

20 BASIC PRINCIPLES OF THERMODYNAMICS

The equations of motion, which involve forces or stresses, are based entirely upon Newton's second law. The concept of a traction vector acting on a surface is based on Newton's third law that relates action and reaction. The concept of strains relies entirely upon certain kinematic considerations. Thus, both stresses and strains are based upon certain laws of nature that we accept as *axioms*, i.e. postulates that everybody accepts as being true.

When relating stresses and strains via the constitutive equations, we are leaving the firm background that the laws of nature provide. In fact, constitutive theories are our imagination of how materials behave when exposed to certain load conditions. We have discussed a number of such constitutive theories and even though we have relied on certain experimental evidence and have tried to be as consistent as possible, it is evident that the constitutive modeling considered so far is based to a certain extent on a framework that is not as firmly rooted in fundamental principles as we would like it to be.

In order to obtain a more fundamental basis for constitutive modeling, it seems intriguing to investigate whether *thermodynamics* may provide this basis. Thermodynamics deals with relations between heat and mechanical work and it is based on two fundamental laws of nature, the *first* and *second law of thermodynamics*; these laws are accepted as axioms just like, for instance, Newton's second law.

It turns out to be possible to derive constitutive theories from thermodynamics and in this chapter we will first discuss some fundamental results of thermodynamics. In the next chapters, we will then discuss in detail various ramifications for constitutive modeling. It appears that the constitutive theories discussed previously can also be derived from thermodynamical principles. This not only supports the relevance of our previous discussion, but it also makes for a completely new approach to derive other and more advanced constitutive theories. Moreover, it turns out that, with this thermodynamic basis, it is possible to combine various material behaviors in a straightforward manner. As an example, we may establish a constitutive theory that combines plasticity and damage.

Without the thermodynamic basis such a combined model is rather difficult to establish, but with the thermodynamic formulation the establishment turns out to be pretty straightforward.

One may ask why we have chosen not to start with the thermodynamic formulation right from the beginning of this exposition. The answer is threefold: first of all, the thermodynamic formulation is rather abstract whereas the previous discussion of various constitutive theories has relied heavily on simple experimental evidence and direct physical considerations; secondly, when the thermodynamic formulation is used to establish once more the previously discussed models (as well as providing a number of new theories) it will - hopefully - enlighten the reader; thirdly - and this may be the most important point - with the background obtained up to now, the reader will have a much better background to understand and fully appreciate why the thermodynamic formulation takes the specific forms that we will discuss.

In this chapter, we will introduce various concepts like temperature, heat, entropy, etc. that enter thermodynamics. For evident reasons, we will confine our attention to mechanical and heat processes and exclude electric, magnetic, chemical and ion diffusion processes. For introductions to traditional thermodynamics that do not focus on the implications for constitutive modeling of solid materials, we may refer, for instance, to Sears (1959), Schmidt (1963) and Çengel and Boles (1994). In the book of Kestin (1979), some attention is given to solid materials. Even though we will take advantage of these viewpoints, for evident reasons we will focus here on a thermodynamic formulation that is of direct relevance for establishing constitutive theories for solid materials. Within this scope, there exist many different approaches to thermodynamics and the reader may, for instance, consult Truesdell and Toupin (1960), de Groot and Mazur (1962), Truesdell (1969), Malvern (1969), Oden (1972), Eringen (1975a), Lavenda (1978), Lemaitre and Chaboche (1990), Maugin (1992) and Haupt (2000). Most of these expositions are quite formal and abstract. Here we have chosen to adopt the simplest possible approach that, hopefully, appeals to the physical insight of the reader so that new concepts like heat, temperature, entropy, etc. not only become quantities that the reader may manipulate with in various equations, but also become concepts of physical relevance.

In the next chapters, we will then take full advantage of thermodynamics and illustrate its extreme importance for constitutive modeling.

20.1 Temperature - Absolute temperature

One of the fundamental characteristics of a body is how hot or cold it is. The familiar concept of *temperature* quantifies this degree of hotness or coldness and the temperature T is simply the real number indicated on a thermometer. If the body gets hotter, its temperature rises; if it gets colder, its temperature falls. However, the *scale* with which we measure the temperature is arbitrary -

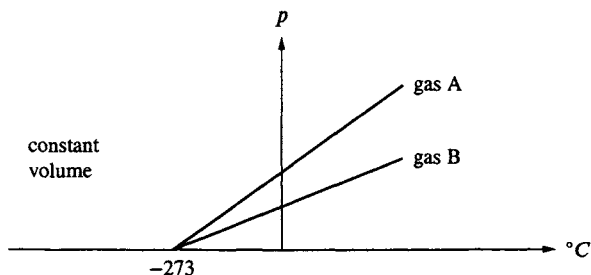


Figure 20.1: Relation between gas pressure and gas temperature for constant volume.

familiar examples are degrees Fahrenheit and degrees Celsius. In spite of that, experience shows that all temperature scales are related uniquely to each other; this implies that irrespective of the temperature scale used, we measure the same phenomenon.

Temperature may be viewed as an expression of how fast the molecules vibrate

It is an experimental fact that high temperature results in powerful vibrations of the molecules of the body whereas low temperature results in small vibrations of the molecules. It is therefore not surprising that experimental evidence shows that, regardless of the scale used for a thermometer, there is a temperature below which no body can be cooled. At this temperature, no molecular vibrations occur and we therefore have:

Irrespective of the temperature scale used, there exists a temperature below which no body can be cooled

To substantiate this viewpoint, consider a gas that occupies a certain fixed volume. Experience then shows that there is a relation between the pressure p and the temperature T . If this relation is measured in the laboratory, it turns out to be linear, cf. Fig. 20.1. This figure also illustrates that irrespective of what gas we consider, there is a certain temperature at which all gases exhibit a pressure that is nil; this temperature turns out to be -273°C . As a negative gas pressure cannot exist, we are again led to the conclusion that there exists a temperature below which no body can be cooled.

Therefore, irrespective of the temperature scale used, the temperature is bounded below. If we assign the temperature value zero to the greatest lower bound, then the temperature is said to be *absolute* and, instead of the notation T for temperature, we use the notation θ to indicate that the temperature measure

is absolute, i.e.

$$\theta > 0 \quad \text{absolute temperature} \quad (20.1)$$

We conclude that the absolute temperature approaches the value zero at the lowest possible temperature.

As already discussed, the lower bound is about -273°C . If we choose to measure temperature changes by means of degrees Celsius ($^{\circ}\text{C}$) then we can construct an absolute temperature measure by means of so-called *Kelvin degrees* [K] according to

$$K = 273 + ^{\circ}\text{C} ; \quad K > 0 \quad (20.2)$$

Let us recall that degrees Fahrenheit ($^{\circ}\text{F}$) are related to degrees Celsius by $(^{\circ}\text{F} - 32)5/9 = ^{\circ}\text{C}$. Therefore, using degrees Fahrenheit as a measure of temperature changes and noting that -273°C corresponds to $9(-273)/5 + 32 = -459^{\circ}\text{F}$, we may construct another absolute temperature measure $^{\circ}\text{R}$, the *Rankine scale*, by setting $^{\circ}\text{R} = 459 + ^{\circ}\text{F}$, $^{\circ}\text{R} > 0$, but (20.2) is the one usually adopted.

We shall later, in Section 20.10, show that strict thermodynamical considerations also infer the existence of an absolute temperature.

20.2 Heat and heat flow

The incremental mechanical work done by a point force \mathbf{f} , when the point moves the distance $d\mathbf{u}$ is given by the scalar product $d\mathbf{u}^T \mathbf{f}$. Mechanical work is therefore energy that is produced by the displacement of forces.

Experience shows that there is another form of energy, namely that related to *heat*. If two bodies at different temperatures are brought into contact with each other, heat will flow from the hotter body into the colder body. We therefore have:

Heat flow is a transportation of energy and heat flow requires a temperature difference

That heat, in fact, is energy that may even be transformed to mechanical work is illustrated in Fig. 20.2. Here a gas is contained in a cylinder with a weightless piston and a mass M is placed on the piston. In Fig. 20.2a), a Bunsen burner is used to heat the system and due to the increase of gas temperature, the gas expands so that after some time the piston has moved the distance u , cf. Fig. 20.2b). The pressure p is unchanged, since the only mechanical loading is due to the mass M . Due to the heating, the system has performed the mechanical work uMg , where g is the gravity acceleration.

That mechanical work may also be transformed to heat is evident for everybody who has inflated a bicycle tyre by using an ordinary hand pump.

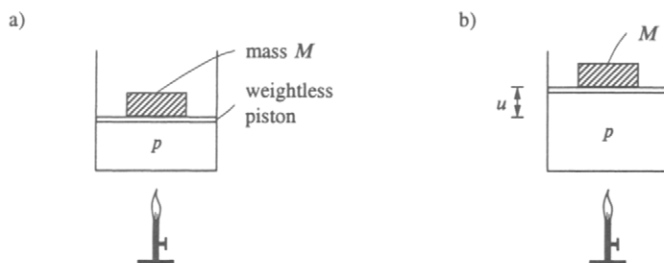


Figure 20.2: Heating of a cylinder containing a gas with the constant pressure p ; a) start of heating; b) end of heating.

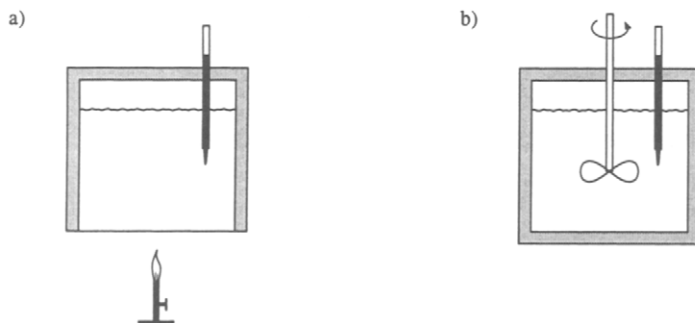


Figure 20.3: Joule's experiment; a) temperature increase by heating; b) same temperature increase by performing mechanical work.

Therefore, heat and mechanical work are of the same nature and both phenomena are referred to as *energy*. Even though heat represents energy, heat can only be measured in terms of a transportation of a certain amount of energy and heat therefore manifests itself in terms of heat flow. Often, in some process between two states, the word heat is used for the total flow of heat that occurs between state 1 and state 2. Heat flow is not to be confused with *heat flux*, which refers to the transportation of heat per unit time.

Heat or heat flow represents energy, but the question remains how we measure heat and how this measurement is related to our usual (SI) concepts of energy. For this purpose, we refer to the celebrated experiment performed by Joule in 1843, see Fig. 20.3. In Fig. 20.3a), a certain amount of water is heated by a Bunsen burner and the temperature then increases. In Fig. 20.3b), mechanical work is supplied to the same amount of water by means of a propeller; due to turbulence and friction in the water, the water temperature then increases. The pressure in the two calorimeters is kept at the same constant level and the

initial temperature of the two water samples is the same. When the temperature increase in the two calorimeters is the same, the mechanical work input is measured. Any physical measurement (pressure, temperature, volume, etc.) of the water in the two calorimeters cannot reveal any difference between the states of the two water samples. This implies that all mechanical work supply in Fig. 20.3b) is equivalent to all heat supply in Fig. 20.3a). As a historical remark, it was then possible to determine that $1 \text{ kcal} = 4.19 \text{ kJ}$, where kcal=kilocalorie and 1 kcal is the amount of heat necessary to increase the temperature of 1 kg of water from 14.5°C to 15.5°C at a pressure of one atmosphere.

With the above observation, the amount of heat flow in any process may now, in principle, be measured; the heat flow in the process in question is applied to the calorimeter in Fig. 20.3a) and by the test set-up in Fig. 20.3b), we are able to measure the amount of heat flow.

We conclude from Joule's experiment that we are able to measure heat; moreover heat and mechanical work are different forms of the same phenomenon, namely energy, that in the SI-system we measure in terms of Joule [$\text{J}=\text{Nm}$].

20.3 State variables and state functions - Introduction to the first law

A specific portion (real or imaginary) of the physical universe - that is, a specific quantity of matter - is called a *system*. By a system, we will here refer to a system that does not exchange matter through its boundary, cf. Fig. 20.4.

In order to describe the system, we need the concept of *state variables*. For simplicity, we will here assume that homogeneous conditions hold for the system. The following definition is used:

State variables are quantities that characterize the state of the system

(20.3)

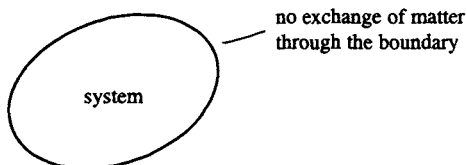


Figure 20.4: Illustration of system.

If in rigid body mechanics we consider a particle as a system, then the current position vector x_i is a state variable. If we consider a gas in a cylinder, state

variables are given by the pressure p , the volume V and the temperature θ . In general, however, the identification of the state variables of a given system is not trivial. Moreover, the choice of state variables for one and the same system depends upon what we are interested in. Consider as an example, a steel bar loaded in uniaxial tension; the steel bar is painted blue. If we are a painter, then the color blue would be a state variable whereas as engineers we may select, for instance, the strain, the stress and the temperature as state variables.

Having established the concept of state variables, we will now introduce the concept of a *state function* according to the following definition:

A state function is a function that only depends on the state of the system and not on the manner in which this state is achieved

(20.4)

As an illustration of a state function, consider a person walking on a mountain from point 1 to point 2. The altitude difference $H_2 - H_1$ is certainly a state function, since it is independent of the specific path the person chooses. However, the walking distance between point 1 and point 2 is not a state function, since it depends on the specific path chosen. Since the state variables characterize the state, we conclude that

State function = function of state variables

(20.5)

In order to arrive at the *first law of thermodynamics*, we first introduce the concept of a *perpetual motion of the first kind*:

A perpetual motion of the first kind is a machine operating in cycles which, in any number of complete cycles, will produce more mechanical work than is absorbed in the form of heat

That the machine operates in cycles means that after one cycle, the machine is in the same condition, i.e. the same state, as before the cycle. One manner in which the first law of thermodynamics is expressed is the following:

A perpetual motion of the first kind is impossible

(20.6)

We will later return to the first law of thermodynamics and evaluate it in greater detail, but already now we will emphasize that the first law of thermodynamics is a postulate. However, all experience supports the first law of thermodynamics and it is therefore accepted as an *axiom* just like Newton's second law. One special occasion where (20.6) becomes evident is where the perpetual motion of the first kind just produces mechanical work without absorbing any heat. There also exists a perpetual motion of the *second* kind and it will be discussed later.

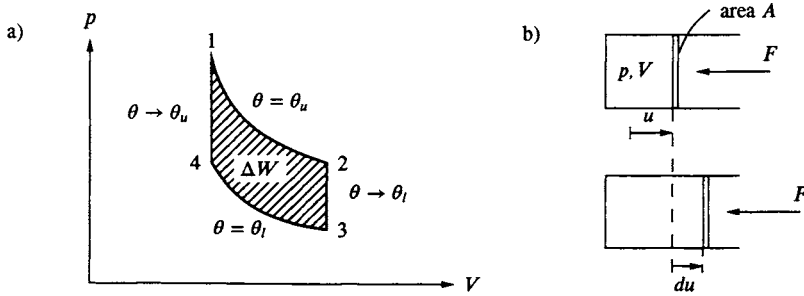


Figure 20.5: a) Complete cycle of gas in a cylinder; b) external force F acting on the piston.

Against this background, we will now prove the important result that neither the mechanical work input nor the heat input to a system are state functions. Referring to Fig. 20.5, let us consider a system in the form of a gas contained in a cylinder with a frictionless piston. Let p , V and θ denote the gas pressure, volume and absolute temperature, respectively. These quantities are taken as state variables that completely define the state of the system. We now perform a cycle via the states 1-2-3-4-1, cf. Fig. 20.5a), so that when returning to state 1, the state is the same as before the cycle.

To gain insight, we may assume that the gas follows the *ideal gas law* given by

$$pV = mR\theta \quad (20.7)$$

where m is the mass of the gas and R denotes the gas constant for the specific gas in question. Along curve 1-2 the gas expands *isothermally*, i.e. at constant temperature. This temperature is denoted by θ_u , where subscript u refers to 'upper'; therefore curve 1-2 is described by $pV = \text{constant}$. This isothermal expansion can be established by bringing the cylinder in contact with a large reservoir having the temperature θ_u . Along curve 2-3, the change is *isochoric*, that is, the volume V is kept constant. The fall in pressure p is obtained by decreasing the temperature from θ_u to θ_l , cf. (20.7); subscript l refers to 'lower'. Along curve 3-4, the gas is compressed isothermally at the temperature θ_l . Finally, the cycle is completed by curve 4-1 where the gas is compressed isochorically by increasing the temperature from θ_l to θ_u .

Referring to Fig. 20.5b), the incremental mechanical work supplied to the system is $-F du$ (minus sign because the force F and the displacement u are measured positively in opposite directions). The incremental mechanical work supplied to the surroundings (i.e. the incremental mechanical work produced by the system) is then given by $F du = p A du = p dV$, i.e. the mechanical work

produced by the system during the cycle is given by the area ΔW shown in Fig. 20.5a). Therefore

$$\text{Mechanical work produced during the cycle} = \Delta W > 0 \quad (20.8)$$

Since the system after the cycle has returned to its original state, we conclude that

$$\boxed{\text{Mechanical work is not a state function}} \quad (20.9)$$

cf. the definition of a state function given by (20.4).

Assume now that heat is a state function. Then, when the cycle has been completed, the total heat input must be zero. However, referring to (20.8) we have then created a machine that during one cycle only produces mechanical work without receiving any heat. This is a perpetual motion of the first kind and according to (20.6) such a machine is impossible. It is therefore concluded that

$$\boxed{\text{Heat is not a state function}} \quad (20.10)$$

20.4 First law of thermodynamics

With these introductory remarks, we are now able to present the first law of thermodynamics in a general form suitable for our purposes.

We consider a region of a body, i.e. a system, and we will first formulate the rate with which mechanical work is performed on the body. With t_i being the traction vector acting on the boundary surface S , b_i the body force per unit volume acting over the region V and \dot{u}_i the displacement rate, we have

$$\begin{aligned} \frac{\delta W}{dt} &= \text{rate of mechanical work input} \\ &= \text{mechanical power input} \\ &= \int_S \dot{u}_i t_i dS + \int_V \dot{u}_i b_i dV \end{aligned} \quad (20.11)$$

We have here chosen to denote this mechanical power input by $\delta W/dt$ instead of dW/dt . If the latter notation was used, this would suggest that the quantity W (the mechanical work) exists in the form of a function that depends on some variables, i.e. that W is a state function. But we have just shown that W is not a state function, cf. (20.9), and this issue is emphasized by the notation $\delta W/dt$. Put another way, dW is not a perfect differential and this is emphasized by writing the incremental mechanical work as δW . If dW were a perfect differential, then there would exist a function W that depends on some variables and W would then be a state function in contrast with our previous findings.

Let us next determine the rate of heat input to the body. Let q_i be the *heat flux vector*; this vector has the direction of the heat flow and its length expresses

the heat per unit time which passes through a unit surface area perpendicular to the direction of heat flow. Let n_i be the unit vector normal to the boundary and directed outwards. Moreover, let r denote the amount of *heat supply* per unit time and unit volume; this quantity represents heat sources within the body (inductive heating, for instance). We then have

$$\begin{aligned}\frac{\delta Q}{dt} &= \text{rate of heat input} \\ &= \int_V r dV - \int_S q_i n_i dS\end{aligned}\quad (20.12)$$

Again we use the notation $\delta Q/dt$ to indicate that heat is not a state function, cf. (20.10), i.e. no function Q exists.

The *kinetic energy* K of the body is defined by

$$K = \frac{1}{2} \int_V \rho \dot{u}_i \dot{u}_i dV \quad (20.13)$$

and it is certainly a state function depending on the velocity \dot{u}_i and the mass density ρ . Since we assume small strains, the mass density ρ can be considered as a constant, i.e.

$$\dot{K} = \int_V \rho \dot{u}_i \ddot{u}_i dV \quad (20.14)$$

We are now in a position to formulate the first law of thermodynamics. It states that

$$\boxed{\dot{K} + \dot{U} = \frac{\delta W}{dt} + \frac{\delta Q}{dt} \quad \text{global form of first law}} \quad (20.15)$$

where U is defined to be the so-called *internal energy* of the body. Moreover, it is postulated that

$$\boxed{\text{The internal energy is a state function}} \quad (20.16)$$

Expression (20.15) is referred to as the *global form* of the first law since it applies to the entire body in question.

The first law of thermodynamics is a postulate which, however, is supported by all experience; it is therefore accepted as an *axiom*. The first law may be viewed as the *principle of conservation of energy*, since it states that the sum of the rate of mechanical work input and the rate of heat input equals the sum of the rate of kinetic energy and rate of internal energy. It is of significant importance that whereas neither mechanical work input nor heat input are state functions, the sum of their rates creates $\dot{K} + \dot{U}$. Here the kinetic energy K is certainly a state function, cf. (20.13), whereas the internal energy U is postulated to be a state function. Therefore, the first law of thermodynamics is not only given by (20.15), but it also defines U to be a state function.

Let us write (20.15) as

$$dK + dU = \delta W + \delta Q \quad (20.17)$$

We then observe, as expected, that the first law excludes the existence of a perpetual motion of the first kind, cf. definition (20.6); integrating (20.17) over one cycle and observing that K and U are state functions, the left-hand side becomes zero, which yields $0 = \Delta W + \Delta Q$ and this expression excludes the existence of a perpetual motion of the first kind. The quantitative formulation of the first law was originally provided by Clausius in 1850.

Expression (20.15) formulates the first law in a global form that applies to the entire body. It turns out to be important to obtain a *local form* of the first law which holds at every point in the body. For this purpose, we first define the *specific internal energy* u per unit mass by

$$U = \int_V \rho u dV \quad (20.18)$$

The specific internal energy u is a state function just like the total internal energy U of the body is a state function.

Since the traction vector is given by $t_i = \sigma_{ij}n_j$, use of Gauss's divergence theorem in (20.11) implies that

$$\frac{\delta W}{dt} = \int_V (\dot{u}_i \sigma_{ij})_{,j} dV + \int_V \dot{u}_i b_i dV \quad (20.19)$$

Likewise, use of Gauss's divergence theorem in (20.12) gives

$$\frac{\delta Q}{dt} = \int_V r dV - \int_V q_{i,i} dV \quad (20.20)$$

Then insertion of (20.14) and (20.18)-(20.20) into (20.15) provides

$$\int_V [\dot{u}_i (\rho \ddot{u}_i - \sigma_{ij,j} - b_i) + \rho \dot{u} - \dot{u}_{i,j} \sigma_{ij} - r + q_{i,i}] dV = 0$$

Taking advantage of the equations of motion, cf. (3.29), we then obtain

$$\int_V (\rho \dot{u} - \dot{\epsilon}_{ij} \sigma_{ij} - r + q_{i,i}) dV = 0$$

Since this expression holds for arbitrary regions V , we conclude that

$$\rho \dot{u} = \dot{\epsilon}_{ij} \sigma_{ij} + r - q_{i,i} \quad \text{local form of first law} \quad (20.21)$$

This is the *local form* of the first law of thermodynamics that holds at every point in the body.

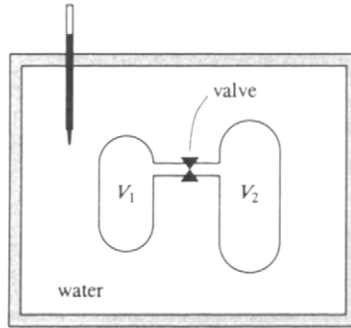


Figure 20.6: Joule's internal energy experiment.

20.5 Ideal gases

In order to introduce the second law of thermodynamics, we shall later use the concept of a *Carnot cycle*. For that purpose, we need information of certain processes performed with *ideal gases*. Ideal gases are described by the *ideal gas law*

$$pV = mR\theta; \quad \text{ideal gas law} \quad (20.22)$$

where p =pressure, V =volume, m =mass of gas, R =gas constant for the gas in question and θ is the absolute temperature. The ideal gas law was formulated preliminarily by Boyle in 1662 and by Mariotte in 1676 and given in its final form by Gay-Lussac in 1802. The ideal gas law applies with close accuracy for gases at not too high a pressure.

The state variables for the ideal gas are p , V and θ and since they are related via (20.22), one may choose, for instance, V and θ . This means that the total internal energy U of a certain amount of gas can be written in general as

$$U = U(V, \theta) \quad (20.23)$$

Note that the total internal energy U refers to a certain amount of matter.

Referring to (20.23) and in order to investigate the internal energy of ideal gases in more detail, Joule performed in 1845 the experiment shown in Fig. 20.6. Two vessels with volumes V_1 and V_2 are placed in a calorimeter filled with water. Initially, the vessel with volume V_1 is occupied by an ideal gas whereas the other vessel is evacuated. The valve connecting the two vessels is then opened and eventually the pressure will be the same in the two vessels. The experiment shows that no temperature change occurs in the calorimeter. Considering the gas as a system, we therefore have $\delta Q = 0$. Moreover, since the vessel walls can be regarded as rigid, the gas has performed no mechanical work on the

surroundings, i.e. $\delta W = 0$. According to the first law (20.17) and waiting until all kinematic energy has disappeared, the total internal energy U is then unchanged. Before opening of the valve, the gas volume is V_1 and after opening of the valve, the gas volume is $V_1 + V_2$. Referring to (20.23) and since the total internal energy is unchanged, we conclude that

$$U = U(\theta); \quad \text{ideal gas} \quad (20.24)$$

Note that the total internal energy U refers to all the particles that constitute the amount of gas considered. This gas amount may be compressed or expanded, but if the temperature is unchanged the total internal energy is also unchanged.

Let us next write the first law (20.17) in a form suitable for gases. Ignoring body forces and since the traction vector is given by $t_i = -pn_i$, (20.11) becomes

$$\frac{\delta W}{dt} = - \int_S \dot{u}_i p n_i dS = -p \int_S \dot{u}_i n_i dS = -p \dot{V}$$

For static conditions, (20.17) then becomes

$$dU = -pdV + \delta Q; \quad \text{for gas} \quad (20.25)$$

Let us next introduce the *specific heat capacity* c of a material. There are different measures of specific heat capacity, but here we will consider the specific heat capacity c_V at constant volume. It is defined as

$$\boxed{\text{The specific heat capacity } c_V \text{ is the amount of heat that must be supplied without change of volume in order to increase the temperature of one unit mass one degree}} \quad (20.26)$$

Note that according to this definition of c_V , the volume is kept constant and this is indicated by the subscript V . Since V is constant, (20.25) implies that $dU = \delta Q$ and according to definition (20.26) we then have

$$dU = \delta Q = mc_V d\theta \quad \text{when } V = \text{constant} \quad (20.27)$$

Following (20.18) and (20.24), we have $U = mu(\theta)$ where u is the internal energy per unit mass. Therefore, we obtain

$$dU = m \frac{du}{d\theta} d\theta$$

and a comparison with (20.27) shows that

$$dU = mc_V d\theta \quad \text{where} \quad c_V = \frac{du}{d\theta}; \quad \text{ideal gas} \quad (20.28)$$

Since (20.24) holds in general for ideal gases, (20.28) also holds in general for ideal gases. However, the material parameter c_V is measured at constant volume

as indicated by (20.27). For ideal gases, c_V can be considered as constant with close accuracy.

For later purposes, we will consider *isothermal processes*, i.e. $\theta = \text{constant}$, for ideal gases and *adiabatic processes*, i.e. $\delta Q = 0$, for ideal gases.

For isothermal processes where $\theta = \text{constant}$, (20.28) yields $dU = 0$ and the first law (20.25) then provides

$$\delta Q = p dV$$

Elimination of the pressure p by means of the gas law (20.22) gives

$$\delta Q = mR\theta \frac{dV}{V} \quad \text{isothermal, ideal gas} \quad (20.29)$$

For adiabatic processes where $\delta Q = 0$, the first law (20.25) gives $dU = -pdV$ which with (20.28) results in

$$mc_V d\theta = -pdV$$

Elimination of the pressure p by means of the gas law (20.22) gives

$$\frac{c_V}{R} \frac{d\theta}{\theta} = -\frac{dV}{V} \quad \text{adiabatic, ideal gas} \quad (20.30)$$

It should be recalled that the only purpose of this section is the establishment of relations (20.29) and (20.30). Advantage will be taken of these results later.

20.6 Reversible and irreversible processes

Let us next introduce the concept of *reversible* and *irreversible processes*. By definition, we have

$$\boxed{\text{A process is reversible if both the system and all its surroundings can be brought back to their initial conditions}} \quad (20.31)$$

This implies that a reversible process is defined as a process that can be reversed without leaving any trace on the system or its surroundings. Moreover

$$\boxed{\text{A process that is not reversible is irreversible}}$$

It should be pointed out that a system may be restored to its initial state following a process, irrespective of whether the process is reversible or irreversible. But for reversible processes, this restoration is made without leaving any trace on the surroundings whereas for irreversible processes, the surroundings will have changed their conditions.

Friction is a familiar form of irreversibility. When two bodies in contact are forced to move relative to each other, a friction force develops which opposes the motion and some mechanical work is needed to overcome this friction force. During the process, this mechanical work is eventually converted to heat and is transferred to the bodies in contact, as evidenced by a temperature increase at the interface. When the direction of the motion is reversed, the bodies can be restored to their initial position, but the interface will not cool during this reversed motion. On the contrary, additional mechanical work is needed to overcome the friction force that also opposes the reversed motion and this additional mechanical work will also be converted to heat and imply a temperature increase of the interface. As a result, the initial position of the bodies has been restored and even the heat developed during the process may be transferred to the surroundings so that the system is in its initial condition. However, the surroundings are not in their initial conditions, since they have received a certain amount of heat; the process is evidently irreversible.

Another form of irreversibility is heat transfer through a finite temperature difference. Consider as an example isothermal expansion or compression of the ideal gas where the heat exchange δQ is given by (20.29). From Fourier's law $\delta Q/\Delta t \sim \Delta\theta$ and a constant temperature difference $\Delta\theta$ between gas and surroundings, we may write in a symbolic form

$$\Delta Q = \text{constant } \Delta\theta \Delta t \quad (20.32)$$

where Δt is the time duration of the heat transfer. When the gas expands, (20.29) shows that $\delta Q > 0$, i.e. the gas temperature is lower than the temperature of the reservoir. When the gas is compressed, (20.29) provides $\delta Q < 0$, i.e. the gas temperature is higher than the reservoir. Since the reservoir temperature is assumed to be constant, the same gas temperature during expansion and compression can only be achieved by letting $\Delta\theta \rightarrow 0$, but since ΔQ is a finite quantity, (20.32) shows that we must require $\Delta t \rightarrow \infty$. This implies that if the heat transfer during expansion and compression is to be the same, the process must proceed infinitely slowly. A reversible heat transfer can therefore only be achieved if the temperature differences are infinitely small. Conversely, any finite temperature difference will result in an irreversible process.

It appears that reversible processes cannot be achieved in practice. However, reversible processes are important since they may be viewed as theoretical, idealized processes.

An evident example of an irreversible process is Joule's experiment illustrated in Fig. 20.6. Initially, the gas occupies the volume V_1 ; after opening of the valve, the gas occupies the volume $V_1 + V_2$ without leaving any trace on the surroundings. However, the opposite process cannot be imagined; it is not possible to bring the gas back to occupy its initial volume V_1 without changing the condition of the surroundings.

We may conclude that reversible processes are only possible if all changes

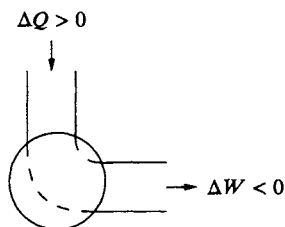


Figure 20.7: Principal sketch of perpetual motion of the second kind.

(of temperature, pressure, etc.) are infinitely small. This implies that a reversible process requires a uniform temperature and no unbalanced forces.

20.7 Introduction to the second law

The second law of thermodynamics can be formulated in various ways. Here we will adopt the most simple and direct physical approach. Just like the first law of thermodynamics was based on the impossibility of a perpetual motion of the first kind, we will base the *second law of thermodynamics* on the impossibility of a *perpetual motion of the second kind*. Let us make the following definition:

A perpetual motion of the second kind is a machine operating in cycles which, in any number of complete cycles, will receive heat from a single heat reservoir and produce an equivalent amount of mechanical work

(20.33)

Such a machine is illustrated in Fig. 20.7. The perpetual motion of the second kind works in cycles; therefore, after one cycle all conditions in the machine are unchanged and from the first law (20.17), we then have $0 = \Delta W + \Delta Q$ where ΔQ is the amount of heat received during one cycle and ΔW is the mechanical work produced during one cycle. Note that per definition, cf. (20.17), ΔW is positive if mechanical work is supplied to the system; in turn, $\Delta W < 0$ then means that the system produces work. We observe that a perpetual motion of the second kind does not violate the first law of thermodynamics. However, it is postulated that

A perpetual motion of the second kind is impossible

(20.34)

This formulation is the famous *Kelvin statement of the second law* from 1851 (William Thomson became Lord Kelvin when he was raised to the peerage); there exist other formulations of the second law - for instance the one proposed

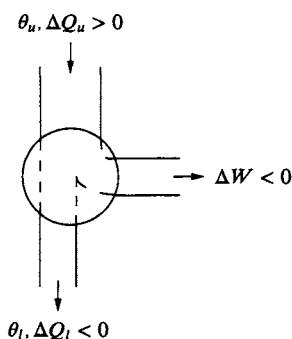


Figure 20.8: Principal sketch of heat engine.

by Clausius in 1850 - but we will later prove that the Kelvin statement and the Clausius statement are identical.

Whereas it is possible to convert mechanical energy completely into heat, cf. for instance the experiment of Joule shown in Fig. 20.3, it is an everyday experience that an amount of heat cannot be converted entirely into mechanical work and this is another, looser formulation of the Kelvin statement.

The impossibility of a perpetual motion of the second kind does not rely as much upon the fact that such a machine has never been constructed, but rather that it has a number of consequences that are in agreement with all experimental evidence and the second law of thermodynamics is therefore accepted as an *axiom*.

According to (20.33) and (20.34), it is impossible to construct a machine that operates in cycles and only receives heat. A machine must therefore also be able to reject heat. A principle sketch of an engine, a *heat engine*, therefore takes the form shown in Fig. 20.8. Here, in one cycle the amount of heat $\Delta Q_u (> 0)$ is supplied to the engine, which produces the mechanical work ΔW (where $\Delta W < 0$) while it rejects the amount of heat ΔQ_l (where $\Delta Q_l < 0$). Note that we measure heat and mechanical work as positive quantities when they are supplied to a system. The temperature θ_u at the reservoir providing the amount of heat ΔQ_u and the temperature θ_l at the reservoir receiving the amount of heat ΔQ_l are conveniently taken as constant temperatures since the heat engine is assumed to operate in cycles; that means, after one cycle, all conditions are assumed to be unchanged.

From the first law (20.17), we have

$$0 = \Delta W + \Delta Q_u + \Delta Q_l \quad (20.35)$$

The *efficiency* η of the heat engine is defined as

$$\boxed{\text{efficiency } \eta = \frac{-\Delta W}{\Delta Q_u}} \quad (20.36)$$

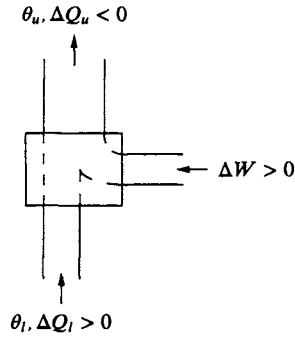


Figure 20.9: Principal sketch of refrigerator.

where it is noted that $-\Delta W > 0$. Combination of (20.35) and (20.36) yields

$$\boxed{\eta = 1 + \frac{\Delta Q_l}{\Delta Q_u}} \quad (20.37)$$

where $\Delta Q_l < 0$ and $\Delta Q_u > 0$.

From (20.36) appears that the efficiency η is a non-negative quantity. If $\eta = 1$, (20.37) shows that $\Delta Q_l = 0$ and the heat engine then turns into a perpetual motion of the second kind that only receives heat from one reservoir (ΔQ_u) and produces an equivalent amount of mechanical work (ΔW). But according to the Kelvin statement (20.34) such a machine is impossible and we conclude that

$$\boxed{0 \leq \eta < 1} \quad (20.38)$$

Evidently, when constructing a heat engine the aim is to achieve an efficiency that is as large as possible, but this efficiency is always smaller than unity. We shall later return to this subject.

A machine that operates in cycles and that represents the opposite of a heat engine is a *refrigerator*, cf. Fig. 20.9. Here, the mechanical work ΔW is supplied to the refrigerator, which receives the amount of heat ΔQ_l from the reservoir having the low temperature θ_l and rejects the amount of heat ΔQ_u to the reservoir having the high temperature θ_u .

Let us next turn to another formulation of the second law. It is an everyday experience that heat does not, by itself, flow from a cold region towards a warmer region. This is the content of the *Clausius statement of the second law* from 1850, which, in a more precise formulation, reads

$$\boxed{\text{It is impossible to construct a machine operating in cycles which, in any number of complete cycles, only results in a transfer of heat from a reservoir at one temperature to a reservoir at a higher temperature}} \quad (20.39)$$

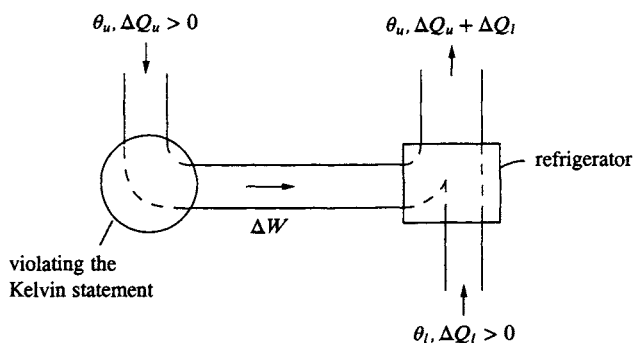


Figure 20.10: Refrigerator is powered by a perpetual motion of the second kind.

We will now prove that the Kelvin statement (20.34) and the Clausius statement (20.39) are equivalent. The proof consists of showing that if it were possible to violate one statement, the other statement would also be violated.

Suppose first that we have a heat engine that violates the Kelvin statement, i.e. it receives the amount of heat $\Delta Q_u (> 0)$ and produces an equivalent amount of mechanical work $\Delta W (< 0)$, where $\Delta W + \Delta Q_u = 0$. As shown in Fig. 20.10, this mechanical work is used to drive a refrigerator, which also receives the amount of heat $\Delta Q_l (> 0)$ at the reservoir having the temperature θ_l . Note that the mechanical work ΔW is considered as a positive quantity when it is supplied to the system (the machine) and as a negative quantity when it is produced by the system. The refrigerator rejects the amount of heat $\Delta Q_u + \Delta Q_l$ to the high-temperature reservoir. The combined result of this machinery is to take the amount of heat ΔQ_l from the low-temperature reservoir and deliver it to the high-temperature reservoir. We have then proved that violation of the Kelvin statement leads to violation of the Clausius statement.

Suppose next that we have a machine that violates the Clausius statement, i.e. it receives the amount of heat ΔQ_l from the low-temperature reservoir and transfers all this heat to the high-temperature reservoir. Referring to Fig. 20.11, this amount of heat ΔQ_l at the high-temperature reservoir as well as the additional amount of heat ΔQ_{add} is supplied to the heat engine that produces the mechanical work ΔW and rejects the amount of heat ΔQ_l to the low-temperature reservoir. The combined result of this machinery is to take the amount of heat ΔQ_{add} from the high-temperature reservoir and produce an equivalent amount of mechanical work ΔW . But this is a perpetual motion of the second kind, which violates the Kelvin statement.

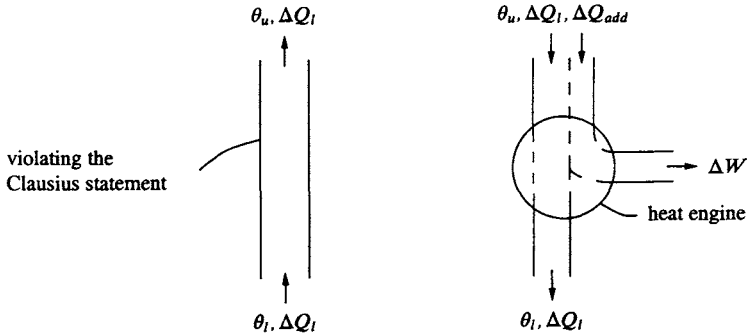


Figure 20.11: Combined effect of machine that violates the Clausius statement with a heat engine.

We have therefore proved that

The Kelvin statement and the Clausius statement of the second law are equivalent statements

20.8 Efficiency of various heat engines

Let us next prove the following statement

The efficiency of an irreversible heat engine is always less than the efficiency of a reversible heat engine operating between the same reservoirs

With evident notation, this statement may be written as

$$\eta_{irr} < \eta_{rev} \quad (20.40)$$

To prove (20.40), consider an irreversible heat engine and a reversible heat engine working between the same reservoirs, as shown in Fig. 20.12. The first law yields

$$0 = \Delta W^{irr} + \Delta Q_u^{irr} + \Delta Q_l^{irr} ; \quad 0 = \Delta W^{rev} + \Delta Q_u^{rev} + \Delta Q_l^{rev} \quad (20.41)$$

The two engines are operated such that they deliver the same mechanical work, i.e.

$$\Delta W^{irr} = \Delta W^{rev} = \Delta W \quad (20.42)$$

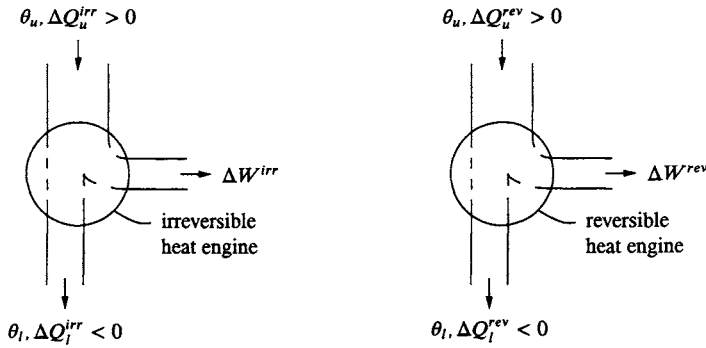


Figure 20.12: Irreversible and reversible heat engine working between the same reservoirs.

From (20.41) then follows that

$$\Delta Q_u^{irr} - \Delta Q_u^{rev} + \Delta Q_l^{irr} - \Delta Q_l^{rev} = 0 \quad (20.43)$$

Since the heat engine to the right in Fig. 20.12 is reversible, it can be reversed and thereby operate as a refrigerator. The irreversible heat engine is now coupled to this refrigerator and due to (20.42), all the mechanical work produced by the irreversible heat engine is used to drive the refrigerator, cf. Fig. 20.13.

Assume that the high-temperature reservoir receives heat from the combined machine, i.e.

$$\Delta Q_u^{irr} - \Delta Q_u^{rev} < 0 \quad (\text{assumption}) \quad (20.44)$$

Due to (20.43), this implies that $\Delta Q_l^{irr} - \Delta Q_l^{rev} > 0$, i.e. the low-temperature reservoir supplies heat to the combined machine. We are then led to a situation where the only result of the combined machine is a transfer of heat from a low-temperature reservoir to a high-temperature reservoir. But according to the Clausius statement (20.39) such a machine is impossible.

Assume next that

$$\Delta Q_u^{irr} - \Delta Q_u^{rev} = 0 \quad (\text{assumption}) \quad (20.45)$$

i.e. the total heat transfer to the high-temperature reservoir is nil. Due to (20.43), the total heat transfer from the low-temperature reservoir is then also nil. Within the combined machine, a number of processes takes place. However, after one cycle all conditions of the combined machine (the system) as well as of the reservoirs (the surroundings) have been restored. According to (20.31), this means that the processes are reversible, but this is in contradiction with the assumption that the combined machine involves an irreversible heat engine.

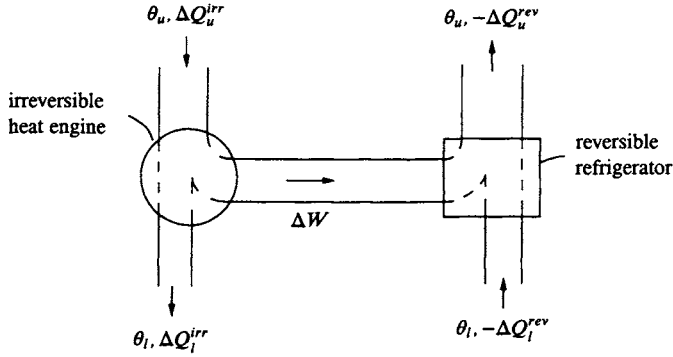


Figure 20.13: Irreversible heat engine driving a (reversible) refrigerator.

Since also (20.45) must be rejected, we are left with

$$\Delta Q_u^{irr} - \Delta Q_u^{rev} > 0 \quad \Rightarrow \quad \frac{\Delta Q_u^{rev}}{\Delta Q_u^{irr}} < 1 \quad (20.46)$$

where it was used that $\Delta Q_u^{irr} > 0$. Use of (20.37) and (20.43) yield

$$\eta_{irr} = \frac{\Delta Q_u^{irr} + \Delta Q_l^{irr}}{\Delta Q_u^{irr}} = \frac{\Delta Q_u^{rev} + \Delta Q_l^{rev}}{\Delta Q_u^{irr}} = \frac{\Delta Q_u^{rev}}{\Delta Q_u^{irr}} \eta_{rev} < \eta_{rev}$$

where advantage was taken of (20.46). This completes the proof of (20.40).

We will also prove that

All reversible heat engines that operate between the same reservoirs have the same efficiency

(20.47)

This statement is quite surprising, since it says that irrespective of how the cycles are devised and irrespective of the working medium used in the heat engines, the efficiency of reversible heat engines is the same, when the two reservoirs are the same.

To prove (20.47), Fig. 20.12 is considered again, but now the irreversible heat engine to the left is replaced by any reversible heat engine. The two heat engines are operated so that they deliver the same mechanical work $\Delta W_{left}^{rev} = \Delta W_{right}^{rev}$, cf. (20.42). The reversible heat engine to the right is again reversed so that it operates as a refrigerator that is driven by the heat engine to the left, cf. Fig. 20.13. Again we assume condition (20.44), which now reads $\Delta Q_u^{left} - \Delta Q_u^{right} < 0$, and again we conclude that this assumption violates the Clausius statement. Since we can choose arbitrarily which of the reversible heat engines that is to work as a refrigerator, we are left with the possibility that $\Delta Q_u^{left} -$

$\Delta Q_u^{right} = 0$. In combination with (20.42) ($\Delta W_{left}^{rev} = \Delta W_{right}^{rev}$), it follows that $\eta_{rev}^{left} = \eta_{rev}^{right}$ and statement (20.47) have then been proved.

For any two given reservoirs, restriction (20.38), i.e. $0 \leq \eta < 1$, holds and we have found that the largest efficiency is provided by a reversible heat engine. Any attempt to construct an efficient heat engine is therefore confined to reduce the irreversibilities as much as possible.

20.9 The Carnot process

It was shown that all reversible heat engines possess the same efficiency. In order to determine this efficiency, we may select any reversible process and the so-called *Carnot process* turns out to be especially convenient for this purpose. The reason is that the Carnot process is devised such that the requirement of reversibility can be fulfilled, at least in principle.

The Carnot process was suggested by Carnot in 1824 and it consists of the following cycle:

Carnot process:

1-2 reversible isothermal expansion

2-3 reversible adiabatic expansion

3-4 reversible isothermal compression

4-1 reversible adiabatic compression

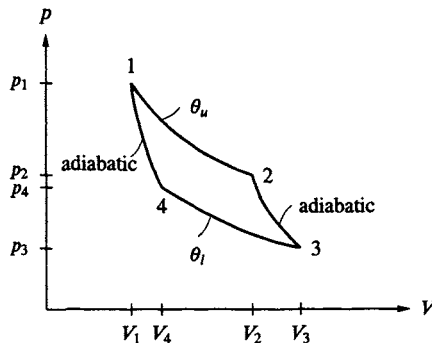


Figure 20.14: Carnot process with ideal gas; reversibility is assumed.

To illustrate this process, we may select as the working medium an ideal gas in a cylinder with a frictionless piston, cf. Fig. 20.14.

Initially in process 1-2, the gas temperature is θ_u and the cylinder are brought into contact with the high-temperature reservoir having the temperature θ_u ; an isothermal expansion is then enforced. In order that the process be reversible,

the difference between the temperature θ_u and the gas temperature should be infinitely small; this requires an infinitely slow expansion. Moreover, a reversible process requires that the piston moves in the cylinder in a frictionless manner. During this isothermal expansion, the gas receives heat from the high-temperature reservoir according to (20.29) and we obtain

$$\Delta Q_u = mR\theta_u \ln \frac{V_2}{V_1} \quad (20.48)$$

In process 2-3, the cylinder is insulated and an expansion occurs. In order that the process be reversible, no friction is allowed and the expansion should proceed infinitely slowly. According to (20.30), the temperature decreases and the expansion is continued until the temperature θ_l has been reached. From (20.30), we obtain

$$-\ln \frac{V_3}{V_2} = \int_{\theta_u}^{\theta_l} \frac{c_V}{R} \frac{d\theta}{\theta}$$

or

$$\ln V_3 = \ln V_2 + \int_{\theta_l}^{\theta_u} \frac{c_V}{R} \frac{d\theta}{\theta} \quad (20.49)$$

where we have changed the integration direction.

In process 3-4, the cylinder is brought into contact with the low-temperature reservoir having the temperature θ_l . A reversible isothermal compression occurs and (20.29) yields that heat is transferred to the low-temperature reservoir, where

$$\Delta Q_l = mR\theta_l \ln \frac{V_4}{V_3} \quad (20.50)$$

Finally in process 4-1, the cylinder is insulated and an adiabatic compression occurs; the process is again reversible. According to (20.30), the temperature then increases and the compression is continued until the temperature θ_u has been reached. From (20.30) follows that

$$-\ln \frac{V_1}{V_4} = \int_{\theta_l}^{\theta_u} \frac{c_V}{R} \frac{d\theta}{\theta}$$

or

$$\ln V_1 = \ln V_4 - \int_{\theta_l}^{\theta_u} \frac{c_V}{R} \frac{d\theta}{\theta} \quad (20.51)$$

From (20.37), (20.48) and (20.50), we obtain

$$\eta_{rev} = 1 + \frac{\theta_l \ln V_4 - \ln V_3}{\theta_u \ln V_2 - \ln V_1}$$

and insertion of (20.49) and (20.51) yields the result

$$\eta_{rev} = 1 - \frac{\theta_l}{\theta_u} \quad (20.52)$$

Therefore, the efficiency of a reversible heat engine is entirely determined by the temperatures of the reservoirs. We have obtained this conclusion by considering a reversible process in terms of a Carnot process using an ideal gas as working medium, but since all reversible heat engines have the same efficiency, (20.52) holds for all reversible heat engines, irrespective of the specific reversible cycle and irrespective of the working medium.

20.10 Thermodynamic temperature scale

The concept of temperature T and absolute temperature θ was discussed in Section 20.1. However, up to now the measurement of temperature hinges on the fact that some properties of a medium change with its coldness or hotness; such a measurement may, for instance, be based on expansion or contraction of mercury in a capillary, as used in a traditional thermometer. As another example, if a vessel of constant volume is filled with ideal gas, then the (absolute) temperature is proportional to the gas pressure, see Fig. 20.1. This means that by measuring the pressure, we can measure the temperature. Such a thermometer is called a *constant-volume gas thermometer* and the corresponding temperature is called the *ideal gas temperature scale*, which, as we have seen, is identical to the absolute temperature, i.e.

*Constant-volume gas thermometer \Rightarrow
ideal gas temperature scale = absolute temperature θ*

However, irrespective of the thermometer we adopt so far, the temperature measurement, in itself, relies on the properties of the substances used in the thermometer.

Theoretically, it would be of importance if the temperature measurement could be performed in such a manner that it is independent of the properties of some substances - at least in principle. Such a temperature scale is called a *thermodynamic temperature scale* and we have

A temperature scale that is independent of the properties of the substances that are used to measure temperature is called a thermodynamic temperature scale

It turns out to be possible to achieve a thermodynamic temperature scale and for that purpose, we first combine (20.37) and (20.52) to obtain

$$\frac{-\Delta Q_l}{\Delta Q_u} = \frac{\theta_l}{\theta_u} \quad \text{reversible machine} \quad (20.53)$$

To derive this relation, we used that for the same two reservoirs, all reversible heat engines have the same efficiency irrespective of their construction, working process and working medium. By specifically choosing a reversible process in terms of a Carnot process using an ideal gas as working medium, (20.53) was then derived. Therefore, (20.53) holds for all reversible machines.

The important point is that the ratio $-\Delta Q_l/\Delta Q_u$ is independent of the nature of the working substances, since the efficiency η_{rev} is so. Since the energy of amounts of heat can be measured directly by means of calorimetry, cf. the Joule test set-up shown in Fig. 20.3, without having defined a temperature scale, the ratio $-\Delta Q_l/\Delta Q_u$ can be measured. If we then consider (20.53) as a matter of definition, then we can measure the temperature ratio θ_l/θ_u only by means of calorimetry. Running a reversible heat engine and since the ratio $-\Delta Q_l/\Delta Q_u$ is independent of the involved substances also the temperature ratio θ_l/θ_u is independent of the involved substances. The thus-defined temperature ratio θ_l/θ_u therefore establishes a thermodynamic temperature scale. In principle, these considerations were put forward by Kelvin in 1854.

Since (20.53) has been shown to be satisfied if temperatures are measured by an ideal gas temperature scale = absolute temperature, we conclude that

$\begin{aligned} \text{Ideal gas temperature scale} &= \text{absolute temperature} \\ &= \text{thermodynamic temperature} \end{aligned}$
--

To be precise, (20.53) only defines the ratio θ_l/θ_u . To identify the thermodynamic temperature scale uniquely, one more piece of information is needed. In 1954, the *triple point of water* (the state at which ice, water and vapor exist in equilibrium) was assigned the value 273 K (273.16 K to be precise) and we are then back to (20.2).

From (20.52), we have

$$\theta_l = \theta_u(1 - \eta_{rev})$$

and since $0 \leq \eta_{rev} < 1$, cf. (20.38), we are led to the conclusion that the lowest attainable temperature θ_l is always greater than zero. This observation supports our previous conclusion given by (20.1).

20.11 Entropy - Clausius's inequality

Relation (20.53) holds when a reversible cycle is performed and it may be written as

$$\frac{\Delta Q_u}{\theta_u} + \frac{\Delta Q_l}{\theta_l} = 0 \quad \text{reversible cycle}$$

To indicate that a cycle is performed, this expression may be written as

$\oint \frac{\delta Q}{\theta} = 0 \quad \text{reversible cycle}$	(20.54)
---	---------

This relation is of significant interest. It was shown previously that heat is not a state function, cf. (20.10), therefore during a cycle we have, in general, $\oint \delta Q \neq 0$. Indeed, this was the motivation for denoting an infinitely small amount of heat by δQ and not dQ , since the latter notation would suggest that there exists a function Q that depends on some variables and then Q would be a state function, in contrast to (20.10). Referring to the discussion following (20.11) and (20.12), an infinitely small amount of heat is not a perfect differential and this is emphasized by using the notation δQ .

Any function, say $z = z(y_\alpha)$, where z depends on some variables y_α , will have the property that during any cycle, we have $\oint dz = 0$. If the variables y_α are state variables, then $z = z(y_\alpha)$ would be a state function. However, whereas heat is not a state function, (20.54) implies that there exists a state function, the *entropy S of the system*, defined by

$$dS = \frac{\delta Q}{\theta} \quad \text{reversible process} \quad (20.55)$$

To check that S is a state function, we calculate the change of S during a reversible cycle and due to (20.54), it follows that $\oint dS = 0$, in accordance with our expectations.

To discuss the concepts of a state function and a perfect differential in more detail, consider the following expression

$$\text{infinitely small quantity} = c_\alpha dy_\alpha \quad (20.56)$$

where the functions c_α depend on the variables y_α . Following, for instance, Kreyszig (1962) we have

A necessary and sufficient condition for (20.56) being a perfect differential is that

$$\frac{\partial c_\alpha}{\partial y_\beta} = \frac{\partial c_\beta}{\partial y_\alpha}$$

(20.57)

We then conclude that (20.56) may be written as

$$\begin{aligned} da &= c_\alpha dy_\alpha && \text{if perfect differential} \\ da &= c_\alpha dy_\alpha && \text{if not a perfect differential} \end{aligned}$$

Any function $z = z(y_\alpha)$ fulfills requirement (20.57) since

$$dz = \frac{\partial z}{\partial y_\alpha} dy_\alpha \quad \text{i.e.} \quad \frac{\partial}{\partial y_\beta} \left(\frac{\partial z}{\partial y_\alpha} \right) = \frac{\partial}{\partial y_\alpha} \left(\frac{\partial z}{\partial y_\beta} \right)$$

On the other hand, consider for instance the expression

$$\delta a = -y_2 dy_1 + y_1 dy_2 \quad (20.58)$$

Since $\partial(-y_2)/\partial y_2 = -1 \neq \partial(y_1)/\partial y_1 = 1$, (20.57) is not fulfilled and the quantity δa is not a perfect differential, as already indicated by the notation δa . However, if (20.58) is multiplied by the factor $1/y_2^2$, we obtain

$$\frac{\delta a}{y_2^2} = -\frac{1}{y_2} dy_1 + \frac{y_1}{y_2^2} dy_2 \quad (20.59)$$

It is now observed that

$$\frac{\partial}{\partial y_2} \left(-\frac{1}{y_2} \right) = \frac{1}{y_2^2} = \frac{\partial}{\partial y_1} \left(\frac{y_1}{y_2^2} \right) = \frac{1}{y_2^2}$$

i.e. (20.57) is fulfilled and, indeed, (20.59) may be integrated to provide

$$db = \frac{\delta a}{y_2^2} \quad \text{where} \quad b = -\frac{y_1}{y_2}$$

In the considered case, we could convert expression (20.58) into a perfect differential by multiplication with a factor, in the present case the factor $1/y_2^2$. Such factor is called an *integrating factor*.

With this discussion, it appears that the factor $1/\theta$ is the integrating factor which for a reversible process transforms the quantity δQ into the perfect differential dS , cf. (20.55).

After these preliminary remarks, we introduce the *entropy S of the body* in the following manner, as suggested by Clausius in 1865:

$$\boxed{\text{Clausius's inequality} \quad dS \begin{cases} = \frac{\delta Q}{\theta} & \text{reversible process} \\ > \frac{\delta Q}{\theta} & \text{irreversible process} \end{cases}} \quad (20.60)$$

Moreover, irrespective of whether the process is reversible or irreversible, we assume that

$$\boxed{\text{The entropy is a state function}} \quad (20.61)$$

Equations (20.60) and (20.61) express the second law of thermodynamics in a mathematical form. Just like the first law, the second law is a postulate, but since all experimental evidence supports this postulate, it is accepted as an axiom.

To illustrate the use of (20.60) and (20.61) and to show that they contain the various forms of the second law that we discussed previously, consider first a reversible heat engine having performed one cycle in a Carnot process, cf. Fig. 20.14. After one cycle, the system (the machine) has returned to its initial state. Since the entropy S of the system is a state function, it therefore takes the same value before and after the cycle. Therefore, (20.60) yields

$$0 = \oint dS = \oint \frac{\delta Q}{\theta} = \frac{\Delta Q_u}{\theta_u} + \frac{\Delta Q_l}{\theta_l} \quad \text{i.e.} \quad \frac{\Delta Q_l}{\Delta Q_u} = -\frac{\theta_l}{\theta_u}$$

Insertion into (20.37) gives

$$\eta_{rev} = 1 - \frac{\theta_l}{\theta_u}$$

in accordance with (20.52).

Consider next an irreversible heat engine having performed one cycle in a process similar to that of Carnot, but without the assumption of reversibility. Again, the entropy S is a state function and it therefore takes the same value before and after the cycle. Consequently, (20.60) gives

$$0 = \oint dS > \oint \frac{\delta Q}{\theta} = \frac{\Delta Q_u}{\theta_u} + \frac{\Delta Q_l}{\theta_l} \quad \text{i.e.} \quad \frac{\Delta Q_l}{\Delta Q_u} < -\frac{\theta_l}{\theta_u}$$

Insertion into (20.37) then yields

$$\eta_{irr} = 1 + \frac{\Delta Q_l}{\Delta Q_u} < 1 - \frac{\theta_l}{\theta_u} = \eta_{rev}$$

in accordance with (20.40).

It is of interest that whereas the first law postulates the existence of a state function, the internal energy, the second law postulates the existence of another state function, the entropy. The word 'entropy' originates from Greek and means 'change'.

The first law does not discriminate whether a process goes in one or another direction; it simply performs the book-keeping of the various energy changes. On the other hand, the second law is discriminative in the sense that it informs us whether a process is possible or not; a process is only possible if it satisfies Clausius's inequality (20.60).

20.12 Maximum entropy at thermodynamic equilibrium

Since the second law selects the processes that are possible, it indicates a trend in nature. It may therefore be used to determine a state of *thermodynamic equilibrium*. By definition, we have

Consider a system where no change in the boundary conditions occurs, i.e. no mechanical work input and no heat input.

The system is then in thermodynamic equilibrium if no changes of the state variables can occur

(20.62)

Thus thermodynamic equilibrium implicitly refers to static conditions. Since $\delta W = \delta Q = 0$, the first law (20.15) implies that $dU = 0$, i.e. the internal energy is constant. A necessary condition for thermodynamic equilibrium is

therefore that the internal energy is constant. With $\delta Q = 0$, the second law (20.60) gives $dS \geq 0$; therefore, if $\delta W = \delta Q = 0$ then the only processes that are allowable are those which imply that $dS \geq 0$. If it is the case that the entropy takes a maximum value, then any change of the state variables would imply that S decreases, which is impossible, and we therefore have thermodynamic equilibrium. Consequently:

If $\delta W = \delta Q = 0$ and if the entropy has a maximum value, thermodynamic equilibrium exists	(20.63)
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This statement is due to Gibbs and it was formulated in 1876.

20.13 The second law and the Clausius-Duhem inequality

It is timely to establish a form of the second law that is of relevance for constitutive mechanics. First of all, we define the *specific entropy* s per unit mass, i.e.

$S = \int_V \rho s dV$	(20.64)
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The specific entropy s is a state function just like the total entropy S of the body is a state function.

Dividing Clausius's inequality (20.60) by dt , we obtain

$$\dot{S} \geq \frac{1}{\theta} \frac{\delta Q}{dt} \quad (20.65)$$

This expression holds for a homogenous system (body) where the temperature is constant. For a body within which the temperature is allowed to vary we obtain with (20.12)

$\dot{S} \geq \int_V \frac{r}{\theta} dV - \int_S \frac{q_i}{\theta} n_i dS$	<i>global form of second law</i> <i>= Clausius-Duhem inequality</i>	(20.66)
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This is the *global form* of the second law and following the terminology suggested by Truesdell and Toupin (1960), it forms the celebrated *Clausius-Duhem inequality* in its global form. The volume term in (20.66) is often called the *entropy source term* whereas the boundary term in (20.66) often is called the *entropy flux term*.

An important point here is that the temperatures in the previous discussion were the temperatures of the reservoirs, i.e. the temperatures at the boundary of the system. This observation motivates the boundary term $\int_S q_i n_i / \theta dS$ in

(20.66). However, in the previous discussion no reference was made to the temperature within the system (within the heat engine) and one may therefore question the volume term $\int_V r/\theta dV$ in (20.66). If the temperature is constant within the body (the system), (20.66) certainly reduces to (20.65). In general, however, the temperature is not uniform and with the just mentioned remarks of the volume term in (20.66) in mind, it is not evident that the total entropy S obeys inequality (20.66). A further discussion of this delicate problem goes beyond the scope of the present exposition and the interested reader may, for instance, consult Gurtin and Williams (1966), Truesdell (1969) and Hutter (1977). Here, we adopt (20.66) as an axiom and it is the global form of the second law.

According to the divergence theorem of Gauss, we have

$$\int_S \frac{q_i}{\theta} n_i dS = \int_V \left(\frac{q_i}{\theta} \right)_{,i} dV \quad (20.67)$$

Insertion of (20.64) and (20.67) into (20.66) and observing that due to the assumption of small strains, the mass density ρ can be considered as constant, we obtain

$$\int_V \left[\rho \dot{s} - \frac{r}{\theta} + \left(\frac{q_i}{\theta} \right)_{,i} \right] dV \geq 0$$

As this expression holds for arbitrary regions V , it is concluded that

$$\boxed{\rho \dot{s} - \frac{r}{\theta} + \frac{q_{i,i}}{\theta} - \frac{q_i \theta_{,i}}{\theta^2} \geq 0 \quad \begin{array}{l} \text{local form of second law} \\ = \text{Clausius-Duhem inequality} \end{array}} \quad (20.68)$$

This is the *local form* of the second law, i.e. the local form of the Clausius-Duhem inequality that holds at every point in the body.

It is recalled that the equality sign holds for reversible processes whereas the inequality sign holds for irreversible processes. The essence of constitutive mechanics has now been boiled down to fulfillment of the Clausius-Duhem inequality. If our suggestions for constitutive models fulfill this inequality, the models satisfy the second law and thereby fulfill all formal physical requirements. Whether the suggested models provide a close approximation to the actual behavior of the materials in question is another issue where thermodynamics cannot give any help. Therefore

Any constitutive model that fulfills the Clausius-Duhem inequality, fulfills all formal requirements

One may wonder whether fulfillment of the first law also places restrictions on constitutive modeling. However, as we shall see in the next chapter the first law turns into the *heat equation*, which places no restrictions on constitutive modeling, but which instead determines the temperature distribution within the body.

20.14 Various approaches to thermodynamics

The essence of this chapter is the first law in its global and local forms, cf. (20.15) and (20.21), as well as the second law, i.e. the Clausius-Duhem inequality, in its global and local forms, cf. (20.66) and (20.68). Moreover, the specific internal energy u and the specific entropy s are postulated to be state functions, i.e. functions that only depend on the current values of those variables, the state variables, that characterize the state, cf. (20.3) and (20.4).

To achieve to this point, the essential principles of the classic thermodynamics were presented and they served as a physical motivation for these main results. This is in contrast with the mainstream of textbooks within constitutive modeling where the first and second laws are simply presented as principles that must be satisfied. Here, we have taken a somewhat less abstract viewpoint by trying to motivate these laws by various physical arguments and the hope is that a quantity like the entropy will appeal to the physical insight of the reader and not just become an abstract quantity that the reader is able to manipulate in various expressions.

However, it would be unfair not to mention that our approach may be criticized and that other approaches to thermodynamics exist. While the scientific community accepts the first law as truly being an axiom, arguments may be raised against the second law and this manifests itself in different formulations of the second law.

For reversible processes, we could argue strictly that the factor $1/\theta$ is the integrating factor that transforms the quantity δQ into the perfect differential $dS = \delta Q/\theta$, cf. (20.55) and (20.60); this implies that the entropy S certainly is a state function. However, as mentioned in Section 20.6, reversible processes are only possible if all changes (of temperature, pressure, etc.) are infinitely small. This implies that a reversible process requires a uniform temperature and no unbalanced forces. For reversible processes to occur, the body must therefore be subjected to conditions that are in equilibrium and this is the reason why this part of thermodynamics often is termed *thermostatistics*. In that case, we can prove with confidence that the entropy is a state function.

However, for irreversible processes the body is not in equilibrium (in the manner defined above) and it may then be questioned whether the entropy is a state function, cf. for instance Meixner (1970) and Hutter (1977). This is the reason for two schools of thought: the so-called *irreversible thermodynamics* and the so-called *rational thermodynamics*.

The school of irreversible thermodynamics focusses on the fact that under equilibrium (reversible) conditions, the entropy is a state function. Therefore, in irreversible thermodynamics the irreversible processes are thought of as being close to equilibrium and only slight, i.e. linear, deviations are allowed.

Within the school of rational thermodynamics with which names like Truesdell, Coleman, Toupin, Eringen and Noll are associated, it is simply accepted

that the entropy is a state function also for irreversible processes far from equilibrium and the second law is then taken in the form of the Clausius-Duhem inequality. This line of thought then investigates the consequences for constitutive theories when they are to fulfill this inequality. The result is a field theory of great beauty and with very important consequences.

Here, we will adopt in the following chapters the viewpoint of the school of rational thermodynamics, that means accept the first and second laws as stated by (20.16), (20.21) and (20.61), (20.68), respectively. However, instead of simply stating these laws, as it is common in rational thermodynamics, we have tried to provide a physical motivation for these laws. In the present chapter, we have also deviated from the school of rational thermodynamics in another aspect by first introducing the concept of temperature as something we can measure and accept and then obtaining the entropy as a derived, i.e. related, concept. This means that we have used the temperature as a so-called *primitive quantity*. Within rational thermodynamics, the entropy is introduced first as a primitive quantity and the temperature then becomes a derived quantity. However, irrespective of which approach is adopted, the resulting relations become the same, but the present approach has been adopted since it seems to be more appealing to the physical intuition of the reader.