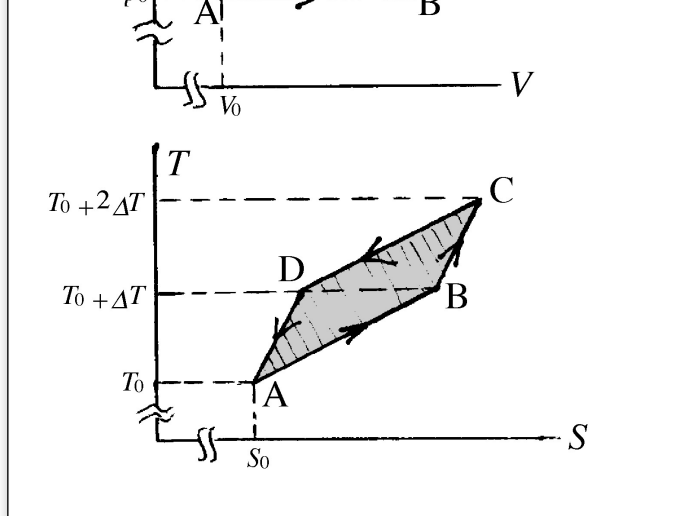
Finally, we consider a heat pump as a third example. The working system is a gas of a fixed amount of substance, Fig. 4.16. We assume that we do not know the characteristic function and instead use the four coefficients  $C_S^p$ ,  $C_S^v$ ,  $\alpha$  and  $\beta$  (one of which depends on the other three).



**Fig. 4.16**  
Cyclic process with a gas

Fig. 4.17 shows the cyclic process in a  $p$ - $V$  and in a  $T$ - $S$  diagram.

The coupling between the variables is expressed by the fact that the slopes of the  $T$ - $S$  curves for  $p = \text{const}$  and  $V = \text{const}$  are different, that is,  $C_S^p$  and  $C_S^v$  are different. A solid is not suitable as a working substance for a heat engine or heat pump, because its volume can practically not be changed, so its energy differential is  $dE = TdS$ .



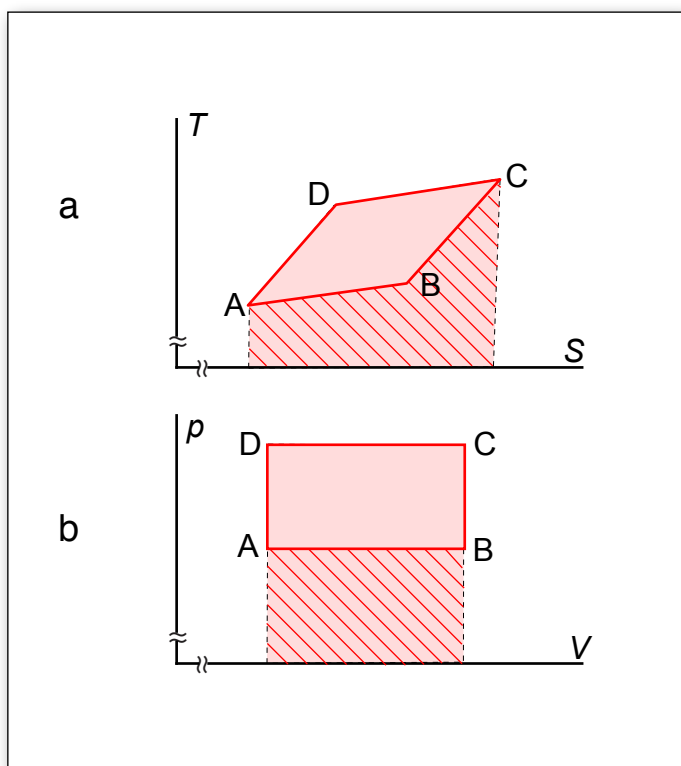
**Fig. 4.17**  
Cyclic process of Fig. 4.16 in a  $p$ - $V$  and in a  $T$ - $S$  Diagramm

## 4.10 Why the energy form heat is not contained in a system

We had already stressed that giving the term  $TdS$  its own name was an unfortunate move. It is a consequence that there are certain expectations that can't be fulfilled – especially the following:

“If a system absorbs heat, the heat must be contained in it after being absorbed.”

To convince ourselves that this proposition is wrong, we look at a gas and bring it from an initial state A to a final state C in two different manners, Fig. 4.18: once passing by B, and once by D, and we ask both times for the absorbed energy.



**Fig. 4.18**

On the way A-B-C the gas absorbs less heat than on the way A-D-C.

On the A-B-C path, the gas absorbs the amount of heat corresponding to the hatched area in Fig. 4.18a, as this area represents  $\int TdS$ . In addition, the gas does (or yields or delivers) work, that is given by the hatched area in Fig. 4.18b.

On the A-D-C path, the gas absorbs the amount of heat corresponding to the pink area in Fig. 4.18a and does the work corresponding to the pink area in Fig. 4.18b.

Initial and final state are the same for both process paths, but the absorbed heat is different. By how much has the heat of the gas increased? Obviously a meaningless question. The same applies to the work.

On the other hand, all questions about the values of the normal physical quantities, the “state quantities”, make sense:

By how much has the entropy or the volume increased?

How much have the temperature and pressure values changed?

In the case of substance-like quantities, the question may and should even be formulated as follows: “How much of it is within the system?” or “How much is contained in it?”.

### 4.11 Equilibria

We consider two systems A and B, whose energy differentials have a term  $\eta dY$  in common, i.e. it is

$$dE_A = \eta_A dY_A + \dots$$

$$dE_B = \eta_B dY_B + \dots$$

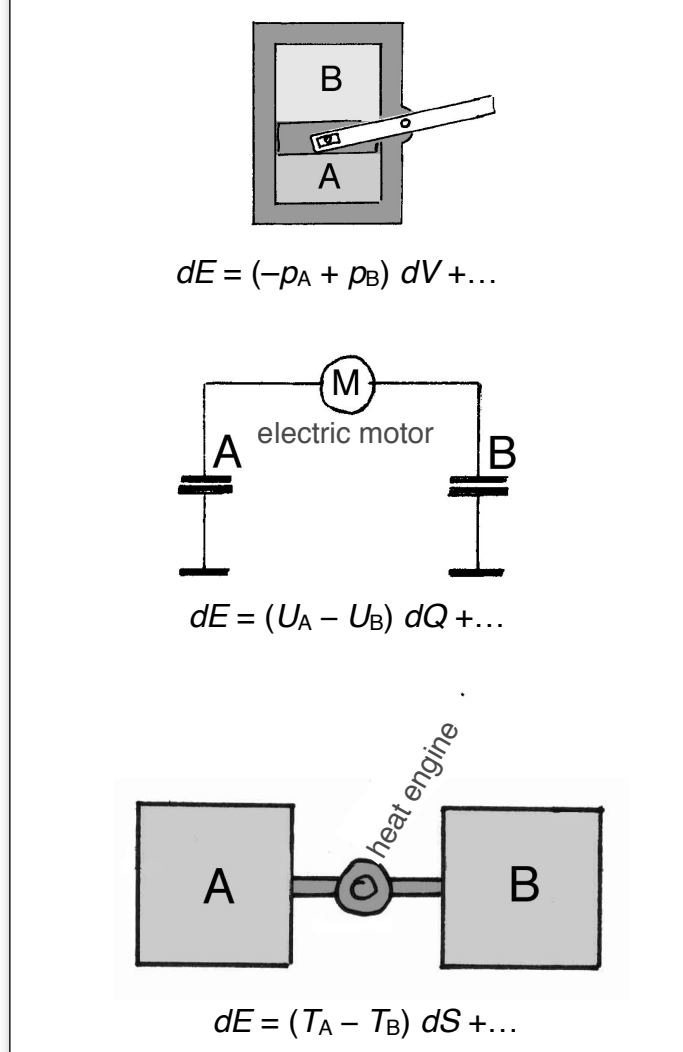
The two systems are now coupled to each other in such a way that the sum of the extensive variables is constant:

$$Y_A + Y_B = \text{const} \Rightarrow dY_A = -dY_B = dY$$

The energy differential of the overall system is therefore:

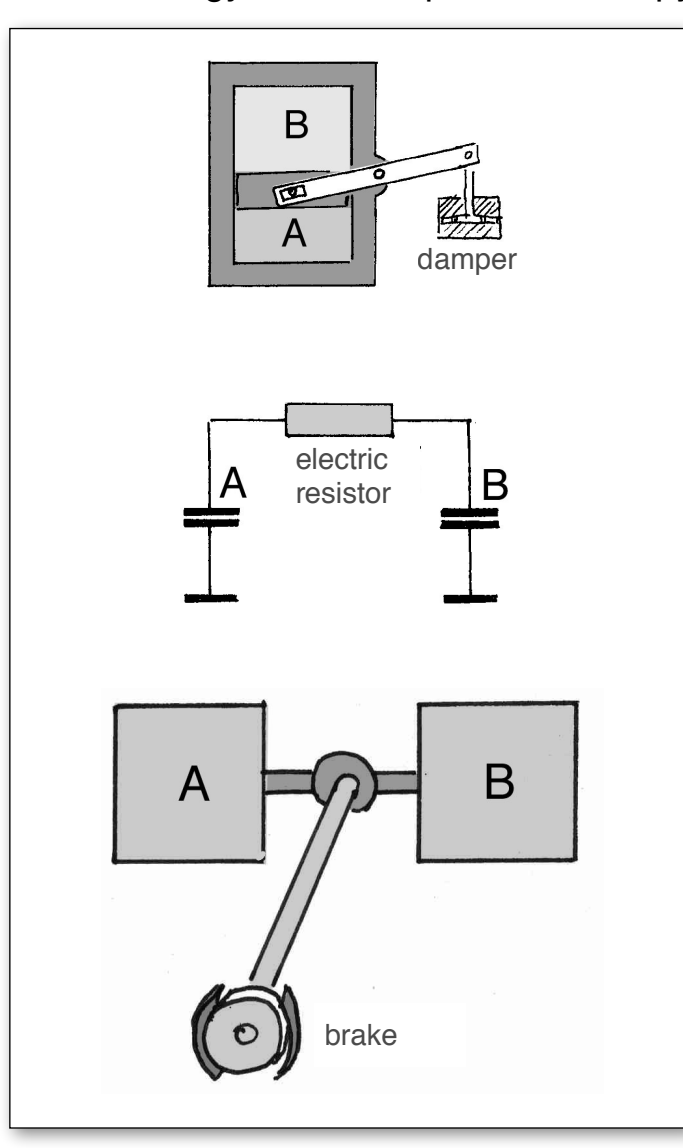
$$dE = (\eta_A - \eta_B) dY + \dots$$

Fig. 4.19 shows three examples.



**Fig. 4.19**  
Three systems consisting of coupled subsystems.

Let us now consider processes in which  $dE < 0$  and in which the released energy is used to produce entropy, Fig. 4.20.



**Fig. 4.20**  
The systems shown in Fig. 4.19 each with a dissipator.

In practice, the “dissipators” shown in the three figures (damper, electric resistor and brake) can also be omitted, because possibilities for entropy production are almost always present anyway.

If we include the dissipator in our system, the energy differential becomes zero and we have

$$(-p_A + p_B)dV + TdS_{\text{prod}} = 0$$

$$(U_A - U_B)dQ + TdS_{\text{prod}} = 0$$

$$(T_A - T_B)dS + TdS_{\text{prod}} = 0$$

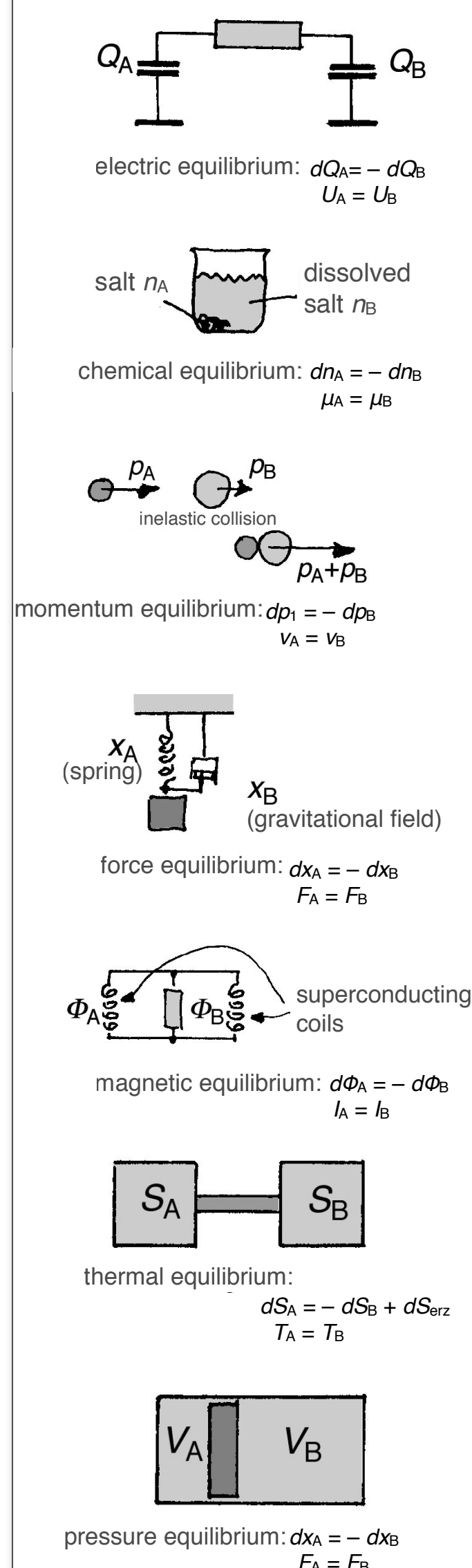
or in general:

$$(\eta_A - \eta_B)dY + TdS_{\text{prod}} = 0$$

Since these processes are associated with entropy production, they run by themselves, but only if  $(\eta_A - \eta_B)dY$  is not zero.

In this product, the second factor,  $dY$ , could be zero. That would simply mean that the process is inhibited. We assume that this is not the case. At some point, however, the first factor  $(\eta_A - \eta_B)$  becomes zero, and the process comes to a halt: there is *equilibrium* between the subsystems with regard to the variable  $Y$ .

In other words, equilibrium exists between two subsystems only with respect to the exchange of a certain extensive variable. There is no equilibrium per se. One must therefore distinguish between different types of equilibria, Fig. 4.21.

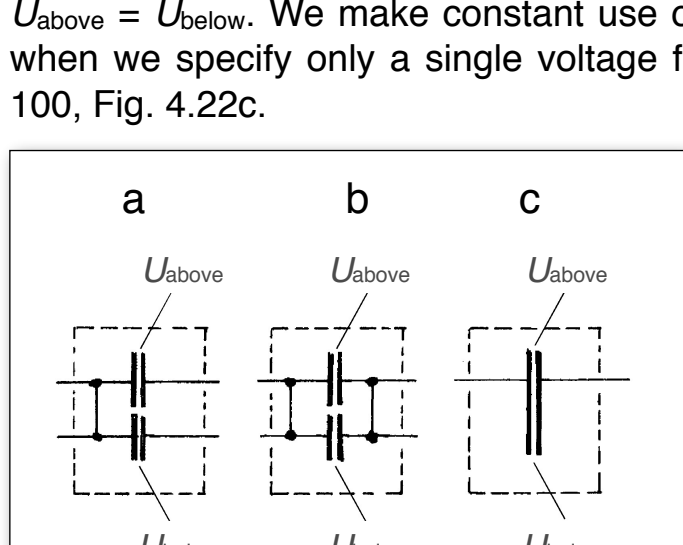


**Fig. 4.21**  
Several types of equilibrium

The total energy of the two subsystems, without the dissipator, decreases during the process of establishing the equilibrium. The state of equilibrium is therefore a state of *minimum energy*. Dissipation often takes place within systems A and B. Then the dissipator can no longer be separated, the produced entropy remains stuck in the system. In this case  $dE = 0$  and  $dS > 0$ , the equilibrium state is now the state of *maximum entropy*.

Equilibria are particularly important for the number of independent variables in a system.

The system in Fig. 4.22a has two independent variables:  $U_{\text{above}}$  and  $U_{\text{below}}$ . In Fig. 4.22b the two capacitors are always in electrical equilibrium, the system has only one independent variable left:  $U_{\text{above}} = U_{\text{below}}$ . We make constant use of this property, for example when we specify only a single voltage for a capacitor and not 2 or 100, Fig. 4.22c.



**Fig. 4.22**  
(a) System with two independent variables.  
(b) Both capacitors are always in electrical equilibrium.  
(c) The parts of the capacitor are always in electrical equilibrium.

Also if we say that the gas in a container has the temperature  $T$ , we make use of the fact that all spatial areas of the gas are in thermal and pressure equilibrium with each other. Sometimes several subsystems are in the same place and they are either in equilibrium or they are not: electrons and phonons (lattice vibrations) of a solid are normally in thermal equilibrium, the solid has a single temperature. However, the subsystems can be brought out of equilibrium so that they have different temperatures.

The existence of equilibria is the reason why the state of a gas consisting of  $10^{23}$  molecules and correspondingly many variables can be described with only 3 independent variables, namely  $S$ ,  $V$  and  $n$ .

## 4.12 Flow equilibria

When an equilibrium is establishing, entropy is produced as much as the system allows. Once the equilibrium is reached, no further entropy production is possible, and the entropy production rate  $\Sigma_S$  becomes zero.

However, it often happens that a system goes through states and finally comes to a standstill in a state in which  $\Sigma_S$  is not equal to zero. The term “standstill” means that all variables of the system assume constant values over time. Such a state is called a *steady state* or sometimes *flow equilibrium*.

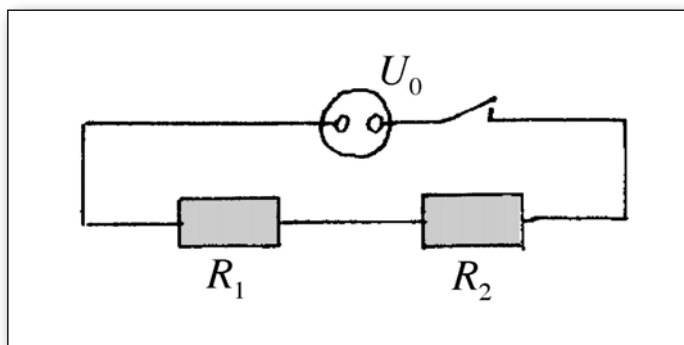
*Steady state:*

Values of variables are constant over time, but  $\Sigma_S \neq 0$

Since the entropy production rate is not zero, the system must be constantly supplied with energy:

$$P = T \cdot \Sigma_S$$

An equilibrium is always established between subsystems. We consider the simplest case, namely that there are only two subsystems, Fig. 4.23. Two resistors are connected in series to a power supply unit which delivers a constant voltage  $U_0$ .



**Fig. 4.23**

When the switch is closed, the voltage  $U_0$  is distributed over the resistors so that  $U_1/R_1 = U_2/R_2$ .

When the switch is closed, the voltage is distributed over the resistors:

$$U_0 + U_1 + U_2 = 0 \quad (4.15)$$

As is well known, it is distributed in such a way that the following applies

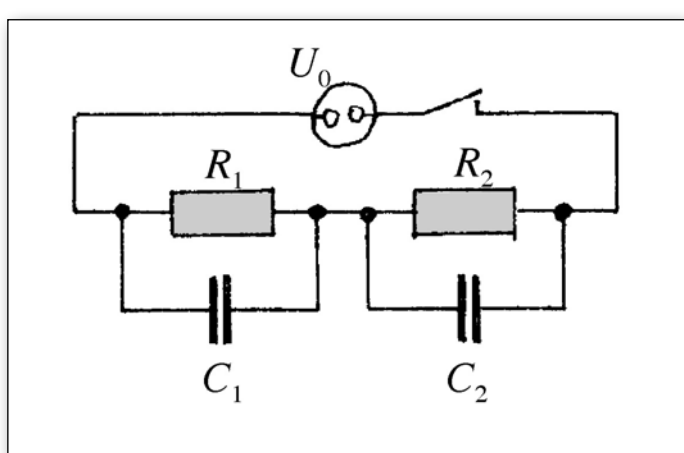
$$\frac{U_1}{R_1} = \frac{U_2}{R_2} \quad (4.16)$$

From equations (4.15) and (4.16) together we obtain the values of  $U_1$  and  $U_2$ :

$$U_1 = -\frac{R_1}{R_1 + R_2} U_0 \quad (4.17)$$

$$U_2 = -\frac{R_2}{R_1 + R_2} U_0$$

Now the distribution of the voltage  $U_0$  over the two resistors can be considered a process. In a real circuit, the capacitances between the different parts of the circuit are not zero, and we can draw a more precise picture of the circuit by taking into account two of these capacitances, Fig. 4.24.



**Fig. 4.24**

More realistic representation of the circuit shown in Fig. 4.23. Two capacitances are shown. It can be seen that the values of the voltages at the two resistors result from the establishment of an equilibrium.

The distribution of  $U_0$  over  $R_1$  and  $R_2$  is now time-dependent:

$$U_0 + U_1(t) + U_2(t) = 0$$

The steady-state voltages adjust with the time constant

$$\frac{C_1 + C_2}{\frac{1}{R_1} + \frac{1}{R_2}}$$

So we obtain

$$\frac{U_1(t = \infty)}{R_1} = \frac{U_2(t = \infty)}{R_2}$$

The state reached for  $t \rightarrow \infty$  is a steady state, because all physical quantities have time-constant values, whereas in the resistors entropy is produced.

It is now found that the energy dissipated in the two resistors, and thus the total entropy produced, reaches a minimum value in the steady state (compared to the states that are passed through when the equilibrium is establishing). We will prove this claim.

The energy dissipated per time in the two resistors taken together is

$$P = \frac{U_1^2}{R_1} + \frac{U_2^2}{R_2}$$

With equation (4.15) we get

$$P = \frac{U_1^2}{R_1} + \frac{(U_0 + U_1)^2}{R_2}$$

In order to obtain  $U_1^{\min}$ , for which  $P$  admits a minimum value, we set  $dP/dU_1 = 0$ :

$$\frac{2U_1^{\min}}{R_1} + \frac{2(U_0 + U_1^{\min})}{R_2} = 0$$

and obtain

$$U_1^{\min} = -\frac{R_1}{R_1 + R_2} U_0$$

and with (4.15)

$$U_2^{\min} = -\frac{R_2}{R_1 + R_2} U_0$$

i.e. the same expressions as (4.17).

The result can be generalized to more than two resistors connected in series:

A voltage distributes over resistors connected in series in such a way that the total entropy production becomes minimal.

Analogue statements can be formulated for other “driving forces”, i.e. differences of intensive quantities.

In addition, a similar consideration results in

An electric current distributes over resistors connected in parallel in such a way that the total entropy production becomes minimal.

Here, too, we have a steady state. Also this statement can be translated to other currents.

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# 5

## The ideal gas

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## 5.1 The ideal gas law

For a diluted gas, the relation between  $p$ ,  $V$ ,  $n$  and  $T$  is experimentally found to be:

$$p \cdot V = R \cdot n \cdot T$$

where

$$R = 8.31441 \text{ J/(mol} \cdot \text{K)}$$

This relationship is called the *ideal gas law*. Because of its universal character it is also called the *general gas equation*. Any substance can be brought in two ways into states where it fulfills the ideal gas law:

- by sufficient dilution;
- by a sufficiently high temperature.

In both ways, the mean interaction energy of the particles becomes small against their mean kinetic energy. However, raising the temperature can cause the substance to disintegrate (e.g. atoms are ionized) and thus  $n$  increases. This does not change the fact that the substance fulfills the gas equation – but then at higher temperatures one does not have the same substance as at lower temperatures.

The different dependencies contained in the equation have been discovered by different researchers and have different names:

$$p \sim \frac{1}{V} \quad \text{Boyle-Mariotte law (Robert Boyle 1627 - 1691, Edmé Mariotte 1620 - 1684)}$$

$$V \sim T \quad \text{Gay - Lussac's law, was not discovered by Gay - Lussac (1778 - 1850), but by Amontons (1663 - 1705)}$$

$$V \sim n \quad \text{Avogadro's law (Earl Amedeo di Quaregna e di Cerreto 1776 - 1856)}$$

Avogadro's discovery was not simply that for a substance the volume is proportional to the amount of substance – this is trivial because of the homogeneity of the gases –, it was the insight that the proportionality factor depends only on  $p$  and  $T$ , and not on the nature of the gas. For the volume of an ideal gas of 1 mol under normal conditions, i.e. at

$$p = 101\,325 \text{ Pa}, \quad T = 273.15 \text{ K}$$

we obtain

$$V = R \frac{n \cdot T}{p} = \frac{8.31441 \text{ J/(mol} \cdot \text{K)} \cdot 1 \text{ mol} \cdot 273.15 \text{ K}}{101\,325 \text{ Pa}} = 0.02241 \text{ m}^3$$

With  $\rho_n = n/V$  we can write the ideal as law in such a way that it does no longer contain substance-like quantities but only local quantities:

$$p = \rho_n \cdot R \cdot T$$

Some of the coefficients introduced in section 4.8 can be calculated from the gas law:

$$\kappa = -\frac{1}{V} \frac{\partial V(T,p)}{\partial p} = \frac{1}{V} \frac{RnT}{p^2} = \frac{1}{p}$$

$$\alpha = \frac{1}{V} \frac{\partial V(T,p)}{\partial T} = \frac{1}{V} \frac{Rn}{p} = \frac{1}{T}$$

$$\beta = \frac{\partial p(T,V)}{\partial T} = \frac{Rn}{V} = \frac{p}{T}$$

For ideal gases  $\beta = \alpha \cdot p$ . It is easy to verify that the general relationship  $\beta = \alpha/\kappa$  is fulfilled.

From

$$C_S^p - C_S^V = \frac{V\alpha^2}{\kappa}$$

we get

$$C_S^p - C_S^V = R \frac{n}{T}$$

## 5.2 Consequences of the ideal gas law

We study the quantities  $E$ ,  $S$  and  $\mu$  as a function of  $p$  and  $V$  at fixed temperature and at fixed amount of substance. Therefore, we use  $V$ ,  $T$  and  $n$  or  $p$ ,  $T$  and  $n$  as independent variables. For the sake of clarity, we sometimes omit the variable  $n$  in expressions such as  $E(T, V, n)$ ; we simply write  $E(T, V)$ .

*Energy as a function of volume and pressure at constant temperature*

We first ask for the  $V$  dependence of energy. With the rules of differential calculus (Falk-Ruppel p. 401, Job p. 51) we get:

$$\frac{\partial E(T, V)}{\partial V} = \frac{\partial E(S, V)}{\partial V} + \frac{\partial E(S, V)}{\partial S} \cdot \frac{\partial S(T, V)}{\partial V}$$

With equations (4.1) and (4.2) (section 4.6) we can write:

$$\frac{\partial E(S, V)}{\partial V} = -p(S, V)$$

$$\frac{\partial E(S, V)}{\partial S} = T(S, V)$$

By using the flip rule (section 4.7) we replace

$$\frac{\partial S(T, V)}{\partial V} = \frac{\partial p(T, V)}{\partial T}$$

and obtain

$$\frac{\partial E(T, V)}{\partial V} = -p + T \cdot \frac{\partial p(T, V)}{\partial T} \quad (5.1)$$

With the ideal gas law the second term on the right side becomes

$$T \cdot \frac{\partial p(T, V)}{\partial T} = T \cdot \frac{Rn}{V} = p$$

So equation (5.1) becomes

$$\frac{\partial E(T, V)}{\partial V} = 0 \quad (5.2)$$

or

$$E(V, T) - E(V_0, T) = 0$$

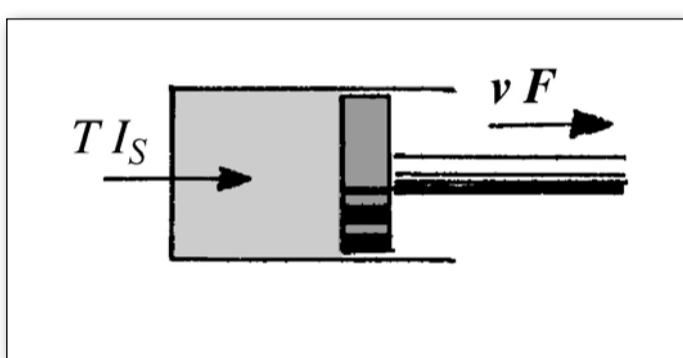
We now obtain (with the rules of differential calculus)

$$\frac{\partial E(T, V)}{\partial V} = - \frac{\partial E(T, V)}{\partial T} \cdot \frac{\partial T(E, V)}{\partial V}$$

Since  $\partial E(T, V)/\partial T \neq 0$ , with (5.2) we get

$$\frac{\partial T(E, V)}{\partial V} = 0$$

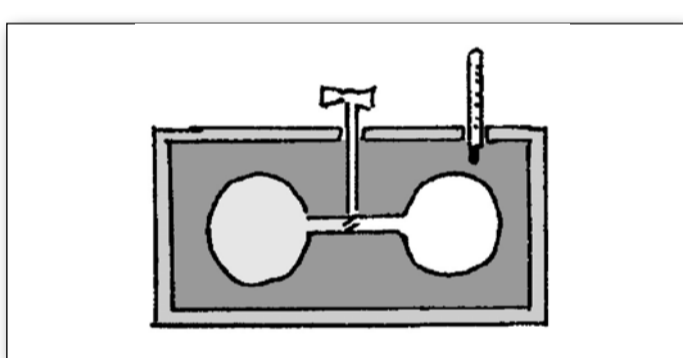
Thus, for  $E = \text{const}$  the temperature of an ideal gas is independent of the volume, or in other words, the temperature remains constant during an isoenergetic expansion or compression of an ideal gas. *Isoenergetic* means: The energy has the same value in the initial and final state, no matter how the process is realized:



**Fig. 5.1**

The gas gives off energy via the piston with the energy carrier momentum and absorbs energy via the walls with the carrier entropy.

- Let the gas push a piston in a cylinder, Fig. 5.1. Thereby it releases the energy  $dE = vdp$ . It obtains this energy with entropy that enters the cylinder:  $dE = TdS$ .
- A historically important realization of the isoenergetic expansion is the free expansion carried out by Gay-Lussac, Fig. 5.2: The gas in the left tank expands into the empty right tank. The temperature is the same at the end as at the beginning.



**Fig. 5.2**

Gay-Lussac experiment: The gas expands into the vacuum.

Finally, we obtain the dependence of the energy on pressure at constant temperature. With the chain rule and with (5.2) we get

$$\frac{\partial E(p, T)}{\partial p} = \frac{\partial E(T, V(p, T))}{\partial p} = \frac{\partial E(T, V)}{\partial V} \cdot \frac{\partial V(p, T)}{\partial p} = 0$$

or

$$E(p, T) - E(p_0, T) = 0$$

*Entropy as a function of volume and pressure at constant temperature*

For the calculation of the volume dependence of the entropy we again consider the isoenergetic expansion, realized reversibly as in Fig. 5.1. The energy flowing into the gas together with entropy is equal to the energy flowing out with momentum. So it is

$$dE = TdS - pdV = 0$$

or

$$TdS = pdV$$

With the ideal gas law we have

$$dS = n \cdot R \cdot \frac{dV}{V}$$

and from this

$$S(V, T) - S(V_0, T) = n \cdot R \cdot \ln \frac{V}{V_0} \quad (5.3)$$

Thus, for  $T = \text{const}$  the entropy increases logarithmically with the volume. With the ideal gas law we also obtain from (5.3)

$$S(p, T) - S(p_0, T) = n \cdot R \cdot \ln \frac{p_0}{p}$$

*The chemical potential as a function of volume and pressure at constant temperature*

With the ideal gas law we calculate:

$$\frac{\partial V(T, p, n)}{\partial n} = \frac{RT}{p}$$

and with the Maxwell relation (4.5c) (section 4.7): we obtain

$$\frac{\partial \mu(T, p, n)}{\partial p} = \frac{RT}{p}$$

Integration gives

$$\mu(T, p) - \mu(T, p_0) = RT \ln \frac{p}{p_0}$$

Thus, at  $T = \text{const}$  the chemical potential increases logarithmically with pressure. With the ideal gas law we also obtain

$$\mu(T, V) - \mu(T, V_0) = RT \ln \frac{V_0}{V}$$

### 5.3 Dissolved substances as ideal gases

The ideal gas law always applies when a substance is sufficiently diluted. It does not matter how the dilution is achieved. We had previously assumed that the substance existed as a pure gas of low density. The material was diluted in vacuum, so to speak. However, the validity of the gas law does not change if a substance is diluted in a material solvent. Sugar in an aqueous sugar solution,  $\text{Na}^+$  ions in an aqueous saline solution, alcohol dissolved in water or water dissolved in alcohol also obey the ideal gas law

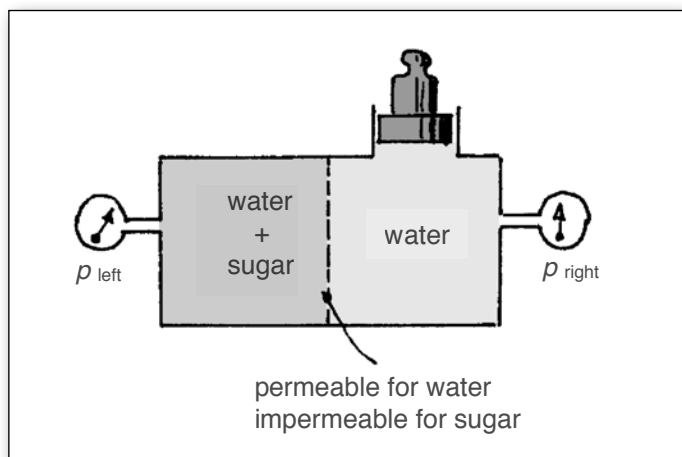
$$p \cdot V = n \cdot R \cdot T.$$

In the case of a solution the molar density

$$\rho_n = \frac{n}{V} = c$$

is called *concentration*.

The experimental proof of the validity of the gas law is, however, somewhat more difficult for these gases than for gases in a vacuum: In order to measure the pressure of the *solute* (the dissolved substance) alone, the so-called *osmotic pressure*, a wall is required which is permeable to the solvent but impermeable to what is dissolved. Such a *diaphragm* has the unpleasant property of having a high flow resistance even for the material it lets through. Therefore, the pressures establish only slowly. In the experiment shown in Figure 5.3, the pressure of the gas “sugar” is given by the difference  $\Delta p$  of the pressure gauge readings.



**Fig. 5.3**

The left pressure gauge shows a value higher by the osmotic pressure than the right one.

We have

$$p_{\text{left}} = p_{\text{water left}} + p_{\text{sugar left}}$$

$$p_{\text{right}} = p_{\text{water right}}$$

Since the diaphragm is permeable for water, it must be

$$p_{\text{water left}} = p_{\text{water right}}$$

Thus

$$\Delta p = p_{\text{left}} - p_{\text{right}} = p_{\text{sugar left}}$$

The equation for the chemical potential derived in the previous section also applies here. The chemical potential of the dissolved substance as a function of the (osmotic) pressure of the dissolved substance is

$$\mu(T, p) - \mu(T, p_0) = RT \ln \frac{p}{p_0}$$

With  $c = n/V$  and  $p = (n/V) \cdot R \cdot T$  we obtain

$$\mu(T, c) - \mu(T, c_0) = RT \ln \frac{c}{c_0}$$



## 5.4 Mixtures of ideal gases

There is a mixture of several ideal gases in one container. In the gas equation  $p \cdot V = R \cdot n \cdot T$  we have to write

$$n = \sum_i n_i$$

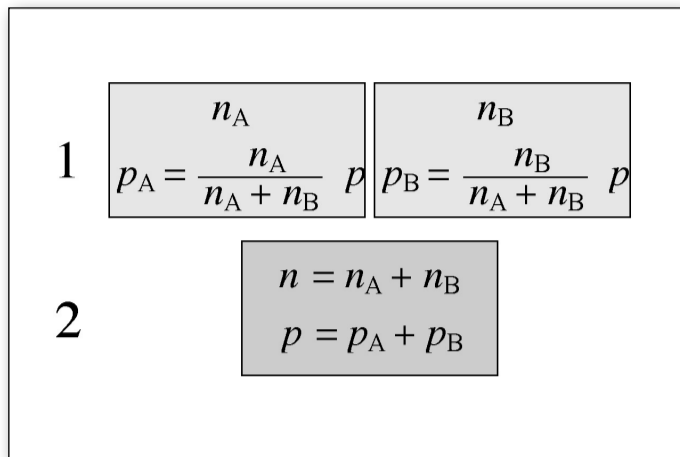
i.e. the amount of substance  $n$  is the sum of the amounts  $n_i$  of the gases  $i$ . The quantities

$$p_i = p \frac{n_i}{n}$$

are called the *partial pressures* of the gases. So we can write

$$p_i \cdot V = R \cdot n_i \cdot T$$

For each gas  $i$  alone a gas equation applies, if the partial pressure of the gas is used. Each gas  $i$  behaves as if it were alone in the container. The two situations 1 and 2 shown in Fig. 5.4 are physically identical.



**Fig. 5.4**

The two situations are identical from the point of view of physics.

Besides the amount of substance, energy and entropy are simply given by the sum of the partial energies or entropies:

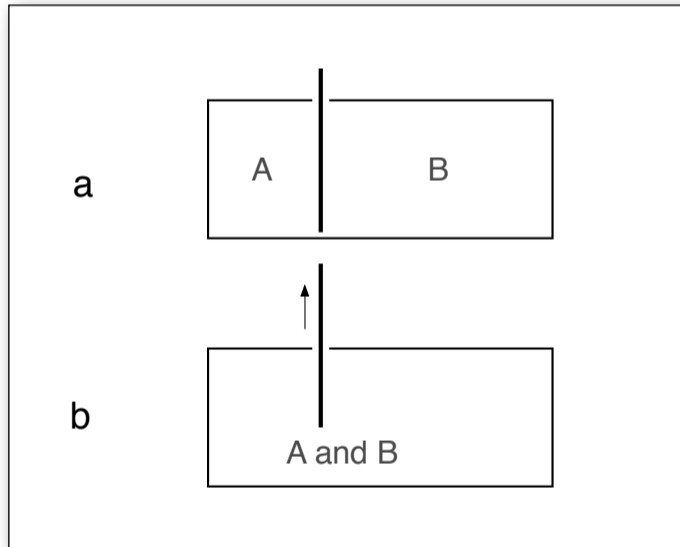
$$n = \sum_i n_i \quad E = \sum_i E_i \quad S = \sum_i S_i$$

A mixture of two gases can also be described as follows: It represents two gases in the same region of space, which are in thermal equilibrium. They are in thermal equilibrium because entropy can pass from one to the other. They are not in pressure equilibrium, because the volume of each of the gases is fixed, and they are not in chemical equilibrium, because one cannot transform into the other.

The chemical potential of each gas depends only on the partial pressure of that gas:

$$\mu_i(T, p_i) - \mu_i(T, p_{0i}) = RT \ln \frac{p_i}{p_{0i}}$$

We consider the mixing process shown in Fig. 5.5: In the initial state (1) the gases A and B are separated and have the same pressure  $p_{A1} = p_{B1}$ .



**Fig. 5.5**

The process of mixing is an isoenergetic expansion of both gases.

Then the separating wall is pulled out (b), so in the final state (2) it is

$$V_2 = V_{A1} + V_{B1}.$$

The mixing process is an isoenergetic expansion of both gases to the final volume  $V_2$ , which is nothing new. Therefore,  $T$  remains constant during mixing and the entropy increases (see equation (5.3), section 5.2):

$$\Delta S = R \sum_i n_i \ln \frac{V_2}{V_{i1}}$$

Since the pressures of the gases are the same before mixing, we have

$$\frac{p}{RT} = \frac{n_i}{V_{i1}} = \frac{n}{V_2}$$

and we obtain

$$\Delta S = R \sum_i n_i \ln \frac{n}{n_i}$$

The quotient  $x_i = n_i/n$  is called the *mole fraction*. With this we obtain the *entropy of mixing*

$$\Delta S = -nR \sum_i x_i \ln x_i$$

We will encounter this relationship again in statistical physics and information theory.

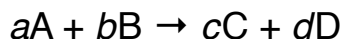
Although the relation between the variables of one partial gas is as if there were no other gases present, one can well distinguish between a free expansion into the vacuum and a free expansion into another gas: The second process is a diffusion process, it has a much greater reaction resistance than the first.

The last equation makes a statement that may be perceived as paradoxical (Gibbs' paradox): If the two gases A and B (Fig. 5.5) are identical, pulling out the wall does not result in any process at all. If, on the other hand, the gases differ in the smallest conceivable characteristic,  $\Delta S$  assumes a value independent of this characteristic. But can't one type of gas be transformed into another by continuously changing one characteristic? Thermodynamics teaches us that the answer is "no". It thus requires the quantization of physical quantities. One of the gases could be e.g. orthohydrogen, the other parahydrogen. There can be no continuous transition between ortho- and parahydrogen, i.e. no type of hydrogen whose nuclear spin has a sharp value between 0 and  $\hbar$  (but  $\neq 0$  and  $\neq \hbar$ ).

## 5.5 The law of mass action

For the sake of clarity, we limit ourselves to four reaction partners A, B, C and D. The generalization of the following calculations is obvious.

All partners of the reaction



are supposed to be ideal gases or exist in a diluted solution.

In chemical equilibrium the chemical potential difference

$$\begin{aligned} \Delta\mu(T, p_A, p_B, p_C, p_D) \\ = a\mu_A(T, p_A) + b\mu_B(T, p_B) - c\mu_C(T, p_C) - d\mu_D(T, p_D) \end{aligned}$$

is zero. Here,  $p_A$ ,  $p_B$ ,  $p_C$  and  $p_D$  are the partial pressures of the gases A, B, C, and D. We express every chemical potential on the right side by

$$\mu_i(T, p_i) = \mu_i(T, p_0) + RT \ln \frac{p_i}{p_0}$$

and obtain (for the case of chemical equilibrium)

$$\begin{aligned} \overbrace{a\mu_A(T, p_0) + b\mu_B(T, p_0) - c\mu_C(T, p_0) - d\mu_D(T, p_0)}^{\Delta\mu'(T, p_0)} \\ + RT \left( a \ln \frac{p_A}{p_0} + b \ln \frac{p_B}{p_0} - c \ln \frac{p_C}{p_0} - d \ln \frac{p_D}{p_0} \right) = 0 \end{aligned}$$

We call  $\Delta\mu'(T, p_0)$  the chemical potential difference in the case that each reaction partner has the partial pressure  $p_0$ , and obtain

$$\exp\left(-\frac{\Delta\mu'(T, p_0)}{RT}\right) = \frac{\left(\frac{p_A}{p_0}\right)^a \cdot \left(\frac{p_B}{p_0}\right)^b}{\left(\frac{p_C}{p_0}\right)^c \cdot \left(\frac{p_D}{p_0}\right)^d}$$

The expression on the left side only depends on temperature, but not on the partial pressures  $p_A$ ,  $p_B$ ,  $p_C$  and  $p_D$ . We designate it  $K(T)$  and obtain the *law of mass action*:

$$\frac{\left(\frac{p_A}{p_0}\right)^a \cdot \left(\frac{p_B}{p_0}\right)^b}{\left(\frac{p_C}{p_0}\right)^c \cdot \left(\frac{p_D}{p_0}\right)^d} = K(T)$$

If three partial pressures are given (or  $n - 1$  if  $n$  substances are involved), the fourth ( $n$ -th) follows from the law of mass action.

## 5.6 The second equation of state $S = S(T, p, n)$

A system with the energy differential

$$dE = TdS - pdV + \mu dn$$

is characterized by three state functions, e.g.  $V = V(T, p, n)$ ,  $S = S(T, p, n)$  and  $\mu = \mu(T, p, n)$ . We have dealt with the first of these and now turn to the second one, namely  $S = S(T, p, n)$ . It is determined by further experience. However, the  $p$ -dependence of  $S(T, p, n)$  is already known because of the Maxwell relation (4.5a)

$$-\frac{\partial S(T, p, n)}{\partial p} = \frac{\partial V(T, p, n)}{\partial T}$$

With the ideal gas law (our first equation of state) we get

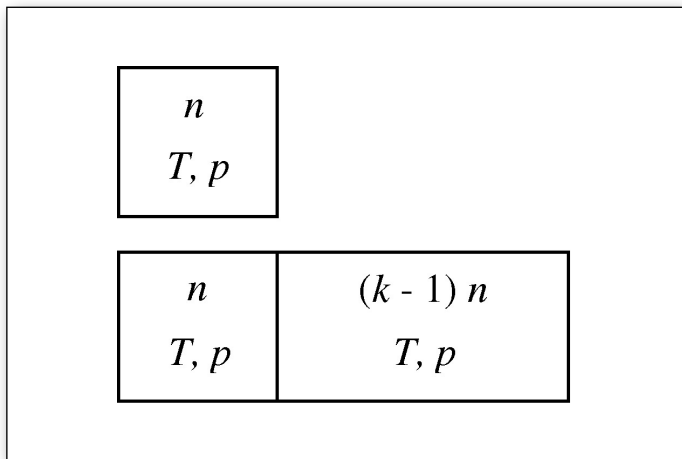
$$\frac{\partial S(T, p, n)}{\partial p} = -\frac{Rn}{p}$$

and by integrating

$$S(T, p, n) = n \cdot R \cdot \ln \frac{p_0}{p} + S(T, p_0, n) \quad (5.4)$$

Only the  $n$ - and  $T$ -dependence of  $S$  are yet unknown. Both are obtained from the experiment.

The  $n$ -dependence results from the homogeneity of the gas: If the amount of the gas is increased by a factor  $k$  while leaving  $T$  and  $p$  constant, the entropy increases by the same factor  $k$ . One can imagine that one has simply placed a new system next to the old one, Fig. 5.6.



**Fig. 5.6**

For fixed temperature and fixed pressure the entropy is proportional to the amount of substance.

Experience shows that the new and the old system do not influence each other. In mathematical symbols:

$$S(T, p, n) = n \cdot \hat{S}(T, p) \quad (5.5)$$

The  $T$ -dependence of  $S$  finally contains the whole individuality of the gas; it is complicated. Under certain conditions, however, a simple analytical expression can also be specified for it. In addition to

$$C_S^p = \frac{\partial S(T, p, n)}{\partial T}$$

we also consider

$$C_S^v = \frac{\partial S(T, V, n)}{\partial T}$$

For the ideal gas, the knowledge of  $C_S^p$  is equivalent to that of  $C_S^v$ , because the following applies (see section 5.1)

$$C_S^p - C_S^v = R \frac{n}{T}$$

Now, the experiment shows

$$C_S^v \geq \frac{3}{2} R \frac{n}{T} \quad C_S^p \geq \frac{5}{2} R \frac{n}{T} \quad \text{in general}$$

$$C_S^v = \frac{3}{2} R \frac{n}{T} \quad C_S^p = \frac{5}{2} R \frac{n}{T} \quad \text{for monoatomic gases (noble gases, Hg vapor)}$$

$$C_S^v \approx \frac{5}{2} R \frac{n}{T} \quad C_S^p \approx \frac{7}{2} R \frac{n}{T} \quad \text{for diatomic gases (only in a restricted temperature range)}$$

For  $c_v$  and  $c_p$  we thus obtain (see section 2.12)

$$c_v = \frac{3}{2} R \quad c_p = \frac{5}{2} R \quad \text{for monoatomic gases}$$

$$c_v \approx \frac{5}{2} R \quad c_p \approx \frac{7}{2} R \quad \text{for diatomic gases}$$

and for all gases we have

$$c_v - c_p = R \quad (5.6)$$

Thus,  $c_p$  and  $c_v$  are temperature-independent, and we can write

$$\frac{\partial S(T, p, n)}{\partial T} = c_p \frac{n}{T}$$

and integrate:

$$S(T, p, n) = c_p \cdot n \cdot \ln \frac{T}{T_0} + S(T_0, p, n) \quad (5.7)$$

From (5.4) and (5.7) we get

$$S(T, p, n) - S(T_0, p_0, n) = n \cdot \left( R \ln \frac{p_0}{p} + c_p \ln \frac{T}{T_0} \right) \quad (5.8)$$

and with (5.5)

$$S(T, p, n) = n \cdot \left( R \ln \frac{p_0}{p} + c_p \ln \frac{T}{T_0} + \hat{S}(T_0, p_0) \right)$$

In an analogue manner one gets

$$S(T, V, n) - S(T_0, V_0, n) = n \cdot \left( R \ln \frac{V}{V_0} + c_v \ln \frac{T}{T_0} \right) \quad (5.9)$$

and

$$S(T, V, n) = n \cdot \left( R \ln \frac{V}{V_0} + c_v \ln \frac{T}{T_0} + \hat{S}(T_0, V_0) \right)$$

## 5.7 Isothermal, isentropic, isobaric and isochoric processes of the ideal gas

We are looking for the  $p$ - $V$  relationship at constant temperature and constant entropy: isotherms and isentropics. Again we always consider processes with  $n = \text{const}$ . To obtain the isotherms, we write the ideal gas law in the form

$$p(V, T) = p_0 V_0 \frac{T}{T_0} \cdot \frac{1}{V}$$

or

$$p(V, T) = f(T) \cdot \frac{1}{V} \quad \text{isothermals}$$

To calculate the isentropics, we introduce an abbreviation:

$$\frac{c_p}{c_v} = \gamma$$

and transform equation (5.9) with the aid of (5.6)

$$\begin{aligned} S(T, V) - S(T_0, V_0) &= n \cdot \left( (c_p - c_v) \cdot \ln \frac{V}{V_0} + c_v \ln \frac{T}{T_0} \right) \\ &= n c_v \cdot \left[ (\gamma - 1) \cdot \ln \frac{V}{V_0} + \ln \frac{T}{T_0} \right] \\ &= n c_v \cdot \ln \left[ \left( \frac{V}{V_0} \right)^{\gamma-1} \cdot \frac{T}{T_0} \right] \end{aligned} \quad (5.10)$$

From this follows with the ideal gas law:

$$S(p, V) - S(p_0, V_0) = n \cdot c_v \cdot \ln \left[ \left( \frac{V}{V_0} \right)^\gamma \cdot \frac{p}{p_0} \right]$$

and finally

$$p(V, S) = p_0 \cdot \left( \frac{V_0}{V} \right)^\gamma \cdot \exp \left( \frac{S - S_0}{n c_v} \right)$$

or

$$p(V, S) = f(S) \cdot \frac{1}{V^\gamma} \quad \text{isentropics}$$

Since  $\gamma > 1$ , the isentropic is steeper than the isothermal at every point of the  $p$ - $V$  diagram.

To calculate the isochorics ( $V = \text{const}$ ) of the ideal gas, we eliminate the temperature in (5.10)

$$T(S, V) = T_0 \cdot \left( \frac{V_0}{V} \right)^{\gamma-1} \cdot \exp \left( \frac{S - S_0}{n c_v} \right)$$

or

$$T(S, V) = f(V) \cdot \exp \left( \frac{S}{n c_v} \right) \quad \text{isochorics}$$

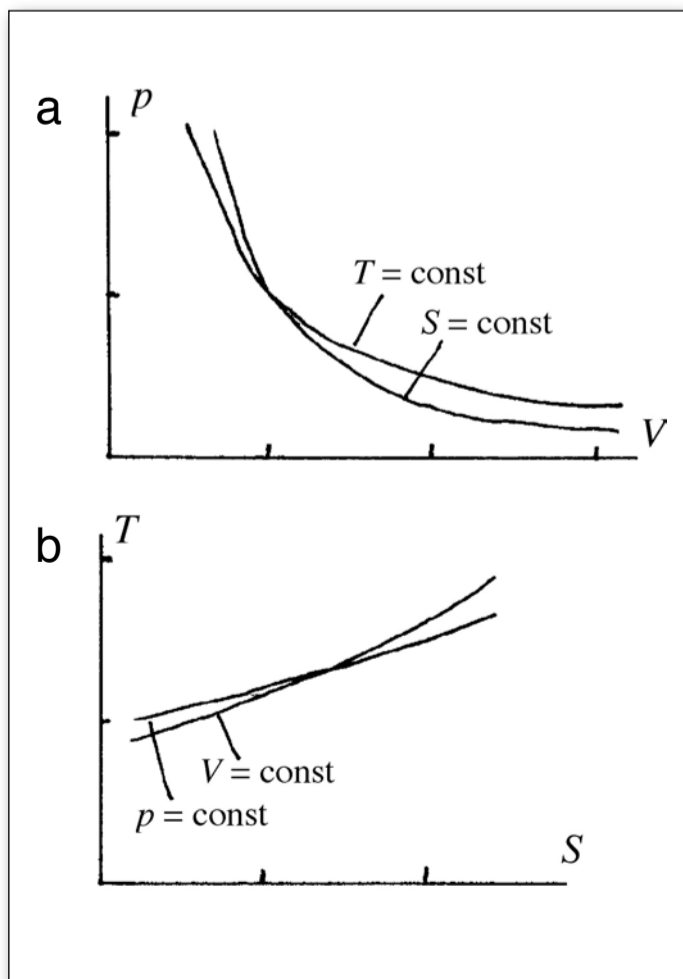
In a similar way we get from (5.8)

$$T(S, p) = T_0 \cdot \left( \frac{p}{p_0} \right)^{1-\frac{1}{\gamma}} \cdot \exp \left( \frac{S - S_0}{n c_p} \right)$$

or

$$T(S, p) = f(p) \cdot \exp \left( \frac{S}{n c_p} \right) \quad \text{isobarics}$$

Fig. 5.7a shows an isothermal and an isentropic in the  $p$ - $V$  diagram, Fig. 5.7b shows an isobaric and an isochoric in the  $T$ - $S$  diagram.



**Fig. 5.7**

(a) Isothermal and Isentropic in the  $p$ - $V$  diagram.  
(b) Isobaric and Isochoric in the  $T$ - $S$  diagram

### 5.8 The third equation of state: $\mu = \mu(T, p, n)$

Two derivatives of this function are already determined by the Maxwell relations (4.5b) and (4.5c), as well as by the equations of state discussed so far:

$$-\frac{\partial\mu(T,p,n)}{\partial T} = \frac{\partial S(T,p,n)}{\partial n} = R \ln \frac{p_0}{p} + c_p \ln \frac{T}{T_0} + \hat{S}(T_0, p_0)$$
$$\frac{\partial\mu(T,p,n)}{\partial p} = \frac{\partial V(T,p,n)}{\partial n} = \frac{RT}{p}$$

The third derivative must be obtained from the experiment. Now, because of the homogeneity of the system,  $\mu$  can no longer depend on  $n$  if  $T$  and  $p$  are fixed. So we have

$$\frac{\partial\mu(T,p,n)}{\partial n} = 0$$

By integrating we obtain:

$$\mu(T,p,n) = RT \ln \frac{p}{p_0} - c_p T \ln \frac{T}{T_0} + (c_p - \hat{S}(T_0, p_0))(T - T_0) + \mu(T_0, p_0) \quad (5.11)$$

We finally obtained the  $T$  dependence of the chemical potential. However, it looks so complicated that one cannot recognize at first sight whether  $\mu$  increases or decreases with  $T$ . The behavior of  $\mu$  as a function of  $T$  can best be seen by looking at the Maxwell relation

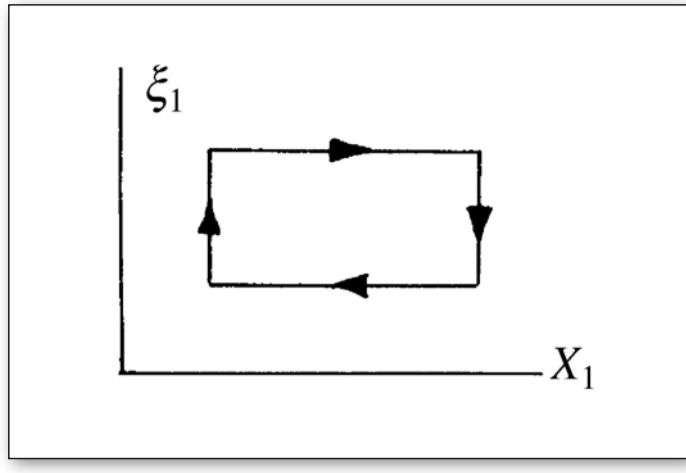
$$-\frac{\partial\mu(T,p,n)}{\partial T} = \frac{\partial S(T,p,n)}{\partial n}$$

The right side simply represents the entropy per amount of substance, and this must always be positive. Thus, the derivative  $\partial\mu(T,p,n)/\partial T$  is negative; for  $p = \text{const}$  and  $n = \text{const}$  the chemical potential decreases with increasing temperature.

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### 5.9 Simple cyclic processes with ideal gases

Cyclic processes of particular technical importance are those in which the energy carrier  $X_1$ , with which the energy arrives, flows into the machine at constant potential  $\xi_{1in}$  and flows out of the machine at constant potential  $\xi_{1out}$ , Fig. 5.8. The  $\xi_1$ - $X_1$  diagram is a rectangle.



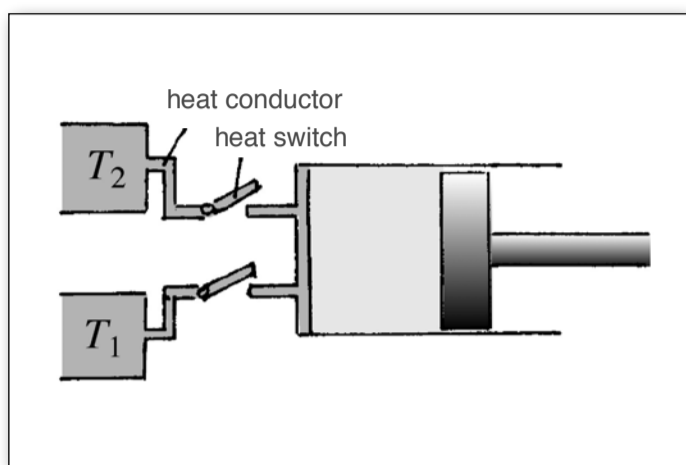
**Fig. 5.8**  
 $\xi_1$ - $X_1$  diagram of a typical cyclic process

We examine three examples. In the first,  $X_1$  is the entropy, the corresponding cyclic process is called the *Carnot cycle*. In the second,  $X_1$  is the amount of substance. Finally, the third is a combination of the first and the second.

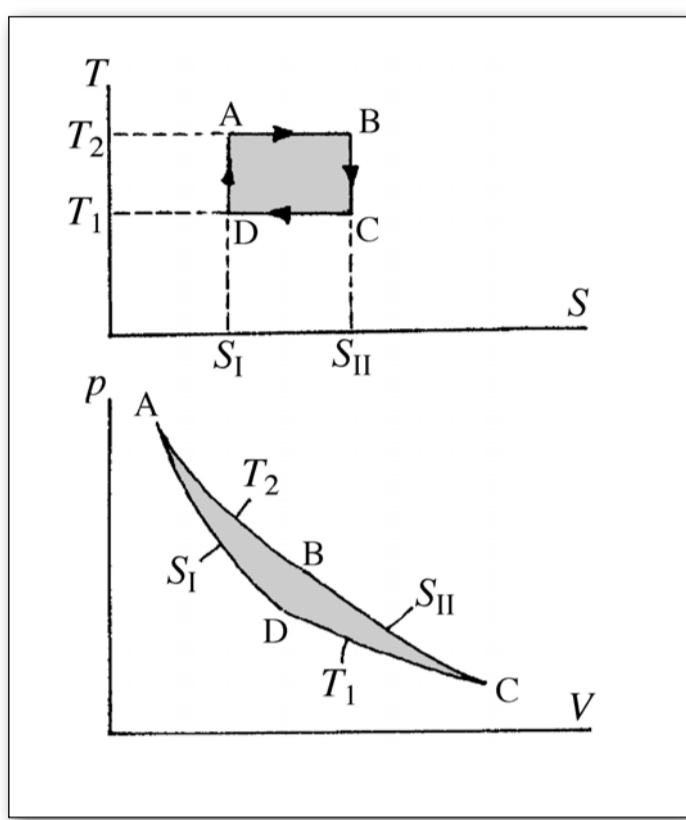
We carry out the three cycles with an ideal gas. The second extensive variable  $X_2$  is the volume in all cases (the corresponding energy carrier is the momentum).

#### Carnot cycle with the ideal gas

Fig. 5.9 shows the machine schematically, Fig. 5.10 shows the process in the  $T$ - $S$  and in the  $p$ - $V$  diagram. The process cycle consists of two isothermals and two isentropics.



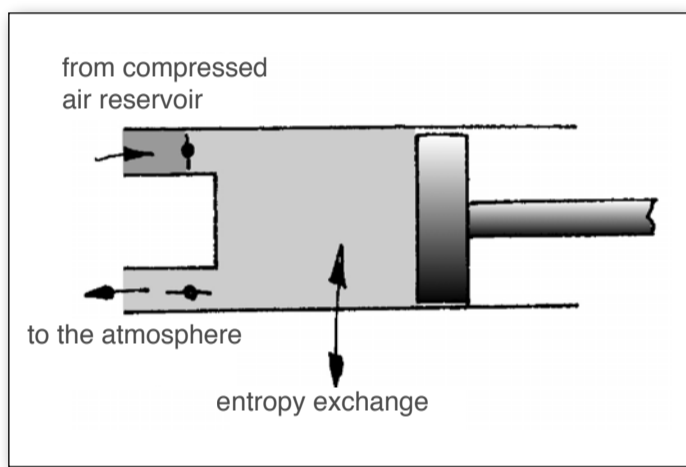
**Fig. 5.9**  
Carnot engine



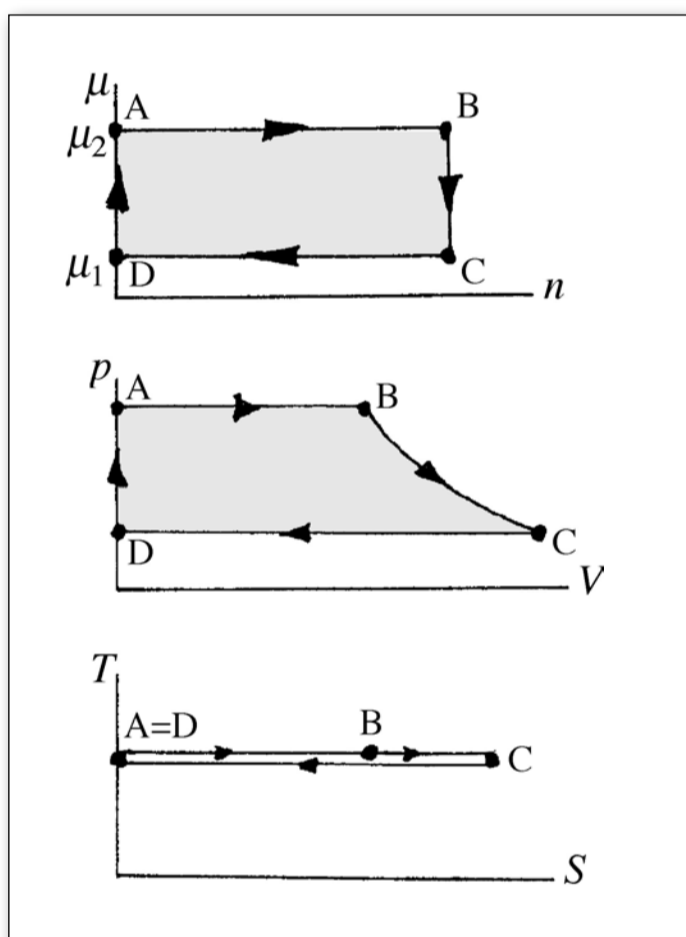
**Fig. 5.10**  
 $T$ - $S$  diagram and  $p$ - $V$  diagram of the Carnot cycle

#### Isothermal compressed air engine

Fig. 5.11 shows the engine schematically, Fig. 5.12 shows the process in the  $\mu$ - $n$ ,  $p$ - $V$  and  $T$ - $S$  diagrams.



**Fig. 5.11**  
Isothermal compressed air engine



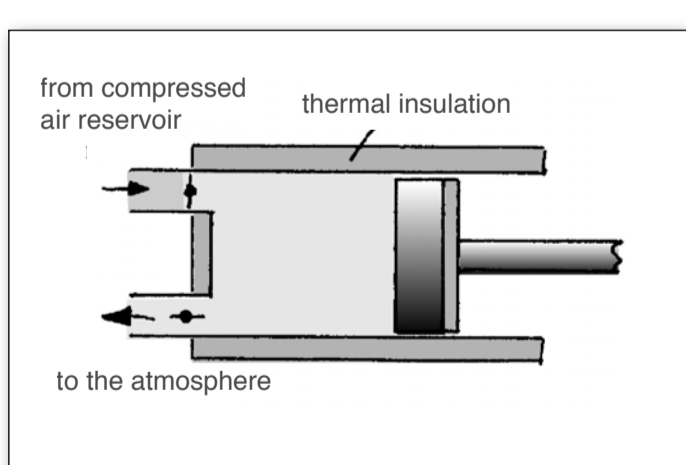
**Fig. 5.12**  
 $\mu$ - $n$ ,  $p$ - $V$  and  $T$ - $S$  diagram of the isothermal compressed air engine

In addition to the extensive quantities  $n$  and  $V$ , the entropy of the gas also changes. However, as can be seen in the  $T$ - $S$  diagram, the entropy always remains at the same thermal potential  $T$ , i.e. the energy that it carries does not change.

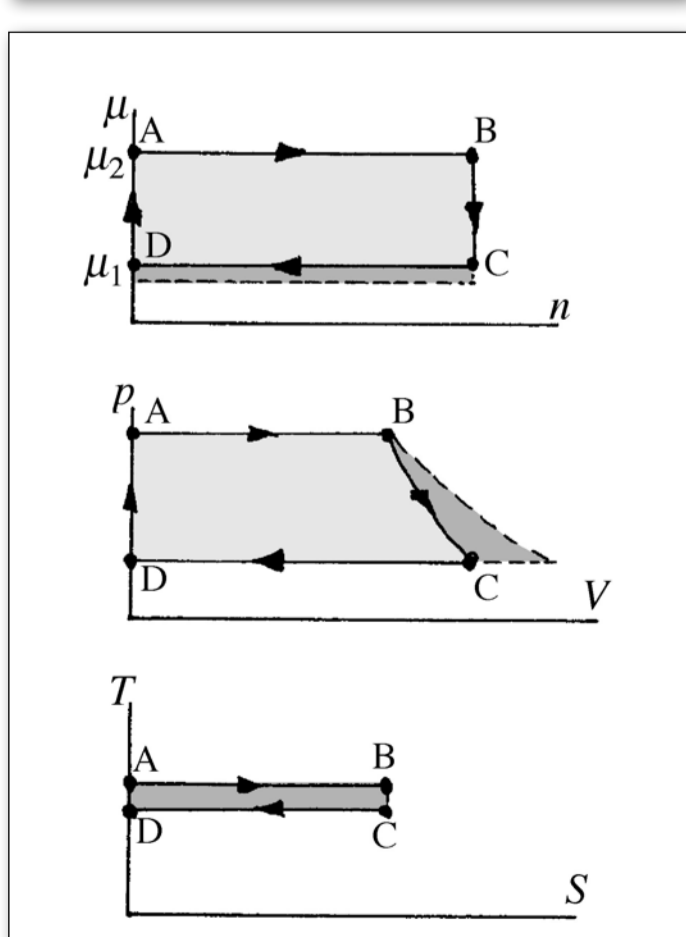
For processes with constant  $\mu$  and constant  $n$ , the technical jargon has not reserved its own "iso word". In process step AB entropy is carried convectively into the cylinder with the inflowing gas, in step BC entropy flows through the cylinder wall into the cylinder. In step CD it is transported out again convectively.

#### Isentropic compressed air engine (steam engine)

The just described cyclic process is difficult to realize, because entropy conduction is a slow process. Real engines (compressed air engines or steam engines) operate mainly isentropically, Fig. 5.13 and 5.14.



**Fig. 5.13**  
Isentropic compressed air engine



**Fig. 5.14**  
 $\mu$ - $n$ ,  $p$ - $V$  and  $T$ - $S$  diagram of the isentropic compressed air engine

The temperature decreases in the expansion step BC. Therefore the chemical potential  $\mu$  is higher at C compared with the isothermal engine. The air (or steam) leaving the engine could still be used: A thermal engine could be operated between the atmospheric air and the air leaving the compressed air engine. This would deliver an amount of energy (in one cycle) that corresponds to the dark area in Fig. 5.14.

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# 6

## Liquid and solid materials

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## 6.1 The chemical potential

Liquids and solids have a particular property: their density can be changed only with difficulty by a change of pressure or by a change of temperature. The following considerations apply to solids only if the problem is isotropic. Both, the coefficients characterizing the solid as well as the mechanical stresses must be direction-independent. Experience shows that

$$\kappa = -\frac{1}{V} \frac{\partial V(T, p, n)}{\partial p} \approx 0$$

$$\alpha = \frac{1}{V} \frac{\partial V(T, p, n)}{\partial T} \approx 0$$

With the Maxwell relation (4.5a)

$$\frac{\partial V(T, p, n)}{\partial T} = -\frac{\partial S(T, p, n)}{\partial p}$$

we obtain

$$\frac{\partial S(T, p, n)}{\partial p} \approx 0$$

Thus entropy is almost pressure-independent. This does not mean that  $S$  is also independent of the volume. In fact, another Maxwell relationship reads

$$\frac{\partial S(T, V, n)}{\partial V} = \frac{\partial p(T, V, n)}{\partial T}$$

and experience shows that  $\partial p(T, V, n)/\partial T$  is large. The fact that  $S$  cannot be changed by changing the volume is simply because the substances under consideration are difficult to compress.

In addition, for liquids and solids we have  $c_p \approx c_v$  (the lower the temperature, the better they coincide). We therefore simply write  $c$  instead  $c_p$  or  $c_v$ .

With the Maxwell relation (4.5c)

$$\frac{\partial V(T, p, n)}{\partial n} = \frac{\partial \mu(T, p, n)}{\partial p}$$

we calculate the pressure dependence of the chemical potential. Because of  $\alpha \approx 0$  and  $\kappa \approx 0$  the quotient

$$\frac{\partial V(T, p, n)}{\partial n} = \hat{V}(T, p)$$

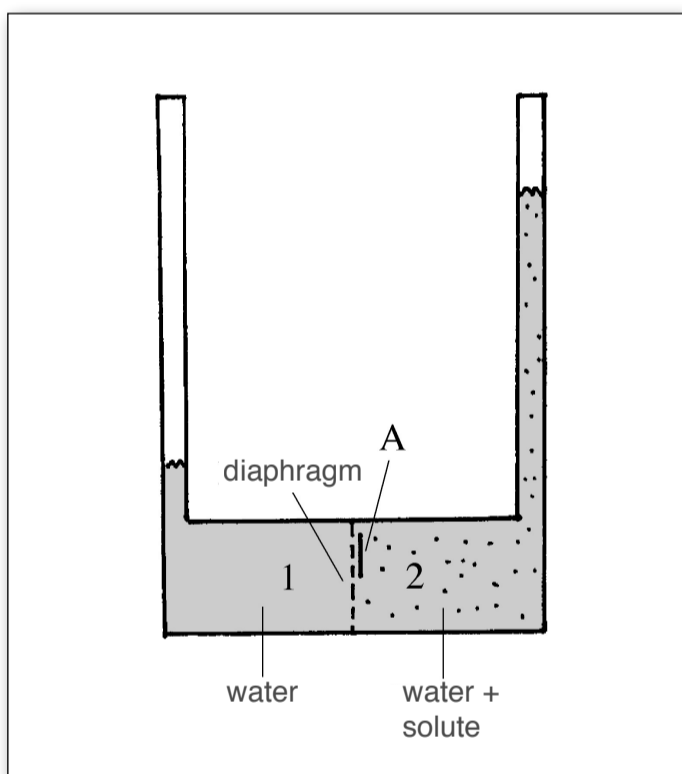
is nearly independent of temperature and pressure and we obtain

$$\mu(p) - \mu(p_0) = \hat{V} \cdot (p - p_0) \quad (6.1)$$

We apply equation (6.1) to an example.

### Lowering of the chemical potential of a liquid by adding a small amount of a foreign substance

If a small amount of a foreign substance (a solute) is dissolved in a liquid (the solvent), the chemical potential of the solvent decreases. We look at the experiment in Fig. 6.1.



**Fig. 6.1**

On the left (1) of the water-permeable diaphragm there is pure water, in the water on the right (2) a foreign substance is dissolved. The chemical potential of water is the same on both sides.

We assume the solvent to be water. For the water chemical equilibrium between the left and the right of the diaphragm will establish:

$$\mu_{\text{H}_2\text{O}, 1} = \mu_{\text{H}_2\text{O}, 2}$$

This means that no more water passes through the diaphragm and the liquid columns on the left and right no longer change their height. The pressure to the right of the diaphragm must now be equal to the sum of the pressure on the left and the pressure of the solute.

$$p_2 = p_1 + p_{\text{solute}}$$

(Two forces act on the surface area  $A$  of the liquid on the right: the force  $p_1 \cdot A$ , which liquid 1 exerts on liquid 2 through the diaphragm and the force  $p_{\text{solute}} \cdot A$ , which the diaphragm itself exerts on the liquid 2.

Now the water on the right of the diaphragm differs from the water on the left in two respects: first, its pressure is higher and second, a foreign substance is dissolved in it. So its chemical potential is

$$\mu_{\text{H}_2\text{O}, 2} = \mu_{\text{H}_2\text{O}, 1} + \frac{V}{n} (p_2 - p_1) + \Delta\mu(n_{\text{solute}})$$

The second summand on the right side of the equation describes the change of the chemical potential due to the increased pressure, the third summand  $\Delta\mu(n_{\text{solute}})$  is the change of the chemical potential due to the foreign substance. In order for the chemical potentials to be equal on the left and right, both "corrections" must add up to zero, i.e. it must be

$$\Delta\mu(n_{\text{solute}}) = -\frac{V}{n} (p_2 - p_1)$$

With the ideal gas law  $p_{\text{solute}} V = R n_{\text{solute}} T$  and with  $p_2 = p_1 + p_{\text{solute}}$  we get

$$\Delta\mu(n_{\text{solute}}) = -\frac{V}{n} \frac{R n_{\text{solute}} T}{V}$$

Now,  $n_{\text{solute}}/n$  is equal to the mole fraction  $x$ , and we obtain

$$\Delta\mu(n_{\text{solute}}) = -xRT$$

The formula tells us that the chemical potential of water in the Rhine is higher than that of water in the North Sea. One could therefore operate a power plant at the mouth of the Rhine in which the Rhine water is lowered to the low North Sea potential and electric charge is pumped up to a high electric potential.

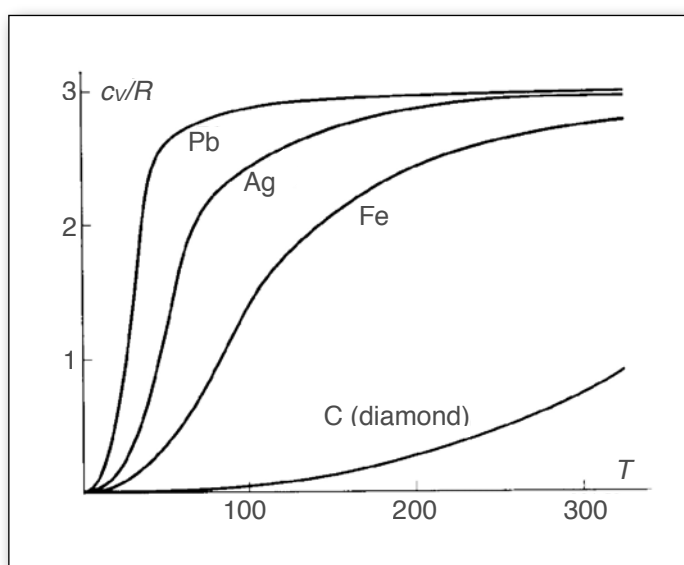


## 6.2 The entropy of solid materials

It is convenient to decompose in our mind a solid material into subsystems: a lattice system, an electron system, a spin system... Each of these subsystems can contribute to the entropy. For many purposes, these systems can be considered separately. Sometimes one of them “does not exist”: Its amount of substance is zero. By “electron system” we mean the so-called free electrons. An electrical insulator has no electron system in this sense.

First we look at the lattice system (the word comes from the fact that the atoms or ions of solids form a crystal lattice). Experience shows that the molar heat capacity for all solids at low temperatures follows Debye’s law, Fig. 6.2:

$$c = \frac{12}{5} \pi^4 R \left( \frac{T}{T_D} \right)^3 \text{ for } T \ll T_D$$



**Fig. 6.2**  
Specific heat capacity as a function of temperature for some solid materials

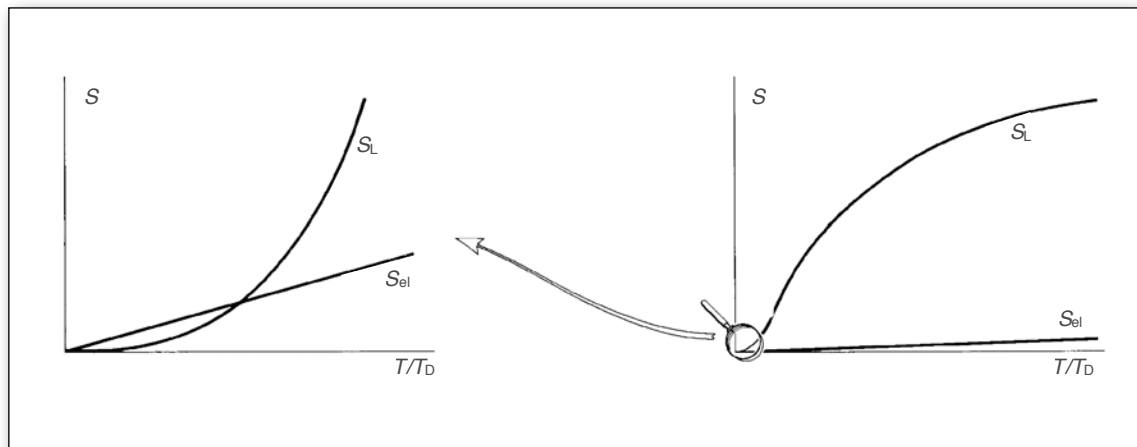
With

$$c = \frac{d\hat{E}}{dT} = T \frac{d\hat{S}}{dT}$$

we get

$$\hat{S} = \int_0^T \frac{c}{T} dT = \frac{12}{5} \pi^4 \frac{R}{T_D^3} \int_0^T T^2 dT = \frac{12}{5} \pi^4 \frac{R}{3} \left( \frac{T}{T_D} \right)^3 = \frac{c}{3}$$

Thus, also the molar entropy increases with the 3rd power of  $T$ , Fig. 6.3.



**Fig. 6.3**  
Entropy of the electron system and the lattice system as a function of temperature for solids

A specific substance is thus characterized solely by  $T_D$ , the *Debye temperature*. Some  $T_D$  values are listed in Table 6.1.

substance	$T_D$ (K)
Pb	88
Ag	215
Cu	315
Fe	453
KBr	177
NaCl	287
Ge	360
diamond	1860

**Table 6.1**  
Debye temperatures

The experiment shows that  $c$  exhibits a simple behavior also for high temperatures: For crystals consisting of a single type of atom,  $c$  approaches asymptotically  $3R$  for increasing temperature, Fig. 6.2:

$$c = 3R \text{ for } T \gg T_D.$$

This is the *Dulong-Petit law*.

The entropy of the electron system is only noticeable at very low temperatures (if the substance has free electrons at all, i.e. if it is a metal). It is proportional to  $T$  and the molar entropy is therefore identical to  $c$ :

$$\hat{S} = c \propto T$$

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# 7

## Phase transitions

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## 7. Phase transitions

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### 7.1 Phases

The word phase has a meaning similar to the word substance. However, since people do not like to say that ice and liquid water are different substances, they prefer to talk about different phases. We do not speak of two different phases if, for example, we have liquid water at 10 °C and liquid water at 20 °C.

In order to pass from one phase to another, the values of any variables undergo discontinuous changes: in the transition of liquid water → gaseous water, for example, the variables molar entropy and molar volume make a jump. But one should not take this definition too seriously: one can avoid the jump in the quoted example by passing around the so-called *critical point*.

The best known phases are the solid, liquid and gaseous phases, in which many substances can be found. In addition, especially solids exist in countless other phases: different crystal modifications; phases in which one part of the crystal lattice (one type of ion) is solid, another is liquid; phases characterized by different states of order of the atomic magnetic or electric moments; phases of the electron system (normal and superconductivity) and many others.

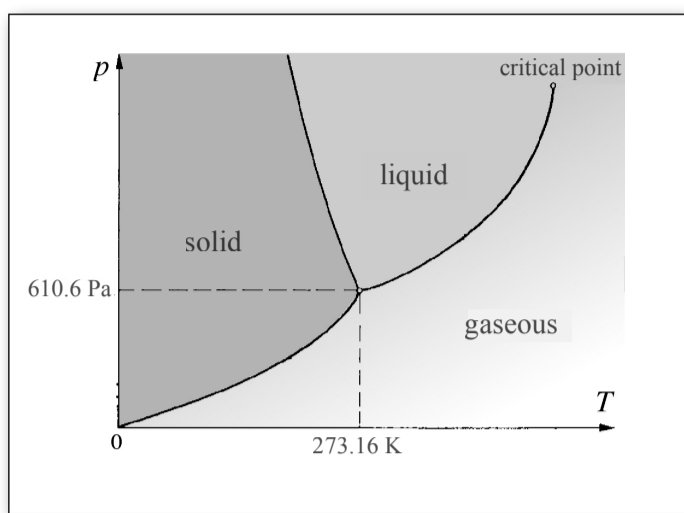
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## 7.2 Phase transitions

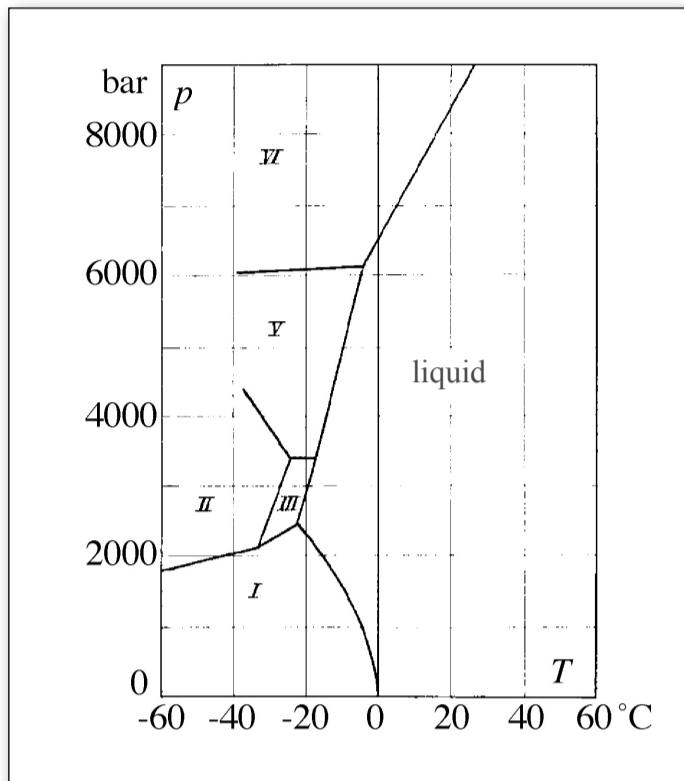
Phase transitions are reactions. If the reaction can run uninhibited, there is chemical equilibrium during the phase transition from phase I to phase II, it is

$$\mu_I(p, T) = \mu_{II}(p, T)$$

This equation defines a relationship between pressure and temperature  $p = p(T)$ . If the function is displayed in a  $p$ - $T$  coordinate system, it is referred to as a *phase diagram*. For pairs of  $p$ - $T$  values that lie on the *coexistence curve*  $p(T)$ , both phases can exist simultaneously. Outside the curve, only one phase is stable. The  $p(T)$  curve that separates the gaseous from the liquid phase is called the *vapor pressure curve* of the substance. In this case, the pressure  $p(T)$  is called the *vapor pressure* (or equilibrium vapor pressure) of the liquid at temperature  $T$ . The vapor pressure curve ends at the critical point (at  $T = T_{cr}$  and  $p = p_{cr}$ ). Figures 7.1 and 7.2 show the phase diagram of water in two different scales.

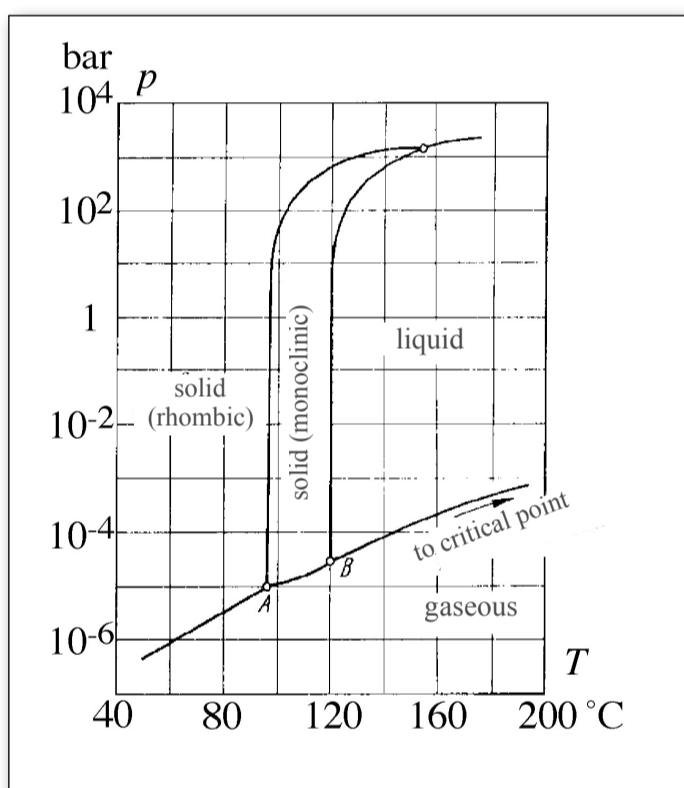


**Fig. 7.1**  
Phase diagram of water



**Fig. 7.2**  
Phase diagram of water

Fig. 7.3 shows the phase diagram of sulfur.



**Fig. 7.3**  
Phase diagram of sulfur

In *triple points*, the chemical potentials of three phases have the same value. This is a condition that defines values for  $p$  and  $T$ . So when a substance is brought into the state in which three phases coexist, a well-defined temperature will establish: a fixed point of temperature. The unit of temperature is defined by the triple point of water (see section 2.4).

Table 7.1 shows the vapor pressure values of water at different temperatures. Table 7.2 lists the vapor pressures of some substances at 20 °C.

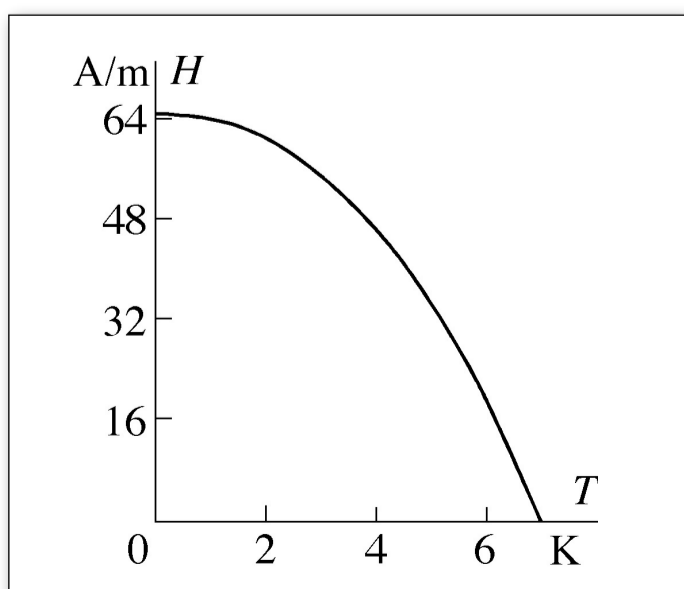
$\vartheta$ (°C)	$p_D$ (Pa)
0	613
20	2333
40	7373
60	$19.92 \cdot 10^3$
80	$47.3 \cdot 10^3$
100	$101.3 \cdot 10^3$
150	$4.76 \cdot 10^5$
300	$8.59 \cdot 10^6$
350	$1.65 \cdot 10^7$

**Table 7.1**  
Vapor pressure of water

substance	$p_D$ (Pa)
ethanol	$5.88 \cdot 10^3$
methanol	$1.25 \cdot 10^4$
benzene	$1.00 \cdot 10^4$
mercury	0.16

**Table 7.2**  
Vapor pressure of some substances at 20 °C

Whether a substance is normal or superconducting at a certain temperature depends on the magnetic field. Fig. 7.4 shows the  $H$ - $T$  phase diagram of lead.

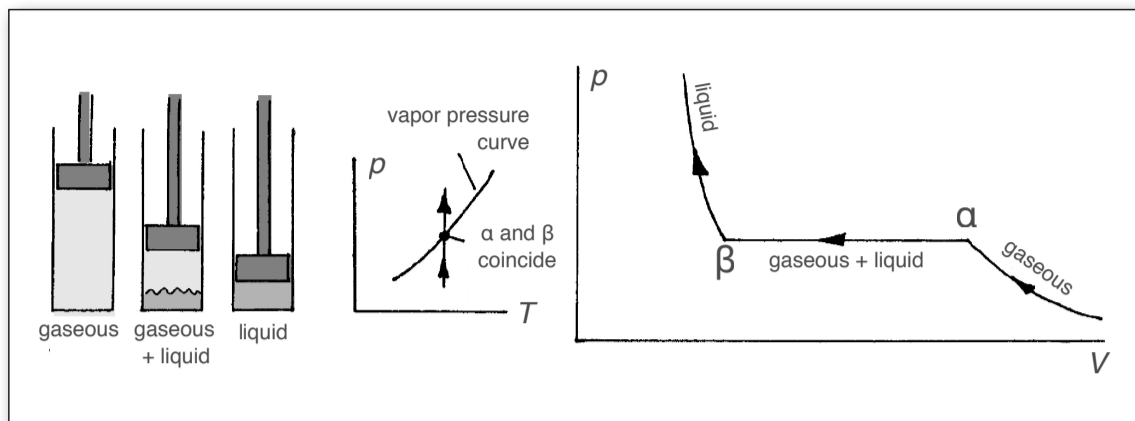


**Fig. 7.4**  
 $H$ - $T$  phase diagram of lead

### 7.3 $\xi$ - $X$ diagrams

In order to better understand how the various variables change during a phase transition, we look at the gaseous-liquid phase transitions in different representations.

First, we decrease the volume of the gas at a fixed temperature, Fig. 7.5.



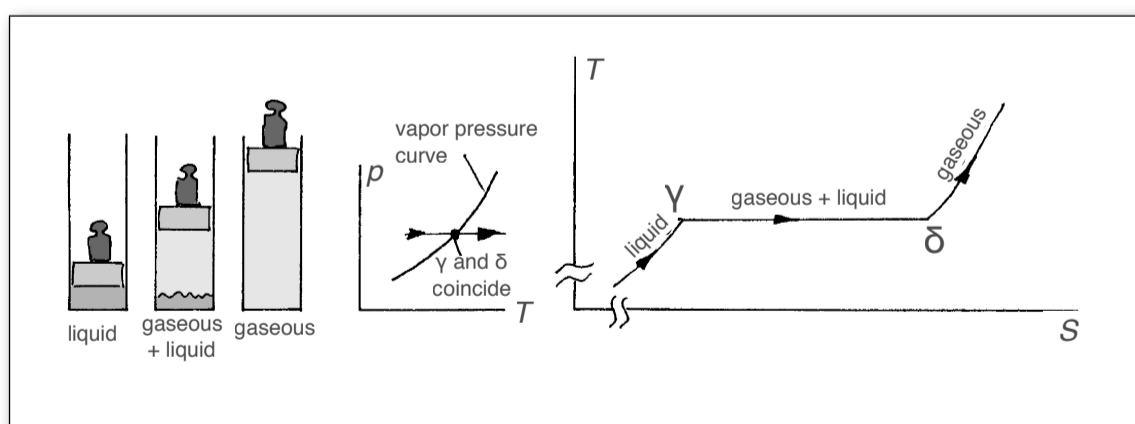
**Fig. 7.5**  
Phase transition at constant temperature

In this process, at first the pressure increases, see the path in the  $p$ - $T$  diagram. When this path reaches the vapor pressure curve, liquefaction begins. In the  $p$ - $V$  diagram we are at the point  $\alpha$ . From now on the pressure does no longer change despite the reduction of the volume. The liquefaction continues until in the point  $\beta$  the whole substance has become liquid. A further reduction of the volume is accompanied by a sharp increase in pressure. In the  $p$ - $T$  diagram we leave the vapor pressure curve. During the transition liquid  $\rightarrow$  gaseous the molar volume changes by a finite amount. Its value is characteristic for the substance, but depends on the temperature. Table 7.3 lists the molar volumes of liquid water (index L) and water vapor (index V) for different temperatures.

$T$ (K)	$\hat{V}_L$ ( $\text{m}^3/\text{mol}$ )	$\hat{V}_V$ ( $\text{m}^3/\text{mol}$ )	$\Delta\hat{S}_{L\rightarrow V}$ (Ct/mol)
312	$1.81 \cdot 10^{-5}$	$3.7 \cdot 10^{-1}$	166
423	$1.97 \cdot 10^{-5}$	$6.85 \cdot 10^{-3}$	79
535	$2.30 \cdot 10^{-5}$	$7.4 \cdot 10^{-4}$	39
647 (= $T_{cr}/\text{K}$ )	$5.66 \cdot 10^{-5}$	$5.66 \cdot 10^{-5}$	0

**Table 7.3**  
Molar volume of liquid water and water vapor, as well as the change of the entropy of the water during the transition

We now supply entropy to the liquid at fixed pressure, Fig. 7.6.



**Fig. 7.6**  
Phase transition at constant pressure

In the process, at first the temperature increases, see the path in the  $p$ - $T$  diagram. When this path reaches the vapor pressure curve, evaporation begins. In the  $T$ - $S$  diagram we are at the point  $\gamma$ . From now on the temperature does no longer change despite the supply of entropy. Evaporation continues until at the point  $\delta$  the whole substance is gaseous. A further entropy supply is accompanied by an increase in temperature; we leave the vapor pressure curve in the  $p$ - $T$  diagram. During the transition liquid  $\rightarrow$  gaseous the molar entropy changes by a finite amount. Its value is characteristic for the substance, but still depends on the temperature. Table 7.3 shows in column 4 this change in the molar entropy of water at different temperatures.

$T\Delta\hat{S}$  is called the molar *heat of evaporation*.

### 7.4 Clausius-Clapeyron relation

The shape of the coexistence curve  $p(T)$  which separates phases I and II depends in a simple way on the values of  $\hat{S}_I - \hat{S}_{II}$  and  $\hat{V}_I - \hat{V}_{II}$ . On the coexistence curve we have  $\mu_I = \mu_{II}$ . Thus we have

$$\frac{d(\mu_I - \mu_{II})}{dT} = 0$$

and therefore

$$\frac{\partial \mu_I(p, T)}{\partial T} + \frac{\partial \mu_I(p, T)}{\partial p} \cdot \frac{dp}{dT} - \frac{\partial \mu_{II}(p, T)}{\partial T} - \frac{\partial \mu_{II}(p, T)}{\partial p} \cdot \frac{dp}{dT} = 0$$

With the Maxwell relations (4.5b) and (4.5c) we obtain

$$-\hat{S}_I(p, T) + \hat{S}_{II}(p, T) + [\hat{V}_I(p, T) - \hat{V}_{II}(p, T)] \cdot \frac{dp}{dT} = 0$$

and thus

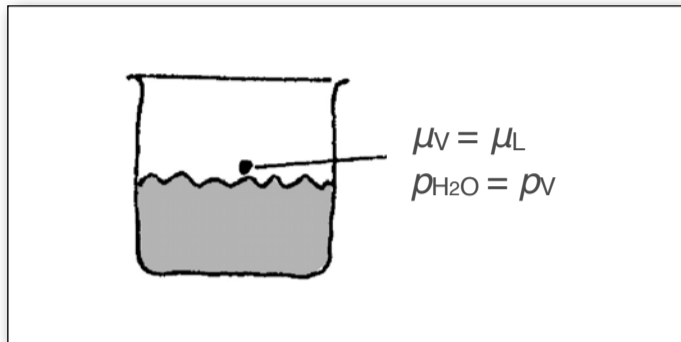
$$\frac{dp}{dT} = \frac{\Delta \hat{S}(T)}{\Delta \hat{V}(T)} \quad \text{Clausius-Clapeyron relation}$$

During evaporation, both the molar entropy and the molar volume increase, i.e. numerator and denominator on the right side of the Clausius-Clapeyron equation have the same sign. So  $dp/dT$  is positive; the boiling temperature increases with increasing pressure. Normally the same applies to melting; the melting pressure curve also has a positive slope. However, water is an exception here, because its volume decreases as it melts (although the molar entropy increases). The melting pressure curve therefore has a negative slope (“anomaly of water”).

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## 7.5 Evaporation and boiling

There is water in a container that is open at the top. The chemical potential of the water vapor  $\mu_V$  directly above the water surface is equal to that of the liquid water  $\mu_L$  below the water surface. The partial pressure of the water vapor is equal to the vapor pressure  $p_V$ , Fig. 7.7. Further up the partial pressure and the chemical potential are lower. There is a chemical potential difference and therefore gaseous water diffuses away from the surface region. In order for the chemical potential at the surface to maintain its equilibrium value, water must pass from the liquid to the gaseous state: It *evaporates*.



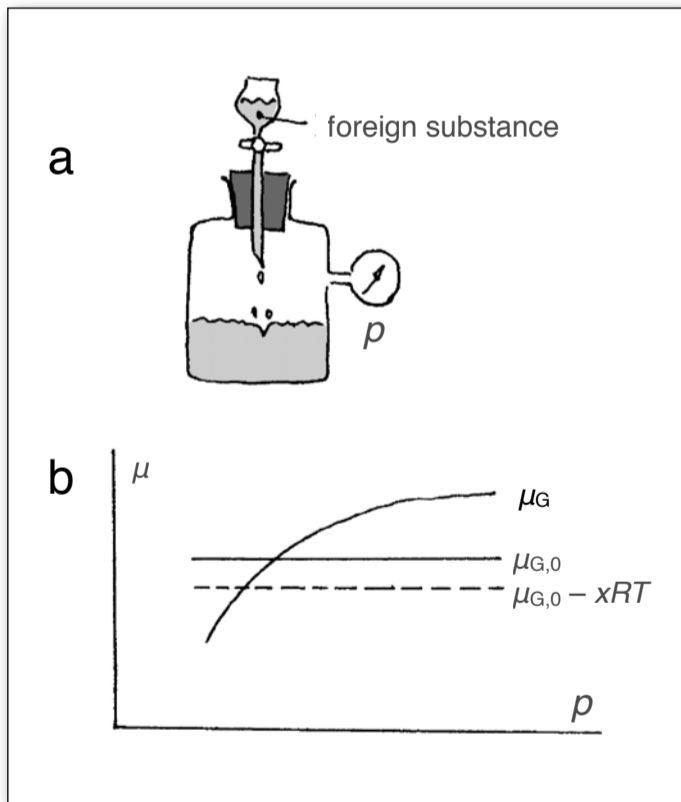
**Fig. 7.7**

The chemical potential of the water vapor just above the surface is equal to that of the liquid water.

The partial pressure of the water above the liquid surface increases with increasing temperature. When it reaches the value of the air pressure, the partial pressure of the “residual air”, i.e. the partial pressure of the non-water components of the air (essentially oxygen and nitrogen) becomes zero. From now on, the water vapor no longer needs to diffuse through the residual air, it pushes it away and flows unhindered upwards. The resistance against the propagation decreases strongly, the flow is practically uninhibited. The speed of evaporation is now only limited by the supply of entropy. We say that the water boils.

If the water is heated from below, as is usual when heating on a stove, the steam must pass through the liquid from below and form bubbles. For this to be possible, the temperature must rise until the vapor pressure equals the pressure in the water at the bottom of the vessel.

We look at a liquid that is in a closed container together with its vapor, Fig. 7.8a.



**Fig. 7.8**

(a) If a foreign substance is dissolved in a liquid, the chemical potential of the liquid decreases.  
(b)  $\mu$ - $p$  diagram

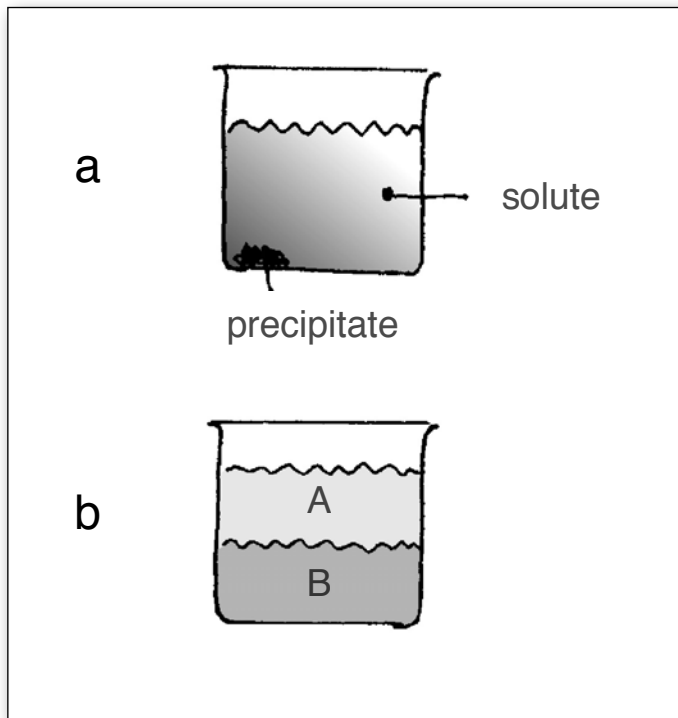
Both have the same chemical potential. Fig. 7.8b shows the  $\mu(p)$  curves (at fixed temperature). If now a foreign substance is dissolved in the liquid, the chemical potential of the liquid (see section 6.1) decreases by  $\Delta\mu = -xRT$  ( $x$  = mole fraction of the solute). The chemical equilibrium between liquid and gas is disturbed. Gas will now condense until the chemical potential of the gas has dropped to its value in the liquid. The vapor pressure has thus been reduced by adding the foreign substance. For this reason, the boiling point of a liquid increases when a foreign substance is added. For the same reason, the melting point decreases when a foreign substance is added to a liquid, such as salt in water.

## 7.6 Solutions

The so-called precipitate and the dissolved substance also form two phases between which a transformation can take place, Fig. 7.9a. Here, too, the transformation comes to a standstill when the chemical potentials have the same value, i.e. when

$$\mu_{\text{precipitate}} = \mu_{\text{solute}}$$

A similar system is formed by two immiscible liquids A and B, Fig. 7.9b.



**Fig. 7.9**

(a) Precipitate and solute establish chemical equilibrium.

(b) Two immiscible liquids. The liquid phase of one substance represents the vacuum for the gaseous phase of the other.

Immiscible does not mean that there is nothing of substance B in liquid A and nothing of substance A in liquid B. In A a small amount of B is dissolved, and in B a small amount of A. B dissolved in A is the “gas phase” of liquid B and A dissolved in B is the “gas phase” of liquid A.

Liquid X represents the “vacuum” for the gas of substance Y. Here the osmotic pressure is a “vapor pressure”. Above  $T_{\text{cr}}$  the two phases of each substance can no longer be distinguished from each other; the two substances become miscible.

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# 8

## Fluid dynamics

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## 8.1 Pipe flow

We consider the flow through a pipe with the following properties: All partial time derivatives are zero, i.e. the flow is stationary. The flow velocity is the same over the entire cross-section of the pipe. The cross-section can be variable, so that the flow velocity in the direction of the pipe axis can change from one cross-section to another. In addition, there is no internal friction and no friction with the wall of the pipe.

For the treatment of flows three kinds of relations are needed:

1. Balance equations for the substance-like quantities  $E$ ,  $S$ ,  $n$  and  $m$ .

In the special case of stationary flows that we consider, the rate of change  $dX/dt$  of the substance-like quantities  $X$  in the balance equation

$$\frac{dX}{dt} = I_X + \Sigma_X$$

is always equal to zero.

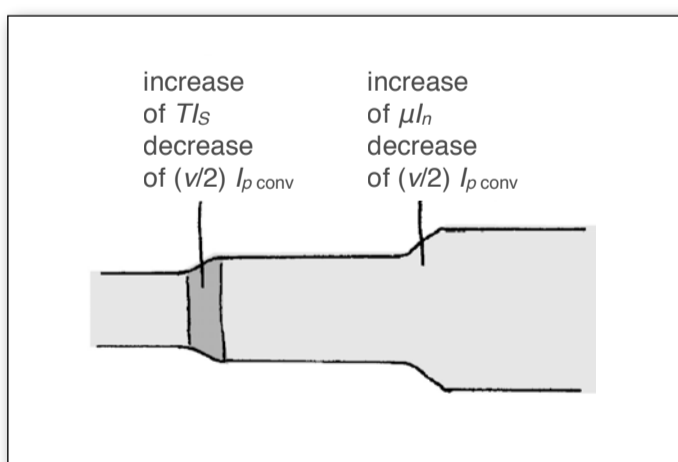
2. The energy differential

In addition to the balance equations of the various substance-like quantities, we also need the couplings between the flows of the substance-like quantities that follow from the energy differential:

$$P = T I_S + \mu I_n + \frac{v^2}{2} I_m \quad (8.1)$$

We know the first two terms on the right side of the equation from earlier times. The third term represents the flow of the kinetic energy. The current  $I_m$  is the current of the inertial mass. We will add another summand later, in which the current of the gravitational mass occurs. Like  $T$  and  $\mu$  the pre-factor  $v^2/2$  of  $I_m$  plays the role of a potential, or a driving force quantity. One could introduce a proper name for it, such as *inertial potential*.

In a flow the energy current  $P$  is often constant along the whole path, but the individual contributions in (8.1) change at locations where the pipe cross-section changes, Fig. 8.1. This can also be expressed as follows: The loading of one energy carrier changes at the expense of the loading of another. The energy is transferred from one carrier to another within the flow.



**Fig. 8.1**

The energy current is the same at each cross-section of the pipe. However, the distribution of the energy flow among the different energy carriers can change

With

$$I_S = \hat{S} \cdot I_n$$

and

$$I_m = \hat{m} \cdot I_n$$

equation (8.1) can be written:

$$P = \left( T \hat{S} + \mu + \frac{v^2}{2} \hat{m} \right) I_n \quad (8.2)$$

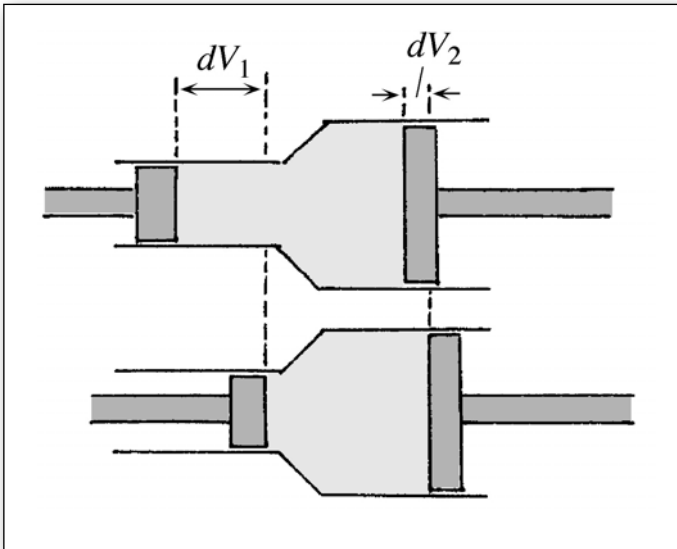
3. Finally, the relations that characterize the specific flowing material (ideal gas, incompressible liquid, etc.) must be given.

## 8.2 Currents without an energy flow through the pipe wall

A simple law applies to flows without an energy transfer through the pipe wall:

$$\hat{E} + p\hat{V} = \text{const}$$

To prove it, we imagine that the flow is realized as shown in Fig. 8.2: by two moving pistons. We assume that no diffusion and no heat conduction takes place in the direction of flow.



**Fig. 8.2**

One can imagine that the energy change in the area between the two pistons is caused by the energy disappearing in the volume element  $dV_1$  and the energy emerging in the volume element  $dV_2$ .

The change  $dE$  of the energy of the system between the two pistons is

$$dE = -p_1 dV_1 - p_2 dV_2$$

One can imagine that the energy change  $dE$  is due to the fact that all the energy  $dE_1$  contained in the volume  $dV_1$  disappears and all the energy  $dE_2$  contained in  $dV_2$  is added, so that

$$dE = dE_1 + dE_2 = -p_1 dV_1 - p_2 dV_2$$

or

$$d(E_1 + p_1 V_1) + d(E_2 + p_2 V_2) = 0$$

If one follows a certain amount of gas on its way from left to right, so for this system we have

$$E + pV = \text{const}$$

or written in molar quantities

$$\hat{E} + p\hat{V} = \text{const}$$

This is an important rule: If the energy current in a flow is constant from one pipe cross-section to another, i.e. if no energy is “taken out or put in from the side”, the expression  $E + pV$  has the same value for both pipe cross-sections.

We used to look at processes where the value of a variable is constant, e.g. isothermal processes ( $T = \text{const}$ ), isentropic processes ( $S = \text{const}$ ), isoenergetic processes ( $E = \text{const}$ ). We are dealing here with a process in which a certain combination of variables is constant, namely  $E + pV$ . To simplify the equations, we give this combination of variables its own symbol:

$$E + pV = H$$

and

$$\hat{E} + p\hat{V} = \hat{H}$$

We remember that this expression is also called enthalpy, and that it is a characteristic function when written as a function of the variables  $S$ ,  $p$  and  $n$ .

### 8.3. Currents of an ideal gas without an energy flow through the pipe wall

In equation (8.2) we insert

$$\begin{aligned}\hat{S}(T, p) &= R \ln \frac{p_0}{p} + c_p \ln \frac{T}{T_0} + \hat{S}(T_0, p_0) \\ \mu(T, p) &= RT \ln \frac{p}{p_0} - c_p T \ln \frac{T}{T_0} - T \hat{S}(T_0, p_0) + c_p (T - T_0) \\ &\quad + T_0 \hat{S}(T_0, p_0) + \mu(T_0, p_0)\end{aligned}$$

and obtain

$$P = \left[ c_p (T - T_0) + T_0 \hat{S}(T_0, p_0) + \mu(T_0, p_0) + \frac{v^2}{2} \hat{m} \right] l_n \quad (8.3)$$

With  $P = \text{const}$  and  $l_n = \text{const}$  we get

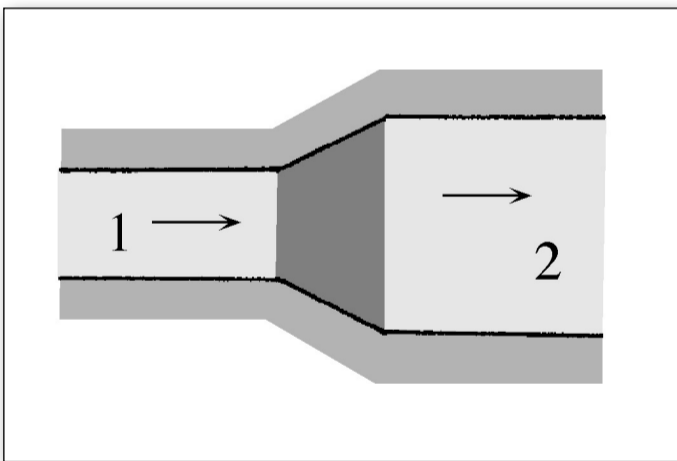
$$c_p (T - T_0) + T_0 \hat{S}(T_0, p_0) + \mu(T_0, p_0) + \frac{v^2}{2} \hat{m} = \text{const}$$

Here and in the following “const” means “has the same value for each cross-section of the pipe”. We now call  $T_0$  that temperature for which the gas has the velocity  $v = 0$  (“boiler state”) and obtain

$$c_p T + \frac{v^2}{2} \hat{m} = c_p T_0 \quad (8.4)$$

Thus, the faster the gas flows, the lower its temperature.

We consider an application of this equation, Fig. 8.3.



**Fig. 8.3**

An ideal gas flows through an expansion valve without being accelerated.

An ideal gas flows through a so-called thermal expansion valve: a flow resistance through which it flows without being accelerated, i.e. without forming a jet or vortex behind it. The valve is thermally insulated against the external environment so that it cannot extract energy from the gas.

The gas expands in the valve: its pressure and density decrease. In order for  $v_1 = v_2$ , the pipe cross-section in the throttle must increase slightly. With the previous equation results

$$c_p (T_1 - T_0) = c_p (T_2 - T_0)$$

and thus

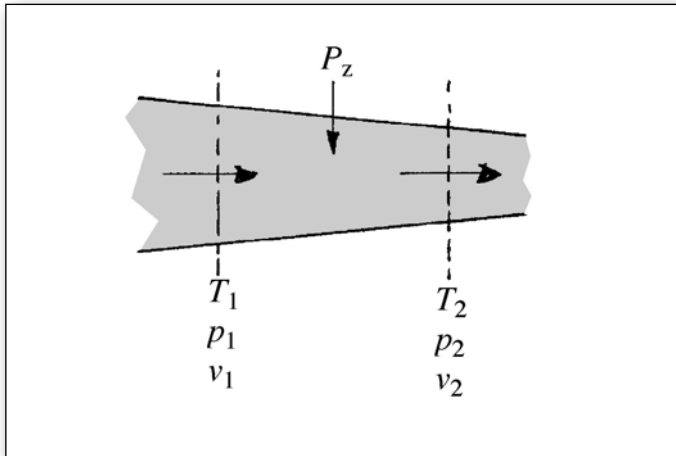
$$T_1 = T_2$$

With the gas equation it follows that the pressure decreases by the same factor by which the molar volume increases.

## 8.4 Isothermal flow of an ideal gas

The balance equation for the energy is, Fig. 8.4:

$$P_2 = P_1 + P_z$$



**Fig. 8.4**

Energy balance of isothermal flow

With (8.3) and with  $T_1 = T_2$  we get

$$\frac{v_2^2}{2} \hat{m} \cdot I_n = \frac{v_1^2}{2} \hat{m} \cdot I_n + T \cdot I_{S,z}$$

Here,  $I_{S,z}$  is the flow of the entropy that must enter or leave the fluid through the pipe walls, in order to keep  $T$  constant.

With

$$I_{S,z} = \hat{S}_z \cdot I_n$$

and

$$\hat{S}_z = R \ln \frac{p_1}{p_2}$$

(since  $T = \text{const}$ ) we obtain

$$\frac{\hat{m}}{2} (v_2^2 - v_1^2) = T \cdot R \cdot \ln \frac{p_1}{p_2}$$

If we take the boiler state as state 1, so that  $v_1 = 0$ , and name  $p_1 = p_0$ ,  $v_2 = v$  and  $p_2 = p$ , then

$$v^2 = \frac{2RT}{\hat{m}} \ln \frac{p_0}{p}$$

Thus, the faster the gas flows, the lower its pressure.

### 8.5 Ideal flow of an incompressible fluid

Since the liquid is not compressed (because it is so difficult), and since  $\partial S(T, p, n)/\partial p \approx 0$ , an isentropic flow is also isothermal. We consider such isentropic-isothermal flows.

With (8.2) we get

$$P = \left( T\hat{S} + \mu + \frac{v^2}{2} \hat{m} \right) l_n = \text{const}$$

and with

$$\hat{S} = \text{const}$$

we obtain

$$\mu + \frac{v^2}{2} \hat{m} = \text{const}$$

With

$$\mu(p) = \hat{V}(p - p_0) + \mu(p_0)$$

(equation (6.1)) we get

$$\hat{V} \cdot p + \frac{v^2}{2} \hat{m} = \text{const}$$

and with

$$\rho_m = \frac{\hat{m}}{\hat{V}}$$

we obtain

$$p + \frac{v^2}{2} \rho_m = \text{const}$$

The equation tells us that the higher the flow velocity, the lower the pressure. In places where a pipe is wide, the pressure is higher than in narrow sections.

---

## 8.6 Flows of liquids in the gravitational field

So far we have implicitly assumed that there is no gravitational field. With the gravitational field, (8.1) becomes

$$P = Tl_s + \mu l_n + \frac{v^2}{2} l_m + gh l_m$$

and

$$P = (T\hat{S} + \mu + \frac{v^2}{2} \hat{m}_{\text{inertial}} + gh\hat{m}_{\text{grav}}) l_n$$

This is the energy current coupled to  $l_n$ . However, a part of it, namely that which has its origin in the gravitational field, does not flow at the same place as  $l_n$ .

With

$$\hat{S} = \text{const}$$

$$\mu(p) = \hat{V}(p - p_0) + \mu(p_0)$$

and

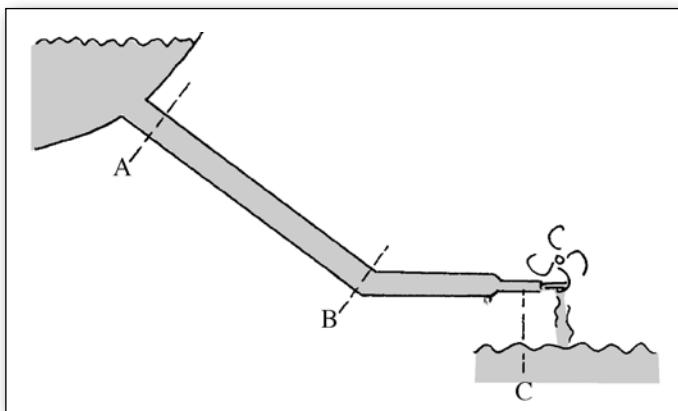
$$\rho_m = \frac{\hat{m}}{\hat{V}}$$

and with  $P = \text{const}$ ,  $l_n = \text{const}$  and  $T = \text{const}$  we get

$$p + \frac{v^2}{2} \rho_m + g \cdot h \cdot \rho_m = \text{const} \quad (8.5)$$

This is the *Bernoulli's equation*.

In the hydroelectric power plant shown in Fig. 8.5, the energy is “transloaded” twice on its way from A to C: On its way from A to B, the loading of  $l_n$  increases at the expense of that of  $l_{m, \text{grav}}$ . In the nozzle the loading of  $l_{m, \text{inertial}}$  increases at the expense of that of  $l_n$ .



**Fig. 8.5**

On the section AB, energy is transloaded from the energy carrier “gravitational mass” to the energy carrier quantity of substance. In the nozzle it changes the carrier again: It is transferred onto the carrier “inertial mass”.

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# 9

## Real gases

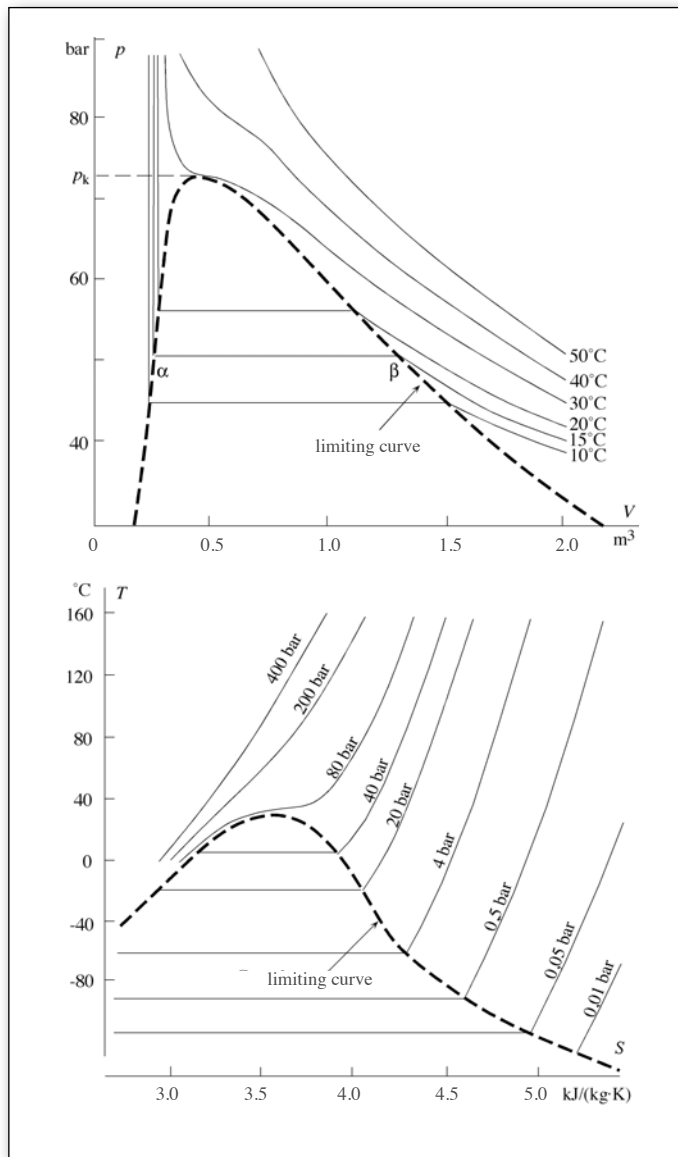
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## 9.1 Critical point

A gas only obeys the equation of state  $pV = nRT$  as long as  $\rho_n$  is small and  $T$  is large.

Fig. 9.1 shows the isotherms of  $\text{CO}_2$  in the  $p$ - $V$  diagram and the isobars in the  $T$ - $S$  diagram for conditions under which  $\text{CO}_2$  is no longer ideal.



**Fig. 9.1**

Carbon dioxide: Isothermals in the  $p$ - $V$  diagram and isobars in the  $T$ - $S$  diagrams

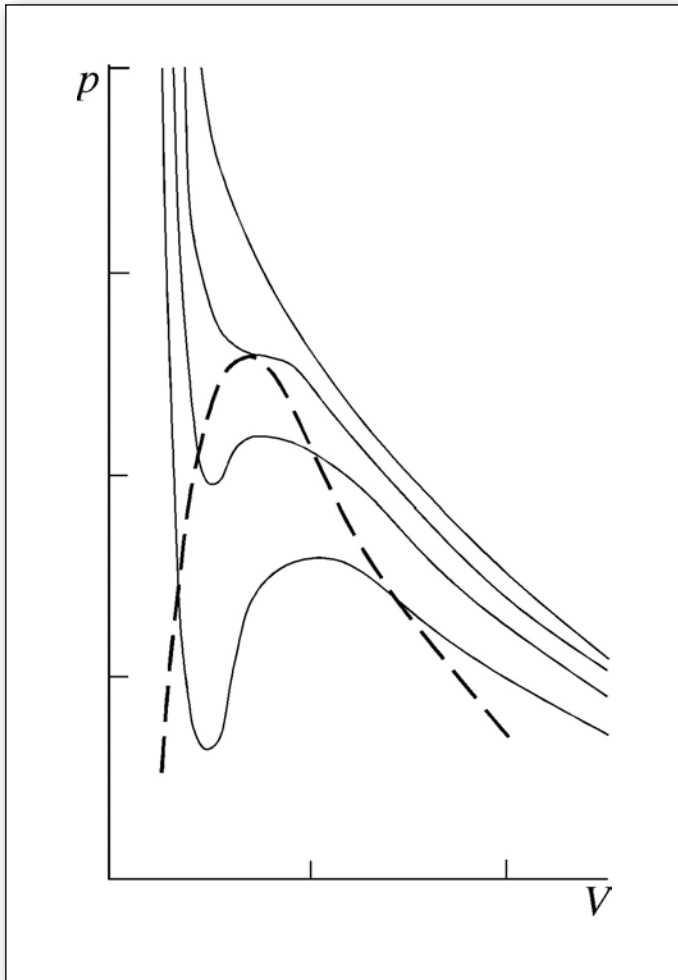
Below the dashed limiting curves, liquid and gas exist simultaneously. If one moves on an isothermal (upper partial picture) from right to left, one enters this coexistence area at point  $\beta$ . The proportion of gas then decreases more and more in favor of the liquid. At  $\alpha$  the phase transition is completed, the whole substance is liquid. The isothermal rises steeply, because the compressibility of the liquid is very low. Isothermals belonging to high temperatures do not cross this area. At these temperatures, it is no longer possible to distinguish between gas and liquid. The temperature from which a phase transition begins to exist is called *critical temperature*  $T_{\text{crit}}$ . The pressure at which the isotherm of the critical temperature touches the coexistence area is called *critical pressure*  $p_{\text{crit}}$ . Water vapor in a state below the limiting curve is called wet vapor.

## 9.2 The van der Waals equation

A gas for which the the ideal gas law no longer applies can be described outside the limiting curve approximately by a somewhat more complicated equation of state, the van der Waals equation:

$$\left(p + \frac{a}{\hat{V}^2}\right) \cdot (\hat{V} - b) = RT$$

$a$  and  $b$  are two constants characterizing the individual gas. Fig. 9.2 shows isothermals according to the van der Waals equation.



**Fig. 9.2**

Isothermals according to the van der Waals equation

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### 9.3 Adiabatic flow of a real gas – the Joule-Thomson effect

We consider the stationary flow of a real gas through a pipe with a dissipative resistance (see section 8.3) and ask for the temperature change of the gas. To exclude the acceleration effect discussed in Section 8.3, the tube at the “resistor” expands so that the flow velocity before and behind it is the same. We ask what change  $dT$  of the temperature results for a given change  $dp$  of the pressure for  $H = \text{const}$ , i.e. we ask for

$$\frac{\partial T(\hat{H}, p)}{\partial p}$$

For this we need

$$d\hat{H}(T, p) = \frac{\partial \hat{H}(T, p)}{\partial p} dp + \frac{\partial \hat{H}(T, p)}{\partial T} dT \quad (9.1)$$

We start with

$$d\hat{H} = Td\hat{S} + \hat{V}dp$$

Comparing with

$$d\hat{H}(\hat{S}, p) = \frac{\partial \hat{H}(\hat{S}, p)}{\partial \hat{S}} d\hat{S} + \frac{\partial \hat{H}(\hat{S}, p)}{\partial p} dp$$

we obtain

$$\frac{\partial \hat{H}(\hat{S}, p)}{\partial \hat{S}} = T \quad \frac{\partial \hat{H}(\hat{S}, p)}{\partial p} = \hat{V} \quad (9.2)$$

We now express the searched derivatives in (9.1) by the known ones in (9.2) using the rules of differential calculus and one of the Maxwell relations:

$$\begin{aligned} \frac{\partial \hat{H}(T, p)}{\partial p} &= \dots = \hat{V} + T \frac{\partial \hat{S}(T, p)}{\partial p} = \hat{V} - T \frac{\partial \hat{V}(T, p)}{\partial T} \\ &= \hat{V} - T\hat{V}\alpha = \hat{V}(1 - T\alpha) \\ \frac{\partial \hat{H}(T, p)}{\partial T} &= T \frac{\partial \hat{S}(T, p)}{\partial T} = c_p \end{aligned}$$

This results in

$$d\hat{H}(T, p) = \hat{V}(1 - \alpha T)dp + c_p dT$$

With

$$d\hat{H}(T, p) = 0$$

we obtain the wanted temperature change:

$$\frac{\partial T(\hat{H}, p)}{\partial p} = \frac{\hat{V}(\alpha T - 1)}{c_p} \quad (9.3)$$

For an ideal gas  $\alpha = 1/T$ . Thus, the temperature change is zero, as was already calculated in section 8.3. In general, the expression (9.3) is negative for high temperatures, i.e. an expansion of the gas results in an increase in temperature. For low temperatures (9.3) is positive: decompression of the gas is accompanied by a temperature decrease. At the *inversion temperature*  $T_i = 1/\alpha$  the temperature remains unchanged, Table 9.1.

substance	$T_i$ (K)
H <sub>2</sub>	224
He	35
O <sub>2</sub>	1041
N <sub>2</sub>	866

**Table 9.1**

Inversion temperatures of several substances

We calculate the inversion temperature for a Van-der-Waals gas. It is

$$T_i = \frac{1}{\alpha} = \frac{1}{\frac{1}{\hat{V}} \frac{\partial \hat{H}(T, p)}{\partial T}} = \hat{V} \frac{\partial T(p, \hat{V})}{\partial \hat{V}} = \frac{\hat{V}}{R} \left[ -\frac{2a}{\hat{V}^3}(\hat{V} - b) + p_i + \frac{a}{\hat{V}^2} \right]$$

We calculate  $p_i$  from the Van-der-Waals equation

$$p_i = \frac{RT_i}{\hat{V} - b} - \frac{a}{\hat{V}^2}$$

and insert in the previous equation

$$T_i = \frac{\hat{V}}{R} \left[ -\frac{2a}{\hat{V}^3}(\hat{V} - b) + \frac{RT_i}{\hat{V} - b} - \frac{a}{\hat{V}^2} + \frac{a}{\hat{V}^2} \right]$$

We thus obtain

$$T_i = \frac{2a(\hat{V} - b)^2}{Rb\hat{V}^2}$$

For gas densities that are not too high we have

$$\hat{V} \gg b$$

and the inversion temperature becomes independent of the molar volume:

$$T_i = \frac{2a}{Rb}$$

The cooling of an expanding gas at  $E + pV = \text{const}$  is called the *Joule-Thomson effect*. It is used in the Linde process for the liquefaction of air.

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# 10

**Combined potentials**

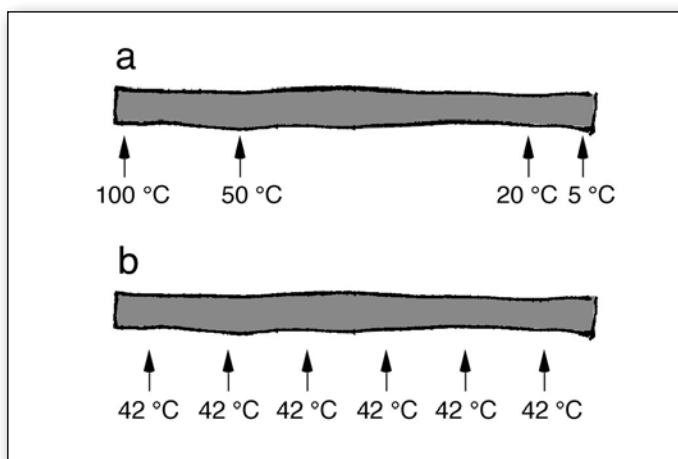
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## 10.1 Once more equilibria

Two subsystems A and B were always involved in the discussion of the equilibria in Section 4.11. We remember: If there is a thermally conductive connection between two bodies A and B, an entropy current flows until the temperatures of A and B have assumed the same value. The state that is then reached, is called thermal equilibrium.

Accordingly, we had defined what we mean by electrical and chemical equilibrium: the state in which two electrical potentials or two chemical potentials have reached the same value.

However, we do not have to limit ourselves to *two* different values of the temperature, the electric potential or the chemical potential. The rod in Fig. 10.1a has a different temperature at each position  $x$ . If we leave it to itself for a while, the temperatures will equalize. At the end all temperature values are the same, Fig. 10.1b. There is thermal equilibrium between all parts of the rod.



**Fig. 10.1**

(a) The rod has a different temperature at each position  $x$ .  
 (b) After a while the temperature is the same everywhere:  $T(x) = \text{const}$ .

Thermal equilibrium:  $T(x) = \text{const}$

Here we had assumed that the temperature would only change in the  $x$ -direction. More generally, we can write:

Thermal equilibrium:  $T(x, y, z) = \text{const}$

Since in the following only gradients of a single direction concern us, we remain with the  $x$ .

Accordingly, we can generalize the definition of chemical and electrical equilibrium:

Chemical equilibrium:  $\mu(x) = \text{const}$

Electric equilibrium:  $\phi(x) = \text{const}$

Also the gravitational potential  $\psi$  can equalize, so that equilibrium is achieved. We call it *gravitational equilibrium*.

Gravitational equilibrium:  $\psi(x) = \text{const}$

## 10.2 Substances and particles – coupling between substance-like quantities

If the extension or the amount of a system does not matter, we speak of a substance. 1 g of air is the same substance as 1 kg of air. In order to characterize a substance, however, it is important to know the relationship between the values of the substance-like quantities:

Water:  $m/n = 18$  g/mol.

Free electrons:  $m/n = 0.55$  mg/mol;  $Q/m = 1.76 \cdot 10^{11}$  C/kg .

Light:  $E/p = 3 \cdot 10^8$  m/s.

Some of the substance-like quantities have a universal quantum. What does that mean? If a system is closed, i.e. if it cannot give away or receive the physical quantity, the value of this quantity is an integer multiple of an elementary quantum, for example:

$$Q = k_1 \cdot e \quad e = 1.60 \cdot 10^{-19} \text{ C} = \text{elementary charge}$$

$$L = k_2 \cdot \frac{\hbar}{2} \quad \hbar = 1.05 \cdot 10^{-34} \text{ Js} = \text{quantum of angular momentum} \\ \text{(Planck constant)}$$

$$n = k_3 \cdot \tau \quad \tau = 1.66 \cdot 10^{-24} \text{ mol} = \text{elementary amount} \\ \text{(1/Avogadro constant)}$$

$$k_1, k_2, k_3 = \text{integers}$$

The quotient  $F = e/\tau = 0.965 \cdot 10^5$  C/mol is called Faraday constant.

A system whose amount of substance has the value  $n = 1$   $\tau$  is called a particle. Under certain circumstances one may imagine it as a small localizable individual; but often this idea fails.

The particle electron, for example, is a system with

$$n = 1\tau, Q = 1e, L = \hbar/2, E = \dots, \text{etc.}$$

Particles for which  $Q \neq 0$ , are called *charge carriers*.

*Examples of charge carriers:*

- free electron
- mobile electron in a semiconductor
- electron hole (or hole) in a semiconductor
- free positron
- Cu<sup>++</sup>-ion in aqueous solution
- myon

Just as an ensemble of values of all substance-like quantities belongs to a certain amount of a substance, an ensemble of currents of substance-like quantities belongs to the flow of a substance. In the case of an electron flow, we are dealing with an electric current (current strength  $I$ ), a mass current (current strength  $I_m$ ), a current of the amount of substance (strength  $I_n$ ), an entropies current (strength  $I_S$ )... Also the various current strengths are related in a characteristic way for a given substance. Thus for a current of free electrons we have  $I/I_m = 1.76 \cdot 10^{11}$  C/kg.

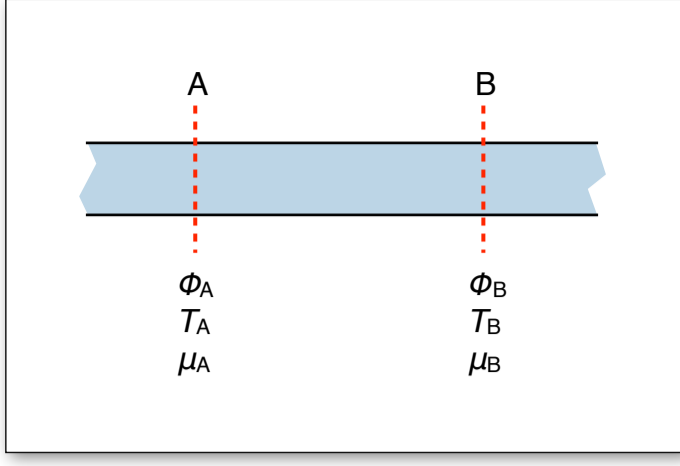
The substance-like quantities are more or less “coupled” to each other. Thus, electric charge is always firmly coupled to the amount of substance and to mass. There is no electric current without a mass flow and without a flow of amount of substance. So there is no pure electric current. It follows that a material or particle flow can be driven in different ways.

One can initiate an electron current, Fig. 10.2,

- by establishing an electrical potential gradient; this potential gradient “pulls” at the charge of the electrons;
- by establishing a gradient of the chemical potential, which pulls on the amount of substance of the electrons;
- by producing a temperature gradient that pulls at the entropy of the electrons.

### 10.3 The electrochemical potential

We consider a current of any charged particles e.g. electrons, between positions A and B of a conductor, fig. 10.2.



**Fig. 10.2**  
A substance flow can have different drives.

If all intensive variables have the same value at A and B, except for the electrical potential  $\Phi$ , i.e. if  $T_A = T_B$ ,  $\mu_A = \mu_B$ , ...,  $\Phi_A \neq \Phi_B$ , the particle flow is driven by the electrical potential difference  $U = \Phi_A - \Phi_B$ . Energy is dissipated in the conductor according to

$$P = T I_{S \text{ prod}} = (\Phi_A - \Phi_B) I.$$

If, on the other hand, all intensive variables except  $\mu$  have the same value at A and B, i.e. if  $T_A = T_B$ ,  $\Phi_A = \Phi_B$ , ...  $\mu_A \neq \mu_B$ , the particle flow is driven by the chemical potential difference  $\Delta\mu = \mu_A - \mu_B$ , and energy is dissipated in the wire according to

$$P = T I_{S \text{ prod}} = (\mu_A - \mu_B) I_n.$$

If both  $\Phi$  and  $\mu$  have different values at A and B, the current has two drives:  $\Delta\Phi$  and  $\Delta\mu$ . These can “pull” the particles in the same direction or in opposite directions.

The dissipated energy is then

$$P = T I_{S \text{ prod}} = (\mu_A - \mu_B) I_n + (\Phi_A - \Phi_B) I.$$

Now  $I$  and  $I_n$  are firmly coupled to each other. One particle ( $n = 1\tau$ ) carries an integer number  $z$  of elementary charges:

$$Q = ze.$$

For electrons, for example,  $z = -1$ .

So it is

$$\frac{Q}{n} = \frac{ze}{\tau}$$

Therefore, the electric current and the current of the amount of substance are also related:

$$\frac{I}{I_n} = \frac{ze}{\tau}$$

and with  $e/\tau = F$  (= Faraday constant) we get

$$I = zF I_n$$

This means that the dissipated energy becomes

$$P = [(\mu_A - \mu_B) + (\Phi_A - \Phi_B) zF] I_n = [(\mu_A + zF\Phi_A) - (\mu_B + zF\Phi_B)] I_n.$$

The quantity

$$\eta = \mu + zF\Phi$$

is called the *electrochemical potential* of the charge carriers. We thus can write

$$P = (\eta_A - \eta_B) I_n$$

The total drive of the particle flow is therefore caused by the electrochemical potential difference

$$\Delta\eta = \eta_A - \eta_B$$

There is no energy dissipation if there is no particle current, and there is no particle current if the driving force  $\Delta\eta = 0$ , i.e. if  $\eta_A = \eta_B$ , or more generally if the electrochemical potential does not depend on the position. We then say that there is *electrochemical equilibrium*.

Electrochemical equilibrium:  $\eta(x) = \text{const}$

Thus, the condition for the current to be zero is not that the electric potential is the same everywhere; it is the electrochemical potential that must be the same everywhere.

As an example, we consider two electric conductors, for example two pieces of wire made of different metals. The chemical potential of the electrons is different in the two metals. So there is a chemical potential difference between the electrons in one metal and those in the other. If we define the chemical potential of free electrons in a vacuum to be 0 G, the values in Table 10.1 apply.

substance	$\mu$ (in kG)
Ag	-460
Cs	-170
Cu	-430
Ni	-445
Pt	-515
W	-435

**Table 10.1**  
Chemical potential of the electrons in some metals

Thus, the chemical potential difference of the electrons in copper and platinum is

$$\mu(\text{Cu}) - \mu(\text{Pt}) = 85 \text{ kG}.$$

If the two pieces of wire are brought into contact with each other, electrons flow from the copper to the platinum according to the chemical potential gradient. This causes the two metals to charge oppositely: the copper becomes positive, the platinum negative. As a result, the electric potential of the copper increases and that of the platinum decreases. That means that we now have an electric drive in the opposite direction of the chemical drive. If

$$F\Delta\Phi = \Delta\mu$$

i.e. if  $\Delta\eta$  is equal to zero, the electric and the chemical drive compensate each other and there will be no longer a flow of electrons. There is *electrochemical equilibrium*.

Thus, there is an electrical potential difference between two pieces of different metals that touch each other. We calculate the *contact voltage* between copper and platinum.

From

$$\eta = 0$$

we get

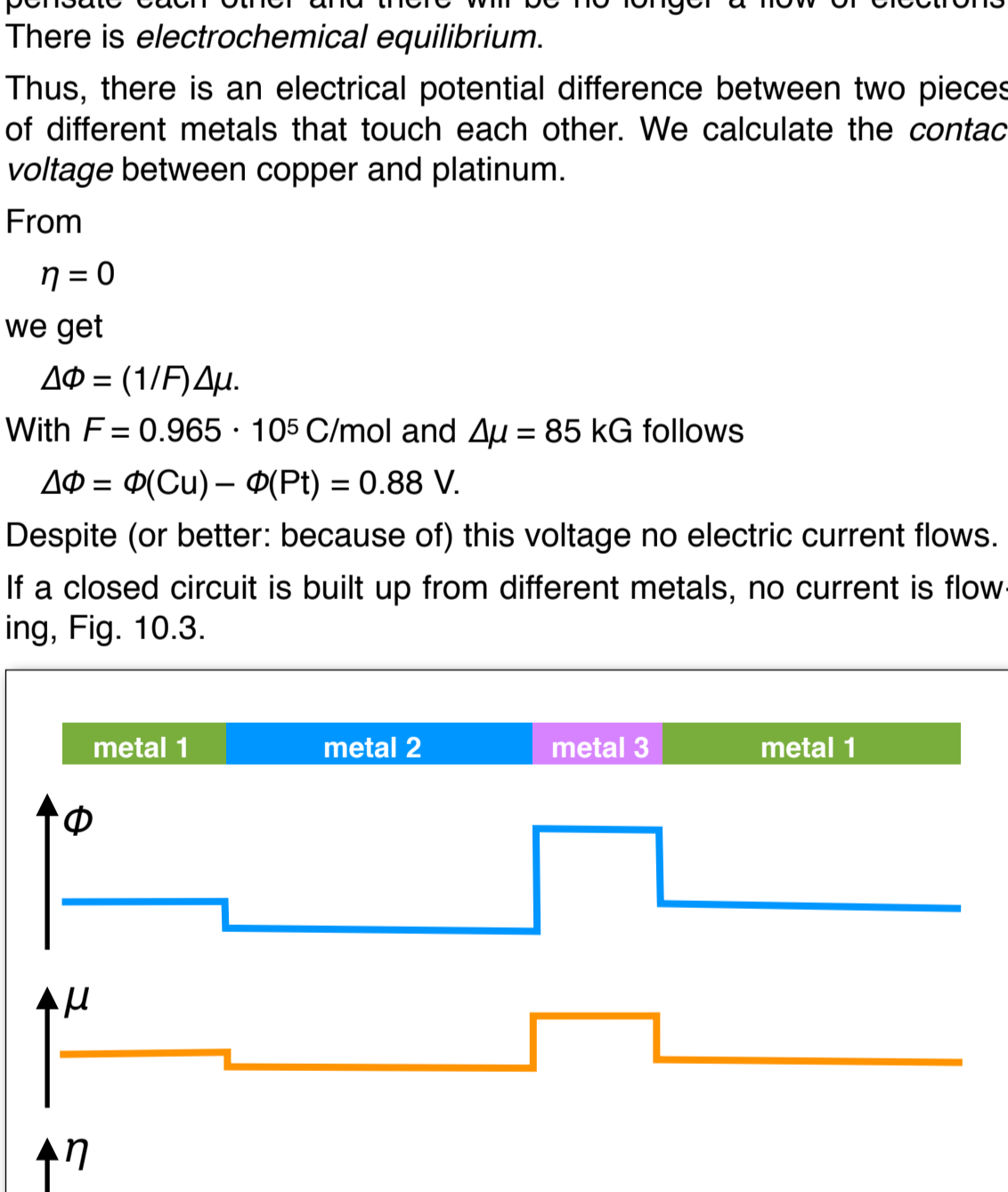
$$\Delta\Phi = (1/F)\Delta\mu.$$

With  $F = 0.965 \cdot 10^5 \text{ C/mol}$  and  $\Delta\mu = 85 \text{ kG}$  follows

$$\Delta\Phi = \Phi(\text{Cu}) - \Phi(\text{Pt}) = 0.88 \text{ V}.$$

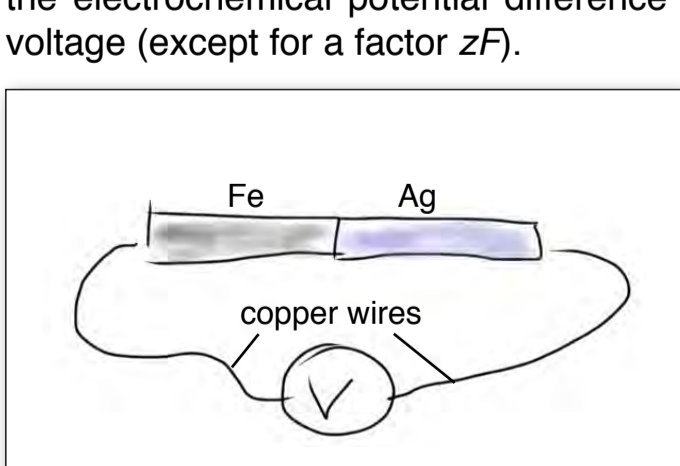
Despite (or better: because of) this voltage no electric current flows.

If a closed circuit is built up from different metals, no current is flowing, Fig. 10.3.



**Fig. 10.3**  
Electric, chemical and electrochemical potential of a closed circuit, which consists only of three conductors of different metals

It is not possible to measure the contact voltage simply with a voltmeter. Figure 10.4 shows why. A voltmeter always indicates the electrochemical potential difference. Only if the chemical potential in the two points between which the voltage is measured, is the same, the electrochemical potential difference is the same as the electric voltage (except for a factor  $zF$ ).



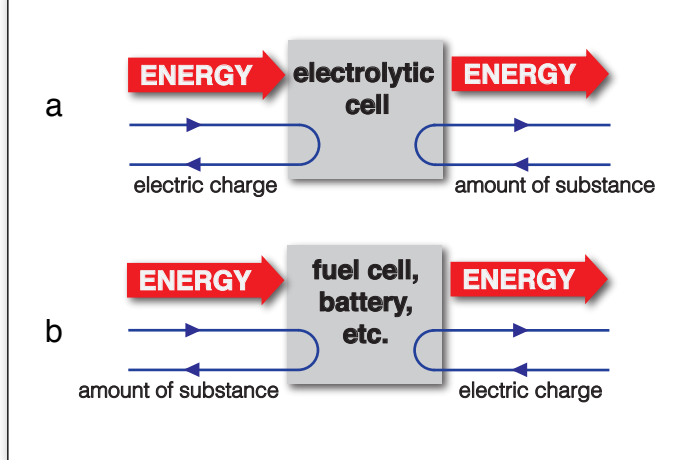
**Fig. 10.4**  
The voltmeter does not measure the electric potential difference between iron and silver but the electrochemical potential difference.

However, if one assumes that a voltmeter measures the electric voltage, there is normally no harm, because in many cases in which one believes that one needs the electric voltage, one actually needs the electrochemical potential difference – for example for the calculation of the electric current  $I$  by means of Ohm’s law.

The electrochemical potential also plays an important role in the pn junction in a semiconductor. The chemical potential of the “holes” is high in the p material and low in the n material. This means that there is a chemical drive for the holes from the p side to the n side. The reverse applies to electrons: A chemical potential gradient acts in such a way that they are driven from the n material to the p material. However, an electric potential difference builds up between the p and n sides of the junction, which keeps the chemical drives balanced; there is no particle flow – neither a flow of electrons nor of holes. The net drive given by the gradient of the electrochemical potential is zero; the electrochemical potential is the same throughout the material, even across the pn junction.

## 10.4 Electrochemical cells

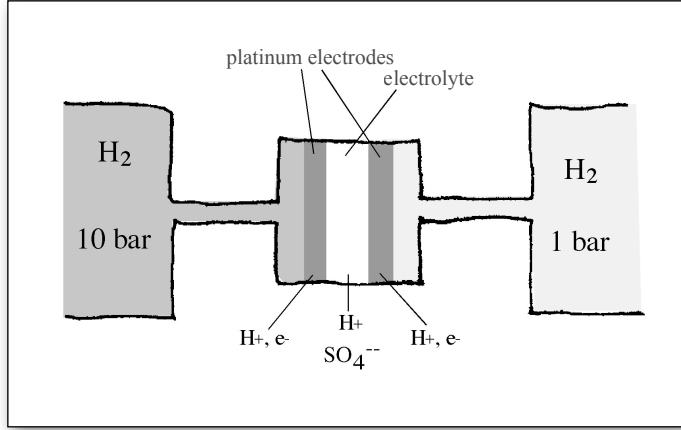
Electrochemical cells are devices that receive energy with the energy carrier amount of substance and release it with the carrier electric charge, or vice versa, Fig. 10.5. They exist in countless variants and have a variety of names. If such a cell works as shown in Figure 10.5a, it is called an electrolytic cell. The various realizations of Fig. 10.5b are called battery, fuel cell etc. Some of these devices are run alternately in one direction or the other. They are then called accumulators or storage batteries.



**Fig. 10.5**  
Electrolytic cell (a) and its reversal (b)

Even if the devices or “cells” are constructed differently, their operating principle is the same in all cases. In the following we will try to understand it by means of a system which is difficult to realize for technical reasons, but which is very transparent, so that one can easily understand how it works.

The cell uses the chemical potential difference that a gas – in our case hydrogen – goes through when it expands, Fig. 10.6.



**Fig. 10.6**  
Electrochemical cell. The chemical potential of the hydrogen is higher in the left reservoir than in the right.

The left reservoir contains hydrogen at high pressure, for example 10 bar. The hydrogen pressure in the right reservoir is low.

The cell has a high pressure hydrogen inlet on its left side and a low pressure hydrogen outlet on its right side. Because of the pressure difference, and thus the chemical potential difference, the hydrogen “wants” to flow through the cell. But that is not easy for it. Behind the inlet is a platinum wall, a so-called electrode. There is another one next to the exit.

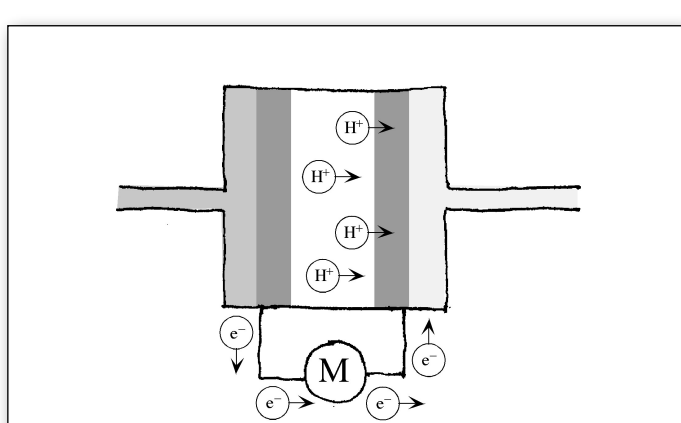
Platinum has the property that it can incorporate hydrogen. There is not enough space between the platinum atoms for the quite large hydrogen molecules. However, at the entry the hydrogen molecules break down into electrons and protons, and these particles can move relatively freely in platinum.

Between the two platinum electrodes is an acid, e.g. sulphuric acid. Acids have the property that they are conductors for protons, but not for electrons.

The hydrogen now wants to go from left to right. To each hydrogen atom belongs a proton and an electron. Protons and electrons are separated from each other in the platinum. The electrons cannot pass through the acid. So couldn't at least the protons follow the chemical drive and flow to the right through the acid? In fact, something is happening that we already know: At the very beginning, a small amount of protons will flow through the acid from the left to the right platinum electrode. In this way, however, an electrical potential difference is built up, which represents a drive for the protons in the opposite direction. After a very short time, the two drives compensate each other and the proton current stops flowing. The protons are in electrochemical equilibrium. This means that the electrical potential of the left platinum electrode is lower than that of the right platinum electrode.

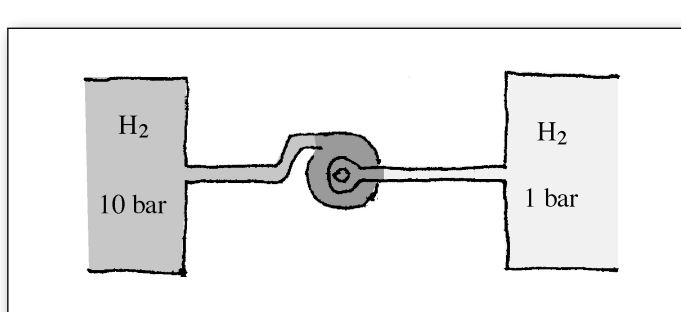
It is now easy to open a path from left to right for the electrons as well: The two platinum electrodes are connected via a copper wire. Copper, like most metals, is a conductor for electrons but not for protons. (We had just come across platinum as an exception, it conducts both electrons and protons.)

This electron current through the copper can now be guided through any electrical energy receiver, e.g. an electric motor, Fig. 10.7.



**Fig. 10.7**  
The electric circuit is closed.

The two hydrogen reservoirs could also have been connected via a turbine. Then the energy corresponding to the chemical potential difference would have been drawn off with the turbine, Fig. 10.8.



**Fig. 10.8**  
One can directly take profit of the chemical potential difference with a turbine.

We realized the pressure equalization differently: We let the two components of hydrogen – the protons and the electrons – go separate ways and extracted all the energy in one of them.

In practice, the cell described here works very poorly because platinum is not as good a conductor for the protons as we have assumed.

A cell very similar to ours is the concentration cell. It exploits the chemical potential difference of dissolved substances with different concentrations. Concentration cells may work, but they are not very efficient. The really good cells exploit more complicated chemical reactions.

Also a chemical reaction is driven by a chemical potential difference. The cells are set up in such a way that the reactants are spatially separated from each other. They can only come together if one of the substances is broken down into electrons plus ions in or on an electrode. The ions pass through the electrolyte, the electrons through the conductor of the outer part of the circuit.

It is not difficult to calculate the voltage if one knows the chemical potential difference of the reaction taking place in the cell. We look at the cell in open circuit conditions. The ions (in a special case protons) are then in electrochemical equilibrium, i.e. the sum

$$\mu + z \cdot F \cdot \phi$$

must have the same value for the left and right platinum electrode:

$$\mu_{\text{left}} + z \cdot F \cdot \phi_{\text{left}} = \mu_{\text{right}} + z \cdot F \cdot \phi_{\text{right}}$$

We call the potential differences

$$\mu_{\text{left}} - \mu_{\text{right}} = \Delta\mu$$

$$\phi_{\text{left}} - \phi_{\text{right}} = \Delta\phi$$

and obtain

$$\Delta\phi = -\frac{\Delta\mu}{z \cdot F}$$

If one knows the reaction, i.e. the chemical potential difference, as well as the number  $z$  of ions per reaction turnover, one can calculate the open circuit voltage of the cell.

We look at the hydrogen cell discussed above as an example. We obtain the chemical potential difference with the equation (see Section 5.2):

$$\Delta\mu = RT \ln \frac{p}{p_0}$$

With

$$p = 10 \text{ bar}$$

$$p_0 = 1 \text{ bar}$$

$$T = 300 \text{ K}$$

$$z = 1$$

$$R = 8.31441 \text{ J}/(\text{mol} \cdot \text{K})$$

and

$$F = 0.965 \cdot 10^5 \text{ C/mol}$$

we get

$$\Delta\phi = 0,060 \text{ V}$$



## 10.5 The gravitochemical potential

We apply the same arguments as in the previous section to the Earth's atmosphere, i.e. air in the gravitational field. Several drives also act on a portion of air: a gradient of the gravitational potential downwards, and a pressure gradient, and thus a chemical potential gradient upwards. The gravitational drive acts on the (gravitational) mass, the chemical potential gradient on the amount of substance. Now mass and amount of substance are firmly coupled to each other. We have:

$$\frac{m}{n} = \hat{m}$$

Here is  $\hat{m}$  the molar mass. The corresponding applies to the currents:

$$\frac{I_m}{I_n} = \hat{m}$$

The vertical distribution of the air is such that a displacement of an air portion from point A to point B, or from B to A does not result in any energy gain, i.e.

$$P = [(\mu_A - \mu_B) + (\psi_A - \psi_B)\hat{m}] I_n = [(\mu_A + \psi_A\hat{m}) - (\mu_B + \psi_B\hat{m})] I_n = 0$$

We call the sum

$$\gamma = \mu + \psi \hat{m}$$

the *gravitochemical potential* of the air. A difference of this magnitude represents a drive for an air portion. If  $\gamma$  has the same value everywhere, the air is in equilibrium, which is a *gravitochemical equilibrium*.

Gravitochemical equilibrium:  $\gamma(z) = \text{const}$

We are interested in the vertical distribution of the air and have therefore designated the position coordinate with  $z$ .

We now express the gravitational potential through the gravitational field strength

$$\psi = g \cdot z$$

and write the gravitochemical potential

$$\gamma = \mu + g \cdot z \cdot \hat{m}$$

If there is gravitochemical equilibrium we have

$$\gamma(z) = \text{const} ,$$

thus

$$\mu(z) + \hat{m} \cdot g \cdot z = \mu(0)$$

or

$$\mu(z) - \mu(0) = -\hat{m} \cdot g \cdot z$$

This means that the chemical potential  $\mu$  decreases linearly with the height  $z$ .

With

$$\mu[p(z)] - \mu[p(0)] = RT \ln \frac{p(z)}{p(0)}$$

see section 5.2, we obtain the pressure as a function of the height (as long as the temperature is the same everywhere):

$$-\hat{m} \cdot g \cdot z = RT \ln \frac{p(z)}{p(0)}$$

or

$$p(z) = p(0) \exp\left(-\frac{\hat{m}gz}{RT}\right)$$

This equation is known as the *barometric formula*. It was derived on the assumption that the temperature does not depend on  $z$ . However, this assumption is completely unrealistic. Strangely enough, the barometric formula is still very popular. We will consider a more realistic distribution of the air in the atmosphere in the next section.

## 10.6 A combination of temperature, gravitational and chemical potential

The calculation we performed in the previous section is unrealistic because we had assumed that no temperature difference builds up when an air portion moves in a vertical direction, i.e. an air flow in a vertical direction is an isothermal process. In fact, the opposite is almost perfectly realized. An air transport is in good approximation an isentropic process. The reason for this is that air is a poor heat conductor and that the air portions under consideration are large. We know that a sweater whose wool with its cavities forms a thin “layer of air” is a very good thermal insulator. In the atmosphere, entropy exchange would have to take place over hundreds of meters if it were to behave isothermal.

So in the following we make the opposite assumption: We assume that the air does not conduct entropy at all. This means that the entropy, just like the mass, is firmly coupled to the amount of substance.

The gradient of the gravitochemical potential is no longer responsible for driving an air flow, but the gradient of a combination of three potential variables: the gravitational potential, the chemical potential and the temperature. We can write this three-potential:

$$\varepsilon = \mu + \hat{m} \psi + \hat{S} T \quad (10.1)$$

where  $\hat{S}$  is the molar entropy.

Thus, the drive for the transport of an air portion would be the gradient

$$\text{grad } \varepsilon = \text{grad } (\mu + \hat{m} \psi + \hat{S} T)$$

Although the molar mass for air has a well-defined value, the value of the molar entropy depends on the history of the air and can have a different value for one air portion than for another, because despite poor thermal conductivity, air can naturally absorb and release entropy. The most effective mechanism for this is the evaporation and condensation of water. In the following we are interested in an important special case: the “dry atmosphere” with the same molar entropy everywhere. So we are looking at an area of the atmosphere where the molar entropy has the same value everywhere. The molar entropy, which is a factor in front of the temperature in equation (10.1), is thus simply constant just as the molar mass in front of the gravitational potential.

The equilibrium of such an atmosphere is then defined by the condition

$$\text{grad } \varepsilon = \text{grad } (\mu + \hat{m} \psi + \hat{S} T) = 0$$

or

$$\varepsilon = \mu + \hat{m} \psi + \hat{S} T = \text{const.}$$

Since the values of our potentials only change in a vertical direction, we write:

$$\varepsilon(z) = \mu(z) + \hat{m} \psi(z) + \hat{S} T(z) = \text{const.}$$

It is now our goal to determine the functions  $\mu(z)$ ,  $\psi(z)$  and  $T(z)$ . For this purpose we use equation 5.8 (section 5.6):

$$S(T, p, n) - S(T_0, p_0, n) = n \cdot \left( R \ln \frac{p_0}{p} + c_p \ln \frac{T}{T_0} \right)$$

Since the molar entropy  $S/n$  is independent of pressure and temperature, we have

$$S(T, p, n) - S(T_0, p_0, n) = 0$$

and thus

$$R \ln \frac{p_0}{p} + c_p \ln \frac{T}{T_0} = 0 \quad (10.2)$$

$p$  and  $T$  therefore depend unambiguously on each other.

In addition, we need the chemical potential of the ideal gas as a function of temperature and pressure (equation (5.11) in Section 5.8):

$$\mu(T, p) = RT \ln \frac{p}{p_0} - c_p T \ln \frac{T}{T_0} + (c_p - \hat{S}(T_0, p_0))(T - T_0) + \mu(T_0, p_0)$$

Inserting (10.2) we obtain

$$\mu(T) = (c_p - \hat{S}(T_0, p_0))(T - T_0) + \mu(T_0, p_0)$$

With the abbreviations

$$\hat{S}(T_0, p_0) = \hat{S}_0 \quad \text{and} \quad \mu(T_0, p_0) = \mu_0$$

we get

$$\mu(z) = (c_p - \hat{S}_0)(T(z) - T_0) + \mu_0 \quad (10.3)$$

Thus our three-potential becomes

$$\begin{aligned} \varepsilon(z) &= \mu(z) + \hat{m} \psi(z) + \hat{S}_0 T(z) \\ &= \hat{m} \psi(z) + \hat{S}_0 T(z) + \mu(z) \end{aligned}$$

and with (10.3)

$$\begin{aligned} \varepsilon(z) &= \hat{m}gz + \hat{S}_0 T(z) + (c_p - \hat{S}_0)(T(z) - T_0) + \mu_0 \\ &= \hat{m}gz + c_p(T(z) - T_0) + \hat{S}_0 T_0 + \mu_0 \end{aligned}$$

If now

$$\varepsilon(z) = \text{const.}$$

we have

$$\varepsilon(z) = \varepsilon(0)$$

and

$$\hat{m}gz + c_p T(z) = c_p T(0)$$

or

$$T(z) = T(0) - \frac{\hat{m}g}{c_p} z \quad (10.4)$$

Therefore, the temperature decreases linearly with altitude. As a numerical value, this gives a temperature decrease of about 1 degree per hundred meters. This temperature decrease is called the dry-adiabatic temperature gradient. It only applies if there are no phase transitions of the water during a vertical air movement. In fact, water evaporates during a downward movement and condenses during an upward movement of the air. As a result, the temperature decrease with height is lower. The approximate value is 0.6 degrees per 100 meters.

Finally, the combination of equations (10.2) and (10.4) provides the pressure decrease with the height:

$$p(z) = p(0) \left( 1 - \frac{\hat{m}g}{c_p T_0} \cdot z \right)^{c_p / R}$$

So not only the pressure, but also the temperature in the atmosphere decreases with the altitude. This stratification corresponds to a three-equilibrium in which gravitational, chemical and thermal drive add up to zero.

## 10.7 A combination of gravitational, inertial and hydrostatic potential – Bernoulli's equation

In Section 8.6 we had become familiar with Bernoulli's equation (8.5):

$$\rho + \frac{v^2}{2} \rho_m + g \cdot z \cdot \rho_m = \text{const}$$

We want to transform this equation a little.

We multiply by the molar volume  $\hat{V} = V/n$ .

We also replace

$$\rho_m \hat{V} = \frac{m}{V} \cdot \frac{V}{n} = \frac{m}{n} = \hat{m}$$

and use equation (6.1) (section 6.1):

$$\mu(p) - \mu(p_0) = \hat{V} \cdot (p - p_0).$$

Thus, Bernoulli's equation becomes

$$\mu + \frac{v^2}{2} \hat{m} + g \cdot z \cdot \hat{m} = \text{const}$$

We want to be a little more precise, because the two molar masses are not the same: the first one is the inertial mass, the second is the gravitational mass.

$$\mu + \frac{v^2}{2} \hat{m}_{\text{inertial}} + g \cdot z \cdot \hat{m}_{\text{grav}} = \text{const}$$

For the term  $v^2/2$  we had in section 8.1 proposed the name inertial potential.  $g \cdot z$  is the gravitational potential.

In this form, the Bernoulli equation allows for a new interpretation: it is an expression of an equilibrium. Here, too, we have a sum of three potentials: the chemical, the inertial and the gravitational potential. The molar masses are constant factors that ensure that all three potentials are measured in the same units.

The equation applies to the frictionless flow of a liquid. We see that the state of such a liquid can be interpreted as an equilibrium. Again, three drives act on three firmly coupled quantities: the amount of substance, the inertial mass and the gravitational mass.

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# 11

**Light as a gas**

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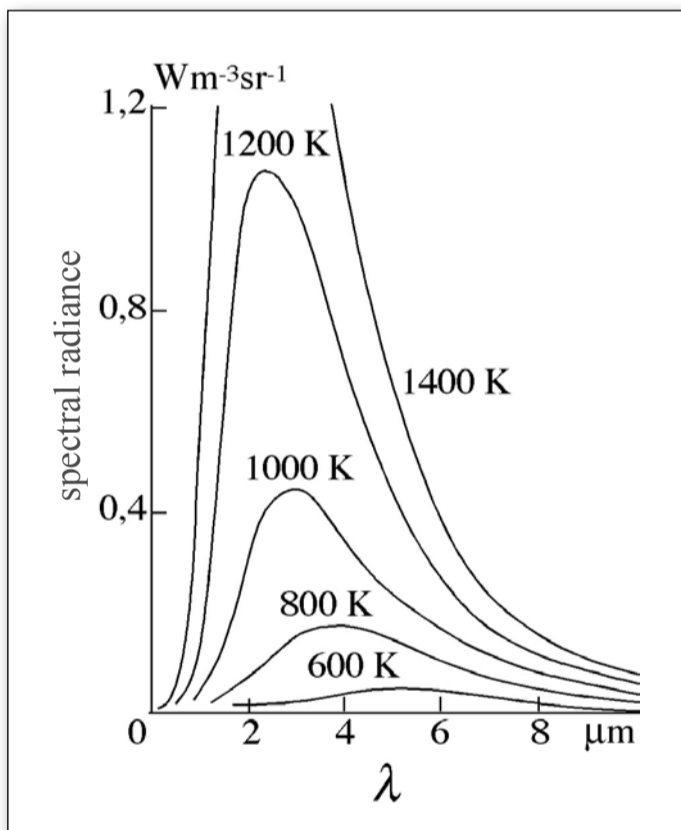
## 11.1 Thermal radiation

There are states of the electromagnetic field that can be described with very few variables, e.g.

- the homogeneous electric field;
- the plane electromagnetic wave.

Another class of states that get along with very few variables is *thermal radiation*. The variables used to describe it are those commonly used in thermodynamics: Energy, entropy, volume, temperature, pressure and chemical potential. Since the light particles, the photons, can fly around freely in an empty box, we also call light a gas. Thermal radiation is present in every empty container whose walls absorb electromagnetic radiation. Every body that absorbs electromagnetic radiation also emits electromagnetic radiation. In the case of thermal equilibrium between wall and radiation, the wall absorbs as much radiation as it emits, and the radiation has the same temperature as the wall. If the wall of the container absorbs radiation of all wavelengths, i.e. if the wall is black, the radiation in the container is called *black-body radiation*.

Black-body radiation can also be present in a container with reflecting walls. For radiation to be described by a single temperature, it must be in thermal and chemical equilibrium with itself. This can be achieved by a tiny particle of dust that absorbs and emits light of any frequency. We imagine the dust particle to be so small that its heat content is small compared to that of the radiation, so that its energy and entropy do not need to be included in the balances. Black-body radiation of 300 K is invisible, it is in the infrared range. The light from the sun is nearly black-body radiation. It has, like the solar surface, a temperature of about 6000 K. Fig. 11.1 shows the spectra of black-body radiation at different temperatures.



**Fig. 11.1**

Spectra of black-body radiation of various temperatures

For the description of light, we will use methods that we have also applied to material gases. First of all, we must refrain from some processes that seem natural to us when dealing with light: So we will not consider a free light beam (e.g. from the sun to the earth) – this corresponds to a free gas beam into the vacuum. We will also not look at selectively absorbing or reflecting walls. If light has a certain wavelength, the light particles (photons) have a certain momentum. A color filter that transmits light of a single wavelength transmits light particles of a particular momentum. In the case of a material gas, this would correspond to a device that only allows molecules of a certain momentum to pass through.

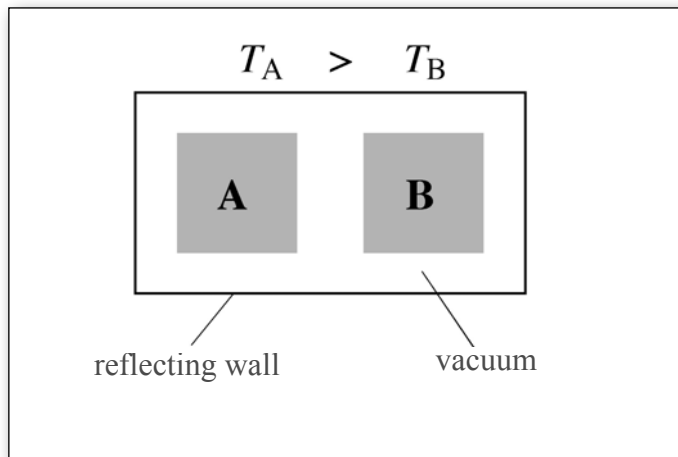
One problem with the handling of light is that it is difficult to measure some parameters that are important for its description: the pressure is usually very low and difficult to measure. The temperature is difficult to measure because the entropy density of light is usually very small. Furthermore, in contrast to material gases, it is almost impossible to perform a process with  $n = \text{const}$  in the laboratory with light.

## 11. Light as a gas

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### 11.2 The entropy of light

The fact that light has entropy and that a light flow is accompanied by an entropy current can easily be seen from the experiment in Fig. 11.2. Experience shows that the two bodies A and B come into thermal equilibrium by radiation flowing from the body with the higher to that with the lower temperature. As  $T_A$  decreases, the entropy  $S_A$  also decreases. Because entropy cannot be destroyed and, apart from radiation, there is no connection through which entropy could flow from body A to body B, the entropy must flow away with the radiation.



**Fig. 11.2**

The temperature of the body at the left decreases. Thus, the radiation must transport entropy.

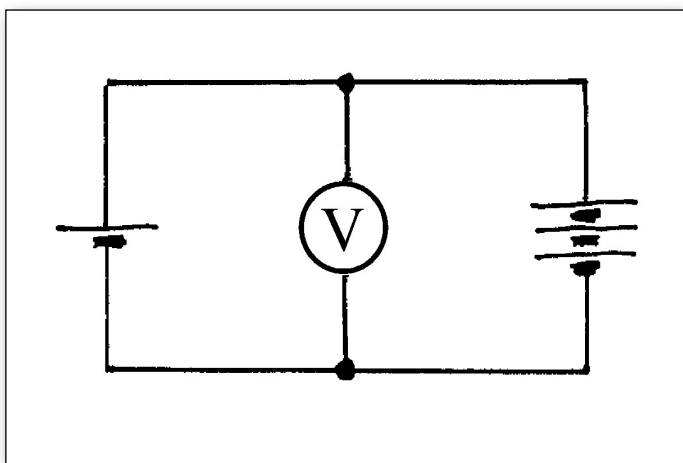
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### 11.3 The temperature of light

Light that is emitted by a body has the same temperature as the body. Thus, the light coming from the surface of the sun has the temperature of the surface of the sun, namely about 6000 K. However, this statement sounds somewhat implausible: If sunlight has this temperature, – wouldn't everything exposed to solar radiation have to burn immediately? And if sunlight has this temperature, then it should be possible to measure it by placing a thermometer in the sunlight.

We want to discuss the problem of measuring the temperature of light. To measure the temperature of a body or other system, the system must be brought into thermal contact with the thermometer being used. If one now holds a thermometer into the solar radiation, the thermometer is in thermal contact not only with the light but also with the air. Whose temperature will it show?

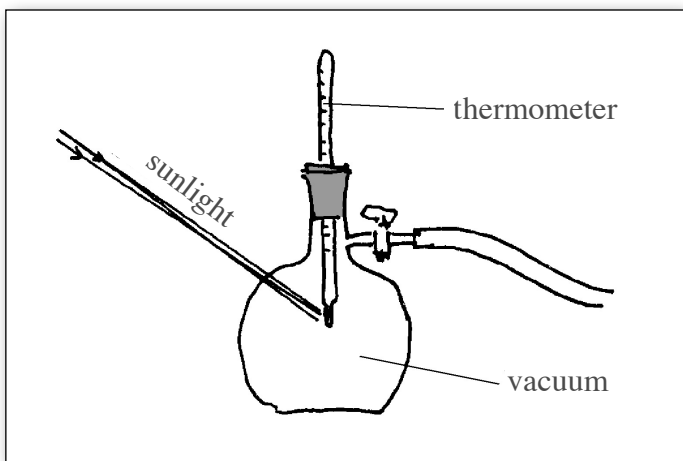
The situation is similar to that shown in Fig. 11.3, where an attempt is made to measure the voltage of two different batteries simultaneously with a single voltmeter. What the voltmeter indicates is not easy to predict. In any case, it will make a compromise between the open circuit voltages of the two batteries. In whose favor the compromise is found depends on the internal resistance of the batteries.



**Fig. 11.3**

One attempts to measure the open circuit voltages of two batteries simultaneously with a voltmeter.

With our thermometer, the compromise is clearly in favor of the air. One can now try to help oneself by placing the thermometer in a transparent, evacuated container, Fig. 11.4.

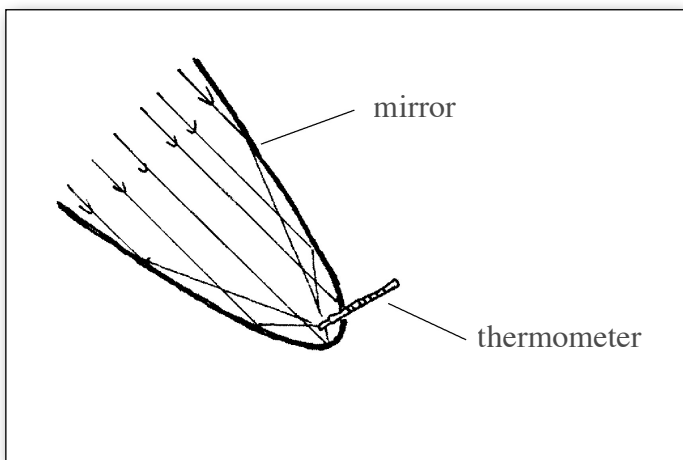


**Fig. 11.4**

Thermal contact with the air has been prevented, but sunlight only comes from a very small range of the solid angle.

However, the temperature value it now displays is still far from the expected 6000 K. The reason is that we missed something else. In fact, the thermometer makes another compromise: it is not only in thermal contact with the sunlight, but also with the radiation from the environment, i.e. radiation at ambient temperature. And while solar radiation only comes from a very small range of the solid angle, the 300 K radiation comes from a very large range. It is therefore normal that this time too the measurement is very much in favor of the ambient temperature.

But how can the temperature of the sunlight be measured? One simply has to make sure that sunlight does not only come from a narrow range of the solid angle, but from all directions, and this is achieved with the help of lenses and mirrors, Fig. 11.5. If, from the thermometer, the sun can be seen in all directions, it will also indicate the temperature of the sun (our normal thermometers are of course no longer suitable for this).



**Fig. 11.5**

The sunlight comes from all directions of the front hemisphere.

### 11.4 The chemical potential of light

We consider a container with reflecting walls with a dust particle filled with radiation whose chemical potential is initially not equal to zero. Since the container has a fixed volume and is energetically insulated, the energy differential reduces to:

$$0 = TdS + \mu dn$$

Because of the dust particle, the amount of substance  $n$  can change. Such a change will occur if thereby the entropy increases, until  $S$  does not increase any further, i.e. until

$$dS = -\frac{\mu}{T} dn$$

has become equal to zero. This is the case when  $\mu$  has become zero (the chemical potential depends on  $n$ ). The resulting light with  $\mu = 0$  is black-body radiation.

For black-body radiation is  $\mu = 0$ .

There is also thermal radiation, i.e. light of a uniform temperature, with  $\mu \neq 0$ . It is obtained by bringing light into equilibrium with another system whose chemical potential is not equal to zero, e.g. the excited electron system of a semiconductor (electrons + holes). This kind of thermal radiation is not called black-body radiation.

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## 11.5 Radiance

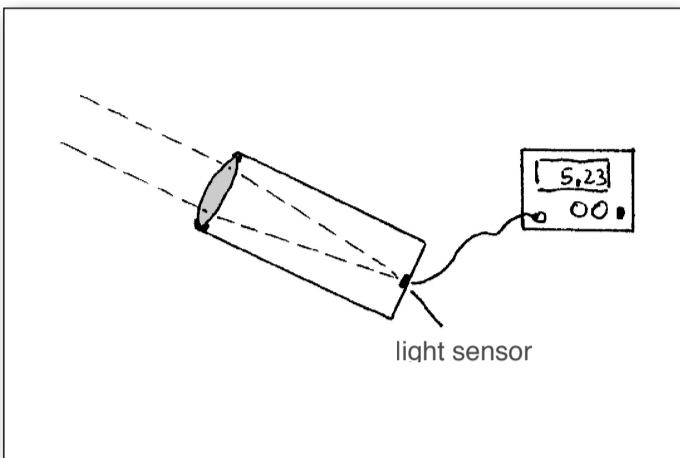
We are looking for a quantity that describes a light field. We are used to describe fields by the distribution of physical quantities in space, more precisely: in positional space. For example, an electric field is described by the spatial distribution of the electric potential  $\Phi(x,y,z)$ , or a material gas by the spatial distribution of its temperature  $T(x,y,z)$  and its pressure  $p(x,y,z)$ .

In a light field, not only the amount of light at each position is of interest, but also the distribution of the light in the different directions at each position. The field quantity we use to describe the light, the *radiance*, is therefore a function of the position and of the direction. We take the energy of light as a measure of the amount of light and define the radiance  $L_E$ :

$$P = \iint_{A \Omega} L_E d\bar{\Omega} d\bar{A}$$

$P$  is the energy current,  $d\bar{\Omega}$  the solid angle element and  $d\bar{A}$  the area of the surface element. The radiance  $L_E$  is therefore the energy current per area and solid angle or the energy current density per solid angle.

One can easily visualize  $L_E$  by looking at a measuring method for the quantity, Fig. 11.6.



**Fig. 11.6**

Measuring radiance. The instrument measures the radiance at the position of the inlet opening and for the direction of the optical axis of the instrument.

The instrument measures the radiance at the position of the lens through which the light enters it and of the direction of the optical axis of the device. By changing the orientation of the instrument at a fixed location, the radiance at this location is obtained as a function of the direction. By shifting it parallel to itself one gets the radiance of a given direction for different positions.

If the device is moved parallel to itself in the direction of its optical axis, i.e. parallel to a light ray, the measured value does not change – if the light is neither scattered nor absorbed. The radiance is constant on a light ray. The displayed value therefore also makes a statement about the surface element from which the light beam comes.  $L_E$  is therefore also called the *surface brightness*.

We consider a container filled with light and look for the relation between  $L_E$  and the energy density  $\rho_E$ . We first introduce the quantity  $\rho_E'$ , defined by

$$\rho_E = \int \rho_E'(\vartheta, \Phi) d\bar{\Omega} \quad (11.1)$$

$\rho_E'(\vartheta, \Phi) d\bar{\Omega}$  is the energy density of that radiation which propagates into the solid angle element of the direction  $(\vartheta, \Phi)$ .

We now assume that the radiation in our container is isotropic, i.e.  $\rho_E'$  is independent of  $\vartheta$  and  $\Phi$ . Then (11.1) can be integrated:

$$\rho_E = 4\pi \rho_E' \quad (11.2)$$

Now the magnitude of the energy current density  $j_E$  of electromagnetic radiation of a single direction is  $j_E = c \cdot \rho_E$ , so in our case it is

$$L_E d\bar{\Omega} = c \cdot \rho_E' \cdot d\bar{\Omega}$$

or

$$L_E = c \cdot \rho_E'$$

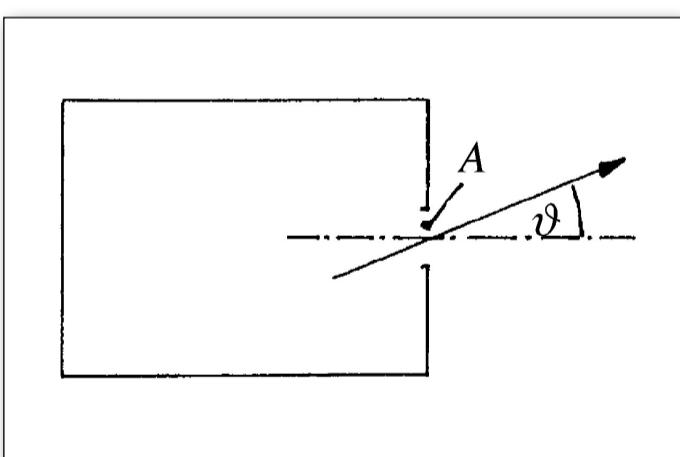
With equation (11.2) we finally obtain

$$\rho_E = \frac{4\pi}{c} L_E \quad (11.3)$$

Instead of the energy, entropy can also be used as a measure of the amount of light. One can thus define an entropy current density per solid angle  $L_S$ , and for the entropy density  $\rho_S$  in the container filled with isotropic light one gets

$$\rho_S = \frac{4\pi}{c} L_S \quad (11.4)$$

We are now looking at a container filled with black-body radiation. We ask how much energy flows through an opening of surface  $A$  out of the container into a solid angle element of the direction  $\vartheta$ , Fig. 11.7.



**Fig. 11.7**

Lambert's law

With

$$d\bar{\Omega} d\bar{A} = d\Omega dA \cos \vartheta$$

we get

$$P = \iint_{A \Omega} L_E d\bar{\Omega} d\bar{A} = \iint_{A \Omega} L_E \cos \vartheta d\Omega dA = A \int_{\Omega} L_E \cos \vartheta d\Omega$$

or

$$dP(\vartheta) = A L_E \cos \vartheta d\Omega$$

The energy current  $dP(\vartheta)$  into a solid angle element  $d\bar{\Omega}$  which lies in the direction  $\vartheta$  is smaller by the factor  $\cos \vartheta$  than that which flows into an equal solid angle element perpendicular to the surface. This statement is known as *Lambert's law*.

For the isotropic radiation of interest to us,  $L_E$  can be drawn in front of the integral, and with

$$d\Omega = \sin \vartheta d\vartheta d\Phi$$

( $\Phi$  = azimuth) we obtain

$$P = A L_E \int_0^{\pi/2} \underbrace{\sin \vartheta \cos \vartheta d\vartheta}_{1/2} \int_0^{2\pi} \underbrace{d\Phi}_{2\pi} = A L_E \pi$$

Dividing this expression by the surface area  $A$  results in the magnitude of the energy current density.

$$j_E = L_E \pi.$$

With equation (11.3) we obtain the relationship between the energy density  $\rho_E$  in the container and the energy current density  $j_E$  of the light exiting through an opening:

$$j_E = \frac{c}{4} \rho_E \quad (11.5)$$

The entropy current density is obtained in an analog way

$$j_S = \frac{c}{4} \rho_S \quad (11.6)$$

## 11. Light as a gas

---

### 11.6 Stefan-Boltzmann law

The energy current per surface area of the light emitted by a black body depends only on the temperature of the body. It was found experimentally

$$j_E = \sigma T^4 \quad \text{with } \sigma = 5.670 \cdot 10^{-8} \text{ Wm}^{-2}\text{K}^{-4} \quad (11.7)$$

This relation is called the *Stefan-Boltzmann law*;  $\sigma$  is the Stefan-Boltzmann constant.

With equation (11.5) follows

$$\rho_E = \frac{4\sigma}{c} T^4$$

We use the abbreviation

$$a = \frac{4\sigma}{c} = 7,566 \cdot 10^{-16} \text{ Jm}^{-3}\text{K}^{-4} \quad (11.8)$$

and obtain

$$\rho_E = aT^4 \quad (11.9)$$

It follows

$$E = aVT^4 \quad (11.10)$$

In addition, with (11.3) we get

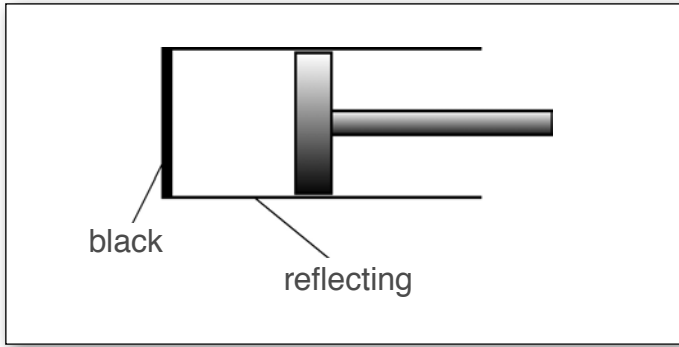
$$L_E = \frac{\sigma}{\pi} T^4$$

In words: Energy density, radiance and total energy in a black body increase with the 4th power of the temperature.

---

## 11.7 Pressure and entropy of thermal radiation as a function of temperature

We consider the black-body radiation in a cylinder whose rear wall is black and at temperature  $T$ , Fig. 11.8. We choose  $T$  and  $V$  as independent variables. If the piston is shifted to the right, the black wall emits more than it absorbs, just so that the newly created volume is filled with radiation of the same density as the radiation had before.



**Fig. 11.8**

When the piston is pulled out, the black surface emits light so that the density of the radiation in the cylinder remains constant.

From the energy differential of the black-body radiation, i.e. of radiation with  $\mu = 0$

$$dE = TdS - pdV$$

we get

$$dS = \frac{1}{T}dE + \frac{p}{T}dV$$

From equation (11.10) we obtain

$$dE(T, V) = 4aVT^3dT + aT^4dV$$

By inserting it into the preceding equation, the following results

$$\begin{aligned} dS(T, V) &= 4aVT^2dT + aT^3dV + \frac{p}{T}dV \\ &= 4aVT^2dT + \left( aT^3 + \frac{p}{T} \right) dV \end{aligned}$$

Comparing with

$$dS(T, V) = \frac{\partial S(T, V)}{\partial T}dT + \frac{\partial S(T, V)}{\partial V}dV$$

we get

$$\frac{\partial S(T, V)}{\partial T} = 4aVT^2 \quad \text{and} \quad \frac{\partial S(T, V)}{\partial V} = aT^3 + \frac{p}{T} \quad (11.11)$$

Partial derivation of the first relationship with respect to  $V$  and the second with respect to  $T$ , and equating results in

$$4aT^2 = 3aT^2 + \frac{1}{T} \frac{dp}{dT} - \frac{p}{T^2}$$

and from this we obtain

$$aT^3 = \frac{dp}{dT} - \frac{p}{T}$$

This differential equation has the solution

$$p = \frac{a}{3}T^4 \quad (11.12)$$

Thus, also the pressure of black-body radiation goes with the 4th power of the temperature. With equation (11.9) we also get

$$p = \frac{\rho_E}{3} \quad (11.13)$$

We will add a plausibility check that delivers the same result.

We decompose the radiation in a rectangular container into 6 parts, each running towards one of the walls. Each component corresponds to a momentum current density, which, according to Maxwell's theory, is equal to the energy density:

$$j_{pi} = \rho_{Ei}$$

With  $\rho_{Ei} = \rho_E/6$  we get

$$j_{pi} = \rho_E/6.$$

The momentum current flowing into the reflecting wall is twice as large as that of the incident radiation, i.e.

$$p = 2j_{pi} = \rho_E/3,$$

that is, the same expression as (11.13).

We finally ask for the entropy density

$$\rho_s(T) = \frac{\partial S(T, V)}{\partial V}$$

of the black-body radiation. With (11.11) and (11.12) we get

$$\rho_s(T) = \frac{4}{3}aT^3$$

From this we obtain the total entropy

$$S = \frac{4}{3}aVT^3$$

The temperature dependence of the entropy is therefore the same as that of a phonon gas in a solid, Section 6.2.

With equation (11.4) follows

$$L_s = \frac{c}{3\pi}aT^3$$

Finally, we obtain the relation between energy and entropy:

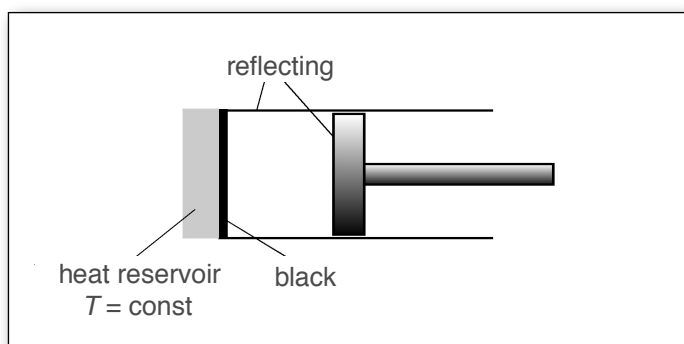
$$E(S, V) = 0,681 \cdot \sqrt[3]{\frac{S^4}{aV}}$$

## 11.8 Isothermal, isentropic and isoenergetic expansion of light

*Isothermal expansion, Fig. 11.9*

The piston is moved. The heat reservoir ensures  $T = \text{const}$ . With the results of the previous section we get:

$$\begin{aligned} E &\sim V \\ S &\sim V \\ \rho_E &= \text{const} \\ \rho_S &= \text{const} \\ p &= \text{const} \end{aligned}$$

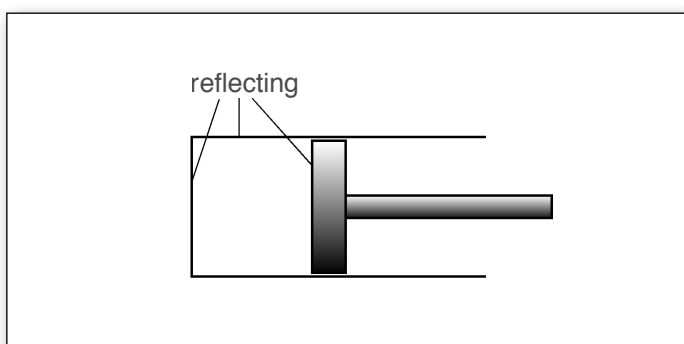


**Fig. 11.9**  
Isothermal expansion of light

*Isentropic expansion, Fig. 11.10*

The reflecting walls ensure  $S = \text{const}$ . During the expansion, the light remains thermal. With the results of the previous section follows:

$$\begin{aligned} V \cdot T^3 &= \text{const} \\ p \cdot V^{4/3} &= \text{const} \\ E/T &= \text{const} \end{aligned}$$



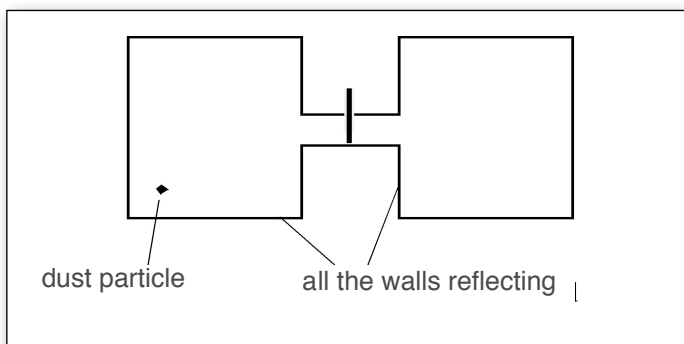
**Fig. 11.10**  
Isentropic expansion of light

*Isoenergetic expansion, Fig. 11.11*

This is the analog to the Gay-Lussac experiment. At first, there is light only in the left container. Then the connection to the right is established. With the results of the previous section:

$$\begin{aligned} V \cdot T^4 &= \text{const} \\ S \cdot T &= \text{const} \\ p \cdot V &= \text{const} \end{aligned}$$

In this expansion,  $T$  decreases according to the first equation. The second tells us that  $S$  increases, as it has to be because of the 2nd law.



**Fig. 11.11**  
Isoenergetic expansion of light

*The cosmic background radiation*

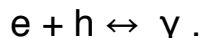
The last two of the processes described above cannot be realized in the laboratory, since even the best mirrors absorb so strongly that the light is always in thermal equilibrium with the cylinder wall. In nature, however, an isentropic expansion is realized: The universe is expanding, and the light that fills the cosmos and had 400,000 years after the Big Bang a temperature of 3000 K continues to cool down. Today its temperature is 2.7 K. It is called *cosmic background radiation*.

*The gas-condensate analogue*

The fact that during the isothermal expansion or compression of light, Fig. 11.9, the values of all intensive variables remain constant and the values of the substance-like quantities are proportional to the volume, is something we know from the material gases: a material gas behaves in the same way when it is in equilibrium with its condensate. The black walls in the experiment with the light correspond to the condensate. When the volume is increased, new light comes out of the walls, when it is reduced it disappears into them. The light reacts with the wall, more precisely: with the electron and phonon system of the wall, and the chemical potentials of light and wall are always equal (and equal to zero). Equation (11.12) corresponds in this picture to the vapor pressure curve.

## 11.9 Light with non-zero chemical potential

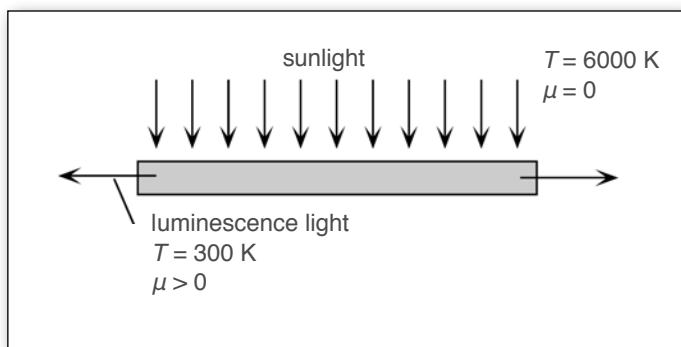
To generate thermal radiation with  $\mu \neq 0$  light is brought into chemical equilibrium with reaction partners whose chemical potential is not equal to zero. For example, the reaction



$e$  and  $h$  are electrons or holes in a semiconductor,  $\gamma$  stands for light. In equilibrium it is

$$\mu_e + \mu_h = \mu_\gamma$$

The values of  $\mu_e$  and  $\mu_h$  are known from solid state physics. If one wishes to generate a light beam with  $\mu \neq 0$ , one reaction partner, namely  $\gamma$ , has to be constantly removed. In order to maintain the concentration of electrons and holes, it is necessary to constantly generate new ones. This can be done, for example, by “pumping” with another light source, such as sunlight. The whole process takes place in a luminescent solid, Fig. 11.12.



**Fig. 11.12**

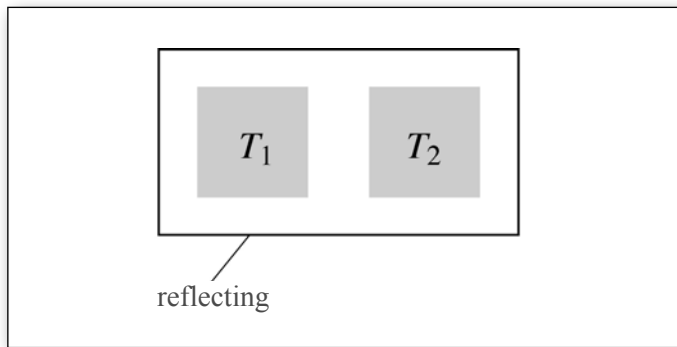
In the luminescent body, the temperature of the light decreases and the chemical potential increases.

The incident light has a high temperature, but  $\mu = 0$ . The emitted light has the temperature of the solid, i.e.  $T \approx 300$  K, but its chemical potential is greater than zero. So the solid body transloads energy – from the carrier entropy to the carrier amount of substance.

Instead of using light, one can also “pump” electrically. This is done in a luminescent diode. This light also has  $T \approx 300$  K and  $\mu > 0$ .

### 11.10 Energy transport with thermal radiation

Two black radiators with different temperatures  $T_1$  and  $T_2$  are located in a reflecting box, so that the radiation emitted by one of them either falls back onto the emitting body or is absorbed by the other body, Fig. 11.13.



**Fig. 11.13**

The radiation emitted by one body is absorbed either by itself or by the other body.

The resulting energy current between the bodies is the sum of one flowing from right to left and one flowing from left to right. The same applies to the entropy current. If the temperatures  $T_1$  and  $T_2$  are not very different, i.e. if  $\Delta T = T_2 - T_1 \ll T_2 = T_1 = T$ , then with (11.7) and (11.8) we get

$$j_E = j_{E2} - j_{E1} = \frac{c}{4} a (T_2^4 - T_1^4) \approx caT^3 \Delta T$$

and with (11.6) and (11.14)

$$j_S = j_{S2} - j_{S1} = \frac{c}{3} a (T_2^3 - T_1^3) \approx caT^2 \Delta T.$$

Thus, for the resulting energy current we get the relation

$$j_E = T \cdot j_S$$

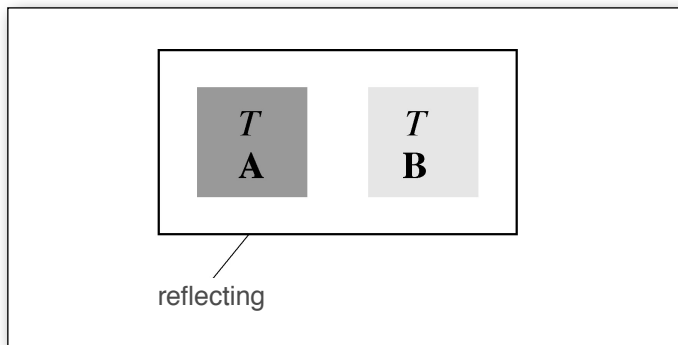
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## 11.11 Kirchhoff's law of radiation

The quotient

$$\alpha = \frac{\text{absorbed energy current}}{\text{incident energy current}}$$

is called the *absorptivity* of a body. Two bodies A and B of the same temperature stand opposite each other in an evacuated container with reflecting walls, Fig. 11.14.



**Fig. 11.14**

Body A is black, it absorbs all radiation, body B does not.

Body A is “black”, it absorbs all radiation, i.e.  $\alpha_A = 1$ . Body B is not black, it only absorbs part of the incoming light and reflects the rest. We call the current density of the energy flowing out of A and B, respectively,  $j_{EA}$  and  $j_{EB}$ . Thus the following applies to the energy flow in the space between the two bodies

$$\text{from left to right: } j_{E\rightarrow} = j_{EA}$$

$$\text{from right to left: } j_{E\leftarrow} = j_{EB} + (1 - \alpha_B) j_{EA}$$

Now no net energy must flow between A and B, otherwise the entropy of the whole arrangement would decrease. So

$$j_{E\rightarrow} = j_{E\leftarrow}$$

and

$$j_{EB} = \alpha_B \cdot j_{EA}$$

We now call  $j_{EA} = j_{E,\text{black}}$ , omit the index B and obtain

$$\frac{j_E}{\alpha} = j_{E,\text{black}}$$

The quotient of the energy current density of the emitted radiation and the absorptivity is the same for all bodies. It only depends on temperature. One can place a color filter in front of each of the two bodies, which transmits radiation of a single frequency  $\nu$ , and reflects the rest. The same consideration as above then shows that the relationship just derived applies to each frequency individually:

$$\frac{dj_E/d\nu}{\alpha} = dj_{E,\text{black}}/d\nu$$

or

$$\frac{dj_E/d\nu}{\alpha} = f(T, \nu)$$

This is *Kirchhoff's law of radiation*.

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# 12

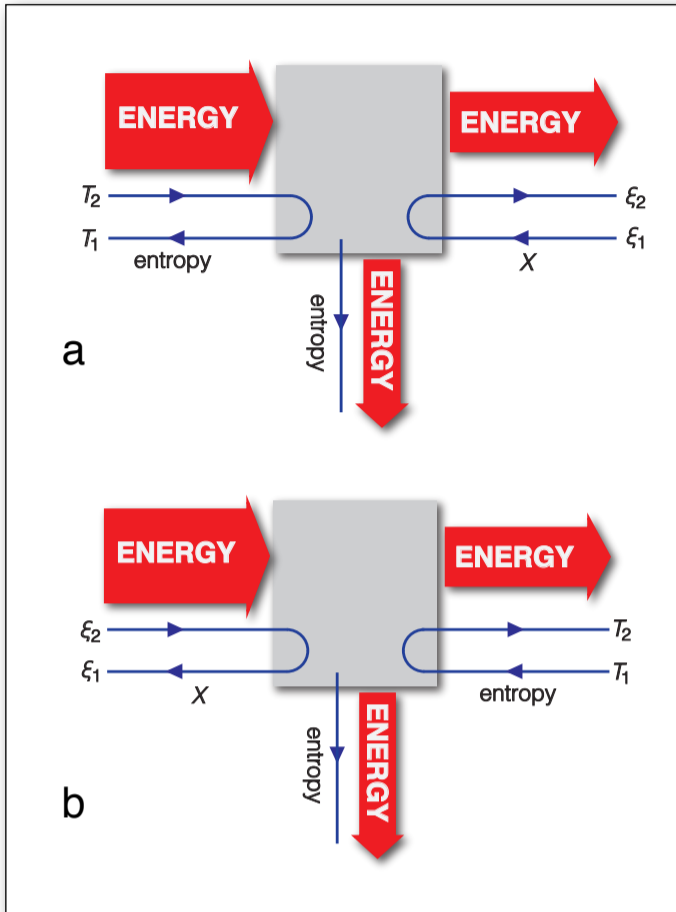
## Heat engines

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## 12.1 Overview

We are dealing with devices and machines in which entropy  $S$  is brought from a high temperature  $T_2$  to a low temperature  $T_1$  and thereby the potential  $\xi$  of another extensive quantity  $X$  is increased, and also with machines in which the opposite happens: the potential of a quantity  $X$  decreases and entropy is raised from low to high “thermal potential  $T$ ”. Such machines can be represented schematically as shown in Figures 12.1a and 12.1b.

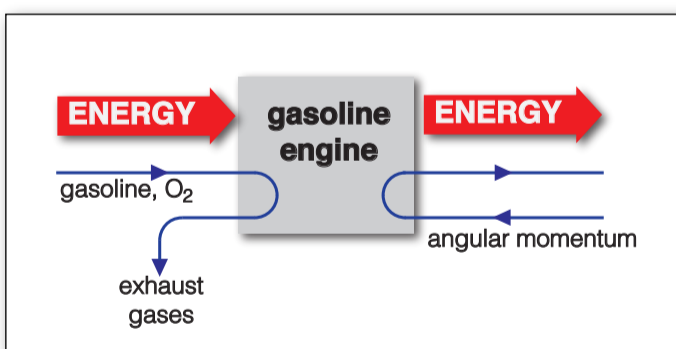


**Fig. 12.1**

(a) Flow diagram of a heat engine;  
(b) Flow diagram of a heat pump

The entropy flowing downwards in the diagrams is the unintentionally produced entropy. If the carrier of the out-flowing energy is angular momentum, the machine is called a *heat engine* or thermal motor. In the case of the solar cell, the thermocouple and the MHD generator, the carrier of the energy flowing out is electric charge.

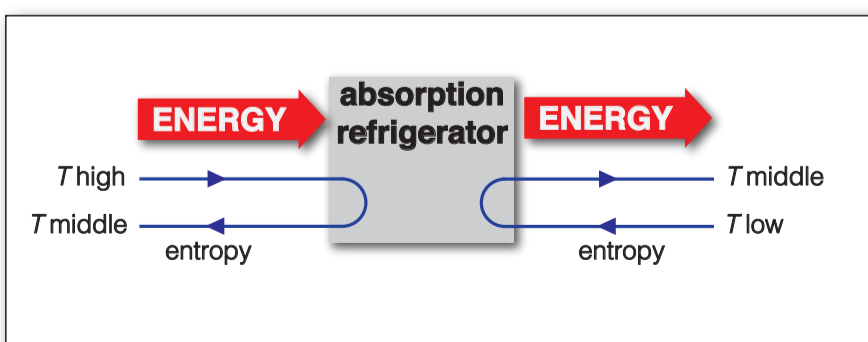
The name of a machine often includes more than what is shown in Fig. 12.1. As is well known, the gasoline engine is a machine into which the energy enters with the carrier gasoline +  $O_2$ , Fig. 12.2. The entropy is generated within the engine.



**Fig. 12.2**

Flow diagram of a gasoline engine

Machines of the type shown in Figure 12.1b are called *heat pumps*. Heat pumps are used for heating and for cooling. There is a special type of heat pump, where the energy carrier is entropy on both sides: the absorption refrigerator, Fig. 12.3. Its structure is analog to that of the electric transformer.



**Fig. 12.3**

Flow diagram of an absorption refrigerator

### 12.2 Why heat engines?

Cars need energy carried by angular momentum. Electricity-based energy is particularly suitable for distribution to many small consumers. But we get our energy from natural sources with other energy carriers.

Our energy sources are of two kinds.

- The inexhaustible sources: One taps into a natural energy flow. This is done in hydro, wind and solar power plants.
- The exhaustible sources: Energy has accumulated on the earth in processes that have lasted billions of years. These stocks are currently being emptied, and on a historical time scale, very quickly. At present, but of course not for much longer, they are man's most important source of energy.

Energy is now being squandered not only in that the natural energy stores are being depleted ruthlessly, but also in that the energy is being transloaded with a poor efficiency from the energy carriers with which it is obtained in nature, to the energy carriers of angular momentum and electricity that people prefer.

We had seen in section 2.7 that the cause of all energy losses is entropy production. However, entropy production is the first step in virtually all technical processes for the exploitation of natural energy reservoirs. In order to obtain energy with the carrier angular momentum or electricity, heat engines are used – machines that need entropy at a high temperature at their input. This entropy is obtained by production, and this is one of the reasons for the poor efficiency of the energy industry. We had seen (equation (2.9) in section 2.7) that this alone is the cause of a factor

$$\eta = \frac{T_2 - T_1}{T_2}$$

to the efficiency. Here  $T_1$  is at best the ambient temperature, i.e. about 300 K, and  $T_2$  the highest temperature that can be technically controlled, i.e. about 800 K. Consequently, just because of the entropy production a factor

$$\eta = \frac{800 \text{ K} - 300 \text{ K}}{800 \text{ K}} \approx 0.63$$

results.

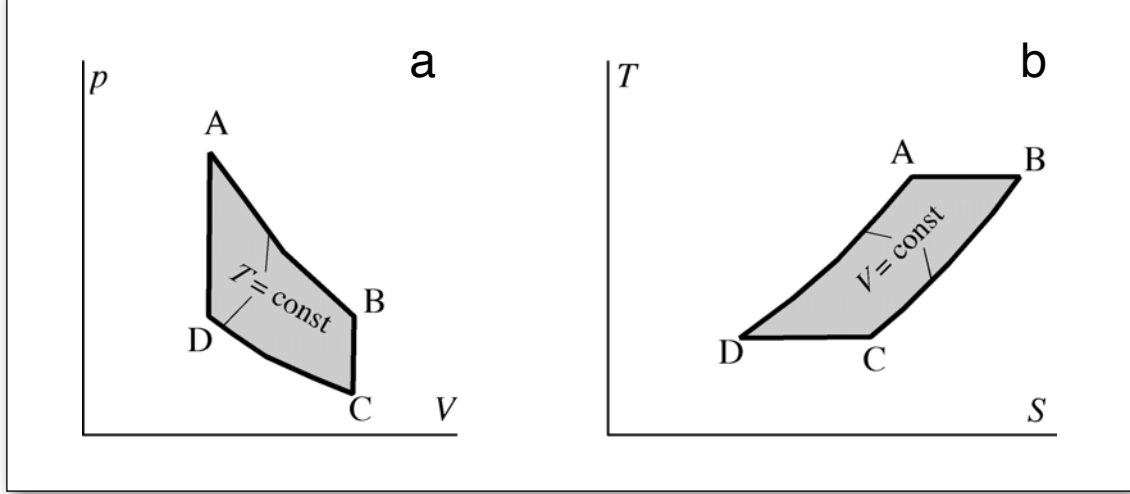
Actually, the efficiency of heat engines is considerably lower: between 0.3 and 0.4.

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## 12.3 External combustion engines

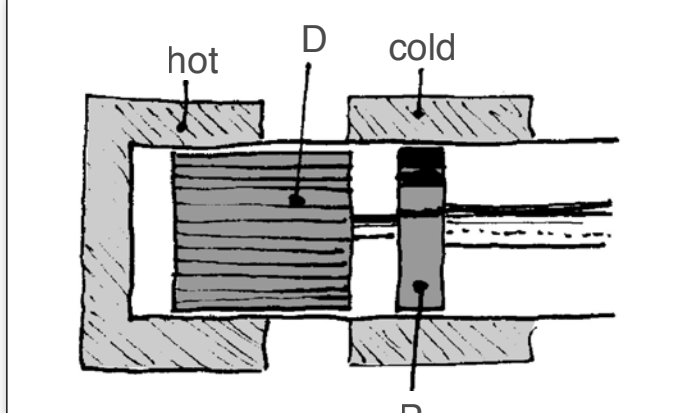
### Cyclically operating machines – the Stirling cycle

Fig. 12.4 shows the  $p$ - $V$  and the  $T$ - $S$  diagram of the idealized Stirling cyclic cycle.



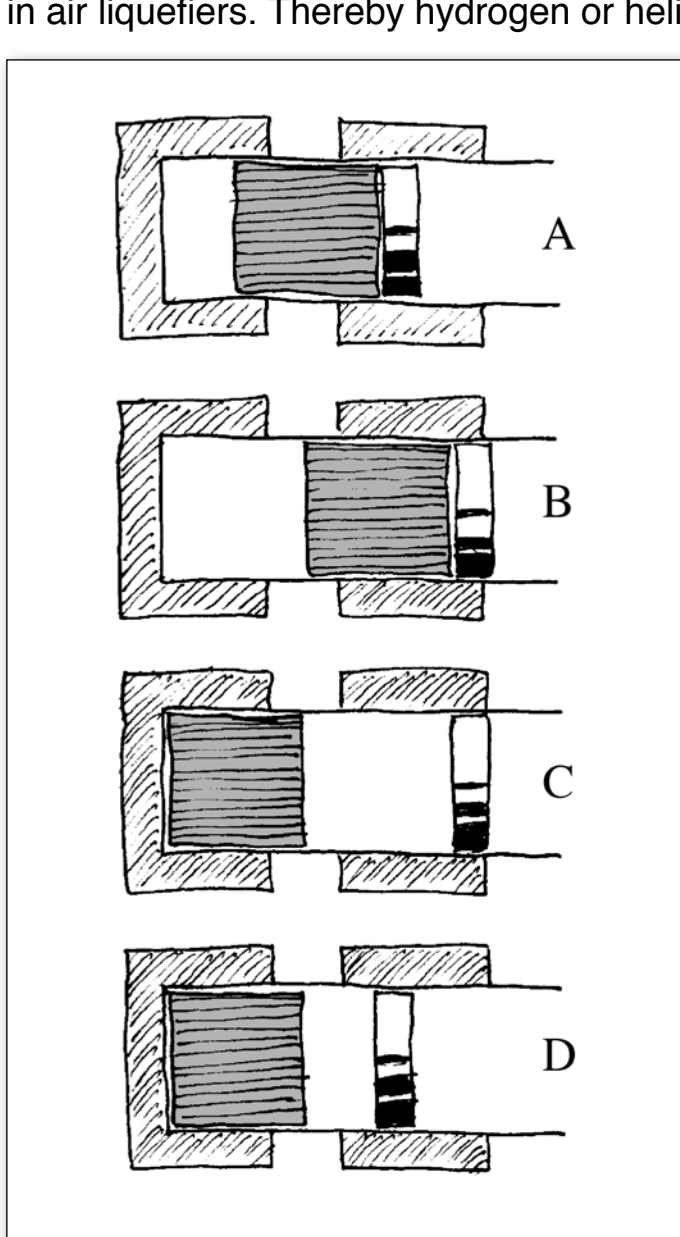
**Fig. 12.4**  
Stirling cycle (a) in the  $p$ - $V$  and (b) in the  $T$ - $S$  diagram

The process is approximately realized in a Stirling or hot air engine, Fig. 12.5. A piston (P) moves back and forth in a cylinder filled with air. The cylinder is heated on the left and cooled on the right. In addition to the piston, the “displacer” (D) also runs back and forth, phase-shifted against the piston. The displacer is permeable to air, but has a large heat capacity and a large surface area, so that it exchanges entropy with the passing air.



**Fig. 12.5**  
Stirling engine

Fig. 12.6 shows the piston and displacer positions corresponding to the four states A to D. The same process running backwards is used in air liquefiers. Thereby hydrogen or helium is the working fluid.



**Fig. 12.6**  
Stirling engine, 4 phases

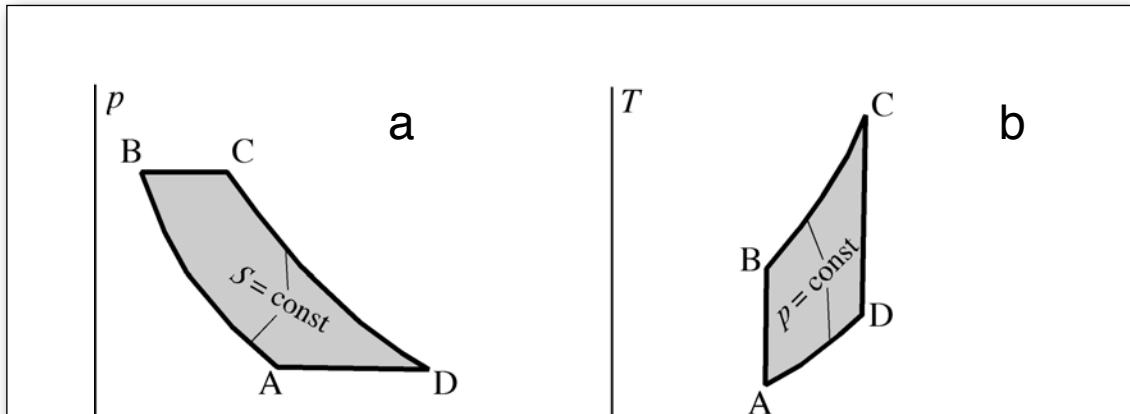
### Continuous flow machines

In a continuous flow machine, the working medium flows in a circuit. The flow is stationary. For a small portion of the working fluid that is traced on its way through the circuit, a closed curve can be specified in the  $p$ - $V$  and  $T$ - $S$  diagrams, just as for the cyclically operating machines.

### The Brayton cycle

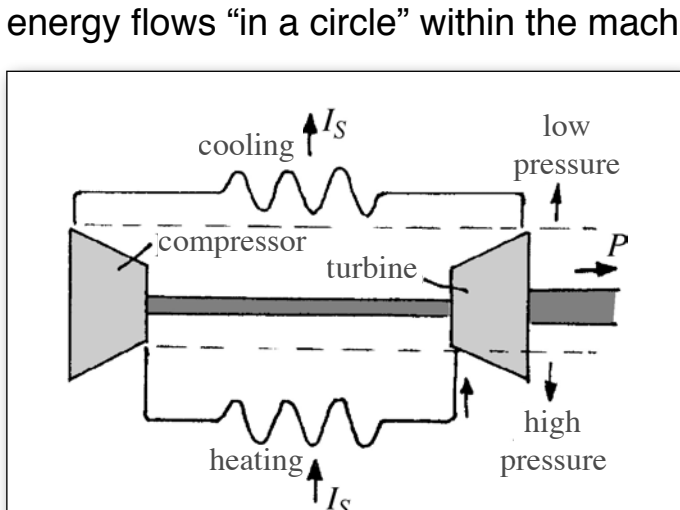
Fig. 12.7 shows the  $p$ - $V$  and the  $T$ - $S$  diagram.

- AB The gaseous working fluid is isentropically compressed.
- BC At constant high pressure entropy is supplied to the gas.
- CD The gas expands isentropically.
- DA The gas releases entropy at low constant pressure.



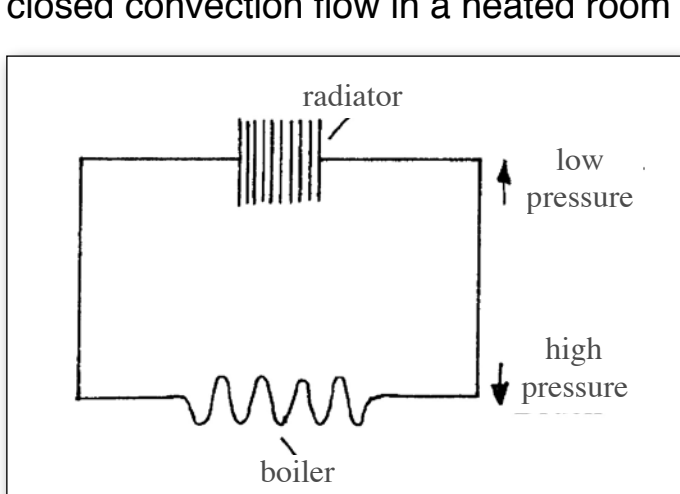
**Fig. 12.7**  
Brayton cycle (a) in the  $p$ - $V$  and (b) in the  $T$ - $S$  diagram

The Brayton cyclic process is realized in a closed-cycle gas turbine plant, Fig. 12.8. The compressor is driven by the turbine. Part of the energy flows “in a circle” within the machine.



**Fig. 12.8**  
Brayton cycle

The self-circulating central heating, Fig. 12.9, also represents an example of this process. The pressure difference between the entropy input and entropy output is provided by the gravitational field. A closed convection flow in a heated room is also such a process.



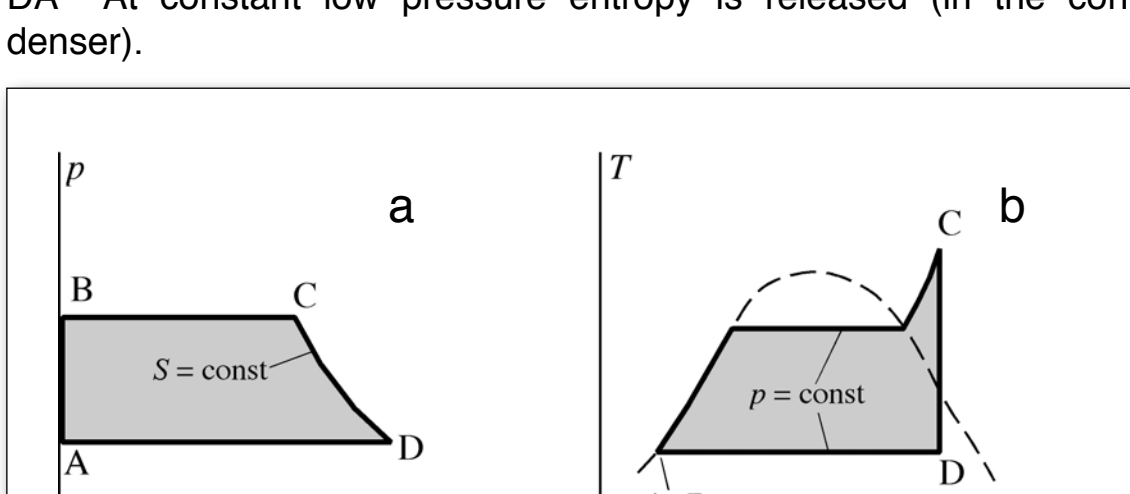
**Fig. 12.9**  
Self-circulating central heating

A more complicated variant of the Brayton cycle is the Ericson cycle. Here, compression and expansion are broken down into sub-steps between which entropy is taken from or supplied to the gas, so that compression and expansion are almost isothermal. This process was used in the helium turbine plant of high-temperature nuclear reactors.

### The Rankine cycle

The Rankine cyclic process is the process that realized in steam engines. It is very similar to the Joule process. It differs from the Joule process in that the working fluid (usually water) makes phase transitions during the cyclic process, Fig. 12.10.

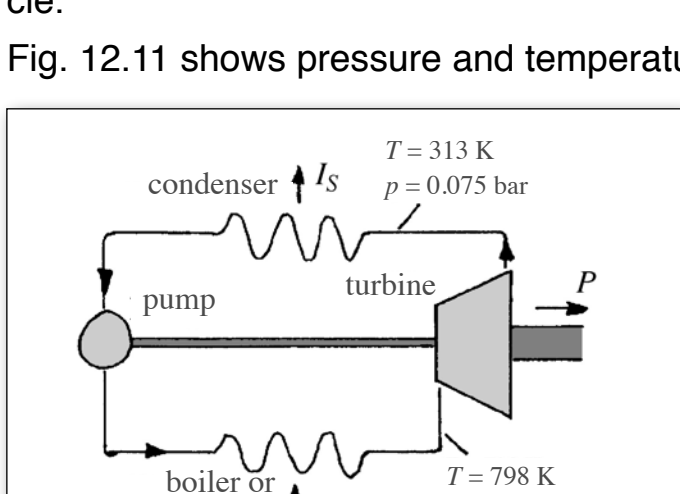
- AB The pressure of the liquid working fluid is isentropically increased (in the feedwater pump).
- BC At constant high pressure entropy is supplied to the fluid (in the boiler or steam generator).
- CD The steam expands isentropically (in the turbine).
- DA At constant low pressure entropy is released (in the condenser).



**Fig. 12.10**  
Rankine cyclic process (a) in the  $p$ - $V$  and (b) in the  $T$ - $S$  diagram

An advantage of this process is that only a feed water pump is required instead of a compressor. As a result, the energy flowing around within the machine is much lower than with the Brayton cycle.

Fig. 12.11 shows pressure and temperature values of a power plant.



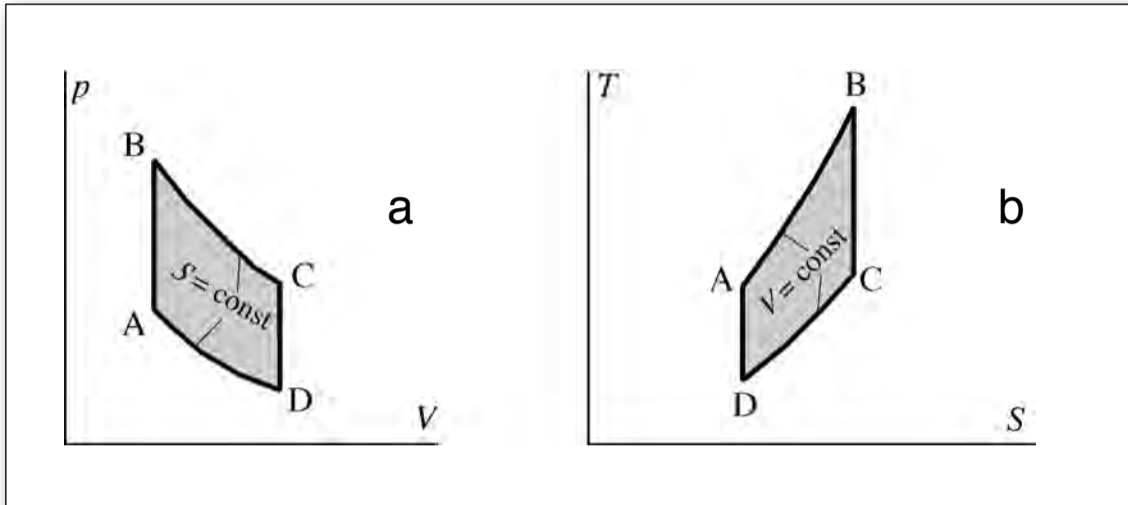
**Fig. 12.11**  
Steam turbine system

Most steam locomotives had no condenser. The steam at the outlet of the engine therefore had to have a pressure  $p > 1$  bar and a temperature  $\vartheta > 100$  °C. The temperature drop between 100 °C and ambient temperature was therefore not exploited.

## 12.4 Internal combustion engines

### Cyclically operating machines – the gasoline engine

Fig. 12.4 shows the  $p$ - $V$  and the  $T$ - $S$  diagram of the Otto cycle which is an idealization of the process that runs in the gasoline engine.



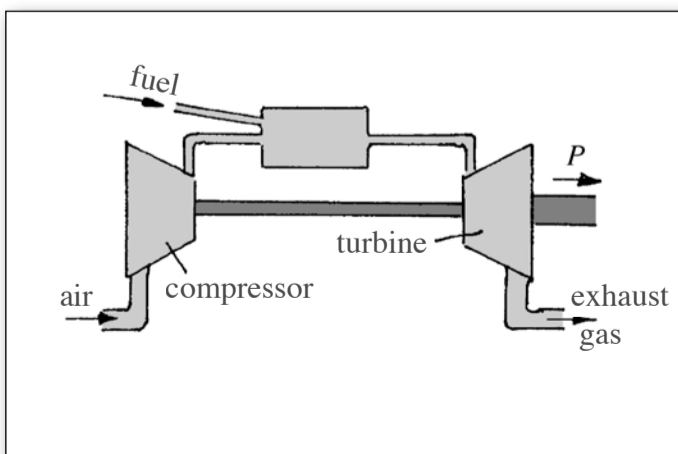
**Fig. 12.12**

Idealized process of the gasoline engine (a) in the  $p$ - $V$  and (b) in the  $T$ - $S$  diagram

The increase in entropy in process step AB is caused by entropy production within the cylinder, by the combustion of gasoline. This happens at the top dead center, and so quickly that the volume practically does not change during the combustion process. BC is the power stroke. The hot gas ( $N_2$ ,  $H_2O$  and  $CO_2$ ) expands. The process step CD does not actually consist of cooling the gas at a fixed volume. Instead, the gas is replaced by fresh, cold gas in a further piston stroke. In process step DA, the fresh gas is isentropically compressed.

### Continuous flow machines – the gas turbine

The process is essentially the same as the Brayton cycle, Fig. 12.13. The working fluid is air – whose oxygen, however, combines with the fuel to other gases ( $H_2O$  and  $CO_2$ ). The compressor compresses air from the surroundings. Entropy is supplied in the combustion chambers by burning the fuel. The hot gases expand in the turbine. In the jet engine, the turbine is designed so that it only drives the compressor. The gas leaving the turbine then has a high velocity relative to the engine. This means that a momentum current flows from the outflowing gas into the engine – and from there into the aircraft.



**Fig. 12.13**

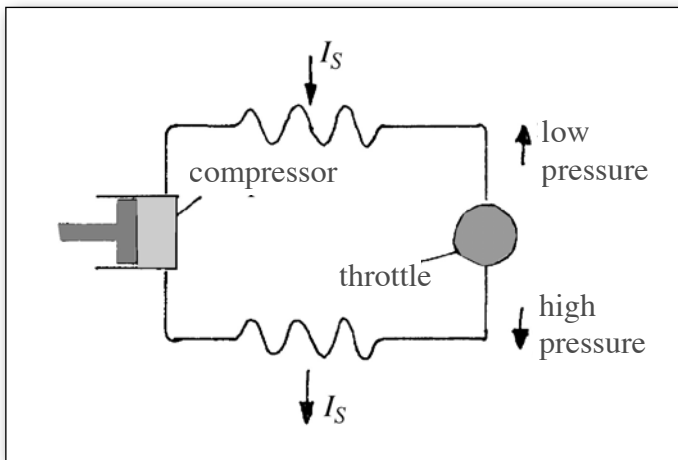
Gas turbine system

## 12.5 Heat pumps

Any heat engine working reversibly can operate as a chiller. Internal combustion engines are not suitable, since irreversibility is fundamental for their operation.

### *Inversed Stirling and Rankine process*

It has already been mentioned that the Stirling engine can operate as a chiller. However, the most common process is the reverse Rankine process: it is used in most refrigerators and freezers, Fig. 12.14. Instead of in an expansion machine, the working fluid expands in a throttle ( $E + pV = \text{const}$ ). This makes the refrigerator less efficient, but it is less complicated.

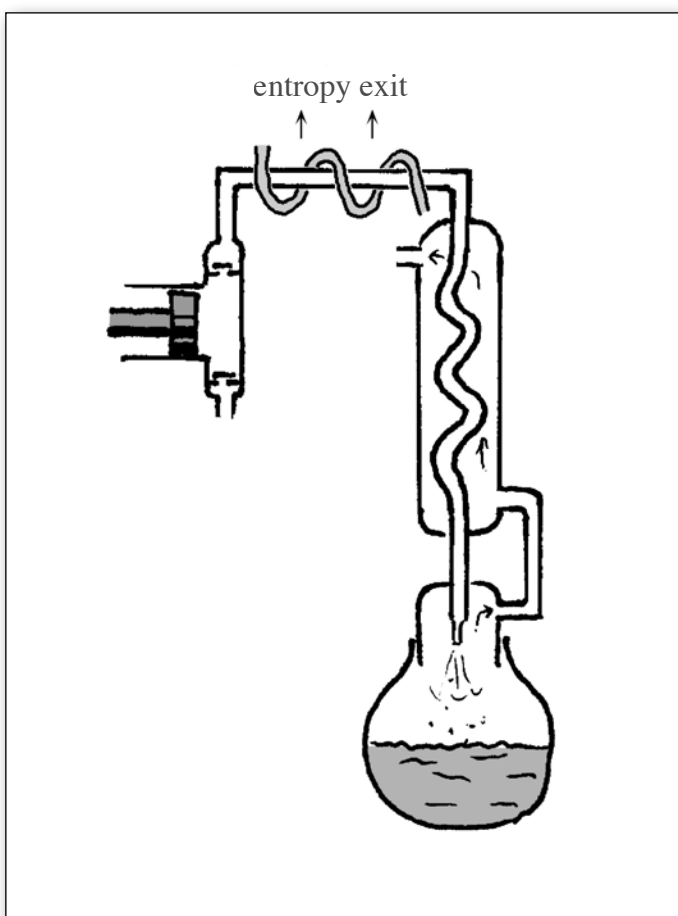


**Fig. 12.14**

In the refrigerator, a Rankine process runs in reverse.

### *The Hampson-Linde cycle*

It is used for the liquefaction of gases, Fig. 12.15. The gas is compressed to 100 to 200 bar and expands in a throttle. It cools down due to the Joule-Thomson effect. This cooled gas is used to pre-cool the incoming gas. As a result, the temperature of the expanded gas becomes lower and lower until part of it finally becomes liquid. Gases whose inversion temperature is below normal temperature, such as  $\text{H}_2$  or  $\text{He}$ , must first be brought below the inversion temperature by another procedure.



**Fig. 12.15**

The Linde-Hampson cycle

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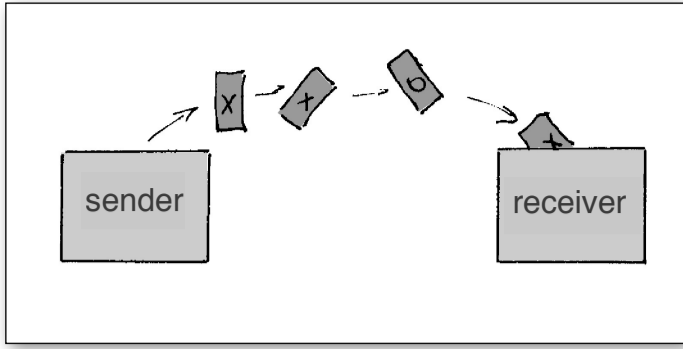
# 13

## Entropy and probability

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### 13.1 Amount of data

We want to transmit messages using cards, Fig. 13.1: Each card can contain one of  $z$  symbols or characters agreed between sender and receiver, e.g. one of the letters of the alphabet.



**Fig. 13.1**  
A data current flows from the sender to the receiver.

We are looking for a measure of the amount of data that is transferred with one card. For simplicity's sake, we first consider the case that there are only two characters, e.g. a cross and a circle. Thus, our *character set* contains  $z = 2$  characters. With one card one of two possible messages can be transmitted; one can choose between two messages. With two cards (sent in order) one can choose between  $2 \cdot 2 = 4$  messages, and with  $n$  cards between  $2^n$  messages.

One could use the number  $N = 2^n$  as a measure for the amount of data transmitted with  $n$  cards. However, the measure defined in this way would have the disadvantage of not being substance-like. This can be seen in the following way.

We send 3 cards first. For 3 cards we have

$$N_a = 2^3 = 8.$$

After that, we'll send two more cards. For two cards alone we have

$$N_b = 2^2 = 4.$$

For all 5 cards together, however

$$N_c = 2^5 = 32.$$

Thus,

$$N_c \neq N_a + N_b.$$

A better measure of the amount of data is the logarithm of the number  $N$  of possible messages. We therefore provisionally define the amount of data  $H$ :

$$H = f \cdot \ln N$$

with  $N =$  number of the possible messages.

The constant  $f$  defines the unit of measurement of  $H$ . For  $N = 2$ , i.e. in the case that a decision is made between two possibilities,  $H = 1$  bit, i.e.

$$1 \text{ bit} = f \cdot \ln 2 \Rightarrow f = \frac{1 \text{ bit}}{\ln 2}$$

With  $n$  cards, an amount of data of

$$H = \frac{1 \text{ bit}}{\ln 2} \ln 2^n = n \text{ bit}$$

will be transferred.

With  $\ln x / \ln 2 = \text{ld } x$  we can also write

$$H = \text{ld } N \text{ bit}$$

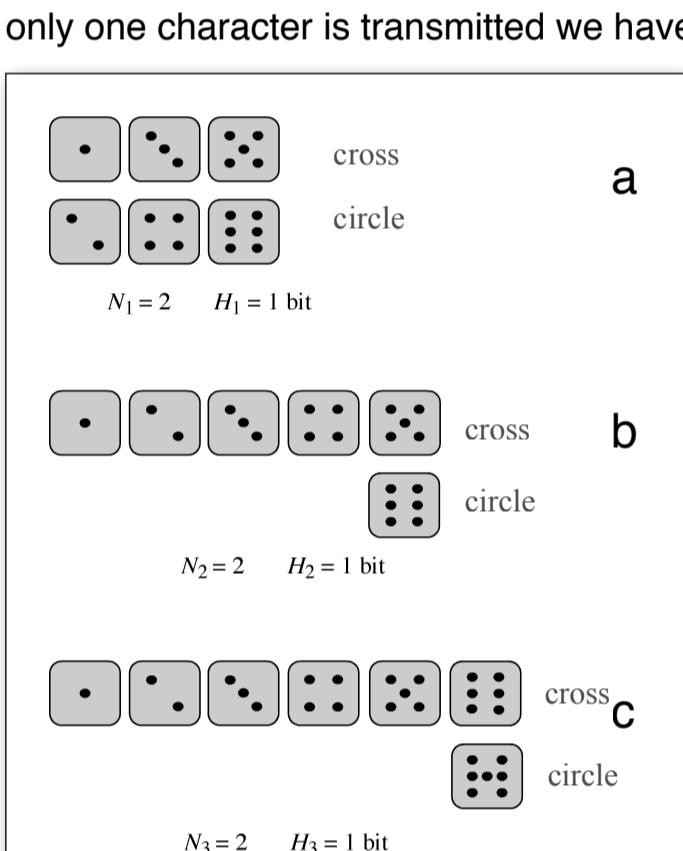
If the number  $z$  of characters of the character set is large, the amount of data per card, and therefore per character, is also large.

With  $z = 32$  we have for one card  $N = 32$ , thus  $H = \text{ld } 32 \text{ bit} = 5 \text{ bit}$ .

Assuming that there are 40 000 Chinese characters, the amount of data transferred with one character is

$$H = \text{ld } 40\,000 \text{ bit} \approx 15 \text{ bit}.$$

We will now convince ourselves that the expression  $f \cdot \ln N$  is still not a good measure of the amount of data. We look at three examples in which one of two possible messages is selected. This means that the character set must contain  $z = 2$  characters. Since each time only one character is transmitted we have  $H = 1$  bit, Fig. 13.2.



**Fig. 13.2**  
Although two characters are used in each case, the amount of data is not the same for the three transmissions (a), (b) and (c).

(a) The sender rolls the dice and tells the receiver whether the result is an even or an odd number.

(b) The sender rolls the dice and tells the receiver whether he has made a 6.

(c) The sender rolls the dice and tells the receiver whether he has rolled a seven.

The formula  $f \cdot \ln N$  returns the same result every time, namely 1 bit. However, from a reasonable amount of data one would expect that

$$H_3 < H_2 < H_1$$

in fact, that even  $H_3 = 0$ , because if the receiver knows the message in advance (in our case, that no seven were rolled), the amount of data he receives with the message should be zero.

A measure that meets this requirement was introduced is:

$$H = -f \cdot \sum_i p_i \ln p_i$$

The sum extends over all possible messages.  $p_i$  is the probability that the message  $i$  will be sent. In the case that all messages are equally likely, we have

$$p_1 = p_2 = p_3 = \dots = p_i = \dots = 1/N,$$

and  $H$  becomes the old expression  $f \cdot \ln N$ .

In our example we have

$$(a) p(\text{pair}) = 0.5 \quad p(\text{impair}) = 0.5 \quad H = 1 \text{ bit}$$

$$(b) p(\text{six}) = 1/6 \quad p(\text{not six}) = 5/6 \quad H = 0.65 \text{ bit}$$

$$(c) p(\text{one to six}) = 1 \quad p(\text{seven}) = 0 \quad H = 0 \text{ bit}$$

The example shows two important properties of this measure of the amount of data:

1) If one of the probabilities is equal to one and all the others equal to zero, we obtain  $H = 0$ :

$$H = -f \cdot \sum_{i=1}^z p_i \ln p_i = -f(z-1) \lim_{p \rightarrow 0} (p \ln p) - f \cdot 1 \cdot \ln 1 = 0,$$

because

$$\lim_{p \rightarrow 0} (p \ln p) = \lim_{p \rightarrow 0} \frac{\ln p}{1/p} = \dots = 0 \quad (\text{l'Hôpital's rule})$$

2) For a given number  $z$  of characters  $H$  is maximum if

$$p_1 = p_2 = p_3 = \dots = p_z.$$

To prove it, the extremum of

$$H(p_1, p_2, \dots, p_z) = -f \cdot \sum_{i=1}^z p_i \ln p_i$$

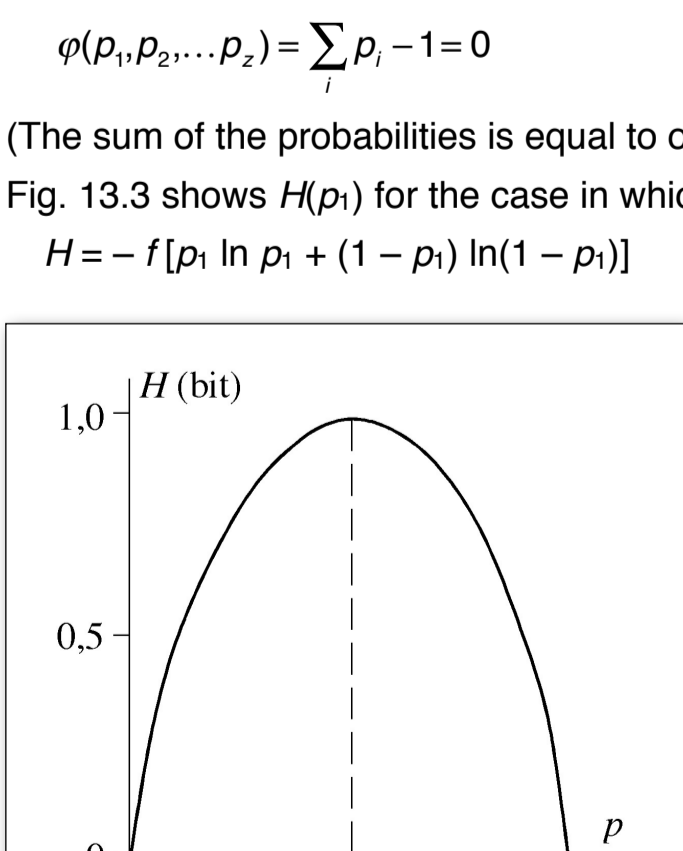
is calculated under the constraint

$$\varphi(p_1, p_2, \dots, p_z) = \sum_i p_i - 1 = 0$$

(The sum of the probabilities is equal to one.)

Fig. 13.3 shows  $H(p_1)$  for the case in which  $z = 2$ :

$$H = -f [p_1 \ln p_1 + (1 - p_1) \ln(1 - p_1)]$$



**Fig. 13.3**  
Amount of data in the case of a transmission with two characters as a function of the probability of the characters

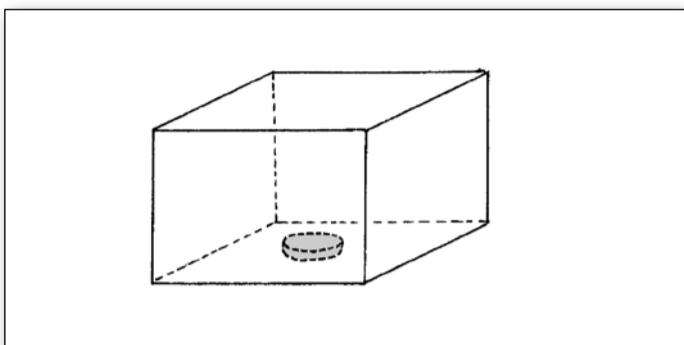
Here we encounter a problem that is also typical for statistical thermodynamics. It is easy to calculate  $H$  for such absurd messages as whether an even or odd number was rolled, because we know the probability distribution of the possible messages. In most cases, however, it is not so easy to specify probabilities.

But how do we know the probabilities of the numbers occurring on the dice? There are two ways for obtaining them: First, we can determine them experimentally. We roll the dice very often and measure the frequency with which the numbers appear. Secondly, we can indicate the probabilities "a priori". We conclude from the symmetry of the dice and the complete indeterminacy of the rolling process that all numbers are equally likely.

## 13.2 Generalization of the concept of state

In section 4.1 we learned: In a particular state, each variable has a specific value. Many real situations cannot be described with this concept of state, namely all those in which the values of variables are not known. We are looking at an example that may seem a bit absurd at first glance, but which makes it easy to explain the problem.

In an opaque box there is a flat magnetic pill whose magnetic moment  $m_0$  is perpendicular to the plane of the disc, Fig. 13.4. Now the box is shaken and placed on the table. We ask for the state of the magnet, whereby we assume that the state is determined only by the value of the magnetic moment.



**Fig. 13.4**

Although one doesn't know which way the magnet is oriented, its state is not completely unknown.

In the sense of our definition of a state given earlier we would have to say: We do not know the state. However, our common sense tells us that we know a lot more than nothing about the magnet, namely

(1) We have either  $m = (0, 0, m_0)$  or  $m = (0, 0, -m_0)$ , but certainly not  $m = (0,5 \cdot m_0, 0, 0)$  etc.

(2) Since we have shaken the box, and since the magnetic disk is symmetrical and neither the box nor the table itself is magnetic, the probability  $p(\uparrow)$  that the magnetic moment points up is 0.5 and the probability that it points down  $p(\downarrow)$  is also 0.5:

$$p(\uparrow) = p(\downarrow) = 0.5$$

We can therefore specify a probability distribution of the values of the variable. This is what we are doing now in order to generalize the concept of state:

In a given state, to the values of each variable belongs a specific probability distribution.

By means of statistical physics it will be possible to specify the state of many systems: the energy and the velocity of the molecules of a gas, the energy of the electrons in a semiconductor, the momentum of the photons in a radiation cavity, the magnetic moment of the particles of a paramagnetic material.

The most important task of statistical physics is to calculate such probability distributions. However, it sounds a bit like magic: One cannot calculate probabilities if one does not enter probabilities somewhere in the calculation – but this is done in statistical physics just the same way as we did with the magnetic disk. The argument is always the same: “The probabilities of all states...[more precise description]... are equal.” The probabilities thus specified are a-priori probabilities. The reason for the equality is: We don't know any reason why they should be different.

Many physicists feel uneasy about this argument. They try to calm down by saying that one can experimentally determine the probabilities, at least in thought. For this one needs the concept of *Gibbs' ensemble*. One imagines that the system to be described exists in a very large number of copies. This is Gibbs' ensemble. The value of the quantity of interest is measured on each copy and a frequency distribution is obtained. This, one says, is equal to the sought-after probability distribution. All statements made about a system are also made about the ensemble. One can say that the ensemble *is* the system. With the help of the ensemble concept one can now describe the state verbally without giving probable values. One specifies the *system preparation*.

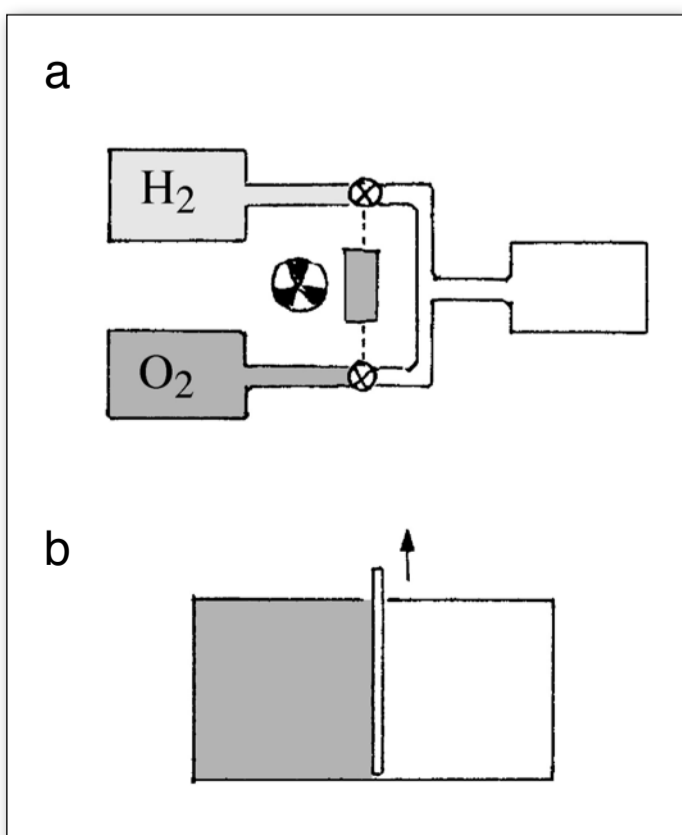
### Examples of system preparations

(1) 1 mol  $H_2$  is in a container which is in thermal contact with a heat reservoir of temperature  $T$ .

(2) One of two valves is opened with the aid of a radioactive material: If a decay takes place within 1 s, 1 mole oxygen flows into a container, if none takes place, 1 mole hydrogen, Fig. 13.5a.

(3) State at time  $t = t_0$ , Fig. 13.5b: In the left compartment there is air of  $T = \dots$ ,  $p = \dots$ . At time  $t_0 - 10^{-8}$  s the wall is pulled out.

(4) Put  $10^5$  molecules one after the other into a container according to the following procedure: Go from your laboratory to the elevator, see how many men and how many women leave. Put one  $O_2$  molecule for each man and one  $N_2$  molecule for each woman into the container. Go back to the elevator etc.



**Fig. 13.5**

(a) In the right container there is with a certain probability pure hydrogen and with another probability pure oxygen.

(b) At time  $t_0$  the gas has partially invaded the right side of the container.



### 13.3 Entropy of a distribution

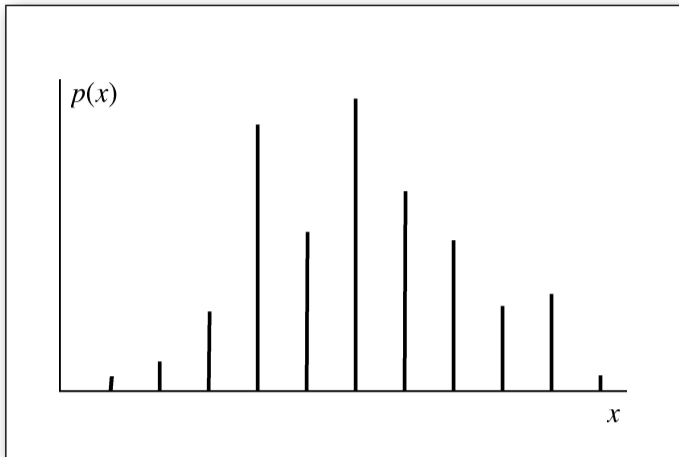
Fig. 13.6 shows the probability distribution  $p(x)$  over the values of a variable  $x$ . With this distribution several quantities or numbers can be defined.

mean of  $x$ : 
$$\bar{x} = \sum_i p(x_i)x_i$$

variance of  $x$ : 
$$S(\Delta x)^2 = \sum_i p(x_i)(x_i - \bar{x})^2$$

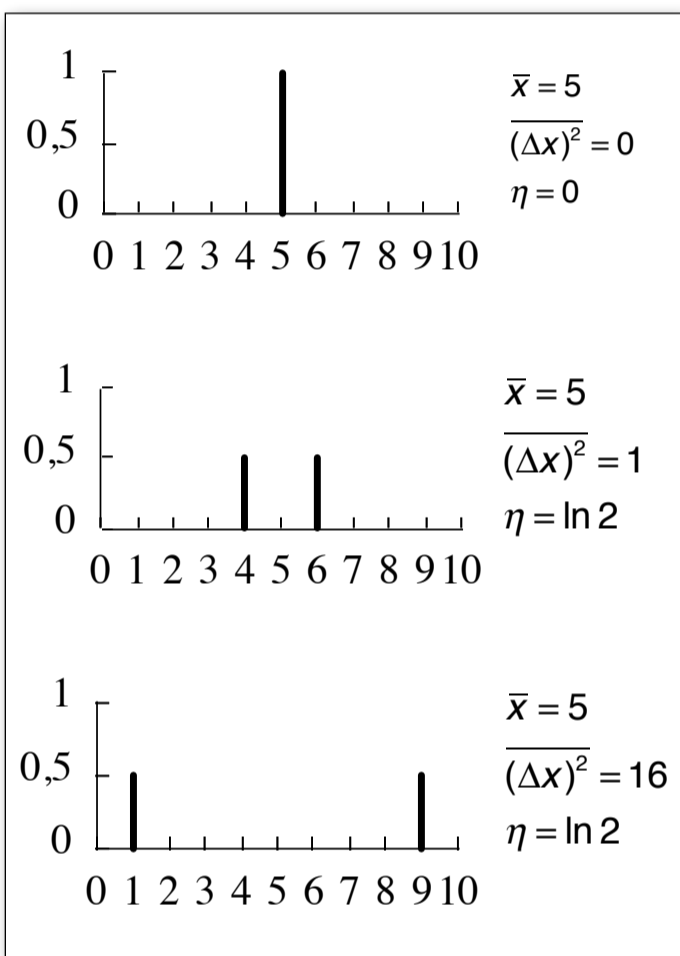
entropy of the distribution: 
$$\eta = -\sum_i p(x_i)\ln p(x_i)$$

The square root of the variance is called the standard deviation.



**Fig. 13.6**  
Different numbers can be calculated from the discrete probability distribution.

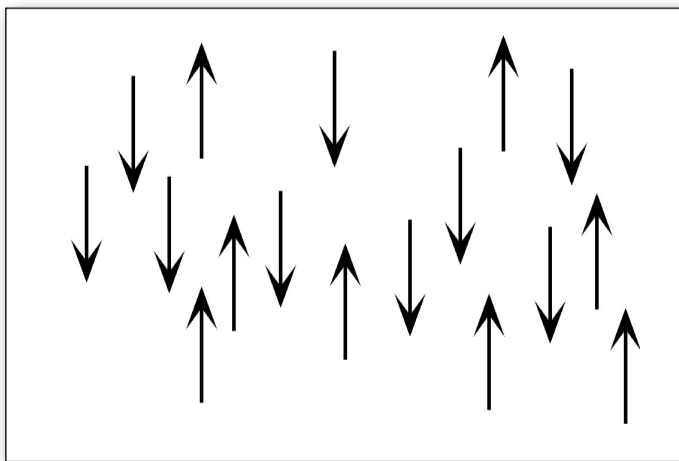
Fig. 13.7 shows three particular distributions, all with the same mean value.



**Fig. 13.7**  
Three probability distributions, all with the same mean, but different variances and different entropies.

The entropy has a finite value only if the distribution is discrete, i.e. if  $x$  can only assume a finite number of different values. The entropy concept defined in this way can be applied to any physical system.

We consider a system with a single independent variable, such as a system of  $N$  particles whose magnetic moments can be oriented in one of two directions: up or down, Fig. 13.8. If the magnitude of the magnetic moment of a single particle is  $m_0$ , the total magnetic moment can assume the values  $Nm_0, (N-2)m_0, (N-4)m_0, \dots, 0, \dots, -(N-4)m_0, -(N-2)m_0, -Nm_0$ .



**Fig. 13.8**  
The only variable of the system is the magnetic moment. The magnetic moment of each particle can only assume two values.

We now describe a state of the system by specifying the system preparation, for example: Bring the system into thermal contact with a heat reservoir of temperature  $T$ . If we do this with all members of Gibbs' ensemble, we obtain a frequency distribution over the values of  $m$  and thus a probability distribution. From this the entropy  $\eta$  could be calculated.

Instead of the cumbersome description of the preparation of the system, we can simply specify the probability distribution  $p(m_i)$ , and calculate the associated entropy. Among the probability distributions over  $m$  there is a class of particular distributions: those where all  $p$  except one are zero. The entropy of such a distribution is zero. Each such distribution corresponds to a particular state. So there is a class of states with entropy zero. If we number the states  $i = 1, \dots$ , we can also say: In the equation

$$\eta = -\sum_i p(x_i)\ln p(x_i)$$

it has to be summed over all states with entropy zero.

### 13.4 The physical entropy of a system

We now claim that the entropy  $\eta$  defined in the previous section is equal to the physical entropy except for a constant factor:

$$S = -k \sum_i p(i) \ln p(i)$$

where

$$k = 1.380 \cdot 10^{-23} \text{ JK}^{-1}$$

is the *Boltzmann constant*

To sum is over all states with  $S = 0$ . We will illustrate this with the example of the previous section. The system consists of four energetically degenerate magnetic moments. The 16 states with entropy zero are listed in Fig. 13.9.

No.	$M$
1	$4M_0$
2	
3	$2M_0$
4	
5	
6	
7	
8	0
9	
10	
11	
12	
13	$-2M_0$
14	
15	
16	$-4M_0$

**Fig. 13.9**

The 16 states with the entropy  $S = 0$  of a system of 4 magnetic moments.

#### 1. $S$ increases spontaneously

We bring the system into a state with  $\eta = 0$ , e.g. into the state with  $p_1 = 1, p_2 = \dots = p_{16} = 0$ . If one now waits for a sufficient time, then finally all probabilities become equal  $p_1 = p_2 = \dots = p_{16} = 1/16$ . Thus  $\eta$  increases from 0 to  $\ln 16$ . The state of maximum entropy is a state of equilibrium: all probabilities  $p_i$  are equal. The entropy  $\eta$ , which we had defined in the previous section, thus has one property in common with the physical entropy  $S$ : If a system is left to itself, it increases.

#### 2. Substancelikeness

We consider the independent systems A and B. We assume that A has  $N_A$  and B has  $N_B$  states with  $\eta = 0$ . Thus

$$\eta_A = -\sum_i p_A(i) \ln p_A(i)$$

$$\eta_B = -\sum_j p_B(j) \ln p_B(j)$$

The system AB consisting of A and B together has  $N_{AB} = N_A \cdot N_B$  states with  $\eta = 0$ . The probability of the state characterized by  $i$  and  $j$  is  $p_A(i) \cdot p_B(j)$ . So it is

$$\begin{aligned} \eta_{AB} &= -\sum_{i,j} p_A(i) \cdot p_B(j) \ln[p_A(i) \cdot p_B(j)] \\ &= -\sum_i p_A(i) \sum_j p_B(j) \ln p_B(j) - \sum_j p_B(j) \sum_i p_A(i) \ln p_A(i) \end{aligned}$$

With

$$\sum_i p_A(i) = 1 \text{ and } \sum_j p_B(j) = 1$$

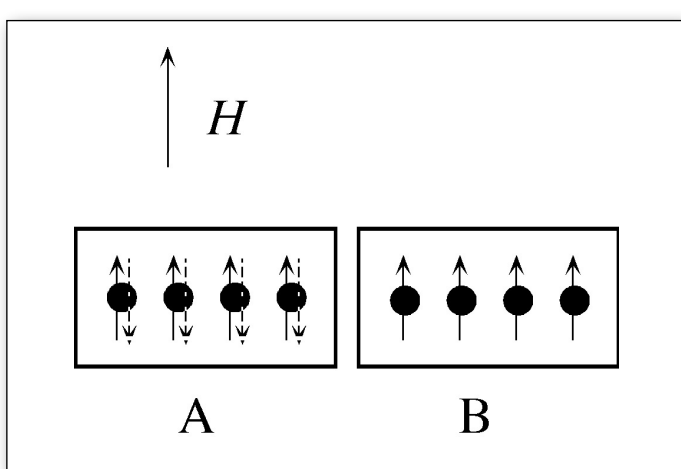
we get

$$\begin{aligned} \eta_{AB} &= -\sum_j p_B(j) \ln p_B(j) - \sum_i p_A(i) \ln p_A(i) \\ &= \eta_A + \eta_B \end{aligned}$$

The entropy  $\eta_{AB}$  of the compound system AB is therefore equal to the sum of the entropies  $\eta_A$  and  $\eta_B$  of the subsystems.

#### 3. If heat flows, $\eta$ also flows

We consider two systems A and B consisting of four magnetic moments each, but this time in an external magnetic field, Fig. 13.10. Thus there is no degeneration.



**Fig. 13.10**

Two systems consisting of four magnetic moments each

The zero point of the energy is set so that  $E = 0$  when the magnetic moments point in the direction of the field vector. If a magnetic moment is reversed, the energy of the system increases by  $E_0$ . The two systems are energetically isolated from each other and from the environment. The initial state is like this: The energy of A is two units  $E_0$ , i.e.  $2E_0$ , the energy of B is zero. Fig. 13.9 shows that A has six states with  $\eta = 0$  (no. 6 to 11) and B has one (no. 1). Each of the systems A and B is in equilibrium, i.e. in the state of maximum entropy. It is therefore (index "in": initial):

$$\eta_A^{\text{in}} = \ln 6 = 1.79 \text{ and } \eta_B^{\text{in}} = \ln 1 = 0.$$

We now bring A and B into thermal contact with each other. We know that (1) entropy  $S$  flows from A to B and (2) entropy  $S$  is produced. We want to check whether this also applies to our statistically defined entropy  $\eta$

By counting, we find that the overall system has 28 states with  $\eta = 0$  (in which  $E = 2E_0$ ). If both sub-systems are in thermal equilibrium, all of them are equally probable and it is (index "fin": final):

$$\eta_{AB}^{\text{fin}} = \ln 28 = 3.33 > \eta_A^{\text{in}} + \eta_B^{\text{in}}$$

In addition we know

$$\eta_A^{\text{fin}} = \eta_B^{\text{fin}} = 0.5 \cdot \eta_{AB}^{\text{fin}} = 0.5 \cdot \ln 28 = 1,67$$

Thus

$$\eta_A^{\text{fin}} < \eta_A^{\text{in}} \text{ and } \eta_B^{\text{fin}} > \eta_B^{\text{in}}$$

Thus the entropy  $\eta$  of A has decreased, that of B has increased. Furthermore, the total entropy  $\eta_{AB}$  has increased – everything as we know it from the physical entropy  $S$ .

## 13. Entropy and probability

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### 13.5 Entropy and temperature

A small class of probability distributions, namely that of equilibrium, can be described very simply: by specifying a single number, the temperature. For an isolated system in equilibrium it is

$$\begin{aligned} p(1) = p(2) = \dots \quad \Rightarrow \quad S &= -k \sum_{i=1}^{\Omega} p(i) \ln p(i) \\ &= -k \Omega \frac{1}{\Omega} \ln \frac{1}{\Omega} \\ S &= k \ln \Omega \end{aligned}$$

With  $dE = TdS$  we obtain

$$kT = \frac{1}{d(\ln \Omega)/dE}$$

---

### 13.6 Entropy and amount of data

From the equality of the expressions for  $S$  and  $H$  it follows that the entropy can be interpreted as an amount of data. If one looks at the four magnetic moments in our example to see how each individual moment is oriented, one obtains the amount of data

$$H = -f \sum p(i) \ln p(i)$$

where  $i$  stands for the states with  $S = 0$ .

Instead of saying “the system contains the entropy  $S$ ” one can also say “the system contains the amount of data  $H$ ”.

If we identify  $S$  and  $H$ , we can write:

$$f = \frac{\text{bit}}{\ln 2} = k = 1.380 \cdot 10^{-23} \text{ JK}^{-1}$$

and thus

$$1 \text{ bit} = 0.9565 \cdot 10^{-23} \text{ JK}^{-1}$$

or

$$1 \text{ bit} \approx 10^{-23} \text{ J/K}$$

The fact that a system containing entropy also contains data does not imply that the system can be used as a technical data store. A data memory should not come into internal equilibrium or into equilibrium with the environment by itself.

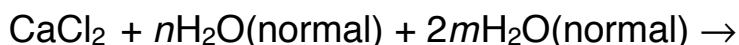
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## Table of chemical potentials and molar entropies

The values in the table are valid for substances under standard conditions, i.e. for a temperature of 25 °C and a pressure of 1 bar. For dissolved substances, the values refer to one-molar solutions: 1 liter of the solution contains 1 mole of the dissolved substance.

For some of the dissolved substances, the molar entropies listed in the table are negative. For example, for  $\text{Ca}^{++}$ :  $S/n = -55,23 \text{ Ct/mol}$ . In fact, of course, there are no negative entropies. The negative value is only the result of an arithmetic trick. In aqueous solutions, ions are surrounded by so-called hydrate shells: A certain number of water molecules are attached to each ion. Ion and hydrate shell together form a kind of large molecule. When dissolving  $\text{CaCl}_2$ , for example, the reaction



takes place.  $\text{CaCl}_2$  transforms into  $\text{Ca}^{++}$  and  $\text{Cl}^-$  ions, and “normal” water is converted into water in the hydrate shells. But now one usually writes this reaction simply like that:



i.e. the water on both sides of the reaction equation is omitted. To ensure that the entropy balance remains correct, the entropy that is released during the formation of the hydrate shell is simply added to the entropy of the ions. The entry in the table under  $\text{Ca}^{++}$  therefore contains the molar entropy of



and under  $\text{Cl}^-$  there is the molar entropy of



Taking these values, the simplified reaction equation can be used to establish the entropy balance of the reaction.

Since the molar entropy of normal water is much greater than that of water in a hydrate shell, it can happen that the total molar entropy listed for an ion is negative.

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Table of chemical potentials and molar entropies

**Ag ... Br (Silver to bromine)**

Formula	Name, phase	$\mu$ in kG	S/n in Ct/mol
<b>Ag</b>	silver, gaseous	245.68	172.89
Ag	solid	0	42.55
Ag <sup>+</sup>	aqueous solution	77.12	72.68
AgBr	solid	-96.9	107.11
AgCl	solid	-109.8	96.23
AgI	solid	-66.19	115.48
AgNO <sub>2</sub>	solid	19.08	128.2
AgNO <sub>3</sub>	solid	-33.47	140.92
AgN <sub>3</sub>	solid	376.14	104.18
Ag <sub>2</sub> CO <sub>3</sub>	solid	-436.81	167.36
Ag <sub>2</sub> O	solid	-11.21	121.34
Ag <sub>2</sub> O <sub>2</sub>	solid	27.61	117.15
Ag <sub>2</sub> O <sub>3</sub>	solid	121.34	100.42
Ag <sub>2</sub> S	orthorhombic, solid	-40.67	144.01
Ag <sub>2</sub> SO <sub>4</sub>	solid	-618.48	200.41
<b>Al</b>	aluminum, gaseous	285.77	164.45
Al	liquid	6.61	35.23
Al	solid	0	28.32
Al <sup>+++</sup>	aqueous solution	-485.34	-321.75
AlBr <sub>3</sub>	solid	-505.01	184.1
Al(CH <sub>3</sub> ) <sub>3</sub>	liquid	-10.04	209.41
AlCl <sub>3</sub>	gaseous	-570.05	314.29
AlCl <sub>3</sub>	solid	-630.06	109.29
AlF <sub>3</sub>	gaseous	-1192.75	276.77
AlF <sub>3</sub>	solid	-1431.15	66.48
AlI <sub>3</sub>	solid	-300.83	158.99
AlN	solid	-287.02	20.17
Al(NO <sub>3</sub> ) <sub>3</sub> · 6H <sub>2</sub> O	solid	-2203.88	467.77
AlO(OH)	boehmite, solid	-912.95	48.45
AlO(OH)	α -biaspore, solid	-920.48	35.27
Al(OH) <sub>3</sub>	hydrargillite, solid	-1143.91	70.12
AlPO <sub>4</sub>	berlinite, solid	-1601.22	90.79
Al <sub>2</sub> Cl <sub>6</sub>	gaseous	-1220.47	489.53
Al <sub>2</sub> O <sub>3</sub>	liquid	-1483.14	99.28
Al <sub>2</sub> O <sub>3</sub>	α , solid	-1581.88	50.94
Al <sub>2</sub> O <sub>3</sub>	γ , solid	-1563.94	52.51
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	solid	-3100.13	239.32
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 6H <sub>2</sub> O	solid	-4622.57	469.03
Al <sub>2</sub> SiO <sub>5</sub>	andalusite, solid	-2597.43	93.22
Al <sub>2</sub> SiO <sub>5</sub>	cyanite, solid	-2596.17	83.81
Al <sub>2</sub> SiO <sub>5</sub> · 2H <sub>2</sub> O	sillimanite, solid	-2625.88	96.19
Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> · 2H <sub>2</sub> O	halloysite, solid	-3759.32	203.34
Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> · 2H <sub>2</sub> O	kaolinite, solid	-3778.15	202.92
Al <sub>4</sub> C <sub>3</sub>	solid	-196.23	88.95
Al <sub>6</sub> Si <sub>2</sub> O <sub>13</sub>	mullite, solid	-6441.94	274.89
<b>Ar</b>	argon, gaseous	0	154.73
Ar	aqueous solution	16.32	59.41
<b>As</b>	arsenic, gaseous	261.08	174.1
As	grey, metallic, solid	0	35.15
AsCl <sub>3</sub>	gaseous	-248.95	327.06
AsCl <sub>3</sub>	liquid	-259.41	216.31
AsF <sub>3</sub>	liquid	-909.14	181.21
AsI <sub>3</sub>	solid	-59.41	213.05
As <sub>2</sub> O <sub>3</sub>	monoclinic, solid	-577.02	117.15
As <sub>2</sub> O <sub>5</sub>	solid	-782.41	105.44
As <sub>2</sub> S <sub>3</sub>	solid	-168.62	163.59
As <sub>4</sub> O <sub>6</sub>	cubic, solid	-1152.52	214.22
<b>Au</b>	gold, gaseous	326.36	180.39
Au	solid	0	47.4
Au <sub>2</sub> O <sub>3</sub>	solid	163.3	125
<b>B</b>	boron, gaseous	511.67	153.34
B	liquid	19.35	14.78
B	solid	0	5.87
BBr <sub>3</sub>	gaseous	-232.46	324.13
BBr <sub>3</sub>	liquid	-238.49	229.7
B(CH <sub>3</sub> ) <sub>3</sub>	gaseous	-35.98	314.64
BCl <sub>3</sub>	gaseous	-387.98	290.07
BCl <sub>3</sub>	liquid	-387.44	206.27
BF <sub>3</sub>	gaseous	-1120.35	254.01
BN	solid	-228.45	14.81
BO <sub>2</sub> H	monoclinic, solid	-723.41	37.66
BO <sub>2</sub> H	orthorhombic, solid	-721.74	50.21
BO <sub>3</sub> H <sub>3</sub>	gaseous	-928.43	295.14
BO <sub>3</sub> H <sub>3</sub>	solid	-969.01	88.83
B <sub>2</sub> Cl <sub>4</sub>	gaseous	-460.66	357.31
B <sub>2</sub> Cl <sub>4</sub>	liquid	-464.84	262.34
B <sub>2</sub> F <sub>4</sub>	gaseous	-1410.43	317.15
B <sub>2</sub> O <sub>3</sub>	gaseous	-822.58	283.67
B <sub>2</sub> O <sub>3</sub>	liquid	-1180.37	78.4
B <sub>2</sub> O <sub>3</sub>	solid	-1193.7	53.97
B <sub>2</sub> O <sub>3</sub>	amorphous	-1182.4	77.82
B <sub>3</sub> N <sub>6</sub> H <sub>6</sub>	liquid	-392.79	199.58
B <sub>4</sub> C	solid	-71.13	27.11
<b>Ba</b>	barium, gaseous	144.77	170.28
Ba	solid	0	66.94
Ba <sup>++</sup>	aqueous solution	-560.66	12.55
BaCO <sub>3</sub>	witherite, solid	-1138.88	112.13
BaCl <sub>2</sub>	solid	-810.86	125.52
BaF <sub>2</sub>	solid	-1148.51	96.23
Bal <sub>2</sub>	solid	-598	167.4
Ba(NO <sub>3</sub> ) <sub>2</sub>	solid	-794.96	213.8
BaO	solid	-528.44	70.29
Ba(OH) <sub>2</sub> · 8H <sub>2</sub> O	solid	-2793.24	426.77
BaS	solid	-456.06	78.24
BaSO <sub>4</sub>	solid	-1353.11	132.21
<b>Be</b>	beryllium, gaseous	289.66	136.17
Be	liquid	9.96	16.54
Be	solid	0	9.54
BeCl <sub>2</sub>	gaseous	-366.1	251.04
BeCl <sub>2</sub>	α , solid	-446.26	82.68
BeF <sub>2</sub>	gaseous	-800.54	227.44
BeF <sub>2</sub>	solid	-979.38	53.35
Be(OH) <sub>2</sub>	gaseous	-625.37	247.69
Be(OH) <sub>2</sub>	α , solid	-814.51	49.37
<b>Bi</b>	bismuth, gaseous	168.2	186.9
Bi	solid	0	56.74
BiClO	solid	-322.17	120.5
BiCl <sub>3</sub>	solid	-315.06	176.98
Bi <sub>2</sub> O <sub>3</sub>	solid	-493.71	151.46
Bi <sub>2</sub> S <sub>3</sub>	solid	-140.58	200.41
<b>Br</b>	bromine, gaseous	82.43	174.91
Br ·	aqueous solution	-103.97	82.42
BrCl	gaseous	-0.96	239.99
BrF	gaseous	-109.16	228.86
BrF <sub>3</sub>	gaseous	-229.45	292.42
BrF <sub>3</sub>	liquid	-240.58	178.24
BrF <sub>5</sub>	gaseous	-350.62	320.08
BrF <sub>5</sub>	liquid	-351.87	225.1
BrH	gaseous	-53.43	198.59
Br <sub>2</sub>	gaseous	3.14	245.35
Br <sub>2</sub>	liquid	0	152.23

Table of chemical potentials and molar entropies

**C (Carbon)**

Formula	Name, phase	$\mu$ in kG	$S/n$ in Ct/mol
<b>C</b>	carbon, gaseous	669.58	157.99
C	diamond, solid	2.9	2.38
C	graphite, solid	0	5.74
CBr <sub>4</sub>	gaseous	66.94	357.94
CBr <sub>4</sub>	monoclinic, solid	47.7	212.55
CCl <sub>2</sub> O	carbonyl chloride, gas	-204.6	283.42
CCl <sub>4</sub>	gaseous	-60.63	309.74
CCl <sub>4</sub>	liquid	-65.27	216.4
CF <sub>4</sub>	gaseous	-878.64	261.5
CH	gaseous	560.75	182.92
CHCl <sub>3</sub>	chloroform, gaseous	-70.41	295.51
CH <sub>2</sub>	gaseous	371.87	181.04
CH <sub>2</sub>	polyethylene, solid	4.4	25.34
CH <sub>2</sub> Cl <sub>2</sub>	dichloromethane, gas	-68.97	270.18
CH <sub>2</sub> O	formaldehyde, gas	-112.97	218.66
CH <sub>2</sub> O <sub>2</sub>	formic acid, gaseous	-350.03	251.6
CH <sub>2</sub> O <sub>2</sub>	formic acid, liquid	-359.57	129
CH <sub>2</sub> O <sub>2</sub>	formic acid, aqueous solution	-372.38	163.18
CH <sub>3</sub>	gaseous	147.92	194.05
CH <sub>3</sub> Br	methyl bromide, gas	-25.94	246.27
CH <sub>3</sub> Cl	chloromethane, gas	-62.95	234.26
CH <sub>3</sub> NO <sub>2</sub>	nitromethane, gas	-6.92	275
CH <sub>3</sub> NO <sub>2</sub>	nitromethane, liquid	-14.55	171.9
CH <sub>3</sub> NO <sub>3</sub>	methyl nitrate, liquid	-40.52	217
CH <sub>4</sub>	methane, gaseous	-50.81	186.1
CH <sub>4</sub> N <sub>2</sub> O	urea, solid	-196.82	104.6
CH <sub>4</sub> O	methanol, gaseous	-162.52	239.7
CH <sub>4</sub> O	methanol, liquid	-166.34	126.7
CO	gaseous	-137.15	197.56
CO <sub>2</sub>	gaseous	-394.36	213.64
CO <sub>2</sub>	aqueous solution	-386	113
CO <sub>3</sub> <sup>-</sup>	carbonate ion, aqueous solution	-527.9	-56.9
CO <sub>3</sub> H <sup>-</sup>	aqueous solution	-586.85	91.21
CS	gaseous	184.1	210.46
CS <sub>2</sub>	gaseous	66.91	237.79
CS <sub>2</sub>	liquid	65.27	151.34
C <sub>2</sub> Cl <sub>2</sub>	dichloroethine, gas	198.41	271.96
C <sub>2</sub> Cl <sub>4</sub>	tetrachloroethene, gas	21.56	343.31
C <sub>2</sub> Cl <sub>6</sub>	hexachloroethane, gaseous	-50	397.77
C <sub>2</sub> H <sub>2</sub>	ethyne, gaseous	209.2	200.83
C <sub>2</sub> H <sub>4</sub>	ethene, gaseous	68.12	219.45
C <sub>2</sub> H <sub>4</sub> O	acetaldehyde, gasf.	-132.92	264.2
C <sub>2</sub> H <sub>4</sub> O	epoxyethane, gaseous	-11.84	243.7
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	acetic acid, gaseous	-378.95	282.5
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	acetic acid, liquid	-389.95	159.83
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	acetic acid, aqu. sol.	-396.56	178.66
C <sub>2</sub> H <sub>5</sub> Cl	ethyl chloride, gaseous	-60.46	275.89
C <sub>2</sub> H <sub>5</sub> Cl	ethyl chloride, liquid	-59.41	190.79
C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> N	aminoacetic acid, solid	-367.02	109.2
C <sub>2</sub> H <sub>6</sub>	ethane, gaseous	-32.62	229.5
C <sub>2</sub> H <sub>6</sub> O	dimethyl ether, gas	-114.07	266.6
C <sub>2</sub> H <sub>6</sub> O	ethanol, gaseous	-168.57	282
C <sub>2</sub> H <sub>6</sub> O	ethanol, liquid	-174.89	160.67
C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	ethylene glycol, liquid	-327.07	179.5
C <sub>3</sub> H <sub>4</sub>	propadiene, gaseous	202.38	234.9
C <sub>3</sub> H <sub>4</sub>	propyne, gaseous	194.16	248.1
C <sub>3</sub> H <sub>6</sub>	propene, gaseous	74.66	226.9
C <sub>3</sub> H <sub>6</sub>	cyclopropane, gaseous	104.11	237.9
C <sub>3</sub> H <sub>6</sub> O	acetone, gaseous	-151.82	294.9
C <sub>3</sub> H <sub>6</sub> O	acetone, liquid	-154.83	200
C <sub>3</sub> H <sub>8</sub>	propane, gaseous	-23.43	269.9
C <sub>4</sub> H <sub>8</sub>	butene-(1), gaseous	72.03	307.4
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	ethyl acetate, liquid	-323.19	259
C <sub>4</sub> H <sub>10</sub>	butane, gaseous	-15.62	310
C <sub>4</sub> H <sub>10</sub>	2-methylpropane, gaseous	-17.92	294.6
C <sub>5</sub> H <sub>10</sub>	cyclopentane, gaseous	38.67	292.9
C <sub>5</sub> H <sub>10</sub>	cyclopentane, liquid	36.49	204.1
C <sub>5</sub> H <sub>12</sub>	pentane, gaseous	-8.11	348.4
C <sub>5</sub> H <sub>12</sub>	pentane, liquid	-9.21	262.7
C <sub>6</sub> H <sub>5</sub> Cl	chlorobenzene, liquid	93.65	194.1
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	nitrobenzene, liquid	141.62	224.3
C <sub>6</sub> H <sub>6</sub>	benzene, gaseous	129.73	269.2
C <sub>6</sub> H <sub>12</sub>	cyclohexane, gaseous	31.75	298.2
C <sub>6</sub> H <sub>12</sub>	cyclohexane, liquid	26.83	204.1
C <sub>6</sub> H <sub>14</sub>	hexane, gaseous	0.3	386.8
C <sub>6</sub> H <sub>14</sub>	hexane, liquid	-4.26	296
C <sub>7</sub> H <sub>8</sub>	methylbenzene, gas	122.39	319.7
C <sub>7</sub> H <sub>8</sub>	methylbenzene, liquid	110.61	219
C <sub>8</sub> H <sub>18</sub>	octane, gaseous	17.44	463.7
C <sub>8</sub> H <sub>18</sub>	octane, liquid	6.41	361.2
C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	sucrose, solid	-1543.52	360

Table of chemical potentials and molar entropies

**Ca ... Fe (Calcium to iron)**

Formula	Name, phase	$\mu$ in kG	S/n in Ct/mol
<b>Ca</b>	calcium, gaseous	145.53	154.78
Ca	liquid	8.19	50.65
Ca	$\alpha$ , solid	0	41.55
Ca	$\beta$ , solid	0.22	42.47
Ca <sup>++</sup>	aqueous solution	-553.04	-55.23
CaBr <sub>2</sub>	solid	-656.05	129.7
CaCO <sub>3</sub>	aragonite, solid	-1127.71	88.7
CaCO <sub>3</sub>	calcite, solid	-1128.76	92.88
CaC <sub>2</sub>	solid	-67.78	70.29
CaCl	gaseous	-130.96	241.42
CaCl <sub>2</sub>	gaseous	-479.18	289.95
CaCl <sub>2</sub>	liquid	-732.16	123.88
CaCl <sub>2</sub>	solid	-750.19	113.8
CaCrO <sub>4</sub>	solid	-1277.38	133.89
CaF <sub>2</sub>	gaseous	-793.27	273.68
CaF <sub>2</sub>	solid	-1161.9	68.87
CaH <sub>2</sub>	solid	-149.79	41.84
CaI <sub>2</sub>	solid	-529.69	142.26
Ca(NO <sub>3</sub> ) <sub>2</sub>	solid	-741.99	193.3
CaO	solid	-604.17	39.75
Ca(OH) <sub>2</sub>	solid	-896.76	76.15
CaPO <sub>4</sub> H	solid	-1679.88	87.86
CaS	solid	-477.39	56.48
CaSO <sub>4</sub>	anhydrite, solid	-1320.3	98.32
CaSO <sub>4</sub> · 2H <sub>2</sub> O	gypsum, solid	-1795.73	193.97
CaSiO <sub>3</sub>	$\alpha$ wollastonite, solid	-1495.36	87.45
CaSiO <sub>3</sub>	$\beta$ wollastonite, solid	-1498.71	82.01
Ca <sub>3</sub> N <sub>2</sub>	solid	-368.61	104.6
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$\alpha$ , solid	-3889.86	241
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$\beta$ , solid	-3899.49	235.98
<b>Cd</b>	cadmium, gaseous	77.45	167.64
Cd	solid	0	51.76
Cd <sup>++</sup>	aqueous solution.	-77.58	-73.22
CdBr <sub>2</sub>	solid	-296.31	137.24
CdCO <sub>3</sub>	solid	-669.44	92.47
CdCl <sub>2</sub>	solid	-343.97	115.27
CdF <sub>2</sub>	solid	-647.68	77.4
CdI <sub>2</sub>	solid	-201.38	161.08
CdO	solid	-228.45	54.81
CdS	solid	-156.48	64.85
CdSO <sub>4</sub>	solid	-822.78	123.04
CdSO <sub>4</sub> · 8/3 H <sub>2</sub> O	solid	-1457.98	229.7
<b>Cl</b>	chlorine, gaseous	105.03	165.1
Cl ·	aqueous solution.	-131.26	56.48
ClF	gaseous	-55.94	217.78
ClF <sub>3</sub>	gaseous	-123.01	281.5
ClF <sub>5</sub>	gaseous	-146.77	310.62
ClH	gaseous	-95.3	186.79
ClO <sub>2</sub>	gaseous	120.5	256.73
Cl <sub>2</sub>	gaseous	0	222.97
Cl <sub>2</sub>	aqueous solution.	6.9	121.34
<b>Co</b>	cobalt, gaseous	380.33	179.41
Co	$\alpha$ , hexagonal, solid	0	30.04
Co	$\beta$ . fcc. solid	0.25	30.71
Co <sup>++</sup>	aqueous solution.	-54.39	-112.97
Co <sup>+++</sup>	aqueous solution.	133.89	-305.43
CoCl <sub>2</sub>	solid	-269.87	109.16
CoF <sub>2</sub>	solid	-647.26	81.96
CoFe <sub>2</sub> O <sub>4</sub>	solid	-1032.61	134.72
CoO	solid	-214.22	52.97
CoSO <sub>4</sub>	solid	-782.41	117.99
Co <sub>3</sub> O <sub>4</sub>	solid	-774.04	102.51
<b>Cr</b>	chromium, gaseous	351.87	174.39
Cr	solid	0	23.77
CrCl <sub>2</sub>	solid	-356.06	115.31
CrCl <sub>2</sub> O <sub>2</sub>	chromyl chloride, liquid	-510.87	221.75
CrCl <sub>3</sub>	solid	-486.18	123.01
CrF <sub>3</sub>	solid	-1087.84	93.89
Cr <sub>2</sub> O <sub>3</sub>	solid	-1058.13	81.17
<b>Cs</b>	cesium, gaseous	49.72	175.49
Cs	liquid	0.03	92.07
Cs	solid	0	85.15
Cs <sup>+</sup>	aqueous solution.	-282.04	133.05
CsBr	solid	-383.25	121.34
CsCl	gaseous	-257.85	255.96
CsCl	solid	-414.37	101.18
CsClO <sub>4</sub>	solid	-306.6	175.27
CsF	gaseous	-373.35	243.09
CsF	solid	-525.39	88.28
CsH	gaseous	101.67	214.43
CsI	solid	-333.46	129.7
<b>Cu</b>	copper, gaseous	298.61	166.27
Cu	liquid	8.37	36.25
Cu	solid	0	33.11
Cu <sup>+</sup>	aqueous solution.	50	40.58
CuBr	solid	-100.83	96.11
CuCO <sub>3</sub> · Cu(OH) <sub>2</sub>	malachite, solid	-893.7	186.19
CuCl	gaseous	63.5	237.09
CuCl	solid	-119.87	86.19
CuCl <sub>2</sub>	solid	-175.73	108.07
CuI	solid	-69.45	96.65
CuN <sub>3</sub>	solid	344.76	100.42
CuO	gaseous	216.93	234.6
CuO	solid	-129.7	42.63
Cu(OH) <sub>2</sub>	solid	-372.74	108.37
CuS	solid	-53.56	66.53
CuSO <sub>4</sub>	solid	-661.91	108.78
CuSO <sub>4</sub> · H <sub>2</sub> O	solid	-918.22	146.02
CuSO <sub>4</sub> · 3H <sub>2</sub> O	solid	-1400.18	221.33
CuSO <sub>4</sub> · 5H <sub>2</sub> O	solid	-1880.06	300.41
Cu <sub>2</sub> O	solid	-146.02	93.14
Cu <sub>2</sub> S	$\alpha$ , solid	-86.19	120.92
<b>F</b>	fluorine, gaseous	61.92	158.64
F ·	aqueous solution.	-278.82	-13.81
FH	gaseous	-273.22	173.67
FH	aqueous solution.	-296.85	88.7
F <sub>2</sub>	gaseous	0	202.67
F <sub>2</sub> O	gaseous	-4.6	247.32
<b>Fe</b>	iron, gaseous	370.7	180.38
Fe	iron, liquid	11.05	34.29
Fe	$\alpha$ , solid	0	27.28
Fe <sup>++</sup>	aqueous solution.	-78.87	-137.65
Fe <sup>+++</sup>	aqueous solution.	-4.6	-315.89
FeCO <sub>3</sub>	siderite, solid	-666.72	92.88
Fe(CO) <sub>5</sub>	liquid	-705.42	338.07
FeCl <sub>2</sub>	gaseous	-159.62	287.48
FeCl <sub>2</sub>	solid	-302.34	117.95
FeCl <sub>3</sub>	gaseous	-247.87	344.1
FeCl <sub>3</sub>	solid	-334.05	142.26
FeCr <sub>2</sub> O <sub>4</sub>	solid	-1343.9	146.02
FeO	gaseous	217.66	241.84
FeO	solid	-245.14	57.49
Fe(OH) <sub>2</sub>	gaseous	-306.63	282.75
Fe(OH) <sub>2</sub>	solid	-492.03	87.86
Fe(OH) <sub>3</sub>	solid	-705.56	104.6
FeS	pyrrhotite, solid	-100.42	60.29
FeSO <sub>4</sub>	solid	-820.9	107.53
FeS <sub>2</sub>	pyrite, solid	-166.94	52.93
Fe <sub>2</sub> O <sub>3</sub>	hematite, solid	-742.24	87.4
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	solid	-2263.05	307.52
Fe <sub>2</sub> SiO <sub>4</sub>	fayalite, solid	-1379.05	145.18
Fe <sub>3</sub> C	cementite, solid	20.08	104.6
Fe <sub>3</sub> O <sub>4</sub>	magnetite, solid	-1015.46	146.44



Table of chemical potentials and molar entropies

**Ga ... Li (Gallium to lithium)**

Formula	Name. Phase	$\mu$ in kG	S/n in Ct/mol
<b>Ga</b>	Gallium, gaseous	238.91	168.95
Ga	solid	0	40.88
Ga <sup>+++</sup>	aqueous solution	-158.99	-330.54
GaBr <sub>3</sub>	solid	-359.82	179.91
GaCl <sub>3</sub>	solid	-454.8	142.26
GaF <sub>3</sub>	solid	-1085.33	83.68
Ga(OH) <sub>3</sub>	solid	-831.36	100.42
Ga <sub>2</sub> O <sub>3</sub>	rhombohedral, solid	-998.3	84.98
<b>Ge</b>	germanium, gaseous	335.98	167.79
Ge	solid	0	31.09
GeBr <sub>4</sub>	liquid	-331.37	280.75
GeCl <sub>4</sub>	gaseous	-457.31	347.61
GeCl <sub>4</sub>	liquid	-462.33	245.6
GeH <sub>4</sub>	gaseous	113.39	217.02
GeI <sub>4</sub>	solid	-144.35	271.12
GeO	brown, solid	-237.23	50.21
GeO <sub>2</sub>	hexagonal, solid	-497.06	55.27
GeS	solid	-71.55	71.13
<b>H</b>	hydrogen, gaseous	203.26	114.6
H <sup>+</sup>	aqueous solution.	0	0
$\left. \begin{matrix} \text{HCO}_3^- \\ \text{HCl} \end{matrix} \right\} \text{ see } \left\{ \begin{matrix} \text{CO}_3\text{H} \\ \text{ClH} \end{matrix} \right.$			
H <sub>2</sub>	gaseous	0	130.57
H <sub>2</sub>	aqueous solution	18	49
$\left. \begin{matrix} \text{H}_2\text{CO}_3 \\ \text{H}_2\text{O} \\ \dots \end{matrix} \right\} \text{ see } \left\{ \begin{matrix} \text{CO}_3\text{H}_2 \\ \text{OH}_2 \\ \dots \end{matrix} \right.$			
<b>He</b>	helium, gaseous	0	126.04
He	aqueous solution	19.25	55.65
<b>Hg</b>	mercury, gaseous	31.85	174.85
Hg	liquid	0	76.02
Hg <sup>++</sup>	aqueous solution	164.43	-32.22
HgBr <sub>2</sub>	solid	-153.13	171.54
HgCl <sub>2</sub>	solid	-178.66	146.02
HgI <sub>2</sub>	red, solid	-101.67	179.91
HgO	red	-58.56	70.29
HgO	yellow, solid	-58.43	71.13
HgS	red, solid	-50.63	82.42
HgS	black	-47.7	88.28
Hg <sub>2</sub> <sup>++</sup>	aqueous solution	153.55	84.52
Hg <sub>2</sub> Br <sub>2</sub>	solid	-181.08	217.57
Hg <sub>2</sub> CO <sub>3</sub>	solid	-468.19	179.91
Hg <sub>2</sub> Cl <sub>2</sub>	solid	-210.78	192.46
Hg <sub>2</sub> I <sub>2</sub>	solid	-111	233.47
Hg <sub>2</sub> SO <sub>4</sub>	solid	-625.88	200.66
<b>Hf</b>	hafnium, gaseous	576.56	186.78
Hf	solid	0	43.56
HfCl <sub>4</sub>	solid	-901.32	190.79
HfF <sub>4</sub>	monoclinic, solid	-1830.5	112.97
HfO <sub>2</sub>	solid	-1027.17	59.33
<b>I</b>	Iodine, gaseous	70.28	180.68
I <sup>-</sup>	aqueous solution	-51.59	111.29
ICl	gaseous	-5.44	247.44
ICl <sub>3</sub>	solid	-22.34	167.36
IF	gaseous	-118.49	236.06
IF <sub>7</sub>	gaseous	-818.39	346.44
IH	gaseous	1.72	206.48
I <sub>2</sub>	gaseous	19.36	260.58
I <sub>2</sub>	liquid	3.32	150.36
I <sub>2</sub>	solid	0	116.14
I <sub>2</sub>	aqueous solution	16.4	137.24
<b>In</b>	indium, gaseous	208.74	173.68
In	solid	0	57.82
In <sup>+++</sup>	aqueous solution	-106.27	150.62
InBr	solid	-169.03	112.97
InI	solid	-120.5	129.7
In(OH) <sub>3</sub>	solid	-761.49	104.6
In <sub>2</sub> O <sub>3</sub>	solid	-830.73	104.18
In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	solid	-2439.27	271.96
<b>Ir</b>	iridium, gaseous	617.98	193.47
Ir	solid	0	35.48
IrF <sub>6</sub>	solid	-461.66	247.69
<b>K</b>	potassium, gaseous	61.17	160.23
K	liquid	0.26	71.45
K	solid	0	55.81
K <sup>+</sup>	aqueous solution	-283.26	102.51
KAl(SO <sub>4</sub> ) <sub>2</sub>	solid	-2235.47	204.6
KBF <sub>4</sub>	solid	-1785	133.89
KBr	solid	-379.2	96.44
KBrO <sub>3</sub>	solid	-243.51	149.16
KCl	gaseous	-233.41	238.99
KCl	liquid	-395.11	86.65
KCl	solid	-408.32	82.68
KClO <sub>3</sub>	solid	-289.91	142.97
KClO <sub>4</sub>	solid	-304.18	151.04
KF	gaseous	-344.8	226.5
KF	solid	-533.13	66.57
KF <sub>2</sub> H	solid	-852.41	104.27
KI	gaseous	-165.9	258.17
KI	solid	-322.29	104.35
KIO <sub>3</sub>	solid	-425.51	151.46
KH	solid	-34.04	50.21
KMnO <sub>4</sub>	solid	-713.79	171.71
KNO <sub>2</sub>	solid	-306.6	152.09
KNO <sub>3</sub>	solid	-393.13	132.93
KOH	gaseous	-235.46	244.35
KOH	liquid	-317.87	98.4
KOH	solid	-379.05	79.29
KSO <sub>4</sub> H	solid	-1031.36	138.07
K <sub>2</sub> CO <sub>3</sub>	liquid	-1049.44	170.37
K <sub>2</sub> CO <sub>3</sub>	solid	-1064.59	155.52
K <sub>2</sub> O	solid	-322.11	94.14
K <sub>2</sub> O <sub>2</sub>	solid	-429.79	112.97
K <sub>2</sub> CrO <sub>4</sub>	solid	-1295.78	200.12
K <sub>2</sub> PtCl <sub>6</sub>	solid	-1109.18	333.88
K <sub>2</sub> SO <sub>4</sub>	solid	-1316.37	175.73
<b>Kr</b>	krypton, gaseous	0	163.97
Kr	aqueous solution	15.06	61.5
<b>La</b>	lanthanum, gaseous	330.54	182.3
La	solid	0	57.32
La <sup>+++</sup>	aqueous solution	-723.41	-184.1
<b>Li</b>	lithium, gaseous	128.04	138.67
Li	liquid	0.93	33.94
Li	solid	0	29.1
Li <sup>+</sup>	aqueous solution	-293.8	14.23
LiCl	gaseous	-217.26	212.81
LiCl	solid	-384.03	59.3
LiF	gaseous	-361.57	200.16
LiF	solid	-588.67	35.66
LiH	gaseous	117.84	170.8
LiH	solid	-68.46	20.04
Lil	gaseous	-134.22	232.12
Lil	solid	-269.66	85.77
LiOH	gaseous	-252.42	217.57
LiOH	solid	-438.73	42.78
Li <sub>2</sub> CO <sub>3</sub>	solid	-1132.44	90.37
Li <sub>2</sub> CO <sub>3</sub>	liquid	-1105.55	127.29
Li <sub>2</sub> O	gaseous	-187.31	229
Li <sub>2</sub> O	solid	-562.11	37.89

Table of chemical potentials and molar entropies

**Mg ... Ni (Magnesium to nickel)**

Formula	Name, phase	$\mu$ in kG	S/n in Ct/mol
<b>Mg</b>	magnesium, gaseous	113.07	148.55
Mg	liquid	6.1	42.51
Mg	solid	0	32.69
Mg <sup>++</sup>	aqueous solution	-456.01	-117.99
MgCO <sub>3</sub>	solid	-1029.26	65.69
MgCl <sub>2</sub>	gaseous	-398.8	276.91
MgCl <sub>2</sub>	liquid	-563.96	129.49
MgCl <sub>2</sub>	solid	-592.12	89.63
MgF <sub>2</sub>	gaseous	-731.5	258.3
MgF <sub>2</sub>	solid	-1071.12	57.24
MgI <sub>2</sub>	solid	-358.15	129.7
Mg(NO <sub>3</sub> ) <sub>2</sub>	solid	-588.4	164.01
MgO	gaseous	-21.48	221.29
MgO	liquid	-502.46	50.35
MgO	solid	-568.96	26.94
Mg(OH) <sub>2</sub>	gaseous	-542.06	273.63
Mg(OH) <sub>2</sub>	solid	-833.69	63.18
MgS	solid	-341.72	46.02
MgSO <sub>4</sub>	solid	-1147.51	91.4
MgSiO <sub>3</sub>	liquid	-1415.39	92.52
MgSiO <sub>3</sub>	solid	-1462.07	67.77
Mg <sub>2</sub> SiO <sub>4</sub>	liquid	-2003.19	123.04
Mg <sub>2</sub> SiO <sub>4</sub>	solid	-2057.93	95.14
<b>Mn</b>	manganese, gaseous	238.49	173.59
Mn	$\alpha$ , solid	0	32.01
Mn <sup>++</sup>	aqueous solution	-228.03	-73.64
MnCO <sub>3</sub>	solid	-816.72	85.77
MnCl <sub>2</sub>	solid	-440.53	118.24
MnO	solid	-362.92	59.71
MnO <sub>2</sub>	solid	-465.18	53.05
Mn(OH) <sub>2</sub>	precipitated, amorphous	-615.05	99.16
MnS	green, solid	-218.4	78.24
MnSO <sub>4</sub>	solid	-957.42	112.13
MnSiO <sub>3</sub>	solid	-1240.56	89.12
Mn <sub>2</sub> O <sub>3</sub>	solid	-881.15	110.46
Mn <sub>2</sub> SiO <sub>4</sub>	solid	-1632.18	163.18
Mn <sub>3</sub> O <sub>4</sub>	solid	-1283.23	155.64
<b>Mo</b>	molybdenum, gaseous	612.54	181.84
Mo	solid	0	28.66
Mo(CO) <sub>6</sub>	solid	-877.8	325.93
MoF <sub>6</sub>	liquid	-1473.1	259.66
MoO <sub>2</sub>	solid	-533.04	46.28
MoO <sub>3</sub>	solid	-668.02	77.74
MoS <sub>2</sub>	solid	-225.94	62.59
<b>N</b>	nitrogen, gaseous	455.58	153.19
NFO	gaseous	-51.04	247.99
NF <sub>3</sub>	gaseous	-83.26	260.62
NH <sub>3</sub>	gaseous	-16.48	192.34
NH <sub>3</sub>	aqueous solution	-26.57	111.29
NH <sub>4</sub> <sup>+</sup>	aqueous solution	-79.37	113.39
NH <sub>4</sub> Cl	$\alpha$ , solid	-203.19	94.98
NH <sub>4</sub> NO <sub>3</sub>	solid	-184.01	151.08
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	solid	-1214.35	151.9
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	solid	-899.9	220.3
NO	gaseous	86.57	210.65
NOCl	nitrosyl chloride, gas	66.11	261.63
NO <sub>2</sub>	gaseous	51.3	239.95
NO <sub>2</sub> <sup>-</sup>	aqueous solution	-37.24	140.16
NO <sub>2</sub> H	cis, gaseous	-42.97	248.66
NO <sub>2</sub> H	trans, gaseous	-45.27	249.12
NO <sub>3</sub> <sup>-</sup>	aqueous solution	-111.34	146.44
NO <sub>3</sub> H	gaseous	-74.77	266.27
NO <sub>3</sub> H	liquid	-80.79	155.6
N <sub>2</sub>	gaseous	0	191.5
<b>Na</b>	sodium, gaseous	77.3	153.61
Na	liquid	0.5	57.85
Na	solid	0	51.45
Na <sup>+</sup>	aqueous solution	-261.89	58.99
NaBH <sub>4</sub>	solid	-127.11	101.39
NaBr	gaseous	-177.78	241.12
NaBr	solid	-349.26	86.82
NaCO <sub>3</sub> H	Na bicarbonate, solid	-851.86	102.09
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	Na acetate, solid	-608.84	123.1
NaCl	gaseous	-201.32	229.7
NaCl	liquid	-365.68	95.06
NaCl	solid	-384.04	72.13
NaClO <sub>4</sub>	solid	-254.32	142.26
NaF	gaseous	-309.74	217.5
NaF	solid	-545.09	51.21
NaI	solid	-284.57	98.32
NaNO <sub>3</sub>	solid	-365.89	116.32
NaOH	gaseous	-215.93	236.4
NaOH	liquid	-375.13	74.17
NaOH	solid	-380.19	64.43
NaSO <sub>4</sub> H	Na bisulfate, solid	-992.86	112.97
Na <sub>2</sub> CO <sub>3</sub>	liquid	-1031.88	155.39
Na <sub>2</sub> CO <sub>3</sub>	solid	-1048.08	138.78
Na <sub>2</sub> CO <sub>3</sub> · 10 H <sub>2</sub> O	solid	-3428.2	564
Na <sub>2</sub> Cl <sub>2</sub>	gaseous	-565.94	325.52
Na <sub>2</sub> O	solid	-379.11	75.04
Na <sub>2</sub> O <sub>2</sub>	solid	-449.66	94.81
Na <sub>2</sub> S	solid	-361.36	97.91
Na <sub>2</sub> SO <sub>3</sub>	solid	-1002.07	146.02
Na <sub>2</sub> SO <sub>4</sub>	thenardite, solid	-1269.35	149.62
Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O	solid	-3647.4	592.04
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	solid	-1028.01	154.81
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5H <sub>2</sub> O	liquid	-2227.72	438.69
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5H <sub>2</sub> O	solid	-2230.07	372.38
Na <sub>2</sub> SiO <sub>3</sub>	solid	-1467.38	113.85
Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	solid	-2324.25	164.05
Na <sub>3</sub> AlF <sub>6</sub>	solid	-3114.1	238
Na <sub>3</sub> PO <sub>4</sub>	solid	-1787.16	173.64
<b>Nb</b>	niobium, gaseous	681.16	186.15
Nb	solid	0	36.4
NbBr <sub>5</sub>	solid	-510.45	259.41
NbC	solid	-136.82	35.4
NbCl <sub>3</sub>	solid	-518.82	146.44
NbCl <sub>3</sub> O	solid	-782.41	142.26
NbCl <sub>4</sub>	solid	-606.68	184.1
NbCl <sub>5</sub>	solid	-683.25	210.46
NbF <sub>5</sub>	solid	-1699.12	160.25
NbN	solid	-205.85	34.52
NbO	solid	-378.65	48.12
NbO <sub>2</sub>	solid	-740.57	54.52
Nb <sub>2</sub> O <sub>5</sub>	solid	-1766.07	137.24
<b>Ne</b>	neon, gaseous	0	146.22
Ne	aqueous solution	19.25	66.11
<b>Ni</b>	nickel, gaseous	384.51	182.08
Ni	solid	0	29.87
Ni <sup>++</sup>	aqueous solution	-45.61	-128.87
NiCO <sub>3</sub>	solid	-605.83	87.9
Ni(CO) <sub>4</sub>	gaseous	-587.27	410.45
Ni(CO) <sub>4</sub>	liquid	-588.27	313.38
NiCl <sub>2</sub>	solid	-259.06	97.65
NiF <sub>2</sub>	solid	-604.17	73.6
NiO	solid	-211.71	37.99
Ni(OH) <sub>2</sub>	solid	-447.27	87.86
NiS	solid	-79.5	52.97
NiSO <sub>4</sub>	solid	-759.81	92.05
Ni <sub>3</sub> S <sub>2</sub>	solid	-197.07	133.89

Table of chemical potentials and molar entropies

**O ... Se (Oxygen to selenium)**

Formula	Name, phase	$\mu$ in kG	S/n in Ct/mol
<b>O</b>	oxygen, gaseous	231.75	160.95
OH <sup>-</sup>	aqueous solution	-157.29	-10.75
OH <sub>2</sub>	water, gaseous	-228.59	188.72
OH <sub>2</sub>	liquid	-237.18	69.91
OH <sub>2</sub>	solid	-236.59	44.77
OH <sub>3</sub> <sup>+</sup>	oxonium ion. aqueous solution	-237.18	69.91
O <sub>2</sub>	gaseous	0	205.03
O <sub>2</sub> H <sub>2</sub>	gaseous	-105.6	232.63
O <sub>2</sub> H <sub>2</sub>	liquid	-120.42	109.62
O <sub>2</sub> H <sub>2</sub>	aqueous solution	-134.1	143.93
O <sub>3</sub>	gaseous	163.18	238.82
<b>Os</b>	osmium, gaseous	744.75	192.46
Os	solid	0	32.64
OsO <sub>4</sub>	yellow, solid	-305.01	149.93
OsO <sub>4</sub>	white, solid	-303.76	167.78
<b>P</b>	phosphorus, gaseous	280.02	163.09
P	liquid	0.09	42.89
P	red, solid	-12.13	22.8
P	white, solid	0	41.09
PBr <sub>3</sub>	liquid	-175.73	240.16
PCl <sub>3</sub>	gaseous	-267.78	311.67
PCl <sub>3</sub>	liquid	-272.38	217.15
PCl <sub>3</sub> O	gaseous	-514.32	325.39
PCl <sub>3</sub> O	liquid	-520.91	222.46
PCl <sub>5</sub>	gaseous	-305.01	364.47
PF <sub>3</sub>	gaseous	-897.47	273.13
PF <sub>5</sub>	gaseous	-1520.72	300.7
PH <sub>3</sub>	gaseous	13.39	210.12
PO <sub>4</sub> <sup>3-</sup>	aqueous solution	-1018.8	-221.75
PO <sub>4</sub> H <sup>-</sup>	aqueous solution	-1089.26	-33.47
PO <sub>4</sub> H <sub>2</sub> <sup>-</sup>	aqueous solution	-1130.39	90.37
PO <sub>4</sub> H <sub>3</sub>	liquid	-1118.43	146.44
PO <sub>4</sub> H <sub>3</sub>	solid	-1119.22	110.5
PO <sub>4</sub> H <sub>3</sub>	aqueous solution	-1142.65	158.16
P <sub>4</sub> O <sub>6</sub>	gaseous	-2084.94	345.6
P <sub>4</sub> O <sub>10</sub>	gaseous	-2669.85	403.76
P <sub>4</sub> O <sub>10</sub>	hexagonal, solid	-2697.84	228.86
<b>Pb</b>	lead, gaseous	161.92	175.26
Pb	liquid	2.22	71.72
Pb	solid	0	64.81
Pb <sup>++</sup>	aqueous solution	-24.39	10.46
PbBr <sub>2</sub>	solid	-261.92	161.5
PbCO <sub>3</sub>	solid	-625.51	130.96
PbCl <sub>2</sub>	solid	-314.13	135.98
PbCl <sub>4</sub>	gaseous	-276.2	384.51
PbF <sub>2</sub>	solid	-617.14	110.46
PbI <sub>2</sub>	solid	-173.64	174.85
Pb(N <sub>3</sub> ) <sub>2</sub>	monoclinic, solid	624.67	148.11
Pb(N <sub>3</sub> ) <sub>2</sub>	orthorhombic, solid	622.16	149.37
PbO	gaseous	26.36	239.94
PbO	liquid	-171.19	85.96
PbO	yellow, solid	-187.9	68.7
PbO	red, solid	-188.95	66.53
PbO <sub>2</sub>	solid	-217.36	68.62
Pb(OH) <sub>2</sub>	solid	-421.07	88
PbS	solid	-98.74	91.21
PbSO <sub>4</sub>	solid	-813.2	148.57
PbSiO <sub>3</sub>	solid	-1062.15	109.62
Pb <sub>3</sub> O <sub>4</sub>	solid	-601.24	211.29
<b>Pd</b>	palladium, gaseous	339.74	166.94
Pd	solid	0	37.57
Pd <sup>++</sup>	aqueous solution	176.56	-117.15
PdCl <sub>2</sub>	solid	-125.1	104.6
PdI <sub>2</sub>	solid	-62.76	150.62
PdS	solid	-66.94	46.02
PdS <sub>2</sub>	solid	-74.48	79.5
<b>Pt</b>	platinum, gaseous	520.49	192.3
Pt	solid	0	41.63
PtS	solid	-76.15	55.06
PtS <sub>2</sub>	solid	-99.58	74.68
<b>Rb</b>	rubidium, gaseous	55.86	169.99
Rb	solid	0	69.45
Rb <sup>+</sup>	aqueous solution	-282.21	124.26
RbBr	solid	-378.15	108.28
RbI	solid	-325.52	118.03
<b>Re</b>	rhenium, gaseous	724.67	188.83
Re	solid	0	36.86
ReCl <sub>3</sub>	solid	-188.28	123.85
ReO <sub>2</sub>	solid	-368.19	72.8
Re <sub>2</sub> O <sub>7</sub>	solid	-1066.08	207.11
<b>Rh</b>	rhodium, gaseous	510.87	185.7
Rh	solid	0	31.51
<b>Ru</b>	ruthenium, gaseous	595.8	186.4
Ru	solid	0	28.53
RuO <sub>4</sub>	gaseous	-139.75	289.95
RuO <sub>4</sub>	liquid	-152.3	183.26
RuO <sub>4</sub>	solid	-152.3	146.44
<b>S</b>	sulfur, gaseous	238.28	167.71
S	liquid	0.39	35.31
S	orthorhombic, solid	0	32.07
S	monoclinic, solid	0.04	32.75
S <sup>--</sup>	aqueous solution	85.77	-14.64
SF <sub>6</sub>	gaseous	-1105.41	291.71
SH <sub>2</sub>	gaseous	-33.56	205.69
SH <sub>2</sub>	aqueous solution	-27.87	121.34
SO	gaseous	-19.84	221.84
SO <sub>2</sub>	gaseous	-300.19	248.11
SO <sub>3</sub>	gaseous	-371.08	256.65
SO <sub>3</sub>	β , solid	-368.99	52.3
SO <sub>3</sub> <sup>--</sup>	aqueous solution	-486.6	-29.29
SO <sub>3</sub> H <sup>-</sup>	aqueous solution	-527.81	139.75
SO <sub>3</sub> H <sub>2</sub>	aqueous solution	-537.9	232.21
SO <sub>4</sub> <sup>--</sup>	aqueous solution	-744.63	20.08
SO <sub>4</sub> H <sup>-</sup>	aqueous solution	-756.01	131.8
SO <sub>4</sub> H <sub>2</sub>	gaseous	-656.09	289.11
SO <sub>4</sub> H <sub>2</sub>	liquid	-690.06	156.9
S <sub>2</sub> Cl <sub>2</sub>	gaseous	-31.8	331.37
<b>Sb</b>	antimony, gaseous	222.17	180.16
Sb	solid	0	45.69
SbBr <sub>3</sub>	solid	-239.32	207.11
SbCl <sub>3</sub>	gaseous	-301.25	337.69
SbCl <sub>3</sub>	solid	-323.72	184.1
SbCl <sub>5</sub>	gaseous	-334.34	401.83
SbCl <sub>5</sub>	liquid	-350.2	301.25
Sb <sub>2</sub> O <sub>3</sub>	orthorhombic, solid	-626.55	123.01
Sb <sub>2</sub> O <sub>4</sub>	solid	-795.8	127.19
Sb <sub>2</sub> O <sub>5</sub>	solid	-829.27	125.1
Sb <sub>2</sub> S <sub>3</sub>	black, solid	-173.64	182
Sb <sub>2</sub> Te <sub>3</sub>	solid	-55.23	234.3
Sb <sub>4</sub> O <sub>6</sub>	cubic, solid	-1268.17	220.92
<b>Sc</b>	scandium, gaseous	336.06	174.68
Sc	solid	0	34.64
ScF <sub>3</sub>	solid	-1555.61	92.05
Sc(OH) <sub>3</sub>	solid	-1233.44	100.42
Sc <sub>2</sub> O <sub>3</sub>	solid	-1819.41	77.4
<b>Se</b>	selenium, gaseous	187.07	176.61
Se	hexagonal, black, solid	0	42.44
SeF <sub>6</sub>	gaseous	-1016.71	313.76
SeH <sub>2</sub>	gaseous	15.9	218.91
SeO	gaseous	26.82	233.89

Table of chemical potentials and molar entropies

**Si ... Zr (Silicon to zirconium)**

Formula	Name, phase	$\mu$ in kG	S/n in Ct/mol
<b>Si</b>	silicon, gaseous	411.29	167.86
Si	liquid	40.83	44.46
Si	solid	0	18.83
SiBr <sub>4</sub>	gaseous	-431.79	377.77
SiBr <sub>4</sub>	liquid	-443.92	277.82
SiC	$\alpha$ , hexagonal, solid	-60.25	16.48
SiC	$\beta$ , cubic, solid	-62.76	16.61
SiCl <sub>4</sub>	gaseous	-617.01	330.62
SiCl <sub>4</sub>	liquid	-619.9	239.74
SiF <sub>4</sub>	gaseous	-1572.68	282.38
SiH <sub>4</sub>	gaseous	56.9	204.51
SiO	gaseous	-126.36	211.5
SiO <sub>2</sub>	gaseous	-306.93	228.86
SiO <sub>2</sub>	liquid	-850.21	47.93
SiO <sub>2</sub>	$\alpha$ cristobalite, solid	-853.67	50.05
SiO <sub>2</sub>	$\beta$ cristobalite, solid	-854.54	43.4
SiO <sub>2</sub>	$\alpha$ quartz, solid	-856.67	41.84
SiO <sub>2</sub>	$\beta$ quartz, solid	-856.48	41.46
SiO <sub>3</sub> H <sub>2</sub>	solid	-1092.44	133.89
SiO <sub>4</sub> H <sub>4</sub>	solid	-1333.02	192.46
Si <sub>2</sub> O <sub>5</sub> H <sub>2</sub>	solid	-1943.47	192.46
Si <sub>2</sub> O <sub>7</sub> H <sub>6</sub>	solid	-2425.88	330.54
Si <sub>3</sub> N <sub>4</sub>	solid	-642.66	101.25
<b>Sn</b>	tin, gaseous	267.36	206.03
Sn	$\alpha$ , grey, solid	0.13	44.14
Sn	$\beta$ , white, solid	0	51.55
SnBr <sub>4</sub>	gaseous	-331.37	411.83
SnBr <sub>4</sub>	solid	-350.2	264.43
SnCl <sub>4</sub>	gaseous	-432.21	365.68
SnCl <sub>4</sub>	liquid	-440.16	258.57
SnH <sub>4</sub>	gaseous	188.28	227.57
SnO	solid	-256.9	56.48
SnO <sub>2</sub>	solid	-519.65	52.3
Sn(OH) <sub>2</sub>	precipitated	-491.62	154.81
SnS	solid	-98.32	76.99
<b>Sr</b>	strontium, gaseous	110.04	164.54
Sr	solid	0	54.39
Sr <sup>++</sup>	aqueous solution	-557.31	-39.33
SrCO <sub>3</sub>	strontianite, solid	-1137.63	97.49
SrCl <sub>2</sub>	solid	-781.15	117.15
SrO	solid	-559.82	54.39
SrSO <sub>4</sub>	solid	-1334.28	121.75
<b>Te</b>	tellurium, gaseous	157.11	182.63
Te	solid	0	49.71
TeO <sub>2</sub>	solid	-270.29	79.5
<b>Ti</b>	titanium, gaseous	425.09	180.19
Ti	solid	0	30.63
TiBr <sub>3</sub>	solid	-523.84	176.56
TiBr <sub>4</sub>	solid	-589.53	243.51
TiC	solid	-180.75	24.23
TiCl <sub>2</sub>	solid	-464.42	87.45
TiCl <sub>3</sub>	solid	-653.54	139.75
TiCl <sub>4</sub>	liquid	-737.22	252.34
TiF <sub>4</sub>	amorphous	-1559.38	133.97
TiH <sub>2</sub>	solid	-80.33	29.71
TiI <sub>4</sub>	solid	-371.54	249.37
TiN	solid	-309.62	30.25
TiO	$\alpha$ , solid	-494.97	34.77
TiO <sub>2</sub>	anatase, solid	-884.5	49.92
TiO <sub>2</sub>	rutile, solid	-889.52	50.33
Ti <sub>2</sub> O <sub>3</sub>	solid	-1434.28	78.78
<b>Tl</b>	thallium, gaseous	147.44	180.85
Tl	solid	0	64.18
Tl <sup>+</sup>	aqueous solution	-32.38	125.52
Tl <sup>+++</sup>	aqueous solution	214.64	-192.46
TlBr	solid	-167.36	120.5
TlCl	solid	-184.93	111.25
TlI	solid	-125.39	127.61
TlNO <sub>3</sub>	solid	-152.46	160.67
TlOH	solid	-195.76	87.4
Tl <sub>2</sub> CO <sub>3</sub>	solid	-614.63	155.23
Tl <sub>2</sub> O	solid	-147.28	125.52
Tl <sub>2</sub> S	solid	-93.72	150.62
Tl <sub>2</sub> SO <sub>4</sub>	solid	-830.48	230.54
<b>U</b>	uranium, gaseous	478.82	198.52
U	solid	0	50.33
U <sup>+++</sup>	aqueous solution	-520.49	-125.52
U <sup>+++</sup>	aqueous solution	-579.07	-326.35
UBr <sub>4</sub>	solid	-788.68	242.67
UC <sub>2</sub>	solid	-175.73	58.58
UCl <sub>4</sub>	solid	-962.32	198.32
UCl <sub>6</sub>	solid	-1010.44	285.77
UF <sub>4</sub>	solid	-1761.46	151.04
UF <sub>6</sub>	solid	-2033.42	227.82
UI <sub>4</sub>	solid	-527.6	271.96
UN	solid	-313.8	75.31
UO <sub>2</sub>	solid	-1075.29	77.82
UO <sub>3</sub>	solid	-1184.07	98.62
<b>V</b>	vanadium, gaseous	453.21	182.19
V	solid	0	28.91
V <sup>++</sup>	aqueous solution	-217.57	-129.7
V <sup>+++</sup>	aqueous solution	-242.25	-230.12
VCl <sub>2</sub>	solid	-405.85	97.07
VCl <sub>3</sub>	solid	-511.28	130.96
VCl <sub>3</sub> O	liquid	-668.6	244.35
VCl <sub>4</sub>	liquid	-503.75	255.22
VF <sub>5</sub>	liquid	-1373.19	175.73
VN	solid	-191.21	37.28
VO	solid	-404.17	38.91
VSO <sub>4</sub>	solid	-1169.85	108.78
V <sub>2</sub> O <sub>3</sub>	solid	-1139.3	98.32
V <sub>2</sub> O <sub>4</sub>	$\alpha$ , solid	-1318.38	102.51
V <sub>2</sub> O <sub>5</sub>	solid	-1419.63	130.96
<b>W</b>	tungsten, gaseous	807.09	173.84
W	liquid	43.07	45.7
W	solid	0	32.64
WCl <sub>6</sub>	$\alpha$ , solid	-455.65	238.49
WF <sub>6</sub>	gaseous	-1632.18	340.95
WF <sub>6</sub>	liquid	-1631.47	251.46
WO <sub>2</sub>	solid	-533.92	50.54
WO <sub>3</sub>	solid	-764.08	75.9
<b>Xe</b>	xenon, gaseous	0	169.57
Xe	aqueous solution	13.39	65.69
<b>Zn</b>	zinc, gaseous	95.18	160.87
Zn	solid	0	41.63
Zn <sup>++</sup>	aqueous solution	-147.03	-112.13
ZnBr <sub>2</sub>	solid	-312.13	138.49
ZnCO <sub>3</sub>	solid	-731.57	82.42
ZnCl <sub>2</sub>	solid	-369.43	111.46
ZnF <sub>2</sub>	solid	-713.37	73.68
ZnI <sub>2</sub>	solid	-208.95	161.08
ZnO	solid	-318.32	43.64
Zn(OH) <sub>2</sub>	solid	-555.13	81.59
ZnS	sphalerite, solid	-201.29	57.74
ZnSO <sub>4</sub>	solid	-874.46	119.66
<b>Zr</b>	zirconium, gaseous	566.51	181.25
Zr	solid	0	38.99
ZrC	solid	-199.58	32.17
ZrCl <sub>4</sub>	solid	-889.94	181.59
ZrF <sub>4</sub>	$\beta$ , monoclinic, solid	-1810	104.6
ZrH <sub>2</sub>	solid	-128.87	35.02
ZrN	solid	-336.39	38.87
ZrO <sub>2</sub>	$\alpha$ , monoclinic, solid	-1042.82	50.38

Table of chemical potentials and molar entropies

**Ca ... Fe**

Formula	Name, phase	$\mu$ in kG	S/n in Ct/mol
<b>Ca</b>	calcium, gaseous	145.53	154.78
Ca	liquid	8.19	50.65
Ca	$\alpha$ , solid	0	41.55
Ca	$\beta$ , solid	0.22	42.47
Ca <sup>++</sup>	aqueous solution	-553.04	-55.23
CaBr <sub>2</sub>	solid	-656.05	129.7
CaCO <sub>3</sub>	aragonite, solid	-1127.71	88.7
CaCO <sub>3</sub>	calcite, solid	-1128.76	92.88
CaC <sub>2</sub>	solid	-67.78	70.29
CaCl	gaseous	-130.96	241.42
CaCl <sub>2</sub>	gaseous	-479.18	289.95
CaCl <sub>2</sub>	liquid	-732.16	123.88
CaCl <sub>2</sub>	solid	-750.19	113.8
CaCrO <sub>4</sub>	solid	-1277.38	133.89
CaF <sub>2</sub>	gaseous	-793.27	273.68
CaF <sub>2</sub>	solid	-1161.9	68.87
CaH <sub>2</sub>	solid	-149.79	41.84
CaI <sub>2</sub>	solid	-529.69	142.26
Ca(NO <sub>3</sub> ) <sub>2</sub>	solid	-741.99	193.3
CaO	solid	-604.17	39.75
Ca(OH) <sub>2</sub>	solid	-896.76	76.15
CaPO <sub>4</sub> H	solid	-1679.88	87.86
CaS	solid	-477.39	56.48
CaSO <sub>4</sub>	anhydrite, solid	-1320.3	98.32
CaSO <sub>4</sub> · 2H <sub>2</sub> O	gypsum, solid	-1795.73	193.97
CaSiO <sub>3</sub>	$\alpha$ wollastonite, solid	-1495.36	87.45
CaSiO <sub>3</sub>	$\beta$ wollastonite, solid	-1498.71	82.01
Ca <sub>3</sub> N <sub>2</sub>	solid	-368.61	104.6
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$\alpha$ , solid	-3889.86	241
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$\beta$ , solid	-3899.49	235.98
<b>Cd</b>	cadmium, gaseous	77.45	167.64
Cd	solid	0	51.76
Cd <sup>++</sup>	aqueous solution.	-77.58	-73.22
CdBr <sub>2</sub>	solid	-296.31	137.24
CdCO <sub>3</sub>	solid	-669.44	92.47
CdCl <sub>2</sub>	solid	-343.97	115.27
CdF <sub>2</sub>	solid	-647.68	77.4
CdI <sub>2</sub>	solid	-201.38	161.08
CdO	solid	-228.45	54.81
CdS	solid	-156.48	64.85
CdSO <sub>4</sub>	solid	-822.78	123.04
CdSO <sub>4</sub> · 8/3 H <sub>2</sub> O	solid	-1457.98	229.7
<b>Cl</b>	chlorine, gaseous	105.03	165.1
Cl ·	aqueous solution.	-131.26	56.48
ClF	gaseous	-55.94	217.78
ClF <sub>3</sub>	gaseous	-123.01	281.5
ClF <sub>5</sub>	gaseous	-146.77	310.62
ClH	gaseous	-95.3	186.79
ClO <sub>2</sub>	gaseous	120.5	256.73
Cl <sub>2</sub>	gaseous	0	222.97
Cl <sub>2</sub>	aqueous solution.	6.9	121.34
<b>Co</b>	cobalt, gaseous	380.33	179.41
Co	$\alpha$ , hexagonal, solid	0	30.04
Co	$\beta$ . fcc. solid	0.25	30.71
Co <sup>++</sup>	aqueous solution.	-54.39	-112.97
Co <sup>+++</sup>	aqueous solution.	133.89	-305.43
CoCl <sub>2</sub>	solid	-269.87	109.16
CoF <sub>2</sub>	solid	-647.26	81.96
CoFe <sub>2</sub> O <sub>4</sub>	solid	-1032.61	134.72
CoO	solid	-214.22	52.97
CoSO <sub>4</sub>	solid	-782.41	117.99
Co <sub>3</sub> O <sub>4</sub>	solid	-774.04	102.51
<b>Cr</b>	chromium, gaseous	351.87	174.39
Cr	solid	0	23.77
CrCl <sub>2</sub>	solid	-356.06	115.31
CrCl <sub>2</sub> O <sub>2</sub>	chromyl chloride, liquid	-510.87	221.75
CrCl <sub>3</sub>	solid	-486.18	123.01
CrF <sub>3</sub>	solid	-1087.84	93.89
Cr <sub>2</sub> O <sub>3</sub>	solid	-1058.13	81.17
<b>Cs</b>	cesium, gaseous	49.72	175.49
Cs	liquid	0.03	92.07
Cs	solid	0	85.15
Cs <sup>+</sup>	aqueous solution.	-282.04	133.05
CsBr	solid	-383.25	121.34
CsCl	gaseous	-257.85	255.96
CsCl	solid	-414.37	101.18
CsClO <sub>4</sub>	solid	-306.6	175.27
CsF	gaseous	-373.35	243.09
CsF	solid	-525.39	88.28
CsH	gaseous	101.67	214.43
CsI	solid	-333.46	129.7
<b>Cu</b>	copper, gaseous	298.61	166.27
Cu	liquid	8.37	36.25
Cu	solid	0	33.11
Cu <sup>+</sup>	aqueous solution.	50	40.58
CuBr	solid	-100.83	96.11
CuCO <sub>3</sub> · Cu(OH) <sub>2</sub>	malachite, solid	-893.7	186.19
CuCl	gaseous	63.5	237.09
CuCl	solid	-119.87	86.19
CuCl <sub>2</sub>	solid	-175.73	108.07
CuI	solid	-69.45	96.65
CuN <sub>3</sub>	solid	344.76	100.42
CuO	gaseous	216.93	234.6
CuO	solid	-129.7	42.63
Cu(OH) <sub>2</sub>	solid	-372.74	108.37
CuS	solid	-53.56	66.53
CuSO <sub>4</sub>	solid	-661.91	108.78
CuSO <sub>4</sub> · H <sub>2</sub> O	solid	-918.22	146.02
CuSO <sub>4</sub> · 3H <sub>2</sub> O	solid	-1400.18	221.33
CuSO <sub>4</sub> · 5H <sub>2</sub> O	solid	-1880.06	300.41
Cu <sub>2</sub> O	solid	-146.02	93.14
Cu <sub>2</sub> S	$\alpha$ , solid	-86.19	120.92
<b>F</b>	fluorine, gaseous	61.92	158.64
F ·	aqueous solution.	-278.82	-13.81
FH	gaseous	-273.22	173.67
FH	aqueous solution.	-296.85	88.7
F <sub>2</sub>	gaseous	0	202.67
F <sub>2</sub> O	gaseous	-4.6	247.32
<b>Fe</b>	iron, gaseous	370.7	180.38
Fe	iron, liquid	11.05	34.29
Fe	$\alpha$ , solid	0	27.28
Fe <sup>++</sup>	aqueous solution.	-78.87	-137.65
Fe <sup>+++</sup>	aqueous solution.	-4.6	-315.89
FeCO <sub>3</sub>	siderite, solid	-666.72	92.88
Fe(CO) <sub>5</sub>	liquid	-705.42	338.07
FeCl <sub>2</sub>	gaseous	-159.62	287.48
FeCl <sub>2</sub>	solid	-302.34	117.95
FeCl <sub>3</sub>	gaseous	-247.87	344.1
FeCl <sub>3</sub>	solid	-334.05	142.26
FeCr <sub>2</sub> O <sub>4</sub>	solid	-1343.9	146.02
FeO	gaseous	217.66	241.84
FeO	solid	-245.14	57.49
Fe(OH) <sub>2</sub>	gaseous	-306.63	282.75
Fe(OH) <sub>2</sub>	solid	-492.03	87.86
Fe(OH) <sub>3</sub>	solid	-705.56	104.6
FeS	pyrrhotite, solid	-100.42	60.29
FeSO <sub>4</sub>	solid	-820.9	107.53
FeS <sub>2</sub>	pyrite, solid	-166.94	52.93
Fe <sub>2</sub> O <sub>3</sub>	hematite, solid	-742.24	87.4
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	solid	-2263.05	307.52
Fe <sub>2</sub> SiO <sub>4</sub>	fayalite, solid	-1379.05	145.18
Fe <sub>3</sub> C	cementite, solid	20.08	104.6
Fe <sub>3</sub> O <sub>4</sub>	magnetite, solid	-1015.46	146.44

Table of chemical potentials and molar entropies

**Ga ... Li**

Formula	Name. Phase	$\mu$ in kG	S/n in Ct/mol
<b>Ga</b>	Gallium, gaseous	238.91	168.95
Ga	solid	0	40.88
Ga <sup>+++</sup>	aqueous solution	-158.99	-330.54
GaBr <sub>3</sub>	solid	-359.82	179.91
GaCl <sub>3</sub>	solid	-454.8	142.26
GaF <sub>3</sub>	solid	-1085.33	83.68
Ga(OH) <sub>3</sub>	solid	-831.36	100.42
Ga <sub>2</sub> O <sub>3</sub>	rhombohedral, solid	-998.3	84.98
<b>Ge</b>	germanium, gaseous	335.98	167.79
Ge	solid	0	31.09
GeBr <sub>4</sub>	liquid	-331.37	280.75
GeCl <sub>4</sub>	gaseous	-457.31	347.61
GeCl <sub>4</sub>	liquid	-462.33	245.6
GeH <sub>4</sub>	gaseous	113.39	217.02
GeI <sub>4</sub>	solid	-144.35	271.12
GeO	brown, solid	-237.23	50.21
GeO <sub>2</sub>	hexagonal, solid	-497.06	55.27
GeS	solid	-71.55	71.13
<b>H</b>	hydrogen, gaseous	203.26	114.6
H <sup>+</sup>	aqueous solution.	0	0
HCO <sub>3</sub> <sup>-</sup> HCl	see {CO <sub>3</sub> H <sup>+</sup> ClH		
H <sub>2</sub>	gaseous	0	130.57
H <sub>2</sub>	aqueous solution	18	49
H <sub>2</sub> CO <sub>3</sub> H <sub>2</sub> O ...	see {CO <sub>3</sub> H <sub>2</sub> OH <sub>2</sub> ...		
<b>He</b>	helium, gaseous	0	126.04
He	aqueous solution	19.25	55.65
<b>Hg</b>	mercury, gaseous	31.85	174.85
Hg	liquid	0	76.02
Hg <sup>++</sup>	aqueous solution	164.43	-32.22
HgBr <sub>2</sub>	solid	-153.13	171.54
HgCl <sub>2</sub>	solid	-178.66	146.02
HgI <sub>2</sub>	red, solid	-101.67	179.91
HgO	red	-58.56	70.29
HgO	yellow, solid	-58.43	71.13
HgS	red, solid	-50.63	82.42
HgS	black	-47.7	88.28
Hg <sub>2</sub> <sup>++</sup>	aqueous solution	153.55	84.52
Hg <sub>2</sub> Br <sub>2</sub>	solid	-181.08	217.57
Hg <sub>2</sub> CO <sub>3</sub>	solid	-468.19	179.91
Hg <sub>2</sub> Cl <sub>2</sub>	solid	-210.78	192.46
Hg <sub>2</sub> I <sub>2</sub>	solid	-111	233.47
Hg <sub>2</sub> SO <sub>4</sub>	solid	-625.88	200.66
<b>Hf</b>	hafnium, gaseous	576.56	186.78
Hf	solid	0	43.56
HfCl <sub>4</sub>	solid	-901.32	190.79
HfF <sub>4</sub>	monoclinic, solid	-1830.5	112.97
HfO <sub>2</sub>	solid	-1027.17	59.33
<b>I</b>	Iodine, gaseous	70.28	180.68
I <sup>-</sup>	aqueous solution	-51.59	111.29
ICl	gaseous	-5.44	247.44
ICl <sub>3</sub>	solid	-22.34	167.36
IF	gaseous	-118.49	236.06
IF <sub>7</sub>	gaseous	-818.39	346.44
IH	gaseous	1.72	206.48
I <sub>2</sub>	gaseous	19.36	260.58
I <sub>2</sub>	liquid	3.32	150.36
I <sub>2</sub>	solid	0	116.14
I <sub>2</sub>	aqueous solution	16.4	137.24
<b>In</b>	indium, gaseous	208.74	173.68
In	solid	0	57.82
In <sup>+++</sup>	aqueous solution	-106.27	150.62
InBr	solid	-169.03	112.97
InI	solid	-120.5	129.7
In(OH) <sub>3</sub>	solid	-761.49	104.6
In <sub>2</sub> O <sub>3</sub>	solid	-830.73	104.18
In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	solid	-2439.27	271.96
<b>Ir</b>	iridium, gaseous	617.98	193.47
Ir	solid	0	35.48
IrF <sub>6</sub>	solid	-461.66	247.69
<b>K</b>	potassium, gaseous	61.17	160.23
K	liquid	0.26	71.45
K	solid	0	55.81
K <sup>+</sup>	aqueous solution	-283.26	102.51
KAl(SO <sub>4</sub> ) <sub>2</sub>	solid	-2235.47	204.6
KBF <sub>4</sub>	solid	-1785	133.89
KBr	solid	-379.2	96.44
KBrO <sub>3</sub>	solid	-243.51	149.16
KCl	gaseous	-233.41	238.99
KCl	liquid	-395.11	86.65
KCl	solid	-408.32	82.68
KClO <sub>3</sub>	solid	-289.91	142.97
KClO <sub>4</sub>	solid	-304.18	151.04
KF	gaseous	-344.8	226.5
KF	solid	-533.13	66.57
KF <sub>2</sub> H	solid	-852.41	104.27
KI	gaseous	-165.9	258.17
KI	solid	-322.29	104.35
KIO <sub>3</sub>	solid	-425.51	151.46
KH	solid	-34.04	50.21
KMnO <sub>4</sub>	solid	-713.79	171.71
KNO <sub>2</sub>	solid	-306.6	152.09
KNO <sub>3</sub>	solid	-393.13	132.93
KOH	gaseous	-235.46	244.35
KOH	liquid	-317.87	98.4
KOH	solid	-379.05	79.29
KSO <sub>4</sub> H	solid	-1031.36	138.07
K <sub>2</sub> CO <sub>3</sub>	liquid	-1049.44	170.37
K <sub>2</sub> CO <sub>3</sub>	solid	-1064.59	155.52
K <sub>2</sub> O	solid	-322.11	94.14
K <sub>2</sub> O <sub>2</sub>	solid	-429.79	112.97
K <sub>2</sub> CrO <sub>4</sub>	solid	-1295.78	200.12
K <sub>2</sub> PtCl <sub>6</sub>	solid	-1109.18	333.88
K <sub>2</sub> SO <sub>4</sub>	solid	-1316.37	175.73
<b>Kr</b>	krypton, gaseous	0	163.97
Kr	aqueous solution	15.06	61.5
<b>La</b>	lanthanum, gaseous	330.54	182.3
La	solid	0	57.32
La <sup>+++</sup>	aqueous solution	-723.41	-184.1
<b>Li</b>	lithium, gaseous	128.04	138.67
Li	liquid	0.93	33.94
Li	solid	0	29.1
Li <sup>+</sup>	aqueous solution	-293.8	14.23
LiCl	gaseous	-217.26	212.81
LiCl	solid	-384.03	59.3
LiF	gaseous	-361.57	200.16
LiF	solid	-588.67	35.66
LiH	gaseous	117.84	170.8
LiH	solid	-68.46	20.04
Lil	gaseous	-134.22	232.12
Lil	solid	-269.66	85.77
LiOH	gaseous	-252.42	217.57
LiOH	solid	-438.73	42.78
Li <sub>2</sub> CO <sub>3</sub>	solid	-1132.44	90.37
Li <sub>2</sub> CO <sub>3</sub>	liquid	-1105.55	127.29
Li <sub>2</sub> O	gaseous	-187.31	229
Li <sub>2</sub> O	solid	-562.11	37.89

Table of chemical potentials and molar entropies

**Mg ... Ni**

Formula	Name, phase	$\mu$ in kG	S/n in Ct/mol
<b>Mg</b>	magnesium, gaseous	113.07	148.55
Mg	liquid	6.1	42.51
Mg	solid	0	32.69
Mg <sup>++</sup>	aqueous solution	-456.01	-117.99
MgCO <sub>3</sub>	solid	-1029.26	65.69
MgCl <sub>2</sub>	gaseous	-398.8	276.91
MgCl <sub>2</sub>	liquid	-563.96	129.49
MgCl <sub>2</sub>	solid	-592.12	89.63
MgF <sub>2</sub>	gaseous	-731.5	258.3
MgF <sub>2</sub>	solid	-1071.12	57.24
MgI <sub>2</sub>	solid	-358.15	129.7
Mg(NO <sub>3</sub> ) <sub>2</sub>	solid	-588.4	164.01
MgO	gaseous	-21.48	221.29
MgO	liquid	-502.46	50.35
MgO	solid	-568.96	26.94
Mg(OH) <sub>2</sub>	gaseous	-542.06	273.63
Mg(OH) <sub>2</sub>	solid	-833.69	63.18
MgS	solid	-341.72	46.02
MgSO <sub>4</sub>	solid	-1147.51	91.4
MgSiO <sub>3</sub>	liquid	-1415.39	92.52
MgSiO <sub>3</sub>	solid	-1462.07	67.77
Mg <sub>2</sub> SiO <sub>4</sub>	liquid	-2003.19	123.04
Mg <sub>2</sub> SiO <sub>4</sub>	solid	-2057.93	95.14
<b>Mn</b>	manganese, gaseous	238.49	173.59
Mn	$\alpha$ , solid	0	32.01
Mn <sup>++</sup>	aqueous solution	-228.03	-73.64
MnCO <sub>3</sub>	solid	-816.72	85.77
MnCl <sub>2</sub>	solid	-440.53	118.24
MnO	solid	-362.92	59.71
MnO <sub>2</sub>	solid	-465.18	53.05
Mn(OH) <sub>2</sub>	precipitated, amorphous	-615.05	99.16
MnS	green, solid	-218.4	78.24
MnSO <sub>4</sub>	solid	-957.42	112.13
MnSiO <sub>3</sub>	solid	-1240.56	89.12
Mn <sub>2</sub> O <sub>3</sub>	solid	-881.15	110.46
Mn <sub>2</sub> SiO <sub>4</sub>	solid	-1632.18	163.18
Mn <sub>3</sub> O <sub>4</sub>	solid	-1283.23	155.64
<b>Mo</b>	molybdenum, gaseous	612.54	181.84
Mo	solid	0	28.66
Mo(CO) <sub>6</sub>	solid	-877.8	325.93
MoF <sub>6</sub>	liquid	-1473.1	259.66
MoO <sub>2</sub>	solid	-533.04	46.28
MoO <sub>3</sub>	solid	-668.02	77.74
MoS <sub>2</sub>	solid	-225.94	62.59
<b>N</b>	nitrogen, gaseous	455.58	153.19
NFO	gaseous	-51.04	247.99
NF <sub>3</sub>	gaseous	-83.26	260.62
NH <sub>3</sub>	gaseous	-16.48	192.34
NH <sub>3</sub>	aqueous solution	-26.57	111.29
NH <sub>4</sub> <sup>+</sup>	aqueous solution	-79.37	113.39
NH <sub>4</sub> Cl	$\alpha$ , solid	-203.19	94.98
NH <sub>4</sub> NO <sub>3</sub>	solid	-184.01	151.08
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	solid	-1214.35	151.9
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	solid	-899.9	220.3
NO	gaseous	86.57	210.65
NOCl	nitrosyl chloride, gas	66.11	261.63
NO <sub>2</sub>	gaseous	51.3	239.95
NO <sub>2</sub> <sup>-</sup>	aqueous solution	-37.24	140.16
NO <sub>2</sub> H	cis, gaseous	-42.97	248.66
NO <sub>2</sub> H	trans, gaseous	-45.27	249.12
NO <sub>3</sub> <sup>-</sup>	aqueous solution	-111.34	146.44
NO <sub>3</sub> H	gaseous	-74.77	266.27
NO <sub>3</sub> H	liquid	-80.79	155.6
N <sub>2</sub>	gaseous	0	191.5
<b>Na</b>	sodium, gaseous	77.3	153.61
Na	liquid	0.5	57.85
Na	solid	0	51.45
Na <sup>+</sup>	aqueous solution	-261.89	58.99
NaBH <sub>4</sub>	solid	-127.11	101.39
NaBr	gaseous	-177.78	241.12
NaBr	solid	-349.26	86.82
NaCO <sub>3</sub> H	Na bicarbonate, solid	-851.86	102.09
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	Na acetate, solid	-608.84	123.1
NaCl	gaseous	-201.32	229.7
NaCl	liquid	-365.68	95.06
NaCl	solid	-384.04	72.13
NaClO <sub>4</sub>	solid	-254.32	142.26
NaF	gaseous	-309.74	217.5
NaF	solid	-545.09	51.21
NaI	solid	-284.57	98.32
NaNO <sub>3</sub>	solid	-365.89	116.32
NaOH	gaseous	-215.93	236.4
NaOH	liquid	-375.13	74.17
NaOH	solid	-380.19	64.43
NaSO <sub>4</sub> H	Na bisulfate, solid	-992.86	112.97
Na <sub>2</sub> CO <sub>3</sub>	liquid	-1031.88	155.39
Na <sub>2</sub> CO <sub>3</sub>	solid	-1048.08	138.78
Na <sub>2</sub> CO <sub>3</sub> · 10 H <sub>2</sub> O	solid	-3428.2	564
Na <sub>2</sub> Cl <sub>2</sub>	gaseous	-565.94	325.52
Na <sub>2</sub> O	solid	-379.11	75.04
Na <sub>2</sub> O <sub>2</sub>	solid	-449.66	94.81
Na <sub>2</sub> S	solid	-361.36	97.91
Na <sub>2</sub> SO <sub>3</sub>	solid	-1002.07	146.02
Na <sub>2</sub> SO <sub>4</sub>	thenardite, solid	-1269.35	149.62
Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O	solid	-3647.4	592.04
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	solid	-1028.01	154.81
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5H <sub>2</sub> O	liquid	-2227.72	438.69
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5H <sub>2</sub> O	solid	-2230.07	372.38
Na <sub>2</sub> SiO <sub>3</sub>	solid	-1467.38	113.85
Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	solid	-2324.25	164.05
Na <sub>3</sub> AlF <sub>6</sub>	solid	-3114.1	238
Na <sub>3</sub> PO <sub>4</sub>	solid	-1787.16	173.64
<b>Nb</b>	niobium, gaseous	681.16	186.15
Nb	solid	0	36.4
NbBr <sub>5</sub>	solid	-510.45	259.41
NbC	solid	-136.82	35.4
NbCl <sub>3</sub>	solid	-518.82	146.44
NbCl <sub>3</sub> O	solid	-782.41	142.26
NbCl <sub>4</sub>	solid	-606.68	184.1
NbCl <sub>5</sub>	solid	-683.25	210.46
NbF <sub>5</sub>	solid	-1699.12	160.25
NbN	solid	-205.85	34.52
NbO	solid	-378.65	48.12
NbO <sub>2</sub>	solid	-740.57	54.52
Nb <sub>2</sub> O <sub>5</sub>	solid	-1766.07	137.24
<b>Ne</b>	neon, gaseous	0	146.22
Ne	aqueous solution	19.25	66.11
<b>Ni</b>	nickel, gaseous	384.51	182.08
Ni	solid	0	29.87
Ni <sup>++</sup>	aqueous solution	-45.61	-128.87
NiCO <sub>3</sub>	solid	-605.83	87.9
Ni(CO) <sub>4</sub>	gaseous	-587.27	410.45
Ni(CO) <sub>4</sub>	liquid	-588.27	313.38
NiCl <sub>2</sub>	solid	-259.06	97.65
NiF <sub>2</sub>	solid	-604.17	73.6
NiO	solid	-211.71	37.99
Ni(OH) <sub>2</sub>	solid	-447.27	87.86
NiS	solid	-79.5	52.97
NiSO <sub>4</sub>	solid	-759.81	92.05
Ni <sub>3</sub> S <sub>2</sub>	solid	-197.07	133.89

Table of chemical potentials and molar entropies

**Si ... Zr**

Formula	Name, phase	$\mu$ in kG	S/n in Ct/mol
<b>Si</b>	silicon, gaseous	411.29	167.86
Si	liquid	40.83	44.46
Si	solid	0	18.83
SiBr <sub>4</sub>	gaseous	-431.79	377.77
SiBr <sub>4</sub>	liquid	-443.92	277.82
SiC	$\alpha$ , hexagonal, solid	-60.25	16.48
SiC	$\beta$ , cubic, solid	-62.76	16.61
SiCl <sub>4</sub>	gaseous	-617.01	330.62
SiCl <sub>4</sub>	liquid	-619.9	239.74
SiF <sub>4</sub>	gaseous	-1572.68	282.38
SiH <sub>4</sub>	gaseous	56.9	204.51
SiO	gaseous	-126.36	211.5
SiO <sub>2</sub>	gaseous	-306.93	228.86
SiO <sub>2</sub>	liquid	-850.21	47.93
SiO <sub>2</sub>	$\alpha$ cristobalite, solid	-853.67	50.05
SiO <sub>2</sub>	$\beta$ cristobalite, solid	-854.54	43.4
SiO <sub>2</sub>	$\alpha$ quartz, solid	-856.67	41.84
SiO <sub>2</sub>	$\beta$ quartz, solid	-856.48	41.46
SiO <sub>3</sub> H <sub>2</sub>	solid	-1092.44	133.89
SiO <sub>4</sub> H <sub>4</sub>	solid	-1333.02	192.46
Si <sub>2</sub> O <sub>5</sub> H <sub>2</sub>	solid	-1943.47	192.46
Si <sub>2</sub> O <sub>7</sub> H <sub>6</sub>	solid	-2425.88	330.54
Si <sub>3</sub> N <sub>4</sub>	solid	-642.66	101.25
<b>Sn</b>	tin, gaseous	267.36	206.03
Sn	$\alpha$ , grey, solid	0.13	44.14
Sn	$\beta$ , white, solid	0	51.55
SnBr <sub>4</sub>	gaseous	-331.37	411.83
SnBr <sub>4</sub>	solid	-350.2	264.43
SnCl <sub>4</sub>	gaseous	-432.21	365.68
SnCl <sub>4</sub>	liquid	-440.16	258.57
SnH <sub>4</sub>	gaseous	188.28	227.57
SnO	solid	-256.9	56.48
SnO <sub>2</sub>	solid	-519.65	52.3
Sn(OH) <sub>2</sub>	precipitated	-491.62	154.81
SnS	solid	-98.32	76.99
<b>Sr</b>	strontium, gaseous	110.04	164.54
Sr	solid	0	54.39
Sr <sup>++</sup>	aqueous solution	-557.31	-39.33
SrCO <sub>3</sub>	strontianite, solid	-1137.63	97.49
SrCl <sub>2</sub>	solid	-781.15	117.15
SrO	solid	-559.82	54.39
SrSO <sub>4</sub>	solid	-1334.28	121.75
<b>Te</b>	tellurium, gaseous	157.11	182.63
Te	solid	0	49.71
TeO <sub>2</sub>	solid	-270.29	79.5
<b>Ti</b>	titanium, gaseous	425.09	180.19
Ti	solid	0	30.63
TiBr <sub>3</sub>	solid	-523.84	176.56
TiBr <sub>4</sub>	solid	-589.53	243.51
TiC	solid	-180.75	24.23
TiCl <sub>2</sub>	solid	-464.42	87.45
TiCl <sub>3</sub>	solid	-653.54	139.75
TiCl <sub>4</sub>	liquid	-737.22	252.34
TiF <sub>4</sub>	amorphous	-1559.38	133.97
TiH <sub>2</sub>	solid	-80.33	29.71
TiI <sub>4</sub>	solid	-371.54	249.37
TiN	solid	-309.62	30.25
TiO	$\alpha$ , solid	-494.97	34.77
TiO <sub>2</sub>	anatase, solid	-884.5	49.92
TiO <sub>2</sub>	rutile, solid	-889.52	50.33
Ti <sub>2</sub> O <sub>3</sub>	solid	-1434.28	78.78
<b>Tl</b>	thallium, gaseous	147.44	180.85
Tl	solid	0	64.18
Tl <sup>+</sup>	aqueous solution	-32.38	125.52
Tl <sup>+++</sup>	aqueous solution	214.64	-192.46
TlBr	solid	-167.36	120.5
TlCl	solid	-184.93	111.25
TlI	solid	-125.39	127.61
TlNO <sub>3</sub>	solid	-152.46	160.67
TlOH	solid	-195.76	87.4
Tl <sub>2</sub> CO <sub>3</sub>	solid	-614.63	155.23
Tl <sub>2</sub> O	solid	-147.28	125.52
Tl <sub>2</sub> S	solid	-93.72	150.62
Tl <sub>2</sub> SO <sub>4</sub>	solid	-830.48	230.54
<b>U</b>	uranium, gaseous	478.82	198.52
U	solid	0	50.33
U <sup>+++</sup>	aqueous solution	-520.49	-125.52
U <sup>+++</sup>	aqueous solution	-579.07	-326.35
UBr <sub>4</sub>	solid	-788.68	242.67
UC <sub>2</sub>	solid	-175.73	58.58
UCl <sub>4</sub>	solid	-962.32	198.32
UCl <sub>6</sub>	solid	-1010.44	285.77
UF <sub>4</sub>	solid	-1761.46	151.04
UF <sub>6</sub>	solid	-2033.42	227.82
UI <sub>4</sub>	solid	-527.6	271.96
UN	solid	-313.8	75.31
UO <sub>2</sub>	solid	-1075.29	77.82
UO <sub>3</sub>	solid	-1184.07	98.62
<b>V</b>	vanadium, gaseous	453.21	182.19
V	solid	0	28.91
V <sup>++</sup>	aqueous solution	-217.57	-129.7
V <sup>+++</sup>	aqueous solution	-242.25	-230.12
VCl <sub>2</sub>	solid	-405.85	97.07
VCl <sub>3</sub>	solid	-511.28	130.96
VCl <sub>3</sub> O	liquid	-668.6	244.35
VCl <sub>4</sub>	liquid	-503.75	255.22
VF <sub>5</sub>	liquid	-1373.19	175.73
VN	solid	-191.21	37.28
VO	solid	-404.17	38.91
VSO <sub>4</sub>	solid	-1169.85	108.78
V <sub>2</sub> O <sub>3</sub>	solid	-1139.3	98.32
V <sub>2</sub> O <sub>4</sub>	$\alpha$ , solid	-1318.38	102.51
V <sub>2</sub> O <sub>5</sub>	solid	-1419.63	130.96
<b>W</b>	tungsten, gaseous	807.09	173.84
W	liquid	43.07	45.7
W	solid	0	32.64
WCl <sub>6</sub>	$\alpha$ , solid	-455.65	238.49
WF <sub>6</sub>	gaseous	-1632.18	340.95
WF <sub>6</sub>	liquid	-1631.47	251.46
WO <sub>2</sub>	solid	-533.92	50.54
WO <sub>3</sub>	solid	-764.08	75.9
<b>Xe</b>	xenon, gaseous	0	169.57
Xe	aqueous solution	13.39	65.69
<b>Zn</b>	zinc, gaseous	95.18	160.87
Zn	solid	0	41.63
Zn <sup>++</sup>	aqueous solution	-147.03	-112.13
ZnBr <sub>2</sub>	solid	-312.13	138.49
ZnCO <sub>3</sub>	solid	-731.57	82.42
ZnCl <sub>2</sub>	solid	-369.43	111.46
ZnF <sub>2</sub>	solid	-713.37	73.68
ZnI <sub>2</sub>	solid	-208.95	161.08
ZnO	solid	-318.32	43.64
Zn(OH) <sub>2</sub>	solid	-555.13	81.59
ZnS	sphalerite, solid	-201.29	57.74
ZnSO <sub>4</sub>	solid	-874.46	119.66
<b>Zr</b>	zirconium, gaseous	566.51	181.25
Zr	solid	0	38.99
ZrC	solid	-199.58	32.17
ZrCl <sub>4</sub>	solid	-889.94	181.59
ZrF <sub>4</sub>	$\beta$ , monoclinic, solid	-1810	104.6
ZrH <sub>2</sub>	solid	-128.87	35.02
ZrN	solid	-336.39	38.87
ZrO <sub>2</sub>	$\alpha$ , monoclinic, solid	-1042.82	50.38



## Literature

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I thank my teacher Gottfried Falk, from whom I learned thermodynamics, and my friend and colleague Georg Job, from whom I learned how simple thermodynamics can be.

The present course is based on the following three books:

G. FALK, Theoretische Physik, II Thermodynamik, Heidelberger Taschenbücher, Springer-Verlag 1968.

G. JOB, Neudarstellung der Wärmelehre – die Entropie als Wärme, Akademische Verlagsgesellschaft Frankfurt am Main, 1972.

G. FALK, W. RUPPEL, Energie und Entropie, Springer-Verlag, 1976.

In the meantime, further books have been written, which are based on Job's ideas.

First, there is one written by Job himself, together with Regina Rüffler, which is aimed at physicochemists.

G. JOB, R. RÜFFLER, Physical chemistry from a different angle, Springer, New York, 2016.

Then by Hans Fuchs a work whose target group are mainly engineers:

H. U. FUCHS, The dynamics of heat, Springer, New York 1996.

And finally a work by Christoph Strunk for physicists:

C. STRUNK, Moderne Thermodynamik, De Gruyter, Berlin 2015

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