Chapter 3
The First Law of Thermodynamics

3.1 Conservation of Energy

It is our daily experience that heat can be converted to work, and that work can be converted to heat. A propeller mounted over a burning candle will spin when the heated air rises due to buoyancy: heat is converted to work. Rubbing your hands makes them warmer: work is converted to heat. Humankind has a long and rich history of making use of both conversions. Friction between a fast spun stick and a resting piece of wood is used since millennia to create a fire. Technical applications of heat to work conversions are abundant through history, and our modern life is unthinkable without heat engines such as steam and gas turbines for generation of electricity, or car and aircraft engines for transport. In cooling engines work is used to withdraw heat, such as in refrigerators or in air conditioning devices.

The evaporation of water to steam by heating provides a large change in volume and/or pressure. Devices using this effect were known already more than 2000 years ago, but they became prevalent with the development of the steam engine. Thermodynamics was initially developed to better understand the processes in steam engines and other conversion devices, so that the understanding can be used to improve the engines.

While the heat-to-work and work-to-heat conversions are readily observable in simple and more complex processes, the governing law is not at all obvious from simple observation. It required groundbreaking thinking and careful experiments to unveil the *law of conservation of energy.* Due to its importance in thermodynamics, it is also known as the *First Law of Thermodynamics.*

Expressed in words, the *First Law of Thermodynamics* reads:

> *Energy cannot be produced nor destroyed, it can only be transferred, or converted from one form to another. In short, energy is conserved.*

It took quite some time to formulate the first law in this simple form, the credit for finding and formulating it goes to Robert Meyer (1814-1878), James

H. Struchtrup, *Thermodynamics and Energy Conversion*,

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Prescott Joule (1818-1889), and Hermann Helmholtz (1821-1894). Through careful measurements and analysis, they recognized that thermal energy, mechanical energy, and electrical energy can be transformed into each other, which implies that energy can be transferred by doing work, as in mechanics, and by heat transfer.

The first law is generally valid, no violation was ever observed. As knowledge of physics has developed, other forms of energy had to be included, such as radiative energy, nuclear energy, or the mass-energy equivalence of the theory of relativity, but there is no doubt today that energy is conserved under all circumstances.

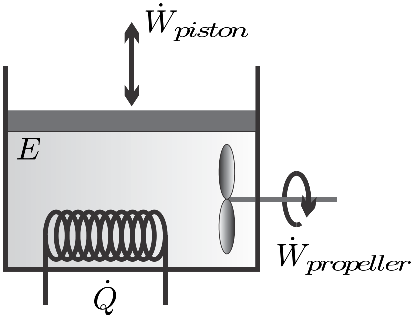

Fig. 3.1 Closed system with energy E exchanging work $\dot{W}$ and heat $\dot{Q}$ with its surroundings

We formulate the first law for the simple closed system, depicted again in Fig. 3.1, where all three possibilities to manipulate the system from the outside are indicated. For this system, the conservation law for energy reads

$$\frac{dE}{dt} = \dot{Q} - \dot{W} \,, \tag{3.1}$$

where E is the total energy of the system, $\dot{Q}$ is the heat transfer rate in or out of the system, and $\dot{W} = \dot{W}_{piston} + \dot{W}_{propeller}$ is the total power—the work per unit time—exchanged with the surroundings.

This equation states that the change of the system's energy in time (dE/dt) is equal to the energy transferred by heat and work per unit time ($\dot{Q} - \dot{W}$). The sign convention used is such that heat transferred *into* the system is positive, and work done *by* the system is positive.

The SI unit of energy, work, and heat is the Joule, $1\,\mathrm{J} = 1\,\mathrm{N\,m} = 1\frac{\mathrm{kg\,m^2}}{\mathrm{s^2}}$; the SI unit of power and heat transfer rate is the Watt, $1\,\mathrm{W} = 1\frac{\mathrm{J}}{\mathrm{s}}$.

All contributions to the first law (3.1), i.e., energy, work and heat, will be discussed in detail in the following sections.

3.2 Total Energy

The total energy E of the system is the sum of its kinetic energy E_{kin}, potential energy E_{pot}, and internal—or thermal—energy U,

$$E = U + E_{kin} + E_{pot} \ . \tag{3.2}$$

Presently, these are the only forms of energy that we need for the description of thermal processes; other forms of energy that can be relevant are chemical energy, nuclear energy, radiative energy and electrical energy, which will be introduced when required.

We address the different contributions to energy in the next sections.

3.3 Kinetic Energy

The kinetic energy is well-known from mechanics. For a homogeneous system of mass m and velocity $\mathcal{V}$, kinetic energy is given by

$$E_{kin} = \frac{m}{2}\mathcal{V}^2 \ . \tag{3.3}$$

For inhomogeneous states the total kinetic energy of the system is obtained by integration of the specific kinetic energy e_{kin} over all mass elements $dm = \rho dV$; we have

$$e_{kin} = \frac{1}{2}\mathcal{V}^2 \quad \text{and} \quad E_{kin} = \int \rho e_{kin} dV = \int \frac{\rho}{2}\mathcal{V}^2 dV \ . \tag{3.4}$$

3.4 Potential Energy

Also the potential energy in the gravitational field is well-known from mechanics. For a homogeneous system of mass m , potential energy is given by

$$E_{pot} = mgz \ , \tag{3.5}$$

where z is the elevation of the system's center of mass over a reference height, and $g = 9.81\frac{\mathrm{m}}{\mathrm{s}^2}$ is the gravitational acceleration on Earth.

For inhomogeneous states the total potential energy of the system is obtained by integration of the specific potential energy e_{pot} over all mass elements $dm = \rho dV$; we have

$$e_{pot} = gz \quad \text{and} \quad E_{pot} = \int \rho e_{pot} dV = \int \rho gz dV \ . \tag{3.6}$$

3.5 Internal Energy and the Caloric Equation of State

Even if a macroscopic element of matter is at rest, its atoms move (in a gas or liquid) or vibrate (in a solid) fast, so that each atom has microscopic kinetic energy. Moreover, the atoms are subject to interatomic forces, which contribute microscopic potential energies. These microscopic energies depend on temperature, and the higher the temperature, the higher the average microscopic energy. Since the microscopic kinetic and potential energies cannot be observed macroscopically, one speaks of the *internal energy*, or *thermal energy*, of the material, denoted as U.

For inhomogeneous states the total internal energy of the system is obtained by integration of the specific internal energy u over all mass elements $dm = \rho dV$. For homogeneous and inhomogeneous systems we have

$$U = mu \quad \text{and} \quad U = \int \rho u dV \; . \tag{3.7}$$

Internal energy cannot be measured directly. The *caloric equation of state* relates the specific internal energy u to measurable quantities, it is of the form $u = u\left(T, v\right)$, or $u = u\left(T, p\right)$. Recall that pressure, volume and temperature are related by the thermal equation of state, $p\left(v, T\right)$; therefore it suffices to know two properties in order to determine the others.

The caloric equation of state must be determined by careful measurements, where the response of the system to heat or work supply is evaluated by means of the first law. For most materials the results cannot be easily expressed as equations, and are tabulated in property tables, see Chapter 6. Some simple caloric equations of state will be presented already in Sec. 3.10.

For inhomogeneous states, where the properties are space dependent, we assume the validity of the caloric equation of state in the local volume element dV. This assumption reflects our understanding that the atoms and molecules of the considered substance are interacting frequently, and thus behave as a collective, see Sec. 2.2.

3.6 Work and Power

Work, denoted by W, is the product of a force and the displacement of its point of application. Power, denoted by $\dot{W}$, is work done per unit time, that is the force times the velocity of its point of application. The total work for a process is the time integral of power over the duration $\Delta t = t_2 - t_1$ of the process,

$$W = \int_{t_1}^{t_2} \dot{W} dt \; . \tag{3.8}$$

For the closed system depicted in Fig. 2.1 there are two contributions to work: *moving boundary work*, due to the motion of the piston, and *rotating* *shaft work,* which moves the propeller. Other forms of work, e.g., spring work or electrical work will be discussed as required.

Work and power can be positive or negative. We follow the sign convention that work done *by* the system is positive and work done *to* the system is negative.

Moving boundary work is best computed from a piston-cylinder system, as depicted in Fig. 3.2; however, the subsequent expressions are valid for arbitrary system geometries. The force on the piston of cross section A is pA and thus the work for an infinitesimal displacement ds is given by $\delta W = pAds = pdV$, where $dV = Ads$ is the volume change associated with the displacement. As the piston is moved, the pressure within the system might change. Thus, the work W_{12} for a finite displacement $V_2 - V_1$ must be computed by summing over the infinitesimal contributions δW, that is by integration, $W_{12} = \int \delta W = \int_1^2 pdV$.

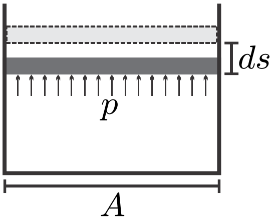

Fig. 3.2 Moving boundary work in a piston-cylinder system at pressure p, piston area A, displacement ds. Work is $\delta W = pdV = pAds$.

The power $\dot{W}$ is obtained from multiplying the force pA with the velocity $\frac{ds}{dt}$ of the piston. Since the cross section does not change, we have $A\frac{ds}{dt} = \frac{dV}{dt}$, and $\dot{W} = p\frac{dV}{dt}$.

Altogether we have the following expressions for moving boundary work with finite and infinitesimal displacement, and for power,

$$W_{12} = \int_1^2 pdV \quad , \quad \delta W = pdV \quad , \quad \dot{W} = p\frac{dV}{dt} \; . \tag{3.9}$$

Here, p is the pressure at the piston; for simplicity we have ignored variations of pressure along the piston surface.

Closed equilibrium systems are characterized by a single homogeneous pressure[1] p, a single homogeneous temperature T, and the volume V. In quasi-static (or reversible) processes, the system passes through a series of equilibrium states which can be indicated in suitable diagrams. Figure 3.3 shows a pressure-volume diagram (p-V-diagram) of two different reversible processes connecting the points $\{p_1, V_1\}$ and $\{p_2, V_2\}$. Due to the relation

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[1] Hydrostatic variation ignored, see Sec. 2.19.

$W_{12} = \int_1^2 pdV$, the work is the area below the respective process curves as indicated by hatching. Obviously, the amount of work depends on the process: work is a path dependent function.

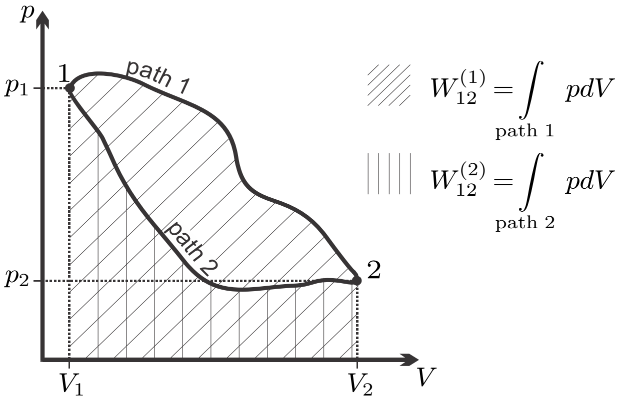

Fig. 3.3 Two reversible processes between points 1 and 2 in the p-V-diagram, and the corresponding moving boundary work

The power transmitted by a rotating shaft is related to the torque **T** and the revolutionary speed $\dot{n}$ (revolutions per unit time) as $\dot{W} = 2\pi\dot{n}\mathbf{T}$, the total work transmitted during a finite time interval is, again, $W_{12} = \int_1^2 \dot{W}dt$. The transmission between the shaft and the working fluid is performed by a propeller (turbines, compressors etc.).

In a closed system the propeller stirs the working fluid and creates inhomogeneous states. Fluid friction transmits fluid motion (i.e., momentum and kinetic energy) from the fluid close to the propeller to the fluid further away. Due to the inherent inhomogeneity, stirring of a fluid in a closed system cannot be a quasi-static process.

This is different in open systems, where fluid is entering and leaving the system. The motion of the fluid can be used to drive the propeller, which decelerates the fluid and transmits work out of the system, or the propeller can provide work to accelerate the fluid. These flow processes can be reversible.

In general, there might be several work interactions $\dot{W}_j$ of the system, then the total work for the system is the sum over all contributions; e.g., for power

$$\dot{W} = \sum_j \dot{W}_j \ . \tag{3.10}$$

Finally we note that mechanical work can be transferred without restrictions between systems in mechanical contact:

> *By using gears and levers, one can transfer work from slow moving to fast moving systems and vice versa, and one can transmit work from high pressure to low pressure systems and vice versa.*

3.7 Exact and Inexact Differentials

Above we have seen that work depends on the process path. In the language of mathematics this implies that the work for an infinitesimal step is not an exact differential, and that is why a Greek delta (δ) is used to denote the work for an infinitesimal change as δW. As will be seen in the next section, heat is path dependent as well.

State properties like pressure, temperature, volume and energy describe the momentary state of the system, or, for inhomogeneous states, the momentary state in the local volume element. State properties have exact differentials for which we write, e.g., dE and dV. The energy change $E_2 - E_1 = \int_1^2 dE$ and the volume change $V_2 - V_1 = \int_1^2 dV$ are independent of the path connecting the states.

It is important to remember that work and heat, as path functions, only describe property *changes*, not states. A state is characterized by state properties (pressure, temperature, etc.), it does not possess work or heat.

Quasi-static (reversible) processes go through well defined equilibrium states, so that the whole process path can be indicated in diagrams, e.g., the p-V-diagram.

Non-equilibrium (irreversible) processes, for which typically the states are different in all volume elements, cannot be drawn into diagrams. Often irreversible processes connect homogeneous equilibrium states which can be indicated in the diagram. We shall use dashed lines to indicate non-equilibrium processes that connect equilibrium states. As an example, Fig. 3.4 shows a p-V-diagram of two processes, one reversible, one irreversible, between the same equilibrium states 1 and 2. We emphasize that the dashed line does not refer to actual states of the system. The corresponding work for the non-equilibrium process cannot be indicated as the area below the curve, since its computation requires the knowledge of the—inhomogeneous!—pressures at the piston surface at all times during the process.

3.8 Heat Transfer

Heat is the transfer of energy due to differences in temperature. Experience shows that for systems in thermal contact the direction of heat transfer is restricted:

> *Heat will always go from hot to cold by itself, but not vice versa.*

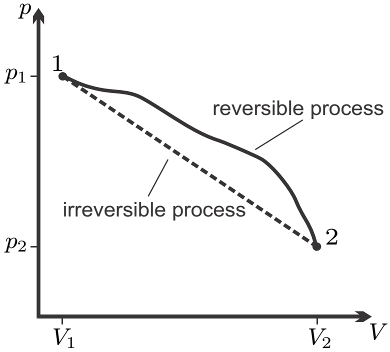

Fig. 3.4 A reversible (quasi-static) and an irreversible (non-equilibrium) process between the equilibrium states 1 and 2

This restriction of direction is an important difference to energy transfer by work between systems in mechanical contact, which is not restricted.

Since heat flows only in response to a temperature difference, a quasi-static (reversible) heat transfer process can only be realized in the limit of infinitesimal temperature differences between the system and the system boundary, and for infinitesimal temperature gradients within the system.

The main heat transfer mechanisms are: (a) Heat conduction, where thermal energy is transmitted by microscopic energy exchange between neighboring particles. (b) Convection, where fluid elements move to hotter or colder parts of the system and then exchange energy with the new neighborhood. (c) Radiative transfer, where electromagnetic radiation that crosses the system boundaries is absorbed or emitted by the matter inside the system. In the present context we do not need to discuss the details of these heat transfer mechanisms, which ultimately describe the same thing: energy transfer driven by temperature difference.

We use the following notation: $\dot{Q}$ denotes the heat transfer rate, that is the amount of energy transferred as heat per unit time. Heat depends on the process path, so that the heat exchanged for an infinitesimal process step, $\delta Q = \dot{Q}dt$, is not an exact differential. The total heat transfer for a process between states 1 and 2 is

$$Q_{12} = \int_1^2 \delta Q = \int_{t_1}^{t_2} \dot{Q} dt \, . \tag{3.11}$$

By convention, heat transferred into the system is positive, heat transferred out of the system is negative.

A process in which no heat transfer takes place, $\dot{Q} = 0$, is called *adiabatic process.*

In general, there might be several heat interactions $\dot{Q}_k$ of the system, then the total heat for the system is the sum over all contributions; e.g., for the heating rate

$$\dot{Q} = \sum_k \dot{Q}_k \, . \tag{3.12}$$

Confusion might result between the use of the word *heat* in everyday language, and its use in thermodynamics. In thermodynamics, *heat* solely describes a means to transfer energy in response to temperature differences. In particular we emphasize that heat is *not* a form of energy, and does not relate to how hot it might be outside. To say "oh, what a heat" is common language, a thermodynamicist will say "oh, it's pretty hot outside", or, even better, "oh, the temperature is pretty high today." A state is characterized by its energy or temperature, a change of state is characterized by heat (transfer).

3.9 The First Law for Reversible Processes

The form (3.1) of the first law is valid for all closed systems. When only reversible processes occur within the system, so that the system is in equilibrium states at any time, the equation can be simplified as follows: From our discussion of equilibrium states we know that for reversible processes the system will be homogeneous, and that all changes must be very slow, which implies very small velocities. Therefore, kinetic energy can be ignored, $E_{kin} = 0$. Stirring, which transfers energy by moving the fluid and friction, is irreversible, hence in a reversible process only moving boundary work can be transferred. As long as the system location does not change, the potential energy does not change, and we can set $E_{pot} = 0$.

With all this, for reversible (quasi-static) processes the first law of thermodynamics reduces to

$$\frac{dU}{dt} = \dot{Q} - p\frac{dV}{dt} \quad \text{or} \quad U_2 - U_1 = Q_{12} - \int_1^2 p dV \, , \tag{3.13}$$

where the second form results from integration over the process duration. We shall later, in particular in Chapter 7, use this equation extensively to study reversible processes in closed systems.

3.10 The Specific Heat at Constant Volume

We consider a closed system heated at constant volume (*isochoric* process), where the first law (3.13) reduces to (recall that $U = mu\,(T, v)$ and $m = const.$)

$$m\left(\frac{\partial u}{\partial T}\right)_v \frac{dT}{dt} = \dot{Q} \, . \tag{3.14}$$

Here, $\left(\frac{\partial u}{\partial T}\right)_v = \frac{\partial u(T,v)}{\partial T}$ denotes the partial derivative of internal energy with temperature at constant specific volume[2] $v = V/m$. This derivative is known as the *specific heat* (or *specific heat capacity*) *at constant volume*,

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v . \tag{3.15}$$

To understand this name for c_v, we rewrite (3.14) as

$$c_v dT = \frac{\dot{Q}dt}{m} = \frac{\delta Q}{m} . \tag{3.16}$$

From this equation we see that c_v is the amount of heat required to increase the temperature of 1 kg of substance by 1 K at constant volume. The specific heat can be measured by controlled heating of a fixed amount of substance in a fixed volume system, and measurement of the ensuing temperature difference; its SI unit is $\left[\frac{\mathrm{kJ}}{\mathrm{kg\,K}}\right]$.

In general, $c_v\left(T, v\right) = \left(\frac{\partial u}{\partial T}\right)_v$ is a function of temperature and specific volume. For incompressible liquids and solids the specific volume is constant, $v = const$, and the specific heat is a function of temperature alone. Interestingly, also for ideal gases the specific heat turns out to be a function of temperature alone, both experimentally and from theoretical considerations. For these materials the internal energy depends only on temperature, and integration gives the caloric equation of state as

$$u\left(T\right) = \int_{T_0}^{T} c_v\left(T'\right) dT' + u_0 . \tag{3.17}$$

Only energy differences can be measured, where the first law is used to evaluate careful experiments. The choice of the energy constant $u_0 = u\left(T_0\right)$ fixes the energy scale. The actual value of this constant will only become relevant for the discussion of chemical reactions. Note that proper mathematical notation requires to distinguish between the actual temperature T of the system, and the integration variable T'.

For materials in which the specific heat varies only slightly with temperature in the interval of interest, the specific heat can be approximated by a suitable constant average c_v^{avg}, so that the caloric equation of state assumes the particularly simple linear form

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[2] Due to the abundance of thermodynamic properties, and the freedom to choose any two of them as variables, one needs to be careful with the notation. In the present context, internal energy depends on two variables, and when a partial derivative is taken with respect to one variable, it is customary to indicate the second variable by a subscript, to condense notation. This notation, where, e.g., $\left(\frac{\partial u}{\partial T}\right)_v = \frac{\partial u(T,v)}{\partial T}$ will be used throughout this text for partial derivatives of properties.

$$u(T) = c_v^{avg}(T - T_0) + u_0 \ . \tag{3.18}$$

This relation for the caloric equation of state will serve us well in our first examples.

For temperatures around the standard environmental temperature $T_0 = 298\,\mathrm{K}$ ($\equiv 25\,°\mathrm{C}$), the specific heat of air is $c_v^{\mathrm{air}} = 0.717\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$, for liquid water one finds $c_w = 4.18\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$. The old unit for heat and thermal energy, the calorie $[\mathrm{cal}]$, is defined such that one calorie is the heat required to raise the temperature of one gram of water by one degree Celsius (from $14.5\,°\mathrm{C}$ to $15.5\,°\mathrm{C}$ at $p_0 = 1\,\mathrm{atm}$), thus $1\,\mathrm{cal} = 4.18\,\mathrm{J}$, and $1\,\mathrm{kcal} = 4.18\,\mathrm{kJ}$.

3.11 Enthalpy

In many thermodynamic calculations one encounters the combination $U+pV$, or the mass divided equivalent $u+pv$, and it is convenient to introduce a name and a symbol for these. We define the total and the specific *enthalpy* as

$$H = U + pV \quad , \quad h = u + pv \ , \tag{3.19}$$

where $H = mh$.

Using enthalpy to replace internal energy, the first law for quasi-static processes assumes the forms[3]

$$\frac{dH}{dt} = \dot{Q} + V\frac{dp}{dt} \quad \text{and} \quad H_2 - H_1 = Q_{12} + \int_1^2 V dp \ . \tag{3.20}$$

As an application we consider a closed system heated at constant pressure (*isobaric* process), so that $\frac{dp}{dt} = 0$. In this case, the first law reduces to $\frac{dH}{dt} = \dot{Q}$, or, since $H = mh(T,p)$,

$$m\left(\frac{\partial h}{\partial T}\right)_p \frac{dT}{dt} = \dot{Q} \ . \tag{3.21}$$

Here $\left(\frac{\partial h}{\partial T}\right)_p = \frac{\partial h(T,p)}{\partial T}$ denotes the partial derivative of specific enthalpy with respect to temperature at constant pressure p. This derivative is known as the *specific heat at constant pressure*

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p \ . \tag{3.22}$$

To understand this name for c_p, we rewrite the above equation as

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[3] From the defintion of enthalpy we have $U = H - pV$, hence $\frac{dU}{dt} = \frac{d(H-pV)}{dt} = \frac{dH}{dt} - p\frac{dV}{dt} - V\frac{dp}{dt}$; inserting this into the first law (3.13) gives the shown result.

$$c_p dT = \frac{\delta Q}{m} \; . \tag{3.23}$$

We see that c_p is the amount of heat required to increase the temperature of 1 kg of substance by 1 K at constant pressure; its SI unit is $\left[\frac{\mathrm{kJ}}{\mathrm{kg\,K}}\right]$.

For an ideal gas the thermal equation of state gives $pv = RT$, and the internal energy $u(T)$ is a function of temperature alone. It follows that for the ideal gas also the enthalpy $h(T) = u + pv = u(T) + RT$ is a function of temperature alone. From the definitions of the specific heats (3.15, 3.22) follows $c_p = c_v + R$; for air at T_0 one finds $c_p^{\mathrm{air}} = 1.004 \frac{\mathrm{kJ}}{\mathrm{kg\,K}}$. For ideal gases enthalpy and specific heat are related as

$$h(T) = \int_{T_0}^{T} c_p(T')\,dT' + h_0 \quad \text{or} \quad h = c_p^{avg}(T - T_0) + h_0 \; , \tag{3.24}$$

where the latter relation holds in case of constant specific heat.

For incompressible solids and liquids ($v = const.$), the specific heats at constant pressure and constant volume agree, since $\left(\frac{\partial pv}{\partial T}\right)_p = p\left(\frac{\partial v}{\partial T}\right)_p = 0$ (also see Sec. 16.7 for a more detailed argument), and one writes the specific heat without an index, $c = c_v = c_p$. The specific heat for water will be denoted as c_w.

While its internal energy depends only on temperature, the enthalpy of an incompressible substance (constant specific volume v) depends on temperature and pressure. Indeed, by its definition $h = u + pv$, enthalpy depends explicitly on pressure. With h_0 as the enthalpy at a reference point (T_0, p_0), the enthalpy for an incompressible solid or liquid with constant specific heat becomes

$$h(T,p) = c^{avg}(T - T_0) + (p - p_0)\,v + h_0 \; . \tag{3.25}$$

Note that no substance is truly incompressible, normally the specific volume changes at least a little bit. This leads to small differences between specific heats which can be ignored as long as the compressibility is sufficiently small.

3.12 Example: Equilibration of Temperature

We apply the first law to the situation depicted in Fig. 2.6. Two bodies A and B that are initially at different temperatures $\bar{T}_A$ and $\bar{T}_B$, respectively, are brought into thermal contact. After a sufficiently long time, we find that both bodies have assumed the common temperature T.

For this problem, kinetic energy is zero, and potential energy does not change. When the system $[A + B]$ is adiabatically enclosed ($\dot{Q} = 0$), and no work is done ($\dot{W} = 0$), the first law of thermodynamics simply states that the energy of the system remains constant,

$$\frac{dU}{dt} = 0 \; .$$

Thus, the energy of the end state is equal to the initial energy, $U_{\text{end}} = U_{\text{init}}$.

For simple incompressible solids the internal energy is given by[4] $U = mcT$, where c denotes the average specific heat (assumed to be a constant) and m is the mass. The internal energy of the system consisting of the two bodies is initially

$$U_{\text{init}} = U_A + U_B = m_A c_A \bar{T}_A + m_B c_B \bar{T}_B \; .$$

To emphasize that the first law does not automatically give equal final temperatures for the two bodies, we write $U_{\text{end}} = m_A c_A T_A + m_B c_B T_B$ with different final temperatures T_A and T_B. We solve for T_A,

$$T_A = \bar{T}_A + \frac{m_B c_B}{m_A c_A} \left(\bar{T}_B - T_B \right) \; , \tag{3.26}$$

and see that there are infinitely many solutions for the final temperatures (T_A, T_B) that fulfill the first law: conservation of energy alone is not sufficient to determine the final equilibrium state.

However, our experience, laid down in the zeroth law, tells us that the final temperatures agree: $T_A = T_B = T$. We find the final temperature as the weighted average of the two initial temperatures,

$$T = \frac{m_A c_A \bar{T}_A + m_B c_B \bar{T}_B}{m_A c_A + m_B c_B} \; ,$$

with the weights given by the thermal masses $m_A c_A$, $m_B c_B$. We shall later employ the second law to find the same result.

As discussed, a thermometer utilizes the equilibration of temperature. The act of measurement should not affect the result. To study the relevant condition, let body B be the thermometer, used to measure the temperature of body A. The final temperature T of body *and* thermometer can be written in the alternative form

$$T = \bar{T}_A + \frac{m_B c_B \left(\bar{T}_B - \bar{T}_A \right)}{m_A c_A + m_B c_B} \; .$$

The measured temperature T is close to the initial temperature $\bar{T}_A$ of body A when $m_B c_B \ll m_A c_A$. It follows that a thermometer should have considerably smaller thermal mass mc than the body whose temperature is to be measured.

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[4] With the energy constant $u_0 = cT_0$.

3.13 Example: Uncontrolled Expansion of a Gas

Our next example concerns the uncontrolled expansion of an ideal gas. For this, we consider an ideal gas in a container which is divided by a membrane, see Fig. 3.5. Initially the gas is contained in one part of the container at $\{T_1, p_1, V_1\}$, while the other part is evacuated. The membrane is destroyed, and the gas expands into the container. The fast motion of the gas is slowed down by internal friction, and in the final homogeneous equilibrium state $\{T_2, p_2, V_2\}$ the gas is at rest and distributed over the total volume of the container. Note that we have no control over the flow after the membrane is destroyed: this is an irreversible process.

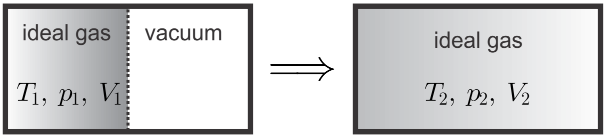

Fig. 3.5 Irreversible adiabatic expansion of an ideal gas

The container is adiabatically enclosed to the exterior, and, since its walls are rigid, no work is transmitted to the exterior. Thus, the first law for closed systems (3.1) reduces to

$$\frac{d\left(U + E_{kin} + E_{pot}\right)}{dt} = 0 \ ,$$

or, after integration,

$$U_2 + E_{kin,2} + E_{pot,2} = U_1 + E_{kin,1} + E_{pot,1} \ .$$

Since the gas it at rest initially and in the end, $E_{kin,1} = E_{kin,2} = 0$, and since potential energy has not changed $E_{pot,1} = E_{pot,2}$, the above reduces to $U_2 = U_1$. With $U = mu$, and $m = const.$, the specific internal energy remains unchanged,

$$u\left(T_1, v_1\right) = u\left(T_2, v_2\right) \ .$$

Measurements for ideal gases show that $T_1 = T_2$, that is the initial and final temperatures of the gas are the same. With this, the previous condition becomes

$$u\left(T_1, v_1\right) = u\left(T_1, v_2\right) \ ,$$

which can only hold if the internal energy of the ideal gas does not depend on volume. This experiment verifies that the internal energy of the ideal gas is independent of volume, and depends only on temperature, $u = u\left(T\right)$.

3.14 Example: Friction Loss

One litre of water in an adiabatic container is stirred such that the initial average velocity of the water is $\mathcal{V}_1 = 5\frac{\mathrm{m}}{\mathrm{s}}$. Stirring stops, and due to internal friction and friction between water and container walls the water will come to rest after a while. The water still moves after the stirrer is removed, but we have no control over the water motion: this is an irreversible process. We compute the change of temperature in the equilibration process.

After stirring stops, the system is isolated, no heat and work are exchanged, $\dot{Q} = \dot{W} = 0$, potential energy remains constant, $\frac{dE_{pot}}{dt} = 0$. The energy balance (3.1) reduces to $\frac{d}{dt}\left(U + E_{kin}\right) = 0$, so that the total energy $U + E_{kin}$ stays constant,

$$U_2 + E_{kin,2} = U_1 + E_{kin,1} \ .$$

From experience we know that in the final homogeneous equilibrium state the water is at rest, $E_{kin,2} = 0$, and we find

$$U_2 - U_1 = mc_w \mathit{\Delta} T = E_{kin,1} = \frac{m}{2}\mathcal{V}_1^2 \ .$$

Mass cancels and we find the temperature difference as

$$\mathit{\Delta} T = \frac{1}{2}\frac{\mathcal{V}_1^2}{c_w} = \frac{1}{2}\frac{25\frac{\mathrm{m}^2}{\mathrm{s}^2}}{4.18\frac{\mathrm{kJ}}{\mathrm{kg}}} = 0.003\,\mathrm{K} \ .$$

For the unit conversion, we have used that $1\frac{\mathrm{kJ}}{\mathrm{kg}} = 10^3\frac{\mathrm{J}}{\mathrm{kg}} = 10^3\frac{\mathrm{m}^2}{\mathrm{s}^2}$. Note that this very small temperature change is due only to the destruction of the initial kinetic energy. Constant stirring of a viscous liquid can increase its temperature considerably; the relevant form for the first law is $\frac{dU}{dt} = -\dot{W}$, or $\frac{dT}{dt} = -\frac{\dot{W}}{mc}$, where $\dot{W}$ is the work required for stirring. A good example from daily life is the kneading of pizza dough, which can become quite warm.

3.15 Example: Heating Problems

3.15.1 Heating of Water

2 litre of water at $T_1 = 20\,°\mathrm{C}$ are heated in a well isolated 2 kW electric kettle. We compute the time required to heat the water to $T_2 = 90\,°\mathrm{C}$.

In this temperature range, liquid water can be well described as an incompressible liquid with mass density $\rho = 1000\frac{\mathrm{kg}}{\mathrm{m}^3}$ and constant specific heat $c_w = 4.18\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$. The mass of water in the heater is $m = \rho V = 2\,\mathrm{kg}$. Since the volume of the water remains unchanged, there is no work done, and with the internal energy $U = mc_w\left(T - T_0\right) + u_0$, the first law reduces to

$$mc_w\frac{dT}{dt} = \dot{Q} \ ,$$

with $\dot{Q} = 2\,\mathrm{kW}$ as given. Separation of variables and integration over the duration of the process gives $mc_w\,(T_2 - T_1) = \dot{Q}\,(t_2 - t_1)$, or

$$\Delta t = t_2 - t_1 = \frac{mc_w}{\dot{Q}}\,(T_2 - T_1) = 292.6\frac{\mathrm{kg}\frac{\mathrm{kJ}}{\mathrm{kg\,K}}}{\mathrm{kW}}\,\mathrm{K} = 292.6\,\mathrm{s}\;.$$

For the unit conversion we have used that $1\,\mathrm{kW} = 1\frac{\mathrm{kJ}}{\mathrm{s}}$.

3.15.2 Heating of Water with Heat Loss

We consider the same problem as above, only that now the water in the heater loses heat to the environment at $T_0 = 20\,^\circ\mathrm{C}$ at a rate of $\dot{Q}_{loss} = \alpha\,(T - T_0)$ with a transfer coefficient $\alpha = 25\frac{\mathrm{W}}{\mathrm{K}}$. The heat loss must be added to the heat supplied by the kettle, so that the first law reads (careful with the sign, the heat loss must be subtracted)

$$mc_w\frac{dT}{dt} = \dot{Q} - \alpha\,(T - T_0)\;.$$

Since T_0, $\dot{Q}$ and α are constant in time, this differential equation can be written in the equivalent form

$$mc_w\frac{d\left(T - T_0 - \frac{\dot{Q}}{\alpha}\right)}{dt} = -\alpha\left(T - T_0 - \frac{\dot{Q}}{\alpha}\right)\;.$$

Integration between $\{t_1, T_1\}$ and $\{t_2, T_2\}$ gives the solution

$$\ln\left(T_2 - T_0 - \frac{\dot{Q}}{\alpha}\right) - \ln\left(T_1 - T_0 - \frac{\dot{Q}}{\alpha}\right) = -\frac{\alpha}{mc_w}\Delta t\;,$$

or, solved for Δt

$$\Delta t = \frac{mc_w}{\alpha}\ln\frac{T_1 - T_0 - \frac{\dot{Q}}{\alpha}}{T_2 - T_0 - \frac{\dot{Q}}{\alpha}} = 695.4\,\mathrm{s}\;.$$

The higher the water temperature becomes, the more heat is lost. With the values given above, for $\Delta t \to \infty$, we find a maximum temperature of $T_2^\infty = T_0 + \frac{\dot{Q}}{\alpha} = 100\,^\circ\mathrm{C}$ (note that $\frac{\dot{Q}}{\alpha} = \frac{2\,\mathrm{kW}}{25\frac{\mathrm{W}}{\mathrm{K}}} = \frac{2000\,\mathrm{W}}{25\frac{\mathrm{W}}{\mathrm{K}}} = 80\,\mathrm{K}$). The chosen value for α is a bit high for a water heater, which normally can bring water to boil and evaporate in finite time.

The heat transfer coefficient α depends on the material, and the system configuration. Our sense of cold or hot is not a sense of temperature, but rather a sense of heat transfer. When we touch an object with large heat transfer coefficient, a large amount of heat is exchanged between our hand

and the object, which feels hotter or colder as an object with smaller heat transfer coefficient at the same temperature. The amount of energy available plays a role as well. A larger amount of heat can be transferred to our hand from an object with large thermal mass mc. Wood feels not as cold as metal of the same temperature.

3.15.3 Isochoric Heating of an Ideal Gas

We consider the air-filled room from a previous example which contains 180.94 kg of air, initially at 20 °C, 1 atm. We now assume the room is perfectly sealed, so that the air volume remains constant, and ask for the total amount of heat that must be supplied to heat the room to 25 °C.

We describe air as an ideal gas with constant specific heat, so its internal energy is given by $U = mc_v (T - T_0) + u_0$, with $c_v = 0.717 \frac{\text{kJ}}{\text{kg K}}$. Since the volume remains constant, no work is done, $W_{12} = \int_1^2 p dV = 0$, and the first law reduces to

$$mc_v \frac{dT}{dt} = \dot{Q} \, .$$

Integration gives

$$Q_{12} = \int_1^2 \dot{Q} dt = mc_v \varDelta T = 648.7 \, \text{kJ} \, .$$

A 2 kW heater would need $\varDelta t = Q_{12}/\dot{Q} = 324$ s to heat the air in the room by 5 °C. The heating of a real room takes longer, since a substantial amount of heat is required to heat the walls, which have a large thermal mass mc, moreover one will expect heat loss through the walls to the colder outside environment.

The pressure after heating is completed, p_2, follows from the ideal gas law $pV = mRT$. Since mass and volume remain constant we have $p/T = mR/V = const$, so that $p_2/T_2 = p_1/T_1$ or $p_2 = p_1 T_2/T_1 = 1.017 \, \text{atm} = 1.0305 \, \text{bar}$ (temperatures in Kelvin!).

3.15.4 Isobaric Heating of an Ideal Gas

Next we ask for the amount of heat required to heat the same amount of air under constant pressure.

In this case, the heat is best computed from the alternative form (3.20) which for constant pressure reduces to

$$\frac{dH}{dt} = \dot{Q} \, ,$$

where $H = mh$ is the enthalpy of the enclosed air, with $h = c_p (T - T_0) + h_0$ and $c_p = 1.004 \frac{\text{kJ}}{\text{kg K}}$. Integration gives

$$Q_{12} = \int_1^2 \dot{Q} dt = mc_p \Delta T = 908.3\,\mathrm{kJ}\,.$$

A 2 kW heater would need $\Delta t = Q_{12}/\dot{Q} = 454\,\mathrm{s}$ to heat the air in the room, provided that no heat loss occurs to and through the walls.

The initial volume is $V_1 = 150\,\mathrm{m}^3$ and the volume after heating follows from the ideal gas law $pV = mRT$. Since pressure and mass remain constant, we have $V_2/T_2 = V_1/T_1$ and find $V_2 = V_1 T_2/T_1 = 152.6\,\mathrm{m}^3$. The expansion of the air requires moving boundary work. Since pressure is constant we find

$$W_{12} = \int_1^2 p dV = p \int_1^2 dV = p\,(V_2 - V_1) = 259.4\,\mathrm{kJ}\,.$$

In the isochoric case all heat supplied goes to increase the internal energy. The heat required for isobaric heating is bigger since, while the increase of internal energy is the same, additional energy is required to provide the expansion work.

Problems

3.1. Tank and Contents

A well-insulated copper tank of mass 12 kg at 27 °C is filled with 4 litres of water at 50 °C. The tank is heated with a 1 kW resistance heater for $2\frac{1}{2}$ minutes, and then left alone. Determine the temperature of the system after equilibrium is established. Is the process reversible or irreversible? For copper: $\rho = 8.9\frac{\mathrm{kg}}{\mathrm{litre}}$, $c_p = 0.386\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$.

3.2. Cooling Process

A $0.5\,\mathrm{m}^3$ block of steel ($\rho = 7.83\frac{\mathrm{kg}}{\mathrm{litre}}$, $c_p = 0.5\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$) initially at 250 °C is heated with a constant rate of $\dot{Q} = 50\,\mathrm{kW}$. How long does it take until the block's temperature is 600 °C?

3.3. Equilibration of Temperature

To warm the water in your bathtub, you decide to heat it by throwing a block of hot iron into the water. When your bathtub holds 150 litres of water initially at 20 °C, and you can heat the iron to 400 °C, what mass should the iron block have so that you can have a bath at 33 °C? Is the process reversible or irreversible? Assume no heat loss to anywhere, and no boiling, evaporation etc.

Specific heats: $c_w = 4.18\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$, $c_{iron} = 0.450\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$.

3.4. Irreversible Expansion

An ideal gas is confined to one side of a rigid, insulated (= no heat transfer, adiabatic) container, divided by a partition. The other side is initially evacuated. The initial state of the gas is $p_1 = 2\,\mathrm{bar}$, $T_1 = 400\,\mathrm{K}$, $V_1 = 0.02\,\mathrm{m}^3$. When the partition is removed, the gas expands to fill the entire container and achieves a final equilibrium pressure of 1.5 bar. Determine the volume of the container.

3.5. Stirring of a Liquid
A thermally insulated 2 litre tank is filled with mercury, which is stirred. When the stirring power is 200 W, how long does it take to raise the temperature of the mercury by 10 °C? Is the process reversible or irreversible?

3.6. Kneading of a Pizza Dough
A high quality kitchen mixer has a 575 W electric motor. Good pizza dough should be kneaded for about 10 minutes. When 2 kg of dough is kneaded in an adiabatically insulated container, and its initial temperature was 20 °C, what temperature will the dough have after kneading?

Assume specific heat of dough as $c = 2.73\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$.

3.7. Measurement of Specific Heat
To measure the specific heat of light oil (incompressible liquid, mass density $0.91\frac{\mathrm{kg}}{\mathrm{litre}}$) two litres of oil are stirred in a well-insulated container for 12.5 minutes. The stirrer consumes a power of 75 W, and it is observed that the temperature rises from 23 °C to 40 °C. Ignore kinetic and potential energies. and determine the specific heat of the oil.

3.8. Ice Cream Maker
An ice maker stirs 5 kg of a fruit-cream-air mixture ($\rho = 570\frac{\mathrm{kg}}{\mathrm{m}^3}$, $c_p = 1.7\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$). The electric motor of the stirrer consumes 575 W of power. It is observed that after 10 minutes the temperature of the ice cream has dropped from $T_1 = -2\,°\mathrm{C}$ to $T_2 = -18\,°\mathrm{C}$. Determine the cooling rate of the ice cream maker.

3.9. Heating of a Room
A room of 300 sq.ft. area and 8 ft height is to be maintained at a constant temperature of 68 °F while the outside temperature is 32 °F. The heat transfer rate to the outside is given by Newton's law of cooling, $\dot{Q} = \alpha\,(T - T_0)$ with $\alpha = 25\frac{\mathrm{W}}{\mathrm{K}}$.

1. Compute the heating power required to maintain the temperature constant.
2. When the heating power is doubled, how long does it take to heat the room from 68 °F to 77 °F?

Convert all results to SI units.

3.10. Isobaric Heating of an Ideal Gas
0.5 kg hydrogen gas (H_2) are enclosed in a piston-cylinder system at 22 °C, 3 atm. In a reversible isobaric process (constant pressure), the hydrogen doubles its volume.

Determine:

1. The initial volume of the system, and the work done in the expansion.
2. The temperature at the end of the expansion, and the heat exchange with the surroundings.

3.11. Isothermal Compression of an Ideal Gas

10 kg helium are enclosed in a piston-cylinder system at 20 °C, 10 bar. In a reversible isothermal process (constant temperature), the helium is compressed to half the original volume. Compute:

1. The initial volume of the system.
2. The work required for compression.
3. The heat exchange with the surroundings.

3.12. Ideal Gas with Non-constant Specific Heat

In a series of experiments you have found that for temperatures in (300 K, 900 K), the specific heat at constant volume of air is $c_v(T) = \left(0.695 + \frac{0.0598T}{1000\,\mathrm{K}}\right)\frac{\mathrm{kJ}}{\mathrm{kg\,K}}$.

1. Make a table with the specific heats $c_v(T)$ and $c_p(T)$, specific internal energy $u(T)$, and specific enthalpy $h(T)$ for temperatures in the range of validity. As reference value chose $u(300\,\mathrm{K}) = 215\frac{\mathrm{kJ}}{\mathrm{kg}}$.
2. 2 kg of air are isobarically heated from 340 K to 860 K. By means of your table, determine the heat supply Q_{12} and the work W_{12}.
3. Redo the calculation under the assumption that the specific heat can be approximated by its value at 300 K (so that it is constant). Determine the relative error for heat and work.

3.13. Work and Heat

A fixed mass m of carbon monoxide (CO) gas at $T_0 = 30\,^\circ\mathrm{C}$ is confined in a piston-cylinder system. The gas undergoes a reversible isothermal process (constant temperature), that is the pressure changes according to the relation $p = mRT_0/V$. The initial and final volumes are $V_1 = 0.1\,\mathrm{m}^3$ and $V_2 = 0.15\,\mathrm{m}^3$ and the initial pressure is $p_1 = 500\,\mathrm{kPa}$.

Consider CO as ideal gas with constant specific heat and molar mass $M = 28\frac{\mathrm{kg}}{\mathrm{kmol}}$. Determine:

1. The mass of CO in the system.
2. The pressure p_2 at the end of the process.
3. The total work required for the process. Show the process in a p-V-diagram.
4. The total heat exchange.

3.14. Work and Heat

Nitrogen (ideal gas with constant specific heats) undergoes a reversible process in a closed system, where the pressure changes according to the relation $p = aV^2 + b$. The initial and final volumes are $V_1 = 0.3\,\mathrm{m}^3$ and $V_2 = 0.1\,\mathrm{m}^3$, and the corresponding pressures are $p_1 = 100\,\mathrm{kPa}$ and $p_2 = 200\,\mathrm{kPa}$; the initial temperature is $T_1 = 30\,^\circ\mathrm{C}$. Determine:

1. The mass of nitrogen in the system.
2. The temperature at the end of the process.
3. The total work required for the process. Show the process in a p-V-diagram.
4. The total heat exchange.

3.15. Work and Heat

Helium, initially at temperature $T_1 = 0\,^\circ\mathrm{C}$ undergoes a reversible process in a closed system, where the pressure changes according to the relation $p = aV^3 + b$. The initial and final volumes are $V_1 = 0.1\,\mathrm{m}^3$ and $V_2 = 0.2\,\mathrm{m}^3$, and the corresponding pressures are $p_1 = 100\,\mathrm{kPa}$ and $p_2 = 40\,\mathrm{kPa}$. For the relevant temperature range helium behaves as an ideal gas. As for all noble gases, its specific heat is constant, $c_v = \frac{3}{2}R$. Determine:

1. The mass of helium in the system.
2. The temperature at the end of the process.
3. The total work required for the process. Show the process in a p-V-diagram.
4. The total heat exchange.