

## Chapter 2

# Basic Concepts and Definitions

Thermodynamics originated from observation of phenomena which occur on the earth in macroscopic systems consisting of a great number of atoms or molecules. Many concepts used in thermodynamics, such as pressure and temperature, are familiar to us from everyday experience. For instance, everybody knows that when two bodies are brought into contact with each other and then isolated from the surroundings, their temperature settles down after some time, which can be easily verified by putting something warm into the fridge. In this chapter, we discuss the concepts of temperature, pressure and thermodynamic equilibrium in a more formal way, and also give definitions of other basic concepts and quantities used in thermodynamics.

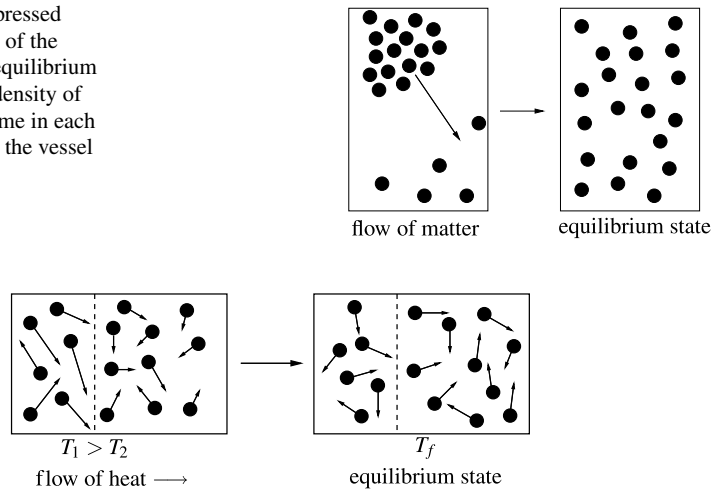
### 2.1 Concept of Thermodynamic Equilibrium

The concept of thermodynamic equilibrium is fundamental to thermodynamics.

**Definition 2.1** *Thermodynamic equilibrium* refers to particular states of a macroscopic system, called equilibrium states, which are independent of time (stationary states) and in which no macroscopic flow of any physical quantity exists.

Note that a stationary state does not have to be an equilibrium state because a steady macroscopic flow of heat or matter, or another physical quantity, may exist in the system. For instance, if we keep the two ends of a wire at different and constant temperatures then heat flows through the wire but the temperature gradient along it does not depend on time. Thus, it is a stationary state but not an equilibrium state because of the heat flow.

**Fig. 2.1** Gas compressed initially in one part of the vessel tends to an equilibrium state in which the density of molecules is the same in each macroscopic part of the vessel



**Fig. 2.2** Vessel with a gas is divided with a stiff wall permeable to heat (*broken line*). The *arrows* represent the velocities of molecules. The system tends to the equilibrium state due to the flow of heat from the part of higher temperature  $T_1$  to the part of lower temperature  $T_2$ . In equilibrium, the temperature in both parts has the same value  $T_f$

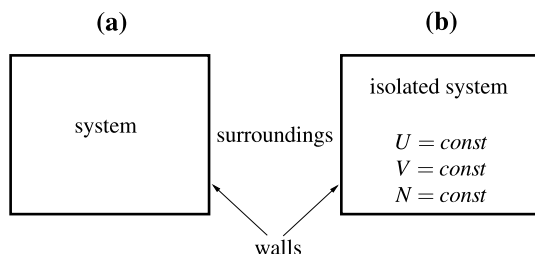
### The fundamental postulate of thermodynamics

Every isolated macroscopic system reaches eventually thermodynamic equilibrium independently of the initial state of the system.

This postulate applies to systems observed in the scale of Earth and nothing indicates that it can also be applied to systems in the cosmic scale and to the whole Universe, in particular.

Two examples how systems reach their equilibrium states are shown in Figs. 2.1 and 2.2. In Fig. 2.1 (on the left), the gas has been compressed in one part of the vessel, so its density in that part is larger than in the rest of the vessel. When the dividing wall is removed the gas is not in an equilibrium state because of a macroscopic flow of matter from the region of higher density to the region of lower density. After some time the densities equalize and the system reaches the equilibrium state (on the right).

Figure 2.2 shows a gas in a vessel divided into two parts with a stiff wall permeable to heat. Initially the temperature in both parts is the same. Then the gas in the left part is heated quickly, so its temperature  $T_1$  is higher than the temperature  $T_2$  in the right part. When the heating stops the system tends to the equilibrium state. The heat flows from the high temperature region to the low temperature region. Since an increase in the temperature means an increase in the kinetic energy of molecules, the flow of heat is associated with a transfer of the kinetic energy from molecules in the left part to molecules in the right part. It occurs through collisions of molecules



**Fig. 2.3** The system is separated by walls from the surroundings. The walls can be movable, can conduct heat or can be permeable to matter. The system interacts with the surroundings through the walls. If the walls are stiff and do not allow neither heat nor matter to pass through them then the system is said to be isolated

with the dividing wall. When the equilibrium state is reached the temperature in both parts is the same.

### 2.1.1 System and Surroundings

The *system* is a separate part of the world (Fig. 2.3a). Everything that does not belong to the system is called the *surroundings*. The system is separated from the surroundings by *walls*. These concepts are present in discussions of all phenomena described by thermodynamics. The wall is called *adiabatic* if it is impermeable to heat. The wall is called *diathermal* if it permits a heat flow. Finally, the wall can be permeable to matter or not. The system with all walls impermeable to matter is a *closed system*. The system is said to interact with the surroundings if any change in the surroundings causes a measurable effect in the system. A system which does not interact with the surroundings in any way is called an *isolated system*. Thus, the energy, volume and amount of matter do not change in an isolated system.

We consider an isolated macroscopic system, which contains only a pure substance, without any internal walls limiting the motion of molecules, for instance, a pure gas in a vessel. Only a few parameters are needed to completely characterize an equilibrium state of such a simple system (Fig. 2.3b). They are: the *internal energy*  $U$ , which is a sum of the kinetic energy and the potential energy of intermolecular interactions of all molecules in the system, the *volume*  $V$  and the *number of molecules*  $N$ . We accept this empirical fact, confirmed by numerous experiments, as a postulate. Other physical quantities, e.g., pressure, temperature or *entropy* (which will be introduced later on), can be treated as functions of these three parameters. Although energy, volume and number of molecules are also present in classical mechanics, entropy does not have a mechanical counterpart, which means that thermodynamics cannot be reduced to classical mechanics. This is because the number of microscopic variables needed to completely describe the motion of all molecules, i.e., the number of all positions and momenta, is enormous in a macroscopic system. For instance, for 1 mole of a pure substance (18 g in the case of

water) it is of the order  $10^{24}$ . Therefore, the fact that only a few parameters can completely characterize a macroscopic system in thermodynamic equilibrium may seem surprising. However, the remaining microscopic variables play a role in the flow of heat (see Fig. 2.2). They are hidden in the entropy, which means that they have influence on the direction of processes in macroscopic systems.

### 2.1.2 State Parameters and State Functions

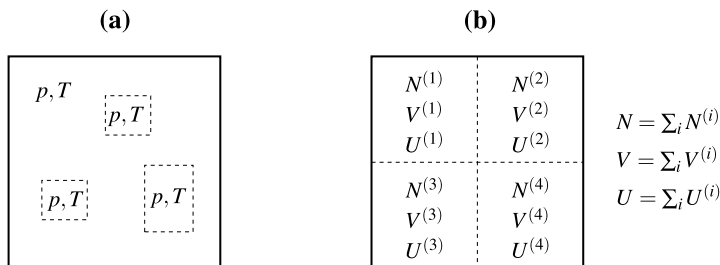
**Definition 2.2** *State parameters* are physical quantities that characterize a system in thermodynamic equilibrium.

For instance, the volume, number of molecules, pressure, temperature and internal energy are state parameters. Not all state parameters are independent. As we have already mentioned, to completely characterize an isolated system in thermodynamic equilibrium only three parameters are needed:  $U$ ,  $V$  and  $N$ . Other quantities, e.g., the pressure  $p$  and temperature  $T$ , are functions of these three parameters. However, it depends on the actual physical situation which parameters are treated as independent variables. For instance, if energy can be transferred between the system and surroundings in the form of heat it is easier to control the temperature of the system than its internal energy. Then  $T$ ,  $V$  and  $N$  are treated as independent variables. In the case of a gas closed in a cylinder with a movable piston, which remains in thermal contact with the surroundings, the pressure and temperature of the system can be easily controlled.

**Definition 2.3** *State function* is a physical quantity which assumes a definite value for each equilibrium state of a system, independent of the way that state is reached.

It follows from the definition of state parameters that they are also state functions because their values depend only on the state of the system. In thermodynamics, quantities which are not state functions are also considered. They depend on the way a given equilibrium state is reached. The best known examples of such quantities are work and heat.

**Intensive and Extensive State Parameters** We consider a system in thermodynamic equilibrium. Each macroscopic part of the system is called a *subsystem*. If the system is in equilibrium the same applies to its all subsystems. In Fig. 2.4a, the system is divided into several subsystems but the boundaries between the subsystems are only imaginary. An *intensive parameter* is a physical quantity which has the same value in each subsystem, therefore, it cannot depend on the mass of a given subsystem. In consequence, intensive parameters do not depend on the mass of the whole system. For instance, temperature, pressure and *chemical potential* (discussed later on) are intensive parameters.



**Fig. 2.4** (a) System in thermodynamic equilibrium is divided into several subsystems. An intensive parameter, e.g., the pressure  $p$  or temperature  $T$ , has the same value in all subsystems. (b) In a composite system, the value of an extensive parameter, e.g., the number of molecules  $N$ , volume  $V$  and internal energy  $U$ , is the sum of contributions from all subsystems

Imagine now that we form a composite system made up of several identical systems, which become subsystems of the composite system (Fig. 2.4b). Then the volume of the composite system is the sum of the volumes of its subsystems and the same concerns the number of molecules. Also the internal energy and entropy have this property. In general, a physical quantity whose value for the composite system is the sum of its values in individual subsystems is called an *extensive parameter*. This means that for an extensive parameter  $X$  we have

$$X = \sum_i X^{(i)}, \quad (2.1)$$

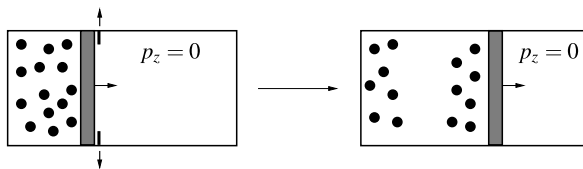
where the index  $i$  numbers the subsystems and  $X^{(i)}$  is the value of  $X$  in the  $i$ th subsystem. It follows from the above definition that extensive parameters are proportional to the mass of the system.

### 2.1.3 Thermodynamic Processes

**Definition 2.4** *Thermodynamic process* is a change occurring in a system between the initial and final equilibrium states.

The process is called *adiabatic* if there is no flow of heat between the system and surroundings. The process is said to be: *isochoric*, if it occurs at constant volume, *isothermal*, if it occurs at constant temperature, and *isobaric*, if it occurs at constant pressure.

According to Definition 2.4, the initial and final states of the system are equilibrium states. However, the intermediate states are not equilibrium states, in general. Real processes proceed at a finite rate and the system cannot reach thermodynamic equilibrium during the process. However, we feel intuitively that the slower the process is, the more time the system has to approach thermodynamic equilibrium at each successive stage of the process. In the framework of thermodynamics, only



**Fig. 2.5** Irreversible expansion of a gas to the vacuum. The piston divides the system into two parts. The *left part* is occupied by a gas and the *right part* is empty. When the piston is released a spontaneous process of gas expansion occurs. The process is irreversible because at any moment the system is not in thermodynamic equilibrium and the gas pressure is not well defined during the process. Inhomogeneities in the molecular density may form during the process

equilibrium states are considered. Any description of non-equilibrium states would involve many more parameters than in the case of equilibrium states. Therefore, it is convenient to consider an idealized process which proceeds infinitely slowly and can be treated as an approximation of real slow processes. Such an infinitely slow process is called a *quasi-static* process.

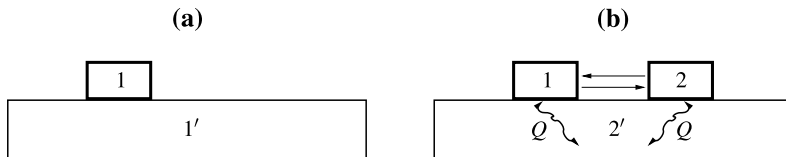
**Definition 2.5** *Quasi-static* process is a sequence of successive equilibrium states of a system.

Differently from real processes, time does not appear in a quasi-static process. The latter proceeds simply from one equilibrium state of the system to another equilibrium state in a continuous manner. A real process can be approximated by a quasi-static process if it is sufficiently slow. In practice, the process is said to be slow if it lasts much longer than the longest characteristic time of a given system. Imagine, for instance, that we move the piston to compress a gas in a vessel. Then we should compare the time of compression with the time the sound needs to reach the wall opposite to the piston. For a system of a length of 3 m and for the speed of sound of  $332 \text{ m s}^{-1}$ , we find that the longest characteristic time of the system is of the order  $10^{-2} \text{ s}$ . If we moved the piston with the speed of sound then regions of a higher and lower density would form in the system, and the energy of the sound wave would be dissipated. At any moment of the process, the system would not be in thermodynamic equilibrium (cf. Fig. 2.5).

Mathematically a quasi-static process is represented by a curve in the space of equilibrium states. The dimension of this space is equal to the number of independent state parameters needed to define an equilibrium state of a given system. If  $X$  denotes a state parameter then a change in  $X$  in a thermodynamic process is denoted by  $\Delta X$ , where

$$\Delta X = X_f - X_i, \quad (2.2)$$

and  $X_i$  and  $X_f$  are the values of  $X$  in the initial and final state, respectively. In calculations, instead of finite changes of parameters, we often consider *infinitesimal*, i.e., infinitely small changes. For the parameter  $X$ , an infinitesimal change of the parameter is denoted by the symbol  $dX$ . Such a procedure is justified, since according to



**Fig. 2.6** Example of an irreversible process. **(a)** Initially the block is in the state 1 and the surroundings, i.e., the substrate is in the state  $1'$ . **(b)** The block moves on a rough surface towards the state 2 and then back from 2 to 1. In both cases, heat is produced because of the friction. The heat is transferred to the surroundings, which causes that the surroundings do not return to the original state even though the block does

Definition 2.5 we can consider processes between two arbitrarily close equilibrium states.

**Definition 2.6** *Reversible process* is a process to which a reverse process exists that restores the original states of both the system and surroundings.

In other words, if in a given process the systems goes from the state 1 to the state 2 and the surroundings go from the state  $1'$  to the state  $2'$  then the process is reversible, provided that there exists a process that simultaneously brings the system from 2 to 1 and the surroundings from  $2'$  to  $1'$ . A process that is not reversible is called an *irreversible* process. Irreversibility is often associated with dissipation of energy in the form of heat. All real processes are irreversible. Two examples are shown in Figs. 2.5 and 2.6. In Fig. 2.6 a block moves on a rough surface. Because of friction heat is produced during this process. The block can be moved back to its original position but due to the friction some amount of heat is transferred to the surroundings independently of the direction of the motion, which means that the surroundings do not return to their initial state.

In order a given process could be considered reversible, it must proceed without friction (dissipation of energy) and at a vanishing rate. Thus, any reversible process is also a quasi-static process, which means that during the process the system passes over successive equilibrium states. However, it does not follow from Definition 2.5 that the reverse statement is also true. Only the second law of thermodynamics, which postulates the existence of entropy as an additional function of state (see Chap. 4), provides a deeper understanding of reversible and irreversible processes. In particular, in Sect. 4.2.1, we derive an expression for an infinitesimal flow of heat in reversible processes (see (4.24)). Since a quasi-static process is an idealization of a real process, and not only a mathematical concept, it must be in agreement with the formula mentioned above. In Chap. 4, we show that quasi-static processes are also reversible processes.

Even though reversible processes are only idealizations of real processes, they actually enable us to calculate changes in state functions in real processes. If a given equilibrium state is reached as a result of an irreversible process then, in general, we cannot calculate directly how state functions have changed in the process. However, according to Definition 2.3, state functions do not depend on the process. Thus, if

we can find a reversible process from a given initial state to a given final state then we can calculate the change in any state function in the reversible process instead of the irreversible one. Examples of such calculations are presented in the following chapters.

### 2.1.4 Calculation of Physical Quantities in Quasi-static Processes

A quasi-static process is defined by a curve in the space of independent state parameters of the system. The curve starts from the initial state  $i$  and ends in the final state  $f$ . During the process the system is all the time in thermodynamic equilibrium, and only its state parameters change. Together with changes in the state parameters also the state functions change. To determine how a state function changes during the whole process, we have to know how it changes if two equilibrium states are infinitesimally close to each other.

Let us assume, for instance, that the independent state parameters are: the internal energy  $U$ , volume  $V$ , and amount of substance  $n$ , where the unit of the latter is the *mole*. The definition of the mole is given in Sect. 2.2.2. Here, it is sufficient to say that the number of molecules  $N$  is proportional to  $n$ , and the proportionality coefficient is a very large number, thus, in practice, we can treat  $n$  as a continuous variable. As a function of state we can take the temperature,  $T = T(U, V, n)$ , for instance. A change in  $T$  in any process amounts to

$$\Delta T = T_f - T_i = T(U_f, V_f, n_f) - T(U_i, V_i, n_i). \quad (2.3)$$

If the process is quasi-static we can express  $\Delta T$  as a sum of successive small steps, which in the limit of infinitesimal steps,  $dT$ , reduces to the integral, i.e.,

$$\Delta T = \int_i^f dT, \quad (2.4)$$

where the integration goes from the initial state to the final state. An infinitesimal change in the temperature is associated with infinitesimal changes in the state parameters, i.e.,

$$dT = T(U + dU, V + dV, n + dn) - T(U, V, n). \quad (2.5)$$

Expanding the first term on the right-hand side in a Taylor series and leaving only the terms linear in the infinitesimal increments of the state parameters, we get

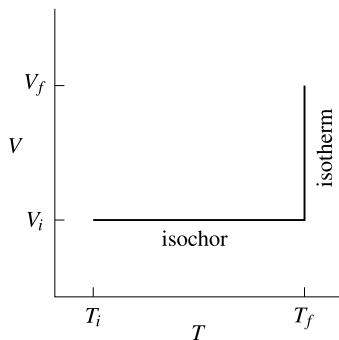
$$dT = \left( \frac{\partial T}{\partial U} \right)_{V,n} dU + \left( \frac{\partial T}{\partial V} \right)_{U,n} dV + \left( \frac{\partial T}{\partial n} \right)_{U,V} dn. \quad (2.6)$$

Since the choice of independent variables can be different, e.g.,  $U$ ,  $p$  and  $n$ , to avoid confusion, the constant parameters at which the differentiation is performed are shown explicitly. For instance,

$$\left( \frac{\partial T}{\partial U} \right)_{V,n} \neq \left( \frac{\partial T}{\partial U} \right)_{p,n}, \quad (2.7)$$



**Fig. 2.7** Example of a quasi-static process in the  $TV$  plane, which consists of an isochoric and isothermal process. First, the temperature changes from  $T_i$  to  $T_f$  at constant volume  $V = V_i$  (the isochor). Then the volume changes from  $V_i$  to  $V_f$  at constant temperature  $T = T_f$  (the isotherm)



thus, the notation  $\partial T/\partial U$  is ambiguous if we do not indicate the other variables.

As we have already mentioned, to define a quasi-static process we have to define a curve (or a path) along which it proceeds in the space of state parameters. For instance, the internal energy  $U$  can be treated as a function of  $T$  and  $V$  if we assume  $n = \text{const}$ . An infinitesimal change in the function  $U(T, V)$  amounts to

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV. \quad (2.8)$$

Here the space of independent state parameters is the subset of the plane:  $T > 0$ ,  $V > 0$ . Often we consider processes in which only one parameter of state varies. In the example considered, it can be an isochoric process, if  $V = \text{const}$ , or an isothermal process, if  $T = \text{const}$ . It can also be a combination of these processes as shown in Fig. 2.7.

**Differentials and Differential Forms** We consider a state function  $Y(X_1, \dots, X_M)$ , where  $X_1, \dots, X_M$  are independent state parameters. An infinitesimal change in  $Y$  in a quasi-static process has the following general form:

$$dY = \sum_{i=1}^M \left(\frac{\partial Y}{\partial X_i}\right)_{X_{j \neq i}} dX_i, \quad (2.9)$$

where the notation  $X_{j \neq i}$  means that the derivative with respect to  $X_i$  is calculated at constant  $X_j$  for  $j \neq i$ . In mathematics  $dY$  is called the *differential* of  $Y$ .<sup>1</sup> To calculate a finite change in  $Y$  in the quasi-static process, we integrate  $dY$  along the path that defines the process in the parameter space:

$$\Delta Y = Y_f - Y_i = \int_i^f dY. \quad (2.10)$$

An important property of the differential is that the above integral does not depend on the path of integration. Otherwise  $Y$  would not be a state function because its value in the final state would depend on the process leading to that state. If we

<sup>1</sup>The term *total differential* is also used.

do not know the explicit form of  $Y$ , but we know all its first derivatives, we can determine  $Y$ , integrating  $dY$  from a selected initial state to a given final state along any path. However, we have to be sure that the coefficients at  $dX_1, \dots, dX_M$  are really the first derivatives of a certain function  $Y$  with respect to the state parameters. Let us denote these coefficients by  $Y_1, \dots, Y_M$ . If they are the first derivatives of  $Y$  then the mixed second order partial derivatives must be equal, thus, the identities

$$\frac{\partial Y_i}{\partial X_j} = \frac{\partial Y_j}{\partial X_i}, \quad (2.11)$$

must hold for all pairs  $i, j = 1, \dots, M$ . It can also be shown that if conditions (2.11) are satisfied then there exists a function  $Y$  such that  $Y_i = \partial Y / \partial X_i$  for  $i = 1, \dots, M$ .

Not all quantities used in thermodynamics are state functions. To explain this, we use a mechanical analogy and compare the work against gravitation with the work against friction forces. In the first case, the work is equal to the change in the potential energy of a body in the gravitational field. As we know it depends only on the space points chosen, which is equivalent to saying that the infinitesimal work performed by the gravitational force is equal to the differential of its potential energy. In the second case, the friction force acts always in the direction opposite to the motion of the body. The infinitesimal work is defined as a scalar product of the friction force and an infinitesimal displacement of the body. However, it cannot be a differential of a certain function because the total work depends on the length of the path along which the body moves.

In thermodynamics, the work  $W$  done on the system and the heat  $Q$  supplied to the system depend on the process, and not only on the initial and final state. This means that they cannot be expressed as changes in some state functions. However, for a quasi-static process, we calculate  $W$  and  $Q$  by integrating infinitesimal contributions, in a similar way as in the case of a state function (see (2.10)), i.e.,

$$W = \int_i^f \mathring{d}W, \quad (2.12)$$

$$Q = \int_i^f \mathring{d}Q. \quad (2.13)$$

We use the notation  $\mathring{d}W$  and  $\mathring{d}Q$  for infinitesimal amounts of work and heat, respectively, to distinguish them from differentials, since the result of integration depends on the path in the space of state parameters. In general, an infinitesimal quantity  $\mathring{d}\omega$  has the following form:

$$\mathring{d}\omega = \sum_{i=1}^M \omega_i dX_i, \quad (2.14)$$

where  $\omega_i = \omega_i(X_1, \dots, X_M)$ . If  $\mathring{d}\omega$  is not a differential of a function then the coefficients  $\omega_i$  do not satisfy conditions (2.11). For instance, if  $\mathring{d}\omega = \omega_1(X_1, X_2)dX_1$ , which means that  $\omega_2 = 0$ , then  $\partial\omega_1/\partial X_2 \neq 0$  and  $\partial\omega_2/\partial X_1 = 0$ . In mathematical

terminology,  $\text{d}\omega$  is called a *differential form*.<sup>2</sup> The differential of a function is simply a special case of a differential form.

An example of a differential form is the work performed on the system (a gas, for instance) whose volume changes by  $\text{d}V$  at the pressure  $p$ . The change in the volume is equal to  $\text{d}V = A \text{d}x$ , where  $A$  denotes the area of the piston and  $\text{d}x$  is its displacement. The force exerted on the piston by the gas amounts to  $pA$ . To compress the gas quasi-statically, the external force must balance exactly the force exerted by the gas, hence, the work performed by the external force amounts to

$$\text{d}W = -p \text{d}V, \quad (2.15)$$

which means that  $\text{d}W > 0$  if  $\text{d}V < 0$ . Since  $V$  is not the only state parameter (the remaining parameters are  $T$  and  $n$ , for instance) conditions (2.11) are not satisfied and  $\text{d}W$  is not a differential of a function. In Chap. 4, we will see that  $\text{d}Q = T \text{d}S$ , where  $S$  stands for the entropy.

## 2.2 Extensive Parameters of State

It took scientists about 300 years, from the times of Galileo to the times of Helmholtz, to establish the parameters needed to describe thermodynamic equilibrium of a system. Nowadays we know that in the case of an isolated system formed by a pure substance, an equilibrium state is defined by three extensive parameters: the volume, internal energy and amount of substance. All other properties of a system in thermodynamic equilibrium can be expressed in terms of these parameters. Below we present a short discussion of these quantities.

### 2.2.1 Volume

We denote the volume by  $V$ . The SI derived unit of volume is the *cubic meter* ( $\text{m}^3$ ) but the volume of gases and liquids is often expressed in litres (L):

$$1 \text{ L} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3 = 1000 \text{ cm}^3.$$

The fact that volume is an extensive parameter follows from its definition. If we form a system made up of subsystems then the volume of the composite system equals the sum of the volumes of all subsystems, provided that they do not overlap. It is a well known geometrical property.

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<sup>2</sup>To be precise, it is a differential form of rank 1 or 1-form.

### 2.2.2 Amount of Substance

The amount of substance is denoted by  $n$ . If there are several chemical components (compounds) in the system we add an index to number them, e.g.,  $n_1, n_2, \dots$  or  $n_A, n_B, \dots$ . The SI base unit for the amount of substance is the *mole* (mol). The amount of substance is also called the *number of moles*.

Here we consider only a pure chemical substance. In everyday live, to specify the amount of a given substance, we usually specify its mass or rather its weight. However, from the stoichiometric point of view, the mass of a substance is not a convenient measure of its amount. In 1811, Amadeo Avogadro formulated a hypothesis that a gas occupying a given volume at a given temperature and pressure always contains the same amount of substance, independently of its kind. *The same amount* was understood in the sense of stoichiometry of chemical reactions. For instance, one portion of  $H_2$  and a half portion of  $O_2$  give one portion of  $H_2O$  in the chemical reaction. In the times of Avogadro, *the portion* was a measure of volume, but it was used to determine the number of moles. At the beginning of the 19th century it was not known that matter consists of atoms or molecules, hence, its amount can be expressed as a number of pieces, e.g., 100 atoms of Ar or 200 molecules of  $H_2O$ . Despite this fact, the concept of the mole was introduced, which actually allowed to measure the amount of substance in pieces. The number of elementary entities, i.e., atoms, molecules, ions, etc., contained in 1 mol of the substance is called the *Avogadro constant*,  $N_A$ . It amounts to

$$N_A = 6.022\,141\,79\,(30) \times 10^{23} \text{ mol}^{-1}, \quad (2.16)$$

which is an enormous number. Having determined the Avogadro constant, we can express the number of elementary entities in the relation to  $N_A$ .

**Definition 2.7** *Amount of substance* is the number of elementary entities divided by the Avogadro constant.

Thus, the amount of substance (number of moles)  $n$  is proportional to the number of elementary entities in the substance, and the proportionality constant is  $N_A^{-1}$ , hence

$$n = \frac{N}{N_A}. \quad (2.17)$$

Since the above relation is the same for all substances, it is necessary to define the elementary entity, e.g.,  $H_2$ , NaCl,  $CO_2$ , etc.

It is needless to say that the modern knowledge of the structure of matter was not available to the inventors of the mole. Their analysis was based mainly on the stoichiometry of chemical reactions. However, the mole as a unit of the amount of substance implicitly contains information about the molecular structure of matter. It is also evident why the mass is not a convenient parameter to measure the amount of substance in chemical reactions. For example, in the reaction of carbon combustion:  $C + O_2 \rightarrow CO_2$ , 1 mol of carbon and 1 mol of oxygen give one mol of carbon dioxide. Expressing the same amounts of the substances in the units of mass, we

have 12 g C and 32 g O<sub>2</sub> which give 44 g CO<sub>2</sub>. No simple proportion can be deduced in this case. However, such a proportion becomes obvious if the amount of substance is expressed in moles.

As in the case of volume, it is quite obvious that the amount of substance is also an extensive parameter. If we form a system composed of two or more subsystems, each of which contains a given number of elementary entities of the same substance, the total number of elementary entities in the system is simply the sum of these numbers. The same concerns the number of moles, which follows from relation (2.17).

### 2.2.3 Internal Energy

The internal energy is denoted by  $U$ . The SI derived unit of energy is the *joule* (J):

$$1 \text{ J} = 1 \text{ N m} = 1 \text{ kg m}^2 \text{ s}^{-2}.$$

Another non-SI unit of energy used in thermodynamics is the calorie (cal). In fact, there are several differently defined calories. One of them is defined as the amount of energy required to warm up one gram of water from 14.5 °C to 15.5 °C at standard atmospheric pressure (101325 Pa), which is

$$1 \text{ cal} = 4.1855 \text{ J}.$$

Another one is the thermochemical calorie:  $1 \text{ cal}_{\text{th}} = 4.184 \text{ J}$ . To express the ionization energy or the energy liberated in nuclear reactions, the electronvolt (eV) is used:

$$1 \text{ eV} \approx 1.602 \times 10^{-19} \text{ J}.$$

It is the amount of energy gained by a single electron in an electric potential difference of one volt (V). The electronvolt is not an SI unit.

Energy is an original concept and neither physics nor chemistry can give us the answer to the question about its nature. They only show how energy can be measured or calculated. We know the kinetic energy of bodies and their gravitational energy. We can calculate the energy of electric charges in an electric field and the energy of magnets in a magnetic field. A few examples of energy calculations are given below. For instance, the kinetic energy of a body of the mass  $m$ , moving with the speed  $v$  small compared to the speed of light, is given by:

$$E = \frac{1}{2}mv^2.$$

A change in the gravitational energy of the same body elevated to the height  $h$  above sea-level amounts to

$$\Delta E = mgh.$$

The energy of a body at rest is given by the famous Einstein equation:

$$E = mc^2,$$

which expresses mass-energy equivalence, where  $m$  is the rest mass of the body and  $c$  is the speed of light. It was derived by Einstein in the framework of the special theory of relativity.

In thermodynamics, we also know some explicit formulae to calculate changes in the internal energy, for instance, a change due to heating of a system. In general, the internal energy of a system,  $U$ , consists of the kinetic energy of molecules and the potential energy of intermolecular interactions. The latter manifests itself, for instance, in the form of heat released during condensation of a gas. We can also include in  $U$  the energy of chemical bonds, which shows up as the heat released or absorbed in chemical reactions, and also the energy of electrons in atoms (ionization energy), etc. The internal energy is a sum of all kinds of energy existing in a given system. However, changes in the internal energy, rather than its absolute value, have physical meaning. In practice, we choose a reference state, to which we assign zero of the internal energy, and determine the energies of other states with respect to the reference state. For instance, if there are no chemical reactions in the system and electron excitations can be neglected then we include in the internal energy only the kinetic energy of atoms or molecules and the potential energy of their mutual interactions and the interactions with external fields (e.g., the gravitational energy).

The internal energy is an extensive parameter, as are volume and amount of substance. This statement is less obvious, however, than in the case of the last two quantities. To show this, we consider a system combined of two identical systems. The internal energy of the composite system can be expressed in the following form:

$$U = U^{(1)} + U^{(2)} + U^{(12)},$$

where  $U^{(1)}$  and  $U^{(2)}$  denote the internal energy of the original systems, and  $U^{(12)}$  comes from the interactions of molecules of system (1) with molecules of system (2). Since intermolecular interactions decay quickly with distance, only the molecules close to the surface of contact can contribute to  $U^{(12)}$ . If  $L$  is the linear size of the system then  $U^{(12)}$  is proportional to  $aL^2$ , where  $a$  is a molecular size, whereas  $U^{(1)} + U^{(2)}$  is proportional to  $L^3$ , hence, the ratio of  $U^{(12)}$  to  $U^{(1)} + U^{(2)}$  is proportional to  $a/L$ . Therefore, all surface effects can be neglected if the system is sufficiently large (macroscopic). In what follows, we always assume that the condition  $L \gg a$  is satisfied and the internal energy is an extensive parameter.

## 2.3 Intensive Parameters of State

In this section, we discuss, in a rather intuitive way, three intensive parameters: the pressure, temperature and chemical potential. Their formal definitions are given in Chaps. 3 and 4. Then, it will turn out that each of these parameters is equal to a derivative of the internal energy with respect to an appropriate extensive parameter. Note that the derivative of one extensive parameter with respect to another extensive parameter must be an intensive parameter because the dependence on the mass of the system cancels out.

We know from everyday experience that if two bodies are brought into thermal contact then a difference between their temperatures causes a flow of heat until the temperature of one body becomes equal to the temperature of the other body. Similarly, a difference in the pressure of a gas on the two sides of a piston causes the action of a force proportional to the piston area and its motion, which stops when the pressure on both sides is the same. This simple observation leads to the conclusion that temperature and pressure are intensive parameters because they have the same values in all subsystems of a given system in thermodynamic equilibrium. Otherwise a macroscopic flow of heat or internal changes in the volume of the subsystems would occur in the system, which would be in contradiction with the definition of thermodynamic equilibrium (see Definition 2.1). A similar argumentation applies to the chemical potential, which we discuss in more detail in Sect. 2.3.3. We will see, however, that the chemical potential of a pure substance is uniquely defined by the temperature and pressure of that substance. Thus, if the temperature and pressure have the same values in all subsystems of a given system then the same is true for the chemical potential. Therefore, it is easier to understand the concept of chemical potential if at least two components are present in the system. For instance, if we add a dye to water and wait for a sufficiently long time we will observe a uniform colour in the whole volume. Even if the temperature and pressure are the same throughout the system we observe a flow of the dye from the regions of higher concentration to the regions of smaller concentration. This process continues until the concentration of the dye becomes uniform. The flow of the dye is caused just by the difference in its chemical potential in various parts of the system.

To summarize, a difference in the temperature is responsible for a flow of heat, a difference in the pressure is responsible for a change in volume (flow of volume), and a difference in the chemical potential of a given component is responsible for a flow of that component. In thermodynamic equilibrium, no flow of any quantity exists, therefore, the temperature, pressure and chemical potential of each component must have the same values in all subsystems of a given system.

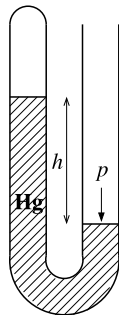
### 2.3.1 Pressure

To define any physical quantity, a method of its measurement must be given. The method can be arbitrary provided that it is reproducible. For instance, Galileo in his studies on the uniformly accelerated motion measured time by means of the amount of water that flowed during the experiment. His measurement of time was reproducible, and the accuracy achieved by Galileo between the 16th and 17th century was comparable with the accuracy of the 19th century watches.

*Pressure* is defined as the normal force acting on a surface, divided by the area of that surface. For the pressure, symbol  $p$  is used. To determine the pressure exerted by a gas on a movable piston of given area, we have to measure the force acting on the piston. The force can be measured with a dynamometer, for instance. The SI derived unit of pressure is the *pascal* (Pa):

$$1 \text{ Pa} = 1 \text{ N m}^{-2} = 1 \text{ kg m}^{-1} \text{ s}^{-2}.$$

**Fig. 2.8** Schematic picture of the mercury barometer used to measure the pressure  $p$ . In the closed part of the tube, the pressure is nearly zero. From the balance of the forces acting on the mercury column of the height  $h$ , we have:  $\rho gh = p$ , where  $\rho$  is the mercury density and  $g$  denotes the gravity of the earth



Other non-SI units of pressure are: the bar (bar),

$$1 \text{ bar} = 10^5 \text{ Pa},$$

the atmosphere (atm),

$$1 \text{ atm} = 101\,325 \text{ Pa},$$

the torr (torr),

$$1 \text{ torr} = \frac{1}{760} \text{ atm} \approx 133.322 \text{ Pa},$$

and the millimeter of mercury (mmHg),

$$1 \text{ mm Hg} \approx 1 \text{ torr}.$$

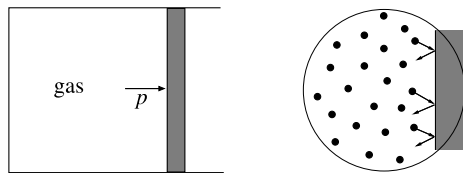
In the mercury barometer, the force exerted by air is balanced by the weight of the mercury column of the height  $h$  in a glass tube (Fig. 2.8). The balance of the forces gives:

$$p = \frac{mg}{A} = \rho gh,$$

where  $m$  is the weight of the mercury column,  $A$  is the area of its cross-section,  $\rho$  is the density of mercury ( $\rho \approx 13.6 \text{ g cm}^{-3}$ ) and  $g \approx 9.81 \text{ m s}^{-2}$  denotes the gravity of the earth. In the past, it was assumed that  $1 \text{ torr} = 1 \text{ mm Hg}$ . However, the density of mercury varies with temperature and the gravity depends on the place on the earth. Nowadays  $1 \text{ torr}$  is defined exactly as  $\frac{1}{760} \text{ atm}$ . Why is mercury used in barometers instead of water, for instance? Water evaporates quickly and its density is too low ( $1 \text{ g cm}^{-3}$ ) to be used as a barometric liquid. It is easy to calculate the height of the barometer if water or flaxseed oil (its density is about  $0.94 \text{ g cm}^{-3}$ ) was used instead of mercury, to measure atmospheric pressure on the earth surface. On the other hand, in the case of low pressure (air pressure decreases with the altitude), the relative accuracy of the mercury barometer worsens because the height of the mercury column decreases. At an altitude of 20 km, the pressure drops to 0.05 atm, and at 700 km it is of the order  $10^{-12} \text{ atm}$  (a state of high vacuum). Such low pressures cannot be measured with the mercury barometer.

The microscopic interpretation of pressure follows from classical and statistical mechanics, and is related to a change in the momentum of molecules that collide





**Fig. 2.9** Gas pressure  $p$  that is measured (*left picture*) results from a great number of molecular collisions with the piston. The *right picture* presents a great magnification of a small fragment of the gas near the piston

with a wall (Fig. 2.9). The change in the momentum per unit time is equal to the force exerted by the molecules on the wall. Thus, to determine the pressure exerted on the wall one needs to calculate the average number of molecular collisions with the wall per unit time.

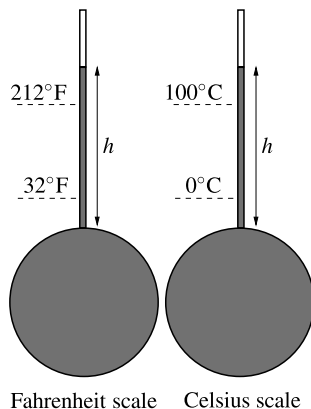
### 2.3.2 Temperature

**Zeroth Law of Thermodynamics and the Empirical Temperature** The zeroth law of thermodynamics, which leads to the concept of *empirical temperature*, was formulated in 1909, which is more than 200 years after the discovery of the thermometer. In order to formulate this law, the state of *thermal equilibrium* is to be defined first. It is a state of thermodynamic equilibrium of a system restricted by diathermal walls, i.e., walls permeable to heat.

#### The Zeroth Law of Thermodynamics

If two systems are in thermal equilibrium with a third system they are also in thermal equilibrium with each other

From the point of view of mathematics, thermal equilibrium between two systems is an *equivalence relation*, and the empirical temperature  $t$  is defined as the *equivalence class* of that relation. All systems that are in thermal equilibrium with one another belong to the same equivalence class, to which a common value of the temperature  $t$  is assigned. Different classes correspond to different values of the empirical temperature. Obviously such an assignment can be done in many ways because it can be based on different reproducible physical phenomena. Thus, it is not surprising that many temperature scales have been in use, for instance, the Celsius and Fahrenheit scales. None of these scales is particularly favoured. For instance, the zero point on the empirical temperature scale is conventional. Only the Kelvin temperature scale is fundamentally different from the empirical scales. It is strictly related to entropy and the second law of thermodynamics, which we discuss in Chap. 4. The temperature on the Kelvin scale is always positive and the zero



**Fig. 2.10** Thermal expansion of liquid is used in both thermometers shown. They are physically identical but one has the Celsius scale and the other has the Fahrenheit scale. The height of the liquid (e.g., mercury) column,  $h$ , shows the temperature measured. The freezing point and boiling point of water correspond to the same values of  $h$  on both thermometers. However, on the Celsius scale we read  $0^\circ\text{C}$  and  $100^\circ\text{C}$ , whereas on the Fahrenheit scale we read  $32^\circ\text{F}$  and  $212^\circ\text{F}$ , respectively

point corresponds to the lowest temperature, which is unattainable experimentally, however.

**Measurement of Temperature** Temperature is one of the intensive parameters that we know very well from everyday life. To measure it we often use mercury thermometers. Nowadays two empirical temperature scales are in common use: the *Celsius scale* in Europe and the *Fahrenheit scale* in the United States.

Celsius chose two reproducible phenomena (which means that they occur always at the same temperatures): the freezing and boiling of water, and assigned to them  $0^\circ\text{C}$  and  $100^\circ\text{C}$ , respectively. Then he divided the scale between these temperatures into 100 equal degrees. Fahrenheit did a similar thing but he chose different phenomena. The temperature  $0^\circ\text{F}$  corresponds to the freezing point of a mixture of water and sal-ammoniac, and the value of  $100^\circ\text{F}$  was assigned to the temperature of his (sick) wife. Fahrenheit also divided his scale into 100 equal degrees. The conversion of one scale to the other is given by the following formula:

$$t_F/^\circ\text{F} = \frac{9}{5}t_C/^\circ\text{C} + 32, \quad (2.18)$$

where  $t_C$  and  $t_F$  denote the temperatures in the Celsius and Fahrenheit scale, respectively. It follows from the comparison of the two scales that  $0^\circ\text{C}$  corresponds to  $32^\circ\text{F}$  and  $100^\circ\text{C}$  corresponds to  $212^\circ\text{F}$ . Figure 2.10 shows that there is no fundamental difference between these two scales.

In the measurement of temperature, a physical phenomenon sensitive to its variation should be used. Such a phenomenon is, for instance: thermal expansion of liquid (used in household thermometers), electric resistance of metals (platinum thermometer), electric potential difference at the junction of two different metals

(thermopile). To measure temperature in the outer space or on the surface of a star, the temperature dependence of the photon–energy distribution is used (pyrometer).

A thermometer based on thermal expansion of liquid is shown in Fig. 2.10. Let us assume that in the range of temperature between  $t_0$  and  $t$ , the volume of the liquid used in the thermometer satisfies the following relation:

$$V = V_0[1 + \alpha(t - t_0)], \quad (2.19)$$

where  $\alpha$  denotes the *thermal expansion coefficient* and the volume  $V_0$  corresponds to the temperature  $t_0$ . Measuring the height of the liquid column,  $h = (V - V_0)/A$ , where  $A$  is the cross-section area of the glass tube, we determine the empirical temperature difference:

$$t - t_0 = \frac{hA}{V_0\alpha}. \quad (2.20)$$

The larger  $V_0$  and smaller  $A$  (narrower tube) are, the more accurate the thermometer is.

In the case of the platinum thermometer, the electric resistance of platinum is measured, which in the range 0–630 °C varies according to the formula:

$$\mathcal{R} = \mathcal{R}_0[1 + a(t - t_0) + b(t - t_0)^2]. \quad (2.21)$$

In order to determine the constants  $\mathcal{R}_0$ ,  $a$  and  $b$ , the following three points are used: the freezing point and boiling point of water and the boiling point of sulphur. These three constant points are needed to calibrate the thermometer. It should be added that a good thermometer must satisfy one more condition. In the measurement of temperature, a flow of heat between the thermometer and the system studied always exists, which disturbs the temperature of the system. To minimize that disturbance, the thermometer should be small compared to the system the temperature of which we measure.

In the case of the thermopile, one measures the electric potential difference  $E$  between two junctions of two different metals, which are placed at different temperatures.  $E$  depends on the temperature difference  $\Delta t$  as follows:

$$E = a + b\Delta t + c(\Delta t)^2. \quad (2.22)$$

One of the junctions can be immersed in a mixture of ice and water, whose temperature is treated as the reference temperature. Using other constant points, it is possible to determine the constants  $a$ ,  $b$  and  $c$ .

**Kelvin Scale** There exists a favoured temperature scale called the *absolute scale* or *Kelvin scale*. The base SI unit of temperature is *kelvin* (K). The temperature that appears in all fundamental laws of nature, called the *absolute temperature* or *thermodynamic temperature*, denoted by  $T$ , is always expressed in the Kelvin scale. Thus, if we use a different temperature scale we have to convert it to the Kelvin scale. For instance, the temperature  $t_C$  in the Celsius scale which corresponds to the temperature  $T$  in the Kelvin scale is obtained from the following formula:

$$T/\text{K} = t_C/^\circ\text{C} + 273.15. \quad (2.23)$$

The temperature  $t_C = 0\text{ }^\circ\text{C}$  corresponds to  $T = 273.15\text{ K}$  and the lower limit of all temperatures, called the *absolute zero* ( $T = 0\text{ K}$ ), corresponds to  $t_C = -273.15\text{ }^\circ\text{C}$ . In Chap. 4, we show that the thermodynamic definition of temperature defines  $T$  up to an arbitrary constant factor, which means that the choice of the temperature unit is arbitrary. However, since the Celsius scale appeared before the Kelvin scale, it was convenient to use the same unit, i.e.,  $1\text{ K}$  and  $1\text{ }^\circ\text{C}$  mean the same temperature difference. Because of this choice, however, the freezing point of water is not an integer in the Kelvin scale.

It had passed more than one hundred years since the first experiments on dilute gases, performed by Boyle at the end of the 17th century, before all relations between pressure, volume and temperature of a dilute gas were discovered. It was found that these three parameters satisfy, to a good approximation, the following equation:

$$pV = B(t_C + 273.15\text{ }^\circ\text{C}), \quad (2.24)$$

where  $B$  is constant for a given amount of gas. Moreover, it was shown that

$$B = nR, \quad (2.25)$$

where  $n$  is the number of moles of the gas, and

$$R = 8.314472(15)\text{ J K}^{-1}\text{ mol}^{-1} \quad (2.26)$$

is called the *gas constant*. It is easy to recognize that the temperature in Eq. (2.24) is actually expressed in the Kelvin scale, hence, (2.24) can be rewritten as follows:

$$pV = nRT. \quad (2.27)$$

Thus, the Kelvin scale can be inferred from the studies of the properties of dilute gases. We notice that the gas constant does not depend on the kind of a gas. This is related to the fact that the amount of substance is expressed in moles. If we used kilograms instead of moles, the value of  $R$  would depend on the molecular mass of a given substance. For instance, it would be 16 times larger for hydrogen ( $\text{H}_2$ ) than for oxygen ( $\text{O}_2$ ).

It follows from (2.27) that for a given amount of a dilute gas and at constant volume, we have

$$\frac{p}{p_0} = \frac{T}{T_0}, \quad (2.28)$$

where  $T_0$  and  $p_0$  define a reference state. This equation shows that measuring the gas pressure, we can determine its temperature  $T$ . To calibrate such a gaseous thermometer, one constant point is to be chosen, for instance, the freezing point of water at atmospheric pressure.<sup>3</sup>

The absolute temperature also appears in the internal energy of a photon gas in thermodynamic equilibrium with the *perfect blackbody*. According to the Stefan–Boltzmann law

$$U = \gamma VT^4, \quad (2.29)$$

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<sup>3</sup>In fact, it should be the *triple point*, i.e., a thermodynamic state in which water vapour, liquid water and ice are in thermodynamic equilibrium (at  $T_0 = 273.16\text{ K}$ ).

where  $\gamma$  is a constant. This energy can be determined from the intensity of the electromagnetic radiation emitted by the perfect blackbody, which means that it absorbs photons independently of their energy. This method can be used, for instance, to determine the temperature of stars. For example, the temperature on the sun surface determined in this way amounts to 6000 K. The thermometers based on the Stefan-Boltzmann law are called *pyrometers*. Expression (2.29) can also be applied in measurements of very high temperatures, at which most of solids melt.

In laboratories, we can obtain both very high and very low temperatures. The lowest temperature obtained on the earth amounts to  $10^{-8}$  K (Boulder Colorado, 1995), and the highest temperature amounts to  $10^{12}$  K (CERN, 2000). In both cases, the amount of substance used in the experiment was very small compared to 1 mol.

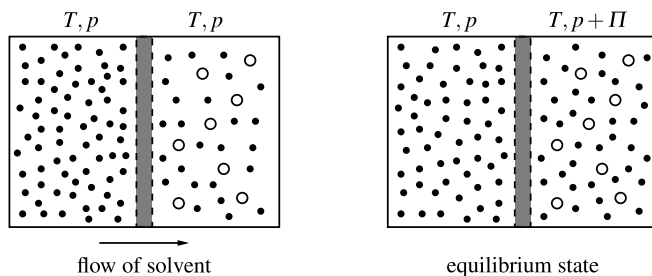
### 2.3.3 Chemical Potential

In a closed system, energy can be transferred only in the form of work or heat. In the general case, also matter can flow between the system and surroundings. To describe thermodynamic equilibrium between the system and surroundings if a flow of matter is possible, we have to introduce an additional intensive parameter, apart from pressure and temperature, which is called the *chemical potential*. In the case of a pure substance, it is just one quantity, denoted by  $\mu$ . In a mixture, each component has its own chemical potential. The SI derived unit of the chemical potential is *joule/mol* (J/mol).

While temperature and pressure are the concepts we are familiar with, it is not the case of the chemical potential. To explain this concept, we recall first that the condition of mechanical equilibrium requires that pressures in all subsystems of a given system are equal. Similarly, thermal equilibrium means that the temperatures of all subsystems are the same. If these conditions are not satisfied simultaneously then heat flows between the subsystems or their volumes change, which means that the system is not in thermodynamic equilibrium.

We consider now a system composed of two subsystems separated by a immobile diathermal wall impermeable to matter. The subsystems are in thermal equilibrium but their pressures can differ because the wall is stiff. We assume that one subsystem is formed by a two-component liquid mixture, in which the number of solvent molecules is much greater than the number of molecules of the other component (the solute). The other subsystem is formed by a pure solvent (Fig. 2.11). We also assume that the temperatures and pressures in both subsystems are initially the same.

What will happen if we replace the wall impermeable to the matter flow with a semi-permeable wall, permeable only to the solvent molecules? Since we have assumed equal temperatures and pressures on both sides of the wall, it may seem that nothing will happen, because the subsystems are in thermal and mechanical equilibrium. Such an answer is wrong, however. In fact, a certain number of the solvent molecules will flow from the subsystem containing the pure solvent to the subsystem containing the mixture. Moreover, this flow causes the pressure of the mixture



**Fig. 2.11** System is divided into two subsystems by an immobile diathermal wall. The *left part* is occupied by a pure solvent (*black circles*), and the *right part* contains a mixture of the solvent with a small amount of a solute (*white circles*). The wall is permeable only to the solvent molecules. Initially the temperatures and pressures in both parts are the same (*left picture*). However, because of the difference in the chemical potential of the solvent, a certain number of the solvent molecules flow to the *right part*. In thermodynamic equilibrium (*right picture*), the chemical potential of the solvent is the same in both subsystems but there is a pressure difference  $\Pi$ , called the *osmotic pressure*

to increase, which is possible because the wall is immobile. The pressure difference between the mixture and the pure solvent is called the *osmotic pressure*.<sup>4</sup> Thus, the flow of the solvent molecules occurs in the direction of increasing pressure, which seems counterintuitive. Apparently *something* is missing in our description of this phenomenon. That what is missing is just the chemical potential. It turns out that the chemical potential of the solvent in a mixture differs from the chemical potential of the pure solvent. In the phenomenon discussed here, the temperature and pressure in the mixture and in the pure solvent are initially the same but the chemical potential of the pure solvent is higher than the chemical potential of the solvent in the mixture, which we explain in Chap. 8. Anyway, the chemical potential difference causes a flow of the solvent in the direction of the lower chemical potential. The flow stops when the chemical potential of the solvent in both subsystems is the same.

If the chemical potential of a given component has the same value in all subsystems then the system is said to be in equilibrium with respect to the flow of that component. This statement concerns only the components whose flow is not restricted by some internal constraints, as in the example above. As we have already mentioned, the chemical potential of a pure substance is a function of temperature and pressure. It depends also on the form in which a given substance exists in given conditions, i.e., as a gas, liquid, or solid. For example, the chemical potentials of liquid water and ice are different functions of temperature and pressure. Therefore, if we ask about the conditions in which liquid water and ice are in thermodynamic equilibrium we have to take into account the equality of chemical potentials, apart from the equality of pressures and temperatures. If the chemical potentials were different then the matter would flow between the liquid and solid, thus, they would

<sup>4</sup>The phenomenon of osmosis is discussed in Chap. 8.

not be in thermodynamic equilibrium. These problems are discussed extensively in Part II, which is devoted to phase transitions.

## 2.4 Equations of State

Having determined all state parameters for a given system in thermodynamic equilibrium: the temperature  $T$ , volume  $V$ , pressure  $p$ , internal energy  $U$ , amount of substance  $n$ , etc., we discover that they are not independent of one another. A relation between the state parameters  $X_1, X_2, X_3, \dots$ :

$$\mathcal{F}(X_1, X_2, X_3, \dots) = 0, \quad (2.30)$$

is called an *equation of state*. A system in thermodynamic equilibrium is uniquely defined by a specified number of independent parameters of state. The remaining parameters of state are functions of the independent parameters. Thus, they are state functions, which can be determined if we know the equations of state.

In general, the equations of state depend on a given substance and on the range of the parameters in which we want to describe that substance. For example, the equations of state of a substance in the gaseous state are different from the equations of state of the same substance in the liquid or solid state. Below we discuss three model systems: the ideal gas, the van der Waals gas and the photon gas, which have different equations of state. The parameters of state that appear in these equations of state are:  $T$ ,  $V$ ,  $p$ ,  $n$  and  $U$ . In the case of the photon gas, there is no dependence on  $n$ , but it is an exception rather than a rule.

### 2.4.1 Ideal Gas

The parameters of state that describe a dilute gas in thermodynamic equilibrium satisfy, to a good approximation, the following equations of state:

$$pV = nRT, \quad (2.31)$$

$$U = \frac{f}{2}nRT. \quad (2.32)$$

$R$  denotes the gas constant (see (2.26)), and  $f$  specifies the number of *degrees of freedom* of a single molecule. For monatomic molecules, e.g., argon,  $f = 3$ . For linear molecules, e.g., oxygen,  $f = 5$ , and for more complex molecules, e.g., methane,  $f = 6$ .<sup>5</sup> A hypothetical gas for which Eqs. (2.31) and (2.32) are satisfied for all

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<sup>5</sup>This follows from the *equipartition theorem*, which is derived in the framework of classical statistical mechanics. According to the equipartition theorem each degree of freedom of the translational or rotational motion of a molecule gives the same contribution to the internal energy, equal to  $RT/2$  per 1 mol. A monatomic molecule has three degrees of freedom related to the translational motion of the center of mass, hence,  $f = 3$ . A linear molecule has, in addition, two independent axes of rotation perpendicular to its symmetry axis, hence,  $f = 3 + 2 = 5$ . Other molecules have three axes of rotation, which gives  $f = 3 + 3 = 6$ .

values of the state parameters is called the *ideal gas*, and (2.31) and (2.32) are the equations of state of the ideal gas. The ideal gas can be treated as a limiting case of a real gas when the pressure  $p \rightarrow 0$ . In a very dilute gas, all intermolecular interactions can be neglected and the only contribution to its internal energy comes from the kinetic energy of molecules.

It follows from the equations of state of the ideal gas that we can choose three independent variables from the five state parameters that appear in these equations. For instance, if we substitute

$$T = 298 \text{ K}, \quad p = 1 \text{ atm}, \quad n = 1 \text{ mol},$$

into (2.31) and (2.32) we get, for  $f = 3$ :

$$V = 0.024453 \text{ m}^3, \quad U = 3716.6 \text{ J}.$$

If we increase the number of moles to  $n = 2$ , keeping  $T$  and  $p$  unchanged, then the volume and internal energy also increase twice.

Choosing  $U$ ,  $V$  and  $n$  as independent variables, we can transform the equations of state of the ideal gas as follows:

$$p = \frac{2U}{fV}, \quad (2.33)$$

$$T = \frac{2U}{fnR}. \quad (2.34)$$

Here the temperature and pressure are treated as functions of state:  $p = p(U, V, n)$  and  $T = T(U, V, n)$ . We use this form of the equations of state in Chap. 4, to calculate the entropy of the ideal gas.

As independent parameters of state we can also choose  $T$ ,  $V$  and  $n$ , and rewrite the equations of state in the following form:

$$p = \frac{nRT}{V}, \quad (2.35)$$

$$U = \frac{f}{2}nRT. \quad (2.36)$$

In this case, the pressure and internal energy are functions of state, which are formally expressed as  $p = p(T, V, n)$  and  $U = U(T, V, n)$ , although  $U$  does not depend on  $V$  for the ideal gas. Relation (2.35) is used, for instance, to calculate the work done during the isothermal compression ( $T = \text{const}$ ) of the ideal gas.

Finally, as independent parameters of state one can choose  $T$ ,  $p$  and  $n$ , which gives

$$V = \frac{nRT}{p}, \quad (2.37)$$

$$U = \frac{f}{2}nRT. \quad (2.38)$$

Here, the volume and internal energy are functions of state:  $V = V(T, p, n)$  and  $U = U(T, p, n)$ , where  $U$  does not depend on  $p$  for the ideal gas. For instance, Eq. (2.37) is used to determine the dependence of the chemical potential of the ideal gas on pressure.



### 2.4.2 Van der Waals Gas

If the gas is not sufficiently dilute the intermolecular interactions cannot be neglected and equations of state (2.31) and (2.32) are not satisfied. Then Eq. (2.31) can be replaced by the *van der Waals equation of state*:

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}. \quad (2.39)$$

It describes some real gases in an approximate way. Moreover, Eq. (2.39) applies not only to gases but, to some extent, also to liquids. In Chap. 6, we show that it explains qualitatively the change of gas into liquid. The constants  $a$  and  $b$  in Eq. (2.39) are to be determined experimentally for a given substance. For example,  $a = 0.1358 \text{ J m}^3 \text{ mol}^{-2}$  and  $b = 3.85 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$  for nitrogen ( $\text{N}_2$ ). For most of simple substances,  $b \approx 3 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$  and  $a$  can vary from  $0.003 \text{ J m}^3 \text{ mol}^{-2}$ , for helium, to  $1 \text{ J m}^3 \text{ mol}^{-2}$ , for Freon.

For the internal energy of the van der Waals gas, the following formula is assumed:

$$U = \frac{f}{2}nRT - \frac{an^2}{V}. \quad (2.40)$$

Equations (2.39) and (2.40) are empirical but they can also be derived from a molecular theory (see Sect. 6.7). We notice that they reduce to the equations of state of the ideal gas when  $a = 0$  and  $b = 0$ . Since the ideal gas model is based on the assumption of non-interacting molecules, the constants  $a$  and  $b$  must be related to intermolecular interactions. The constant  $a$  stands at the term which takes into account, in an approximate way, attraction between molecules. Thus, it is a measure of the strength of attractive forces. The presence of the constant  $b$  stems from the fact that a molecule is not a point object but it occupies some volume. Therefore, it is not possible to compress a given substance into the volume  $nb$  taken up by the molecules themselves because such a state would have infinite pressure.

### 2.4.3 Photon Gas

The photon gas is a system formed by quanta of electromagnetic radiation (photons). As an ordinary gas of molecules, the photon gas has its volume, temperature, internal energy and pressure. However, in contrast to a molecular gas, the number of photons is not conserved. Photons are absorbed and emitted by the walls of a vessel and because of that the number of moles is not a state parameter for the photon gas. The state of thermodynamic equilibrium of the photon gas is called the *blackbody radiation*, and the equations of state have the following form:

$$p = \frac{1}{3}\gamma T^4, \quad (2.41)$$

$$U = \gamma VT^4, \quad (2.42)$$

where  $\gamma \approx 7.56 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4}$ .<sup>6</sup> Thus, the pressure,  $p = p(T, V)$ , and the internal energy,  $U = U(T, V)$ , are state functions, and  $T$  and  $V$  are state parameters. If we treat  $U$  and  $V$  as state parameters, and  $T = T(U, V)$  and  $p = p(U, V)$  as state functions then we obtain

$$p = \frac{U}{3V}, \quad (2.43)$$

$$T = \left( \frac{U}{\gamma V} \right)^{1/4}. \quad (2.44)$$

#### 2.4.4 Equations of State in Terms of Intensive Parameters

Dividing the equations of state of the ideal gas (see (2.31) and (2.32)) by the mole number  $n$ , we get

$$pv = RT, \quad (2.45)$$

$$u = \frac{f}{2} RT, \quad (2.46)$$

where  $v = V/n$  and  $u = U/n$  denote the molar volume and the molar internal energy, respectively. Both  $v$  and  $u$  are intensive parameters, as are temperature and pressure, i.e., they do not depend on the mass of the system. Equations (2.45) and (2.46) provide as much information about properties of the system as Eqs. (2.31) and (2.32) do. This stems from the fact that any macroscopic subsystem of a system in thermodynamic equilibrium have the same physical properties as the whole system. It simplifies the description of thermodynamic systems because the number of independent parameters of state is reduced by one.

Treating in the same way Eqs. (2.39) and (2.40) for the van der Waals gas, we find:

$$p = \frac{RT}{v - b} - \frac{a}{v^2}, \quad (2.47)$$

$$u = \frac{f}{2} RT - \frac{a}{v}. \quad (2.48)$$

In the case of the photon gas, we divide both sides of Eq. (2.42) by  $V$ , which gives  $U/V = \gamma T^4$ . Thus, instead of the molar internal energy, we have the internal energy per unit volume.

The conclusions presented above follow from the definition of extensive and intensive parameters. When we join together  $m$  identical systems, to form a new  $m$  times larger system, the intensive parameters, such as pressure and temperature, do not change, and the extensive parameters, such as volume and internal energy, are

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<sup>6</sup>The constant  $\gamma = 8\pi^5 k_B^4 / (15c^3 h^3)$ , where  $k_B = R/N_A$  is the Boltzmann constant, and  $c$  and  $h$  denote the speed of light in the vacuum and the Planck constant, respectively.

multiplied by  $m$ . For example, if pressure is treated as a function of three extensive parameters:  $U$ ,  $V$  and  $n$ , then

$$p(mU, mV, mn) = p(U, V, n). \quad (2.49)$$

Here  $m > 0$  is an integer but it is easy to show that  $m$  can be treated as a positive real variable. To show this, we consider a large system in thermodynamic equilibrium, which is divided to  $\mathcal{N}$  identical small (but macroscopic) fragments. Then we use  $\mathcal{M}$  fragments, to form a subsystem of the original system. Assuming that the extensive parameters  $U$ ,  $V$  and  $n$  correspond to the large system, for the subsystem, we have  $mU$ ,  $mV$  and  $mn$ , where  $m = \mathcal{M}/\mathcal{N}$  is a rational number. If  $\mathcal{N}$  is a very large number we can assume that  $m$  is practically a continuous variable. Thus, we can substitute  $m = 1/n$  in (2.49), hence,

$$p(u, v, 1) = p(U, V, n), \quad (2.50)$$

i.e.,  $p$  is a state function of two intensive parameters:  $u$  and  $v$ . A similar relation can be derived for temperature.

Then we consider the internal energy as a state function of  $T$ ,  $V$  and  $n$ . Since  $U$  is an extensive parameter, the following identity must hold:

$$U(T, mV, mn) = mU(T, V, n). \quad (2.51)$$

Substituting  $m = 1/n$ , we obtain

$$U(T, V, n) = nU(T, v, 1) = nu(T, v). \quad (2.52)$$

We note finally that relations (2.49)–(2.52) are exact, as they do not refer to any particular form of the equations of state.

## 2.5 Exercises

**2.1** Calculate the kinetic energy of molecules in 22 L of air, assuming that the average speed of molecules is equal to the speed of sound and the density of air is  $10^{-3} \text{ g cm}^{-3}$ . Ignore the fact that air is a mixture of several gases.

**2.2** Calculate the change in the gravitational energy of 1 mol of water transferred from the level  $h = 0$  to the height  $h = 5 \text{ km}$ .

**2.3** Calculate approximately the change in the internal energy of 9 g of water caused by its evaporation. The heat of evaporation amounts to  $40 \text{ kJ mol}^{-1}$ . Compare it with the change in the gravitational energy found in Exercise 2.2 and with the kinetic energy of air. Draw a conclusion about the energy of interactions of water molecules.

**2.4** Calculate approximately the change in the internal energy of 40 g of argon caused by its evaporation. The heat of evaporation amounts to  $6 \text{ kJ mol}^{-1}$ . Compare it with the energy needed to evaporate water. Draw conclusions about the interaction energies of water molecules and argon atoms.

**2.5** Calculate approximately the change in the internal energy of 12 g of carbon caused by its combustion. The heat of combustion amounts to  $400 \text{ kJ mol}^{-1}$ . Compare it with the energy of intermolecular interaction found in Exercise 2.4. Comparing the changes in the internal energy due to evaporation and combustion, draw a conclusion about the energy of chemical bonds and intermolecular interactions.

**2.6** The sun shines due to thermonuclear reactions in which nuclei of light elements combine to form nuclei of heavier elements. As a result of a few nuclear reactions, four hydrogen nuclei (protons) combine to form one nucleus of helium (2 protons and 2 neutrons) and the energy of 26 MeV is released ( $1 \text{ MeV} = 10^6 \text{ eV}$ ,  $1 \text{ eV} \approx 1.6 \times 10^{-19} \text{ J}$ ). Calculate the energy released during the nuclear reaction in 1 mol of hydrogen nuclei (protons).

**2.7** As a result of annihilation, 1 mol of carbon is transformed into the energy of a photon gas. Calculate how much energy has been released. Compare it with the forms of energy discussed previously.

**2.8** One mol of water vapour condenses. Find the change in its volume, assuming  $1 \text{ g cm}^{-3}$  for the density of liquid water and  $10^{-3} \text{ g cm}^{-3}$  for the density of water vapour.

**2.9** In the reaction of ammonia formation, 2 mol of  $\text{NH}_3$  are formed from 1 mol of  $\text{N}_2$  and 3 mol of  $\text{H}_2$ . Find the changes in the total amount of substance in the system and in the amounts of individual components:  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$ .

**2.10** A mixture of three gases: 3 mol of  $\text{H}_2$ , 4 mol of  $\text{H}_2\text{O}$  and 1 mol of Ar, occupies a vessel of the volume of 100 L. A second vessel contains 5 mol of  $\text{H}_2$ , 2 mol of  $\text{H}_2\text{O}$  and 1 mol of Ar, which also occupy 100 L. Then we fuse the vessels. Give the total mole number and the volume of the gases in the fused vessels.

**2.11** There are four vessels, each of which contains the same gas of the internal energy  $U$ , volume  $V$  and mole number  $n$ . Then we fuse the vessels. Find the total internal energy, volume and mole number of the gas in the fused vessels.

**2.12** A man needs 2000 kcal a day, on average, in order his organism could function properly. Calculate the power used up by a man. It is worth mentioning that the first studies on the heat given off by animals were carried out by Lavoisier and Laplace in the 18th century with the use of calorimeters. Thus, thermodynamics provided a basis for the determination of the human diet from the energetic point of view.

**2.13** Why do we use mercury in the barometer instead of water or oil, for instance? What would the height of the barometer have to be if we used flaxseed oil, of the density about  $0.94 \text{ g cm}^{-3}$ , instead of mercury, to measure atmospheric pressure on the earth surface?

**2.14** Is 1 atm a large pressure? What force does air exert on a human body? What would happen to a human body if the pressure of air decreased to the value  $10^{-6}$  atm?

**2.15** Assume you drink water using a 20 cm long straw. What pressure difference do you have to apply with your mouth (when you suck in air in the straw you simply produce an underpressure above the liquid surface), to drink up water?

**2.16** At a depth of 10 m there is a submarine. The pressure of air inside the submarine amounts to 1 atm. A sailor wants to lift the lid to let a diver out into water. The lid area is equal to  $2 \text{ m}^2$ . Calculate the force the sailor has to apply to lift the lid. Explain why to let the diver out of the submarine, the sluice-gate must be filled with water first.

**2.17** Convert  $0^\circ\text{F}$ ,  $70^\circ\text{F}$  and  $451^\circ\text{F}$  to the Celsius scale.

**2.18** What temperature in the Kelvin scale corresponds to  $-273.15^\circ\text{C}$ ?

**2.19** Express the temperature of 0 K in the Fahrenheit scale.

**2.20** Convert  $100^\circ\text{F}$  to the Celsius scale. How do we know that Fahrenheit's wife was sick when he calibrated the thermometer? Is the human body temperature suitable for the calibration of thermometers?

**2.21** How would you calibrate a pyrometer if you know that the temperature of water at the triple point is equal to  $T = 273.16 \text{ K}$ ? You have a means of measuring the energy emitted by the perfect blackbody at a given temperature. The internal energy  $U$  is proportional to the intensity of radiation.

**2.22** Prove that the internal energy per mole does not depend on the size of the system, thus, it is an intensive parameter. Assume that you join together  $m$  identical systems characterized by the same parameters of state:  $U$ ,  $V$  and  $n$ . Calculate the internal energy per mole for each system and for the composite system and compare the results.

**2.23** We have two vessels containing water at the same temperature and pressure. The volume of the vessels amounts to  $V_1 = 18 \text{ cm}^3$  and  $V_2 = 36 \text{ cm}^3$ , respectively, and the density of water is  $\rho = 1 \text{ g cm}^{-3}$ . Calculate the mole number of water and its molar density (the mole number per unit volume) for each vessel. Then we join the vessels together. Calculate the volume, mole number and molar density after the fusion of the vessels. Which of them are extensive parameters and which are intensive parameters? Why is the density  $\rho$  an intensive parameter?

**2.24** Determine the volume per one molecule of  $\text{H}_2\text{O}$  in liquid water. The density of water  $\rho = 1 \text{ g cm}^{-3}$ , the Avogadro constant  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$  and the molar mass of water  $M = 18 \text{ g mol}^{-1}$ .

**2.25** Calculate an infinitesimal increase in the volume,  $dV$ , if the temperature increases by  $dT$ , the pressure increases by  $dp$ , and the mole number  $n$  does not change. Perform the calculations for the ideal gas.

**2.26** Calculate an infinitesimal increase in the internal energy,  $dU$ , if the temperature increases by  $dT$ , the volume increases by  $dV$ , and the mole number  $n$  does not change. Perform the calculations for the van der Waals gas.

**2.27** Calculate an infinitesimal increase in the pressure,  $dp$ , for the photon gas if the temperature increases by  $dT$ .

**2.28** Which of the expressions presented below is a differential of a function of  $x$  and  $y$ : (1)  $d\omega = 2xy^3dx + 3x^2y^2dy$ , (2)  $d\omega = xy^4dx + x^2y^2dy$ . Find this function.

**2.29** Show that in the case of the differential form which is not a differential of a function in Exercise 2.28, the integral  $\int_i^f d\omega$  depends on the path of integration. As the initial point ( $i$ ) and final point ( $f$ ) in the  $xy$  plane assume  $(0, 0)$  and  $(1, 1)$ , respectively. Perform calculations for two paths: (1)  $0 \leq x \leq 1$ ,  $y = 0$  and  $x = 1$ ,  $0 \leq y \leq 1$ , (2)  $0 \leq x \leq 1$ ,  $y = x$ . Verify that in the case of the differential  $df$ , the integral does not depend on the path of integration and is equal to  $\Delta f = f_f - f_i$ .

**2.30** A system that contains 5 mol of a gas in a vessel of the volume  $V = 120$  L and at a temperature of  $25^\circ\text{C}$  is in thermodynamic equilibrium. Then, we let a certain amount of the gas out of the vessel. The pressure of the gas in the new state is equal to  $p = 0.5$  atm. What is the amount of the gas that has escaped?

**2.31** A vessel of the volume 0.1 L is occupied by 1 mol of  $\text{N}_2$  at the temperature  $T = 298$  K. Calculate the pressure and internal energy of the gas. Apply the equation of state of the ideal gas.

**2.32** A vessel of the volume 0.1 L is occupied by 1 mol of  $\text{N}_2$  at the temperature  $T = 298$  K. Calculate the pressure and internal energy of the gas. Apply the van der Waals equation of state with the constants:  $a = 0.1358 \text{ J m}^3 \text{ mol}^{-2}$  and  $b = 3.85 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ . Compare the result with the result of Exercise 2.31.

**2.33** A vessel of the volume 1000 L is occupied by 1 mol of  $\text{N}_2$  at the temperature  $T = 298$  K. Calculate the pressure and internal energy of the gas. Apply the van der Waals equation of state, with the same constants  $a$  and  $b$  as in Exercise 2.32, and then the equation of state of the ideal gas. Compare the result with the results of Exercises 2.31 and 2.32.

**2.34** Calculate the internal energy of a photon gas contained in a vessel of the volume of  $1 \text{ m}^3$ , for two values of the temperature: 298 K and 400 K. Calculate the pressure exerted by the gas on the walls of the vessel.

**2.35** Verify the relations:

$$p(U, V, n) = p(mU, mV, mn) \quad \text{and} \quad U(T, mV, mn) = mU(T, V, n),$$

for the ideal gas and van der Waals gas.

**2.36** Calculate  $-V^{-1}(\partial V/\partial p)_{T,n}$  for the ideal gas and van der Waals gas. Does this expression make sense for the photon gas? Calculate an analogous quantity for the photon gas at constant internal energy  $U$ .

**2.37** Calculate  $V^{-1}(\partial V/\partial T)_{p,n}$  for the ideal gas and  $V^{-1}(\partial V/\partial U)_p$  for the photon gas.

**2.38** Calculate  $(\partial U/\partial T)_{V,n}$  for the ideal gas, van der Waals gas and photon gas.

**2.39** Assuming that most of air is contained in a thin, 10 km in thickness, layer around the earth, the pressure is equal to 1 atm, and the average temperature amounts to 14 °C, calculate the total mole number of gases in the atmosphere. Then assuming that oxygen makes 21 % of air, calculate the amount of oxygen. Living organisms use up  $0.5 \times 10^{16}$  mol of oxygen per year. If the oxygen supply was not renewed in the photosynthesis process, how quickly would it be lacking in the atmosphere?

**2.40** The temperature on the sun surface amounts to about 6000 K. The amount of energy radiated by the sun in the form of photons per unit time and per unit area is given by

$$I = \frac{uc}{4},$$

where  $u$  is the internal energy of the photon gas per unit volume, and  $c = 3 \times 10^8 \text{ m s}^{-1}$  is the speed of light. The radius of the sun is equal to 700 000 km. Calculate the energy  $E$  radiated by the sun during one second. Consider if the mankind will cope with the energetic crisis after the resources of oil have been exhausted.



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