

## Molecular Physics

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### 3.1 KINETIC THEORY OF IDEAL GASES

#### 3.1.1 Introductory remarks

So far, we have considered the behavior of small amounts of particles and can follow almost each of them. We come now to a description of physical systems consisting of enormous numbers of particles, moving chaotically (i.e., randomly) in a limited space. Such objects are referred to as statistical systems, related to which are gases, liquids and real (nonideal) solids. Here, special approaches are necessary. By a thermodynamic system, we understand a set of macroscopic bodies that can accomplish an exchange of energy both among themselves and with bodies that are outside the system. These laws are referred to as statistical ones. In fact, there is a difference between these and Newton's laws that have an exact character; they cannot give any information on a particular particle, but describe the general properties of a system that has a statistical character. Statistical physics, however, operates both by integrated values and allows one to evaluate uncertainties (fluctuations) as well. As a rule, in molecular physics, the latter are negligibly low, therefore we will not pay much attention to them. These systems as a whole are described by a restricted set of parameters unified by corresponding equations of state. Such systems can be in equilibrium states if their parameters do not depend on time, remaining unchanged for an infinitely long time. We will deal mainly with such systems. Very important examples are systems that are in thermal equilibrium with other systems and the environment. The parameters describing such a system, for gases in particular, comprise mass ( $M$ ), pressure ( $p$ ), density ( $\rho$ ), temperature ( $T$ ), and, in some respects, the volume ( $V$ ) that a system can occupy.

Any statistical system can be in various states described by a set of parameters. These parameters do not always have certain values. If, for example, the pressure (or temperature) in different elementary volumes of gas is different, it is impossible to attribute certain general values to the whole gas. Such a state is referred to as nonequilibrium. If such a nonequilibrium closed system is left alone for a period of time, the temperature and/or pressure inside the system will equalize in due course. The system will have passed into a state of equilibrium. From this point of view equilibrium systems possess maximum disorder, whereas nonequilibrium systems have a smaller disorder parameter.

A state in which the parameters are identical at any point of the system is referred to as an equilibrium state; in the absence of external excitement, it remains unchanged in time.

From all possible statistical systems the equilibrium closed systems are allocated. For such systems the physical theory, referred to as equilibrium thermodynamics or simply thermodynamics, is well developed. Thermodynamics is the phenomenological doctrine of heat. Classical thermodynamics asserts that “the isolated thermodynamic system cannot spontaneously change its state”. This statement is sometimes referred to as the zeroth law of thermodynamics, another assertion of which is that “If two thermodynamic systems are in thermodynamic equilibrium with some third body they are in thermodynamic equilibrium with each other”.

The transition of a system from one state to another is called the process. The process consists of a sequence of nonequilibrium stages. If the relaxation time of the system is much less than the time of the external disturbing effects, the system will have enough time to reach equilibrium; such a process consists of a sequence of equilibrium states (strictly speaking, it should be an indefinitely slow process). The process consisting of a continuous sequence of equilibrium states is referred to as the equilibrium or quasi-equilibrium process. Thus only an indefinitely slow process can be equilibrium, although at a slow enough transformation, a real process can come nearer to equilibrium than a closed.

### EXAMPLE E3.1

Determine the average distance  $\langle l \rangle$  between the centers of two neighboring molecules in water vapor at normal conditions and compare it with the diameters of water molecules.

**Solution:** Suppose that all molecules of water vapor are at equal distances to each other; this distance will coincide with an average distance  $\langle l \rangle$ . Each molecule in this case will have a volume  $l^3$ . If  $N$  is the number of molecules then  $V = Nl^3$  is the volume occupied by  $N$  molecules. Dividing this equality by  $V$ , we obtain  $(N/V)l^3 = 1$ ; this is the concentration  $n$  of water molecules and we can obtain  $\langle l \rangle = l = 1/\sqrt[3]{n}$ . If the water vapor is under normal conditions ( $p = 1.013 \times 10^5$  Pa and  $T = 300$  K) the molecule's concentration is known ( $n = n_L = 2.69 \times 10^{25} \text{ m}^{-3}$  is the Loschmidt number.) Executing the calculations we arrive at

$$\langle l \rangle = \frac{1}{\sqrt[3]{n_L}} = \frac{1}{2.69 \times 10^{25}} = 3.33 \times 10^{-9} \text{ m.}$$

The same formula is valid for the estimation of the molecule's diameter in liquid water since in this case, the molecule centers are at distances practically equal to the molecule's diameter  $d = 1/\sqrt[3]{n}$ ; in this case  $n$  is the molecule's concentration in the water. In order to evaluate the diameter of the water molecule one should determine

the molecule concentration in the liquid phase. Since  $n = \rho(N_A/M)$  where  $\rho$  is density of the water then,

$$d = \frac{1}{\sqrt[3]{n}} = \sqrt[3]{\frac{M}{\rho N_A}}$$

Substituting the constants and executing the calculations, we arrive at

$$d = \left( \frac{18 \times 10^{-3}}{6 \times 10^{23} \times 10^3} \right)^{1/3} \approx 3.1 \times 10^{-10} \text{ m.}$$

Thus, under evaporation the average intermolecular distance increases by approximately 11 times.

### EXAMPLE E3.2

Chlorine,  $m = 0.8$  g in weight and at a temperature 2 K is placed in a vessel of capacity  $V$ . Find the pressure of the gas if it is in part dissociated. The degree of dissociation  $\alpha = 0.4$  (i.e., 40% of gas is dissociated).

**Solution:** Partly dissociated gas can be considered as a mixture of two gases: monatomic  $m_{\text{dis}} = \alpha m$  and a mole mass  $M/2$  and nondissociated mass  $m_{\text{nondis}} = m(1-\alpha)$  and mole mass  $M$ .

According to Dalton's law, the pressure is an additive value, i.e., each of the gas components yields "its own pressure": monoatomic  $p_{\text{dis}}$  gas and diatomic gas  $p_{\text{nondis}}$ . Their sum is the total pressure of a mixture of the two component gas  $p = p_{\text{dis}} + p_{\text{nondis}}$ . Find these two values using the ideal gas equation

$$pV = \frac{m}{M} RT.$$

Then,

$$\begin{aligned} p_{\text{dis}} &= \frac{1}{V} \frac{\alpha m}{M/2} RT \text{ and} \\ p_{\text{nondis}} &= \frac{1}{V} \frac{(1-\alpha)m}{M} RT \text{ and} \\ p &= \frac{mRT}{MV} (1+\alpha). \end{aligned}$$

Transform all values into the SI system and execute calculations:

$$p = \frac{8 \times 10^{-4} \times 8.31 \times 2.10^3}{35.5 \times 10^{-3} \times 2 \times 10^{-3}} \text{ Pa} = 2.62 \times 10^5 \text{ Pa.}$$

$$p = 262 \text{ kPa or } P = 2.59 \text{ atm (1 atm} = 1.013 \times 10^5 \text{ Pa).}$$

### 3.1.2 Distribution function

For the definition of the average value of any characteristic of a particle system, statistical physics offers a special function: the so-called function of distribution of particles on a given physical property. We shall consider the notion of the distribution function in more detail.

In a multiparticle system some particles may have different characteristics. To find the distribution of particles of a given system on any characteristic means to find the relative number of particles for which the given physical value has a numerical magnitude lying in the given interval of values. This distribution is nonuniform; for example, the concentration of particles with low speeds is much less than the concentration of particles with average speeds.

We shall designate by  $x$  a value of distribution upon which a system is examined; this can be speed, energy, etc. We shall designate  $dN(x)$  as the number of particles, the parameter  $x$  of which lies in a limit from  $x$  up to  $x + dx$ . Certainly,  $dN(x)$  increases as wider the interval and greater the number of particles in the system; that is  $dN(x) \sim Ndx$  or  $dN(x) = ANdx$ , where  $A$  is the proportionality coefficient. This coefficient should be a function of  $x$  since in identical intervals at different  $x$  intervals, the number of particles can be different, i.e.,  $A = f(x)$ . Then  $dN(x) = f(x)Ndx$ , or

$$\frac{dN(x)}{N} = f(x)dx. \quad (3.1.1)$$

The magnitude  $dN(x)/N$  is a share (or relative amount) of particles, the parameter  $x$  of which lies in an interval from  $x$  to  $x + dx$ .

This quantity can be treated in the probability sense  $w$ . If one managed to measure the property of any specified particle then it is a probability  $dN(x)/N$ , that the particular particle has a property lying in the interval  $x-x + dx$ . Therefore,

$$\frac{dN(x)}{N} = dw(x) = f(x)dx. \quad (3.1.2)$$

The value,

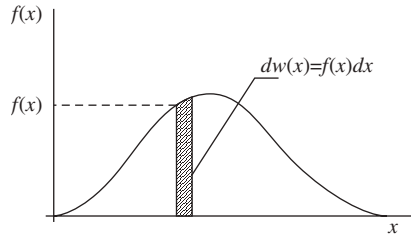
$$f(x) = \frac{dw(x)}{dx} = \frac{dN(x)}{Ndx}, \quad (3.1.3)$$

is referred to as the distribution function density.

Figure 3.1 presents an example of a distribution function. In the graph, the hatched area is  $dw(x) = f(x)dx$ . We also know definitely that a particular particle is in a vessel, therefore,

$$\int f(x)dx = \int dw(x) = 1. \quad (3.1.4)$$

This is the normalization condition.



**Figure 3.1** A model of a distribution function.

Find out how we can determine the average value. Begin first with a case where the values  $x$  can accept any integer data. Then,

$$\langle x \rangle = \frac{x_1 + x_2 + x_3 + \dots + x_N}{N} = \frac{1}{N} \sum_{i=1}^N x_i.$$

If the value  $x_i$  has  $k_i$  particles and the overall measurement is  $N$ , then,

$$\langle x \rangle = \frac{k_1 x_1 + k_2 x_2 + k_3 x_3 + \dots}{k_1 + k_2 + k_3 + \dots} = \frac{1}{N} \sum_{i=1}^N k_i x_i = \sum_{i=1}^N \frac{k_i}{N} x_i = \sum_{i=1}^N \Delta w_i x_i.$$

In the last expression, the fraction  $k_i/N$  under the sum sign expresses the share of particles, which with probability  $\Delta w_i$  determines the value  $x_i$ .

If the property  $x$  can accept a continuous set of values, the summation should be changed to integration:

$$\langle x \rangle = \int x dw(x) = \int x f(x) dx. \quad (3.1.5)$$

Integration is accomplished over all values of  $x$ . If one has to obtain the averaged value of a function, the prescription is the same:

$$\langle \varphi \rangle = \int \varphi(x) f(x) dx, \quad (3.1.6)$$

in the case of normalized  $f(x)$  function, and

$$\langle \varphi(x) \rangle = \frac{\int \varphi(x) f(x) dx}{\int f(x) dx}, \quad (3.1.6')$$

if it is not normalized.

Thus we have obtained a procedure for calculating an averaged value starting with the distribution function, which is supposed to be known.

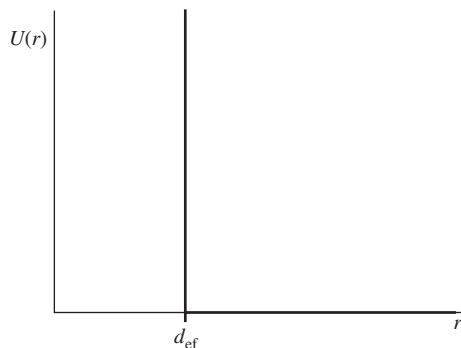
### 3.1.3 An ideal gas model

The simplest gas model is the model of an ideal gas, the essence of which is as follows:

1. A gas is represented by a set of an enormous number of molecules. It allows one to obtain average values of its physical parameters and to reduce deviations (fluctuations) from them. The thermodynamic balance in the ideal gas is established only due to an exchange of energy between molecules at their collisions.
2. Molecules are represented by very small spherical particles, the total volume of which is negligibly small in comparison to the volume that the gas occupies.
3. It is accepted that molecules do not interact at intermolecular distances larger than their effective diameter. The potential curve for the model of the ideal gas looks like that presented in Figure 3.2. If we imagine molecules as “incompressible balls” with radius  $r_0$ , the potential energy of their interaction is equal to zero at distances larger than their diameter  $2r_0$ , and increases sharply at  $r < 2r_0$ .
4. It is supposed that the collisions of molecules occur under the laws of absolute elastic collision (Section 1.5.5).
5. It is supposed also that there is no additional physical influence on the system as a whole.

In this approximation, it is possible to obtain an exact equation (within the framework of statistical laws) of the ideal gas state.

A few words should be added. There are no ideal gases in nature: neither hydrogen gas nor uranium hexafluoride is ideal. There exists only the notion of an ideal gas state. Each gas can be both in the state of an ideal gas or behave as a real gas. All depends on the temperature and pressure. The model of the ideal gas is very convenient for understanding many gas state peculiarities.



**Figure 3.2** Potential curve  $U(r)$  of an ideal gas molecules interaction.

### 3.1.4 General equation of an ideal gas

One of the basic features of gas is its property to exert pressure on the walls of the vessel in which it is contained. Let us determine this pressure for a state of ideal gas. On the way, we shall obtain a number of other important equations. In spite of the fact that we will be using a considerably simplified model, we will obtain results continuous to our exact consideration.

In addition to those simplifications that we have already made when introducing the ideal gas model, we will also make some additional assumptions that will help us to simplify our calculations in order not to lose generality. In particular, we will: (1) count all molecules as identical, spherically symmetric and moving at the same speeds (let this speed be the average root square velocity  $v_{\text{rms}} = \sqrt{\langle v^2 \rangle}$ ); (2) consider that all molecules move with equal probability along three coordinate axes, i.e.,  $1/6$  part of all molecules moves along each direction; one of the axes is chosen to be perpendicular to the vessel wall.

Choose a cylindrical element with the cross-section  $S$  and a side  $l$  in the vessel close to the wall. Each molecule hitting the wall obtains from it a momentum  $\Delta p = -2mv$  (refer to eq. (1.5.18) and Figure 1.37). In turn, the molecule transfers the momentum  $\Delta p = 2mv$  to the vessel's wall. Assuming a molecule-wall interaction time  $\tau$ , we can obtain the force produced by this impact  $F = 2\Delta mv_{\text{rms}}/\tau$ , and acting on the wall by a single molecule. In order to find the total force, we need to find the number of molecules that hit the wall in time  $\tau$ . If we choose a cylinder of length equal to  $l = v_{\text{rms}}\tau$  (Figure 3.3), then all molecules in the cylinder moving toward the wall hit the wall; their number is  $(1/6)n2mv_{\text{rms}}\tau$ . Then the force exerted upon the wall from the molecules in the cylinder will be  $F_p = (1/6)nSv_{\text{rms}}\tau(2mv_{\text{rms}}\tau/\tau) = (1/3)nSv_{\text{rms}}^2m$ , and the pressure will be

$$p = \frac{F}{S} = \frac{2}{3}n \frac{mv_{\text{rms}}^2}{2}. \quad (3.1.7)$$

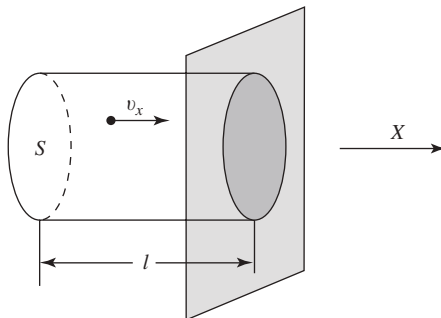


Figure 3.3 Model of gas pressure on a vessel's wall.

Taking into account the fact that the actual speeds of all the molecules vary, we should take the average values of the speed squared,

$$\langle \varepsilon \rangle = \left\langle \frac{mv^2}{2} \right\rangle, \quad (3.1.8)$$

and the pressure,

$$p = \frac{2}{3} n \langle \varepsilon \rangle. \quad (3.1.9)$$

Therefore, the pressure acquired by the ideal gas on the vessel's walls is equal to 2/3 of the volumetric density of the translational kinetic energy of the molecules.

$$p = \frac{2}{3} n \frac{mv^2}{2}. \quad (3.1.10)$$

Since  $n \langle \varepsilon \rangle = N \langle \varepsilon \rangle / V = K / V = w$ , where  $w$  is the volume averaged kinetic energy density. Therefore, the pressure acquired by the ideal gas on the vessel's walls is equal to 2/3 of the volumetric density of the translational kinetic energy.

Another form of this equation can be obtained by its multiplication with volume in moles

$$pV_m = \left(\frac{2}{3}\right) nV_m \langle \varepsilon \rangle. \quad (3.1.11)$$

Since  $pV_m = RT$  and  $nV_m = N_A$ , then  $RT = (2/3)N_A \langle \varepsilon \rangle$ . The ratio  $(R/N_A) = \kappa$  is referred to as the Boltzmann constant ( $1.38 \times 10^{-23}$  J/K). Then,

$$\langle \varepsilon \rangle = \frac{3}{2} \kappa T. \quad (3.1.12)$$

i.e., the average kinetic energy of the translational energy of the molecules of the ideal gas is equal to 2/3 of the product of the Boltzmann constant and absolute temperature. Therefore, product  $\kappa T$  is a measure of the thermal movement of molecules.

It follows from the last formula that absolute temperature  $T$  is a measure of the average kinetic energy of the translational motion of molecules. Two important conclusions follow from this: at zero absolute temperature the translational kinetic energy of each molecule is zero; their motion stops. The second conclusion is that the ideal gas temperature can be measured in energy units. In reality, at a room temperature of 300 K, the averaged value of energy  $\langle \varepsilon \rangle$  is  $1.38 \times 10^{-23} \times 300$  J =  $4 \times 10^{-21}$  J = 25 meV; it is equivalent to saying "the gas energy is 300 K" or "the gas temperature is 25 meV".

There exists a relation between the pressure and absolute temperature. It can be obtained from comparison of eqs. (3.1.11) and (3.1.12). We can obtain

$$p = n \kappa T. \quad (3.1.13)$$



Multiplying this equation by molecule mass  $m$  we can obtain the expression,

$$T = \frac{m p}{\kappa \rho} \quad (3.1.14)$$

### 3.1.5 Absolute temperature

Let us determine the absolute temperature included in expression (3.1.14). Then we will establish the relation between various temperature scales.

It is known, for example, that at water freezing temperatures, the density of air (basically, air consists of nitrogen) at sea level (pressure equals  $10^5$  Pa) is equal to  $1.255 \text{ kg/m}^3$ . The mass of a molecule of nitrogen is  $4.68 \times 10^{-26} \text{ kg}$ . To what absolute temperature in Kelvin's scale (K) does the temperature of water freezing (namely  $0^\circ\text{C}$ ) correspond? From eq. (3.1.14), it follows that  $^\circ\text{C}$  corresponds to zero.

$$T(^{\circ}\text{C}) = \frac{4.68 \times 10^{-26} \times 1.01 \times 10^5}{1.38 \times 10^{-23} \times 1.255} = 273.15 \text{ K.}$$

Thus, according to definition, water freezes at  $273.15 \text{ K}$ . According to the formula (3.1.12) at  $T = 0 \text{ K}$ , any translational motion of molecules stops. Such a temperature is referred to as *absolute zero*. It corresponds to  $-273.15^\circ\text{C}$ .

Both in degrees Kelvin and Celsius, the difference between water freezing and boiling is equal to 100 degrees; therefore, in both of them the measurement of one degree is identical. Therefore between Celsius and Kelvin scale there is a ratio:

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

Experiments show that  $-273.15^\circ\text{C}$  ( $T = 0 \text{ K}$ ) is the lowest possible temperature limit.

In practice, different thermometer approaches are used: at very high temperatures one uses the laws of thermal radiation (refer to Chapter 6.6); at average temperatures—the thermal expansion of hydrogen or helium at constant pressure and at low temperatures—the characteristics of solids according to the laws of quantum physical statistics (refer to Chapter 9.3) are used.

There are other scales of temperature also, for example, some countries use the Réaumur scale ( $^{\circ}\text{R}$ ), and in the English-speaking countries the Fahrenheit scale ( $^{\circ}\text{F}$ ) is used. These scales are connected to the Celsius scale by the equations:

$$T(^{\circ}\text{R}) = \left(\frac{4}{5}\right) T(^{\circ}\text{C})$$

$$T(^{\circ}\text{F}) = \left(\frac{9}{5}\right) T(^{\circ}\text{C}) + 32,$$

where

$$0(^{\circ}\text{C}) = 0(^{\circ}\text{R}) = 32(^{\circ}\text{F}) \text{ and } 100(^{\circ}\text{C}) = 80(^{\circ}\text{R}) = 212(^{\circ}\text{F}).$$

### 3.2 DISTRIBUTION OF MOLECULES OF AN IDEAL GAS IN A FORCE FIELD (BOLTZMANN DISTRIBUTION)

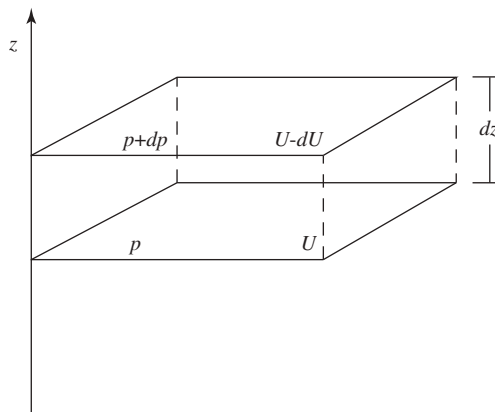
In an ideal gas, a large number of molecules are considered as noninteracting particles, i.e., the potential energy does not appear in this case. However, in an external force field this situation varies and molecules have a potential energy due to the influence of external forces. The question arises as to how molecules are distributed in this external field.

In the absence of any external influence, because of chaotic thermal movement, the gas uniformly fills the given volume. If, however, an ideal gas is in an external force field, the distribution of molecules changes; it becomes dependent upon the potential energy of the molecules in this field.

#### 3.2.1 An ideal gas in a force field: Boltzmann distribution

Let us first find the distribution of a molecule concentration of an ideal gas in a uniform one-dimensional external force field. Consider the field acting on the molecules to be conservative and uniform. Choose a unique  $z$ -axis coinciding with the direction of a force vector, along which we shall examine the molecules' distribution.

In the gas, imagine there to be two identical plates with an area  $S$  that dispose perpendicularly to the  $z$ -axis with a distance  $dz$  between them (Figure 3.4). Because of the action of external forces, the pressure upon the upper plate will be higher than on the lower plate.



**Figure 3.4** Gas in an external force field  $U(z)$ . Boltzmann distribution function.

The pressure difference  $dp$  is equal to the total force working on all molecules being of volume  $S dz$  acting on the plates' areas:

$$dp = \frac{F(z)n(z)S dz}{S} = F(z)n(z) dz \quad (3.2.1)$$

where  $n(z)$  is the molecule concentration at height  $z$  and  $F(z)$  is the force acting on a single molecule in a layer with coordinate  $z$ . According to the problem condition, the force is conservative, which means that the field is potential. In this case, there exists a relation between the force  $F(z)$  and the potential energy  $U(z)$  (1.4.32)  $dF = -dU(z)/dz$ . Therefore,

$$dp = -n(z) \frac{dU(z)}{dz} dz = -n(z) dU(z). \quad (3.2.2)$$

Assume that the gas is ideal and so its pressure and concentration are proportional to each other (eq. (3.1.13) below). The gas is considered to be uniformly spread, therefore, the temperature is the same at all points. From (3.1.13) one obtains

$$dp = \kappa T dn. \quad (3.2.3)$$

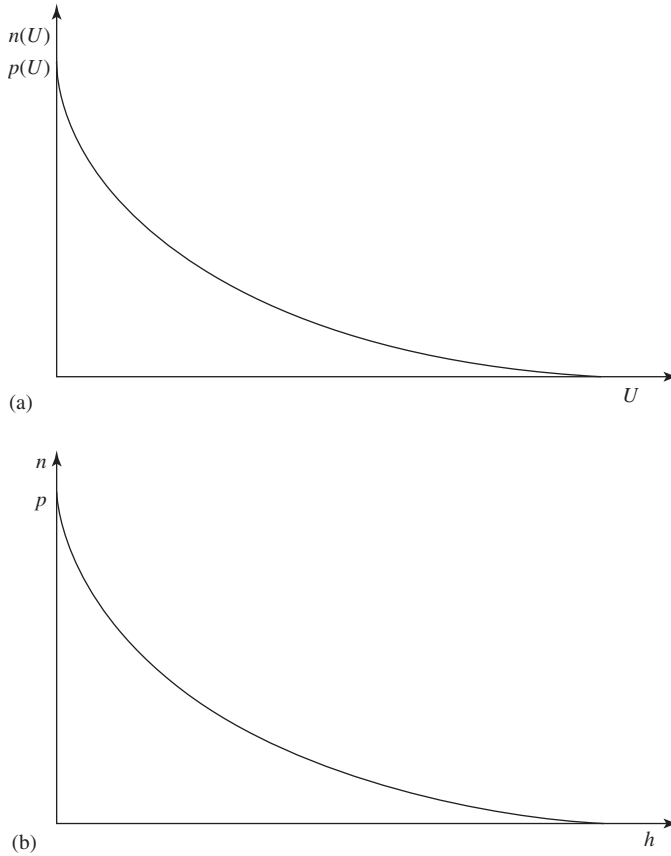
Changing the pressure to concentration in eq. (3.2.2), we obtain  $\kappa T dn = -n dU$ . Separating the variables we obtain  $dn/n = -(dU/\kappa T)$ . Integration gives  $\ln n = (U/\kappa T) + \ln C$ . We can rewrite this expression  $\ln(n(z)/C) = -(U(z)/\kappa T)$ . And further,  $n(z) = C \exp(-(U(z)/\kappa T))$ .

Assume that at a  $z$ -level the concentration is  $n_0$ . Then the constant  $C$  is equal to  $n_0$ . Therefore, finally

$$n(z) = n_0 \exp\left(-\frac{U(z)}{\kappa T}\right). \quad (3.2.4)$$

The expression obtained relates the molecular concentration of the ideal gas in a force field  $n(z)$  as well as  $p(z)$  with the potential energy of a single molecule  $U(z)$  at uniform temperature; the law is referred to as Boltzmann's law (or the Boltzmann distribution). A graph is presented in Figure 3.5a from which it is apparent that the greatest concentration of molecules takes place in those points of a field in which the potential energy is minimum; we accept this potential energy to be the zero level. With an increase in the potential energy, the concentration of molecules decreases. At  $U = \kappa T$ , the molecule concentration will be  $e$  time less than at zero level.

The distribution presented in the figure corresponds to some certain temperature. Figure 3.6 shows the family of curves corresponding to different temperatures. At high enough temperatures, the influence of a force field on the molecule distribution decreases; the energy of chaotic molecular movement also increases. That is, at high temperatures, the concentration of molecules will be equating; gas will regularly fill the whole given



**Figure 3.5** (a) Boltzmann distribution  $n(U)$ ; (b) barometric height distribution function.

volume. On the contrary, a decrease of temperature will lead to a sharp change of concentration with  $z$ . The force field becomes more effective.

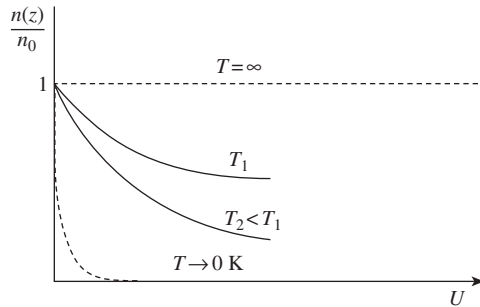
As the concentration of molecules and their pressure are proportional to each other, we can similarly write for pressure:

$$p(z) = p_0 \exp\left(-\frac{U(z)}{\kappa T}\right). \quad (3.2.5)$$

In this formula  $p_0$  and  $p(z)$  are the pressure in the points where the potential energy equals zero and  $U(z)$ , respectively.

### 3.2.2 Barometric height formula

Consider a particular example: the distribution of molecular concentration (or pressure) in a field of gravity not very high above the earth's surface. In this case, the gravitational field



**Figure 3.6** Boltzmann height distribution function at different temperatures.

can be counted as being homogeneous (see Section 1.4.5). Then the potential energy of the gas molecules is described by the formula  $U(h) = mgh$  where  $m$  is the molecules' mass, and  $h$  is the height above the earth's surface. Substituting this expression for potential energy in the general formula we obtain

$$p(h) = p_0 \exp\left(\frac{mgh}{\kappa T}\right). \quad (3.2.6)$$

This is the barometric height formula. It allows us to calculate the atmospheric pressure above the earth's surface, a graph of which (Figure 3.5b) is analogous to that presented in Figure 3.5a. In fact, it is assumed that the atmospheric temperature is constant and convection absent.

The barometric formula can be rewritten in a different form. Remember that  $m/\kappa = (mN_A/\kappa TN_A) = (M/R)$  ( $M$  is a mole mass and  $R$  is the universal gas constant). Therefore,

$$p(h) = p_0 \exp\left(-\frac{Mgh}{RT}\right). \quad (3.2.7)$$

If a gas represents a mixture of different gases (like air), every component should be considered independently. Applying the barometric formula to the partial pressure of every component of the mixture, we can see that the pressure (concentration) of gases with greater mole mass decreases faster than light gases. This should lead to an enrichment of the higher layers of the atmosphere by light gases, for example, hydrogen. This, however, is not the case: tests of air at different heights reveal approximately identical percentages of light and heavy gases. This shows that our approximation is incorrect: the temperature of the atmosphere at different heights is different. Moreover, it is impossible to ignore macroscopic streams of air (convection).

If there was no thermal movement of molecules, they would all fall to the ground under the action of gravitational force, and all the air would concentrate as a layer, several meters in thickness, on the surface of the ground. If there were no gravitational force field, the molecules would scatter throughout open space. The atmosphere is

obliged for its existence to the competition of the thermal chaotic motion of molecules and gravitational forces. Thus, in atmosphere, a quite definite distribution of molecules is established.

Notice that the earth's gravitational field is completely unable to keep gas in a current balance. According to Boltzmann's formula, a nonzero (let it be very small) concentration of molecules is present at any height. In fact, it is possible that as a result of manifold casual collisions a molecule can gain a speed greater than the second space speed ( $v = 11.2$  km/sec) and can leave the earth. Therefore, the earth's atmosphere continuously, but very slowly, loses its light component. The moon, in particular, has already lost its atmosphere as the gravitational field of the moon is much weaker than that of the earth's.

### EXAMPLE E3.3

In the cabin of an airborne plane, the barometer shows an identical pressure of  $p = 79$  kPa all the time because of what the pilot counts as the flying-height  $h_1$  constant. However, the temperature of the outside air changes from  $T_1 = 5^\circ\text{C}$  to  $T_2 = 1^\circ\text{C}$ . What uncertainty  $\Delta h$  in the definition of height has the pilot supposed? Assume pressure  $p_0$  at the ground to be normal.

**Solution:** To find the solution we have to use the barometric height (bh) formula (refer to Section 3.2.2). The barometer can show constant pressure  $p$  at various temperatures  $T_1$  to  $T_2$  onboard only in the case where the plane is not at height  $h$  (which the pilot counts constant), but at some other height  $h_2$ . Write the barometric height formula (3.2.7) for these two heights:

$$p = p_0 \exp\left(-\frac{Mgh_1}{RT_1}\right) \text{ and } p = p_0 \exp\left(-\frac{Mgh_2}{RT_2}\right).$$

Take the logarithm from both sides of equations:

$$\ln \frac{p_0}{p} = \left(\frac{Mgh_1}{RT_1}\right) \text{ and } \ln \frac{p_0}{p} = \left(\frac{Mgh_2}{RT_2}\right).$$

Find the difference of heights

$$\Delta h : \Delta h = h_2 - h_1 = \frac{R \ln(p_0/p)}{Mg} (T_2 - T_1).$$

The test of the measurement units gives the correct values. Substitution of the numerical values give the results  $\Delta h = 28.5$  m. The sign shows that the plane is at a height 28.5 m lower than the height supposed.

### 3.2.3 Centrifugation

One of the practical applications of the Boltzmann distribution is centrifugation, which is used in technology mainly for mixture separation. The basic part of a centrifuge is the cylindrical rotor rotating with high angular velocity relative to the axis of the cylinder; this rotation creates a centrifugal inertia force field. The rotor is filled with mixtures of gases to be processed, suspensions, isotopes mixes, etc., and rotation is started. The particles with the greater weight will concentrate near the rotor walls whereas, the lighter ones concentrate in the center. In this way, the division of the fractions of the mixture is achieved.

There are many types of centrifuge; all are subdivided, first of all, according to the separation factor  $Fr$ , the ratio of centripetal acceleration near the rotor's wall to the acceleration of free fall,  $Fr = a_n/g$ . It can be seen that the separation factor is dimensionless and for normal industrial centrifuges, it is approximately 3500. Usually centrifuges are used for the separation of disperse systems (particles with sizes of 10–50  $\mu\text{m}$ ). In the so-called supercentrifuges,  $Fr$  is about 3500; these are used for separating emulsions and highly disperse (less than 10  $\mu\text{m}$ ) suspensions. In laboratory practice, ultracentrifuges have  $Fr$  reaching  $1.2 \times 10^6 \text{ min}^{-1}$ . These are applied mainly in the research of fibers, viruses and pigments.

Ultracentrifuges are used for isotopes separations. The distribution of molecules along the rotor radius depends on the relative mass of the isotopes. By selecting fractions in the rotor center and at the wall, and repeating the process of centrifugation, it is possible to achieve significant enrichment of gas by a given isotope. The efficiency of division depends on the difference between the masses of two isotopes; therefore, the separation of heavy isotopes is no more complex than separation of light ones.

Let us find the concentration distribution of different particles in a centrifuge depending on the distance of a cylindrical layer from a rotation axis. Choose the reference system connected with the rotor; direct an axis  $r$  along the rotor radius. Such a system is not inertial. Each particle of mass  $m$  at distance  $r$  feels the action of centrifugal force

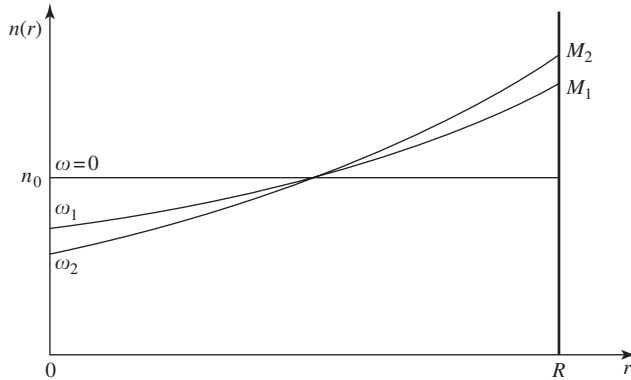
$$F(r) = m\omega^2 r. \quad (3.2.8)$$

Thus, all particles are in centrifugal forces (of inertia). Such a field is not uniform. Nevertheless one can use the concept of potential energy caused by the presence of forces of inertia. Therefore, the relation between centrifugal force and potential energy can be used (see eq. (1.4.32)):

$$dU(r) = -F(r)dr. \quad (3.2.9)$$

After integration we obtain

$$U(r) = \frac{m\omega^2 r^2}{2} + C.$$



**Figure 3.7** Molecule distributions in a centripetal force field.

This expression can be substituted into eq. (3.2.4). We obtain

$$n(r) = C \exp\left(\frac{m\omega^2 r^2}{2\kappa T} - \frac{C_1}{\kappa T}\right) = C \exp\left(-\frac{C_1}{\kappa T}\right) \exp\left(\frac{m\omega^2 r^2}{2\kappa T}\right).$$

Denote the molecule concentration at  $r = 0$  as  $n(0)$ , i.e.  $n(0) = C \exp(-C_1/\kappa T)$ . Then we arrive at

$$n(r) = n(0) \exp\left(\frac{m\omega^2 r^2}{2\kappa T}\right), \quad (3.2.10)$$

and

$$n(r) = n(0) \exp\left(\frac{M\omega^2 r^2}{2RT}\right). \quad (3.2.11)$$

The particle concentration increases with increasing  $r$ . This expression confirms that the heavy particles concentrate near the walls (Figure 3.7).

### EXAMPLE E3.4

Radon ( $M = 0.222$  kg/mole) is placed in a centrifuge's rotor with radius  $R = 0.2$  m at temperature  $T = 300$  K. Determine the ratio of concentration  $n(R)/n(0)$  of radon atoms near the rotor's walls to that on the centrifuge axis if frequency of the rotor rotation is equal to  $n = 12 \times 10^3$  min<sup>-1</sup>.

**Solution:** The most rational way to solve this problem is to use a noninertial system of coordinates in the framework of a D'Alambert principle. We shall connect the coordinates system with the rotating rotor. Radon atoms, in this case, will



possess the so-called centrifugal potential energy that is caused by centrifugal forces of inertia. In this case, a Boltzmann distribution can be given in the form  $n(r) = n(0)e^{-(U_{cf}(r)/\kappa T)}$ , where  $U_{cf}$  is the centrifugal potential energy. First find the expression for the centrifugal force  $F_{cf}$ . It was shown in Section 1.2.1 that centripetal acceleration is  $v^2/r$  and correspondingly, the centripetal force is  $F_{cf} = -ma_n = m(v^2/r) = m(\omega^2 r^2/r) = m\omega^2 r$ . So, centrifugal force is directed along the radius from the rotation axis. According to eq. (1.4.34), the centrifugal force is  $F_{cf} = -(dU_{cf}/dr)$ , therefore  $dU_{cf} = -F_{cf}dr$ . Therefore, after integration  $U(r) = -(1/2)m\omega^2 r^2 + C$ . Accepting  $U(0) = 0 = C$ , we obtain  $U(r) = -(1/2)m\omega^2 r^2$ . The Boltzmann equation in the centrifugal reference system is now  $n(r) = \langle n \rangle e^{2(m\omega^2 r^2/\kappa T)}$ . Because of the fact that we know the rotation frequency  $n$  but not  $\omega$  ( $\omega = 2\pi n$ ) and  $(m/\kappa) = (M/R)$  we finally arrive at  $n(r)/\langle n \rangle = e^{(2\pi^2 M n^2 r^2/\kappa T)}$ . Keeping in mind that  $n = 12 \times 10^3 \text{ min}^{-1} = 200 \text{ s}^{-1}$  and executing calculations we obtain a numerical result

$$\frac{n(R)}{n(0)} = \exp \left[ \frac{2\pi^2 0.222 \times (200)^2 \times (0.2)^2}{8.31 \times 300} \right] = e^{2.81} = 16.6.$$

### 3.2.4 Boltzmann factor

We have started considering the behavior of those systems consisting of an enormous number of particles, for some special cases. In particular, we have obtained the one-dimensional Boltzmann distribution. It is easy to generalize this approach to a system in three-dimensional space. Let  $dN$  be the number of particles near a point  $x, y, z$  in a volume  $dV = dx dy dz$ . Keeping in mind eq. (3.2.4), it is possible to write

$$dN(x, y, z) = n(x, y, z) dV$$

or,

$$dN(x, y, z) = n_0 \exp \left( -\frac{U(x, y, z)}{\kappa T} \right) dx dy dz. \quad (3.2.12)$$

This expression describes the relationship of molecules of ideal gas concentration and their coordinates in an external three-dimensional force field. It can be seen that the probability for the gas particles to be in volume  $dV$  around a point  $x, y, z$  is proportional to the exponential multiplier

$$\exp \left( -\frac{U(x, y, z)}{\kappa T} \right),$$

i.e., the higher the potential energy in a given point of a field, the less the probability of finding molecules there. This multiplier is referred to as the Boltzmann factor (multiplier).

The significance of the Boltzmann factor consists of the fact that it establishes an interrelation between two competing tendencies: the aspiration of the molecules to their ordering under the action of a force field and the tendency to disordering under the action of molecular chaotic thermal motion with average energy  $\kappa T$ . So, if there was no thermal motion ( $\kappa T \rightarrow 0$ ), all molecules would concentrate near a point with  $U \rightarrow 0$ ; if there was no ordering action of a force field, all molecules would scatter uniformly all over space. This particular result is described by the Boltzmann factor. This factor is common in deciding many questions in various areas of physics.

The Boltzmann factor plays an analogous and important role in chemical kinetics. Here, it describes the distribution of molecules on their internal energy. As for the majority of endothermic reactions, overcoming a potential barrier occurs basically due to the energy concentrated on internal degrees of freedom. The Boltzmann factor defines their kinetics. In Figure 7.14, a qualitative example of a potential energy curve of interatomic interactions in a chemically reacting system is presented. Only those molecules that have a sufficient stock of energy are capable of overtaking a potential barrier  $Q$  in height (so-called activation energy) at temperature  $T$ . The Boltzmann probability for a molecule to have the necessary stock of energy at temperature  $T$  is defined by factor

$$\exp \frac{Q}{\kappa T}. \quad (3.2.13)$$

This defines its importance in chemical kinetics. The Boltzmann factor determines the exponential (temperature) part of Arrhenius' formula for the ratios of the majority of chemical reactions.

This factor is common to the solution of many problems in various areas of physics and chemistry.

### 3.3 DISTRIBUTION OF THE KINETIC PARAMETERS OF AN IDEAL GAS' PARTICLES (MAXWELL DISTRIBUTION)

#### 3.3.1 The Maxwellian distribution of the absolute values of molecule velocities

The distribution of molecules based on their potential energy is described by eq. (3.2.4). Compare it to the distribution function definition (Section 3.1.2). These two expressions are almost identical with one exception: in Section 3.1.2, the total number of particles is  $N$  whereas, in eq. (3.2.4) the constant multiplier is  $n_0$  in a point  $U = 0$ . Hence, they differ by a constant term. Therefore, one can write

$$f(x, y, z) = C \exp\left(-\frac{U(x, y, z)}{\kappa T}\right). \quad (3.3.1)$$

i.e., the distribution function of molecules in a force field on coordinates is proportional to the Boltzmann factor. With sufficient evidence, we can assert that the distribution of molecules on the full mechanical energy is described by an analogous expression

$$f(x, y, z, v_x, v_y, v_z) = C' \exp\left(-\frac{E}{\kappa T}\right) = C' \exp\left[-\frac{U(x, y, z) + K(v_x, v_y, v_z)}{\kappa T}\right] \quad (3.3.2)$$

Then,

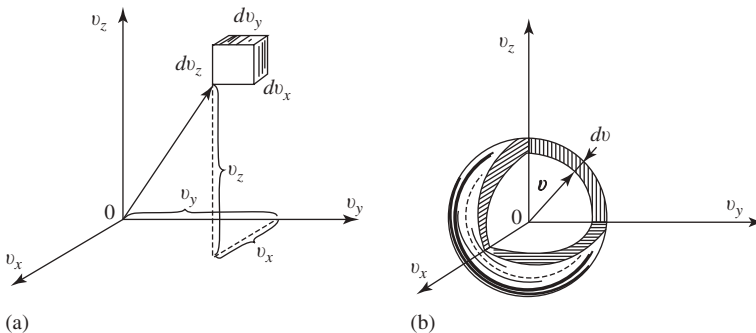
$$dw(x, y, z, v_x, v_y, v_z) = \frac{dN(x, y, z, v_x, v_y, v_z)}{N} = C \exp\left[-\frac{U(x, y, z) + K(v_x, v_y, v_z)}{\kappa T}\right] d\tau. \quad (3.3.3)$$

The formula requires an explanation. Here, there is the full mechanical energy  $U + K = E$ , being a function of the system's state, i.e., dependent on particle coordinates and components of molecular speeds (or momentums). The factor  $d\tau = dx dy dz dv_x dv_y dv_z$  is an element of a configuration space (eq. 1.3.38). Constant  $C'$  is not yet determined, but can be found from normalization. This is the Maxwell–Boltzmann distribution.

The coordinate distribution function has already been obtained (Section 3.2.1). Therefore, this part of the equation can now be withdrawn from consideration, leaving only those terms that depend on the components of the molecules' speed

$$dw(v_x, v_y, v_z) = \frac{dN(v_x, v_y, v_z)}{N} = C \exp\left[-\frac{K(v_x, v_y, v_z)}{\kappa T}\right] dv_x dv_y dv_z. \quad (3.3.4)$$

What is the physical meaning of an elementary volume  $d\tau$ ? To uncover this, let us draw an imaginary coordinate framework (*in a velocity's space*) and allocate the elementary volume in a configuration space (Figure 3.8a). The physical meaning of  $dV = dv_x dv_y dv_z$



**Figure 3.8** Maxwell distribution: the transition from the Cartesian (a) to the spherical symmetric coordinate (b) in the velocities space.

consists of the fact that volume  $d\tau$  takes into account only those molecules whose velocity vectors begin in the origin and ends in an elementary volume  $dV$ ; i.e., these vectors are fixed both in length and in direction.

Remember our problem: we have aimed to derive the distribution of molecules on kinetic energy. The last is defined by the velocity squares, i.e., they are not dependent on the direction of molecular movement. Thus, we are dealing with distribution of the speeds regardless of the direction of molecular movement. This means that from an orthogonal elementary volume we should pass to an elementary volume in the form of a thin spherical layer which takes into account only the vector length  $dV = 4\pi v^2 dv$ . Now we can understand that the function of distribution should look like

$$f(u)du = C'' \exp\left(-\frac{mv^2}{2\kappa T}\right) 4\pi v^2 dv. \quad (3.3.5)$$

We now have to calculate the constant  $C''$ . Keeping in mind a table integral

$$\int_0^{\infty} x^2 \exp(-ax^2) dx = \frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{a^3}},$$

and normalization condition (Section 3.1.5), we obtain  $C'' = (m/2\pi\kappa T)^{3/2}$ . Finally we obtain

$$f(v)dv = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2\pi\kappa T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2\kappa T}\right) dv$$

and

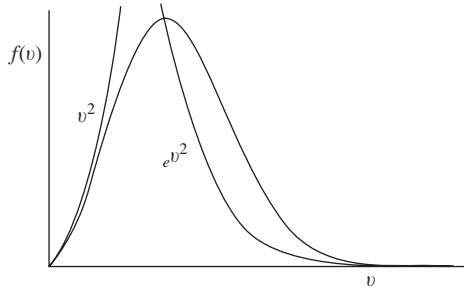
$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2\pi\kappa T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2\kappa T}\right). \quad (3.3.6)$$

This function describes the molecular speeds distribution of the ideal gas. The resultant curve is presented in Figure 3.9 together with the constituent functions.

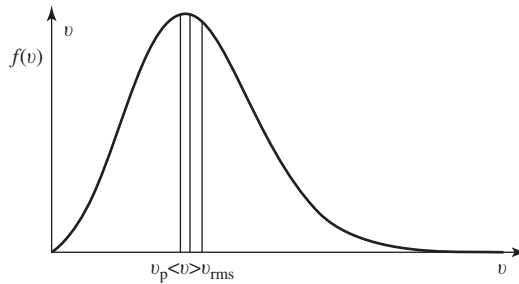
Let us examine the relationship obtained. In the area of small speeds, the exponential multiplier is close to unity. When the speed increases sufficiently the power function increases slowly in comparison with the drop of the exponent. The curve has a well-defined maximum.

There are three characteristic speeds of this distribution: the most probable speed  $v_p$ , the average molecule's speed  $\langle v \rangle$  and the root mean square  $v_{\text{rms}}$  speed. The value of the most probable speed can be found by calculating an extremum of the distribution function:

$$v_p = \sqrt{\frac{2\kappa T}{m}} = \sqrt{\frac{2RT}{M}}. \quad (3.3.7)$$



**Figure 3.9** A Maxwellian distribution  $f(v)$  on molecule's speed.



**Figure 3.10** Maxwell distribution and characteristic speeds: the most probable  $v_p$ , the averaged  $\langle v \rangle$  and root mean square  $v_{rms}$  velocities.

The specified average molecule's speed  $\langle v \rangle$  and the root mean square speed  $v_{rms}$  can be obtained using table integrals

$$\langle v \rangle = \sqrt{\frac{8\kappa T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \tag{3.3.7'}$$

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3\kappa T}{m}} = \sqrt{\frac{3RT}{M}}. \tag{3.3.7''}$$

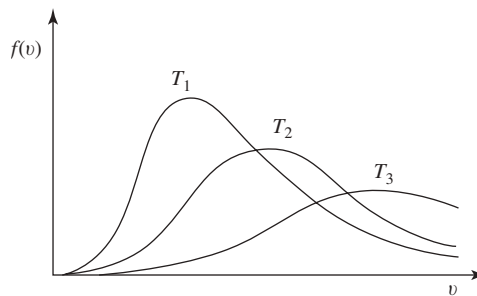
All these values are different, and are presented in Figure 3.10. The geometrical sense of average speed consists of the fact that it divides the area under a curve  $f(v)$  into two equal parts. The root mean square  $v_{rms}$  characterizes the molecular energy and was used in Section 3.1.3.

For instance, we consider the distribution of molecules of nitrogen on their speeds at room temperature. The most probable speed is approximately 420 m/sec. The division of all molecules into groups is shown in Table 3.1. It can be seen from the table that 60% of all molecules are grouped near the central area. The relative number of slow and fast molecules is low. At the same time, at any temperature, there are always some molecules with speeds considerably exceeding the most probable value.

**Table 3.1**

Relative amounts of nitrogen molecules having their speed in given intervals (at room temperature)

Velocity intervals (in m/sec)	Relative amounts of molecules (in%) having their speed in a given interval
0–100	0.6
100–200	5.0
200–300	7.0
300–400	10.0
400–500	20.0
500–600	18.0
600–700	10.0
700–800	9.0
800–900	8.0
900–1000	7.0
Higher than 1000	5.4

**Figure 3.11** Maxwell distribution at different temperatures.

Temperature has an essential influence on the kinetics. From eq. (3.3.7) it can be seen that the maximum of the Maxwellian curve shifts toward the higher speeds (Figure 3.11). Although the curves flatten, the area under every curve (i.e., the overall number of particles) remains the same. When gas is heated, the number of molecules with high speeds increases though their total amounts remain constant.

**EXAMPLE E3.5**

Knowing the molecules' speed distribution find (1) the most probable  $v_p$ , (2) the average speed  $\langle v \rangle$  and (3) the root-mean square  $v_{rms}$  value of speeds.

**Solution:** (1) The molecules' speed distribution is described by eq. (3.3.6). The tabular integrals used are:

$$\int_0^{\infty} x^3 \exp(-ax^2) dx = \frac{1}{2a^{-2}} \quad \text{and} \quad \int_0^{\infty} x^4 \exp(-ax^2) dx = \frac{3\sqrt{\pi}}{8a^{(5/2)}}.$$

In order to find the most probable  $v_p$  speed one should determine the extremum of  $f(v)$ -function, i.e., to calculate the first derivative of that function on  $v$  and equate it to zero. This gives

$$\frac{df(v)}{dv} = 4\pi \left( \frac{m}{2\pi\kappa T} \right)^{3/2} \left[ 2v \exp\left(-\frac{mv^2}{2\kappa T}\right) - v^2 \frac{mv}{\kappa T} \exp\left(-\frac{mv^2}{2\kappa T}\right) \right] = 0.$$

This equation corresponds to three roots: 0,  $\infty$  and  $v_p = \sqrt{2\kappa T/m}$ . The first two of them are trivial, the third is the one sought.

(2). To find  $\langle v \rangle$ , we should use eq. (3.1.5) and calculate an integral  $\langle v \rangle = \int_0^\infty v f(v) dv$ . Therefore,

$$\langle v \rangle = \sqrt{\frac{2m^3}{\pi(\kappa T)^3}} \int_0^\infty v^3 \exp\left(-\frac{mv^2}{2\kappa T}\right) dv = \frac{1}{2} \sqrt{\frac{2m^3}{\pi(\kappa T)^3}} \left( \frac{2\kappa T}{m} \right)^2 = \sqrt{\frac{8\kappa T}{\pi m}}.$$

(3) To find the root mean square speed

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{2m^3}{\pi(\kappa T)^3}} \int_0^\infty v^4 \exp\left(-\frac{mv^2}{2\kappa T}\right) dv = \sqrt{\frac{3\kappa T}{m}}.$$

The relationship between the values are

$$v_p : \langle v \rangle : v_{rms} = \sqrt{2} : \sqrt{8/\pi} : \sqrt{3} = 1.41 : 1.59 : 1.71.$$

### EXAMPLE E3.6

An ideal gas is in normal conditions and occupies a volume  $V=10$  mL. Determine the number of molecules whose speed are in a limit from  $v_1 = 0$  to  $v_2 = 0.01v_p$  ( $v_p = \sqrt{2\kappa T/m}$ , see example E3.5)

**Solution:** The number of molecules whose speeds lie in a narrow interval  $v-v+dv$  can be determined according to an approximate equation  $dN_{v-v+dv} = N f(v) dv$ \* where  $N$  is the total number of molecules in the given volume,  $f(v)$  is the Maxwell distribution function (3.3.6). In order to determine the amount of molecules sought, we have to substitute the distribution function into the expression \* and calculate a corresponding integral. Therefore,

$$\Delta N = \int_0^{\Delta v_p} f(v) dv = \frac{4N}{\sqrt{\pi}} \sqrt{\left( \frac{m}{2\kappa T} \right)^3} \int_0^{\Delta v} v^2 \exp\left(-\frac{mv^2}{2\kappa T}\right) dv.$$

It is impossible to take this integral analytically; however, we can make some simplifications. In particular, since the speed interval lies in very low speed values, we can substitute exponential multiplier by unity (accurate calculations give its magnitude as 1.0001). Besides, the multiplier in brackets can be rewritten as:

$$\left(\frac{m}{2\kappa T}\right)^{3/2} = \frac{1}{v_p^3}.$$

Then the integral can be rewritten as:

$$\Delta N = \frac{4}{\sqrt{\pi}} \frac{N}{v_p} \int_0^{0.01v_p} v^2 dv.$$

After integration we obtain

$$\Delta N = \frac{4}{3\sqrt{\pi}} \frac{N}{v_p^3} v_p^3 10^{-6}.$$

The particle number can be expressed knowing the Loschmidt value (the number of gas particles in  $1\text{cm}^3$  at normal condition),  $n_L = 2.69 \times 10^{19} \text{cm}^{-3}$ . Substituting all intermediate values we arrive at  $\Delta N = 4/(3\sqrt{\pi}) 2.69 \times 10^{19} \times 10 \times 10^{-6} = 6.07 \times 10^{14}$  (molecules).

### EXAMPLE E3.7

Find the share  $\Delta N/N$  of molecules of the ideal gas, speed of which differs from the  $(1/2)v_p$  by not more than 1%.

**Solution:** In order to solve this problem, it is convenient to write the Maxwell distribution using the relative molecular speed  $u$

$$u = v/v_p = \frac{v}{\sqrt{2\kappa T/m}}.$$

The distribution on  $u$  can be found as  $f(u) = (4/\sqrt{\pi})u^2 e^{-u^2}$

The number sought can be written as:  $\Delta N/N = f(u)\Delta u = (4/\sqrt{\pi})u^2 e^{-u^2} \Delta u$ .

Notice that  $u = 1$  at  $v = v_p$ . The magnitude of the interval between  $u$ -limits is  $\Delta u = 0.01$ . The interval to be taken is narrow; therefore, the integral can be approximated accordingly  $\langle u \rangle = \int_{\Delta u} f(u)du \approx f \Delta u$ , i.e.,

$$\frac{\Delta N}{N} = f\left(\frac{1}{2}\right) \times \Delta u = \frac{4}{\sqrt{\pi}} \left(\frac{1}{2}\right)^2 e^{-(1/2)^2} \times 0.01 = \frac{e^{-1/4}}{\sqrt{\pi}} 0.01.$$

Executing calculations we arrive at  $\Delta N/N = (e^{-1/4}/\sqrt{\pi})0.01 = 4.39 \times 10^{-3}$



### 3.3.2 The kinetic energies Maxwellian distribution of molecules

We will now find the distribution function of the values of molecule kinetic energies. For this purpose we shall express the relative number of those molecules having speeds in interval  $v \rightarrow v + dv$  using the kinetic energies expression  $\varepsilon$  corresponding to these speeds. Express the equal number of molecules on velocities and energies

$$f(v)dv = f(\varepsilon)d\varepsilon. \quad (3.3.8)$$

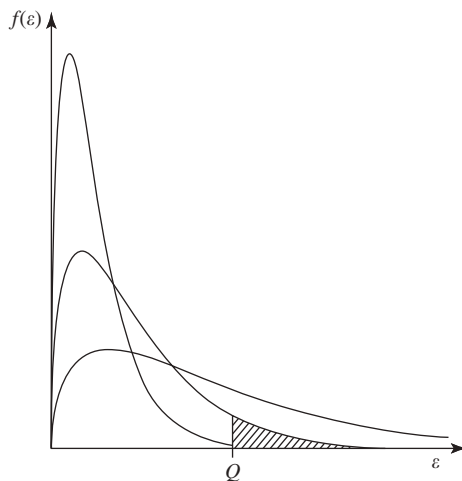
Make a substitution of variables in expression (3.3.6). As  $mv^2/2 = \varepsilon$  then,  $v^2 = 2\varepsilon/m$  and  $v = \sqrt{2/m}\sqrt{\varepsilon}$ . Taking into account eq. (3.3.8.), expression (3.3.6) will then be as follows:

$$f(\varepsilon) = \frac{4}{\sqrt{\pi}} \left( \frac{m}{2\kappa T} \right)^{3/2} \frac{2\varepsilon}{m} \exp\left(-\frac{\varepsilon}{\kappa T}\right) \frac{1}{\sqrt{2m}\sqrt{\varepsilon}} d\varepsilon.$$

Finally, we arrive at

$$f(\varepsilon) = \frac{2}{\sqrt{\pi}\sqrt{(\kappa T)^3}} \sqrt{\varepsilon} \exp\left(-\frac{\varepsilon}{\kappa T}\right). \quad (3.3.9)$$

The distribution function  $f(\varepsilon)$  is presented in Figure 3.12. At small kinetic energy ( $\varepsilon \ll \kappa T$ ), an exponential term is close to 1. Therefore  $f(\varepsilon) \sim \sqrt{\varepsilon}$  (i.e., runs up steeply). At large  $\varepsilon \gg \kappa T$ ,



**Figure 3.12** Maxwell molecular energy distribution.

the exponent  $\exp(-(\varepsilon/\kappa T))$  mostly influences the function. Hence, curve  $f(\varepsilon)$  leaves the origin as  $\sqrt{\varepsilon}$ , passes over a maximum and is exponentially going down toward zero.

The distribution obtained allows us to estimate the concentration of chemically active molecules, which can overcome the activation barrier  $Q$  and get in touch with another molecule to produce a new product. To find the relative concentration of molecules with kinetic energy  $\varepsilon > Q$ , we should calculate an integral

$$\frac{\Delta N}{N} = \int_Q^{\infty} \frac{dN}{N} = \int_Q^{\infty} f(\varepsilon) d\varepsilon. \quad (3.3.10)$$

There are no such integrals in the mathematical tables. We can see that at large  $\varepsilon$ , the main contribution to the result is made by the exponent; the multiplier  $\sqrt{\varepsilon}$  contributes vaguely in comparison with the exponent and can be neglected. Therefore, the situation is simplified and calculation of the integral results in

$$\frac{\Delta N}{N} = \frac{2\sqrt{Q}}{\sqrt{\pi}\sqrt{(\kappa T)^{3/2}}} \int_Q^{\infty} \exp\left(-\frac{\varepsilon}{\kappa T}\right) d\varepsilon = \frac{2}{\sqrt{\pi}} \sqrt{\frac{Q}{\kappa T}} \exp\left(-\frac{Q}{\kappa T}\right). \quad (3.3.11)$$

The number of chemically active particles is not  $N$ , but much less; in Figure 3.12, it is shown by the hatched area. The proportion of such particles can be defined according to eq. (3.3.11); they can overcome activation barrier  $Q$ .

### 3.4 FIRST LAW OF THERMODYNAMICS

#### 3.4.1 Equipartition of energy over degrees of freedom

In order to analyze the energy that molecules can accept, we should first find the number of its degrees of freedom  $i$ , i.e., the number of independent coordinates that describes the position in space of all the molecules' atoms. Remember, the position of atoms in a biatomic fixed material MP (i.e., atom) is defined by three independent coordinates ( $i = 3$ ). The position of a biatomic molecule is described by six degrees of freedom; however, the presence of one interatomic chemical bond reduces this number to five: each bond reduces the  $i$ -number per unit, i.e.,  $i = 3 \times 2 - 1 = 5$  (three translational and two rotary degrees of freedom). For a bent three-atomic molecule  $i = 3 \times 3 - 3 = 6$  (i.e., there are three translational and three rotary degrees of freedom). For any other multinuclear molecule, the numbers of translational and rotary degrees of freedom are all the same (six), because of the presence of chemical bonds.

Apart from translational and rotary movements, intramolecular oscillations of atoms can also exist; there are oscillatory degrees of freedom with doubled  $i$  for the kinetic and potential part of oscillatory energy. However, at not so high temperatures (not appreciably higher than room temperature) intramolecular oscillations are not excited.

On the basis of this simplified model, it would appear that monoatomic molecules, which are essentially point like and have practically zero MI, can store energy only in their translational motion. Maxwell suggested a theorem of equipartition of energy among the degrees of freedom: every degree of freedom can store an equal amount of energy; it is associated with an energy of  $(1/2)\kappa T$  per atom or  $(1/2)RT$  per mole (refer to Section 3.1.4).

### 3.4.2 First law of thermodynamics

Thermodynamics is a section of physics in which physical properties of macroscopic systems are studied on the basis of macroscopic energy transformations, mainly without accounting for their microscopic structure. When investigating the macroscopic properties of thermodynamic systems in gaseous, liquid, solid or plasma states, we are dealing with enormous numbers of particles. Statistical methods consist of averaging the physical characteristics of constituent particles. As a result of such averaging, there appear a small number of parameters describing the state of the system as a whole, these parameters being pressure  $p$ , volume  $V$ , thermodynamic (absolute) temperature  $T$ , and total number of particles  $N$ , or amount of substance  $\nu$ . Such an approach to the description of thermodynamic systems does not examine a particular system's models and its internal structure. Thermodynamics operates with such concepts as internal energy  $U$ , amount of heat  $Q$  and work  $A$  of a thermodynamic system.

In particular, a very important characteristic of a system is its internal energy  $U$ . Internal energy is the total energy of each system component minus its macroscopic kinetic energy as the whole and potential energy in an external force field:

$$U = \sum_{i=1}^N \varepsilon_i + \frac{1}{2} \sum_i^N \sum_j^N U_{ij} (i \neq j). \quad (3.4.1)$$

Internal energy is a function of the system's state. It means that every time the system appears in a given state, its energy takes values corresponding to this state. At the transition of a system from state 1 (characterized by internal energy  $U_1$ ) to state 2 (characterized by internal energy  $U_2$ ), the change of internal energy is defined by the difference of these energies and will not depend on the process by which the given transition is taking place; i.e.,  $\Delta U = U_2 - U_1$ .

In an ideal gas state, interaction between molecules is absent; hence there is no total potential energy in eq. (3.4.1). Then  $U = \sum_i^N \varepsilon_i = N\langle\varepsilon\rangle$  where  $N$  is the total number of particles. Since  $N = (m/M)N_A$  and  $\langle\varepsilon\rangle = 3/2\kappa T$  (see eq. (3.1.12)) then,

$$U = \frac{m}{M} \frac{3}{2} \kappa T \times N_A = \frac{m}{M} \frac{3}{2} RT. \quad (3.4.2)$$

So, the internal energy of a particular amount of ideal gas depends only on its temperature  $T$ .

There are two possible ways of changing the internal energy of a thermodynamic system: (1) by the production of macroscopic work under the action of external forces applied to the system; and (2) by heat exchange.

The process of the heat exchange of contacting bodies not accompanied by the production of macroscopic work is referred to as heat exchange. The energy transferred to a body by another body during heat exchange is referred to as the amount of heat or, simply, heat.

These two methods of energy exchange between macroscopic bodies are qualitatively various and nonequivalent. In fact, the accomplishment of the work of a system can lead to the change of any other kind of energy (potential, internal, etc.), whereas, the energy transferred to a system as heat contributes directly to the increase of the chaotic motion of the system's particles, i.e., it influences the internal system energy only.

Both methods of energy transfer accompany each other; i.e., the heat transferred to a system can contribute to a change of internal energy as well as the system's work against external forces in the framework of the law of energy conservation.

The law of energy conservation is referred to as the first principle of thermodynamics. This law states that: the amount of heat transferred into the system,  $Q$ , goes to the change of internal energy  $dU$  and the work accomplished by the system against external forces  $\delta A$ :

$$\delta Q = \delta U + \delta A. \quad (3.4.3)$$

All values are expressed in the same energy units. Only  $dU$  in this equation is an exact differential because of the fact that  $U$  is an exact function of the system's state; here,  $\delta Q$  and  $dA$  are not the functions of state and mean only a very small quantity.

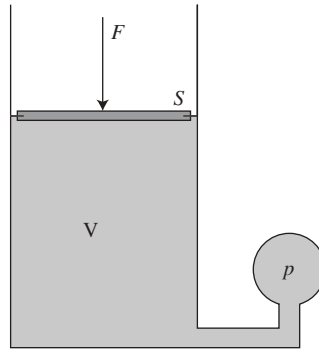
Eq. (3.4.3) enables us to define the internal energy of the system from a thermodynamic position only: internal energy is a body property, the change of which is equal to the difference of heat brought into the system and the work produced against external forces.

The work produced by a system concerns gas compression and/or expansion. For this purpose, we can imagine cylinder with diameter  $S$  with a piston under which there is a gas (Figure 3.13). There is a manometer to measure pressure  $p$ . The cylinder has a ruler on its side to measure piston position (i.e., volume). We shall act on the piston by a force  $F$ . Under the action of this force the piston, having compressed gas, will move on  $dx$ . The work of the force under gas we shall define as  $dA = Fdx$ . Since pressure is  $p = F/S$  then  $F = pS$  and  $dA = pSdl$  is the change of volume under the piston  $dl S = dV$ . The work of external force  $dA$  is equal to the increase of the system's potential energy

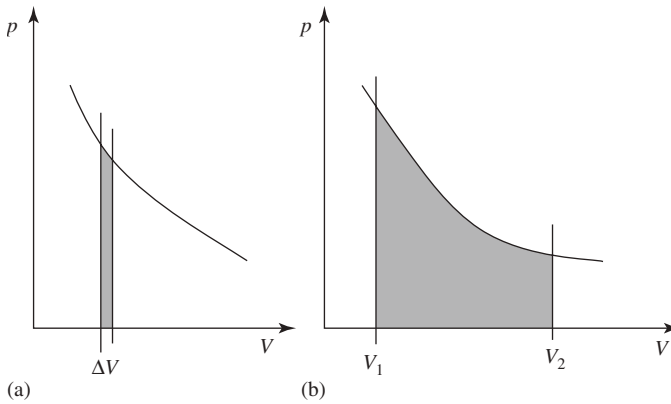
$$dA = pdV. \quad (3.4.4)$$

The same consideration is valid also for the work of gas against external forces.

In the coordinate system  $p(V)$  an elementary equation  $pdV$  is represented in Figure 3.14 as a hatched strip; however, in macroscopic processes integration is often needed to determine the total work (Figures 3.14a and b).



**Figure 3.13** An experimental device.



**Figure 3.14** Work done in processes: (a) elementary volume change  $dV$ ; (b) in a finite process  $\Delta V$ .

### 3.4.3 Heat capacity of an ideal gas: the work of a gas in isoprocesses

Heat capacity is a very important characteristic of a system because it enables the calculation of the amount of heat needed for initiation and maintenance of chemical processes. Consider a case when the amount of particles remains constant. The heat capacity is an amount of thermal energy (of heat) that raises a body's temperature by 1 K. Therefore,

$$c = \frac{dQ}{dT}. \quad (3.4.5)$$

In this form the heat capacity depends of the amount of substance. For uniform systems, a specific heat capacity is used: the heat capacity of a mass unit. Therefore,

$$C_s = \frac{dQ}{m dT} = \frac{c}{m}. \quad (3.4.6)$$

The molar heat capacity relates to one mole of a substance

$$C_v = \frac{dQ}{v dT} = \frac{M}{m} \times \frac{dQ}{dT} = \frac{M}{m} c. \quad (3.4.7)$$

where  $m$  is the mass of the substance and  $v$  is the number of moles. An intercomparison gives

$$c = m C_s, \quad (3.4.8)$$

$$C_v = M C_s, \quad (3.4.9)$$

$$c = \frac{m}{M} C_v. \quad (3.4.10)$$

Consider the particular forms for the work of a gas in isoprocesses on the basis of the first law of thermodynamics.

1. *Isochoric process* ( $V = \text{const.}$ ). In this process gas does not produce any work because  $V = \text{const}$  and correspondingly  $dV = 0$ . This means that all the heat consumed from outside will increase the internal energy:  $\delta Q = dU$  and  $C = dU/dT$ . However, for the closed system of an ideal gas, the change of internal energy means the change of total kinetic energy  $dU = dK$ . Therefore,

$$dU = (C_v)_v dT = \frac{m}{M} \frac{3}{2} R dT. \quad (3.4.11)$$

where,

$$(C_v)_v = \frac{m}{M} \times \frac{3}{2} R = v \frac{3}{2} R. \quad (3.4.12)$$

This is the expression for mole heat capacity  $C_v$  at constant volume. For the isochoric heating of  $v$  moles of an ideal gas for  $\Delta T$ , the thermal energy should obtained

$$\Delta Q = v \frac{3}{2} R \Delta T = v (C_v)_v \Delta T. \quad (3.4.13)$$

2. *Isobaric process* ( $p = \text{const.}$ ). In this case the heat consumed goes toward increasing the internal gas energy  $dU$  and to producing the work  $p dV$ :

$$\delta Q = dU + p dV = d(U + pV). \quad (3.4.14)$$

In thermodynamics, the sum  $U + pV = H$  is referred to as the enthalpy (the heat content) of a system: the enthalpy is a thermodynamic quality, the change of which in an isobaric process is equal to the heat consumed by the heat of the system. Since  $U$  depends only on

temperature, for a molar  $dU = (C)_v dT$  and  $\delta Q = dU + pdV = dU + RdT$ . Dividing the equation by  $dT$  we obtain

$$\left(\frac{\delta Q}{dT}\right)_p = (C)_v + R. \quad (3.4.15)$$

or

$$(C)_p = (C)_v + R. \quad (3.4.16)$$

The work produced by a system in an isobaric process is  $dA = pdV = \nu R dT$  or  $A = \nu R \Delta T = (m/M)R \Delta T$ . In order to heat isobarically an ideal-gas system, one should provide for  $\Delta T$  the heat

$$Q = \nu \left(\frac{5}{2}\right) (C)_p \Delta T = \nu \frac{5}{2} R \Delta T.$$

4. *Adiabatic process.* This process occurs without heat exchange to the environment. Hence, at adiabatic process  $\delta Q = 0$  and, according to the first law of thermodynamics,  $dA = -dU$ . The work of the system against external forces in an adiabatic process is at the expense of internal gas energy change. In practice, the adiabatic process is carried out with a sufficiently fast gas expansion or compression that heat exchange with the environment has no time to take place. Use both expressions  $dA = pdV$  and  $dU = (m/M)dT$ . Therefore,  $pdV = -(m/M)dT(C)_v$ . Using the ideal gas equation, we can write  $(m/M)RdT = d(pV) = pdV + Vdp$ . Combining the two last equations we can write as follows:  $pdV = -((C)_v/R)(pdV + Vdp)$ . Using eq. (3.4.16) we can write

$$\frac{(C)_v}{R} = \frac{(C)_v}{(C)_p - (C)_v} = \frac{1}{\frac{(C)_p}{(C)_v} - 1}.$$

The ratio  $(C)_p/(C)_v$  is usually designated as the adiabatic index

$$\frac{(C)_p}{(C)_v} = \gamma \quad (3.4.17)$$

and referred to as the ratio of specific heats.

Then  $pdV = -(1/(\gamma-1))(pdV + Vdp)$  or  $\gamma pdV - pdV = -pdV - Vdp$ . therefore  $\gamma pdV + Vdp = 0$ . Dividing this equation by  $pV$ , we obtain  $\gamma(dV/V) + dp/p = 0$ . Integration gives  $\gamma \ln V + \ln p = \ln C$ . After exponentiation we arrive at

$$pV^\gamma = \text{const.} \quad (3.4.18)$$

This equation is referred to as the Poisson equation.

The adiabatic graph falls noticeably more steeply than the isothermal curve (Figure 3.15).

For two states with parameters  $p_1V_1$  and  $p_2V_2$  we obtain  $p_1V_1^\gamma$  and  $p_2V_2^\gamma$ . Using these equations and equation we can obtain  $TV^{\gamma-1}=\text{const.}$  and  $T_p^{(\gamma-1/\gamma)}=\text{const.}$  and for volumes:

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1} \quad (3.4.19)$$

and for pressures:

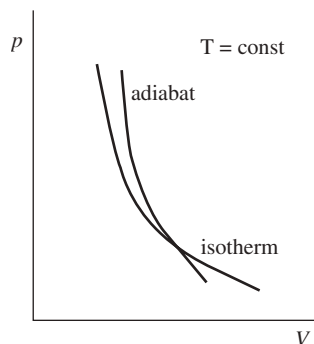
$$\frac{T_2}{T_1} = \left( \frac{p_1}{p_2} \right)^{\frac{\gamma-1}{\gamma}} \quad (3.4.20)$$

Let us find the equations for the work in an adiabatic process. Since  $dA=pdV$  and  $pdV=-(m/M)(C_v)_v dT$ , then  $dA=-(m/M)(C_v)_v dT$ . After integration in the limits  $T_1-T_2$ , we obtain  $A=(m/M)(C_v)_v(T_1-T_2)$ . Taking initial temperature  $T_1$  out of the brackets, we obtain a slightly different expression:  $A=(m/M)(C_v)_v T_1(1-(T_2/T_1))$ . Using one of eqs. (3.4.19), we can obtain an expression for the work as a function of the system's initial and final state; for volumes:

$$A = \frac{m}{M} (C_v)_v T_1 \left[ 1 - \left( \frac{V_1}{V_2} \right)^{\gamma-1} \right] \quad (3.4.21)$$

and for pressures:

$$A = \frac{m}{M} (C_v)_v T_1 \left[ 1 - \left( \frac{p_1}{p_2} \right)^{\frac{\gamma-1}{\gamma}} \right] \quad (3.4.22)$$



**Figure 3.15** Isotherm and adiabatic curve.



Since, in an adiabatic process, the system's temperature changes without consumption of external heat, the heat capacity in this process is equal to zero ( $dQ = 0$  at  $dT \neq 0$ ).

The important property of the heat capacity is its additivity. This means that heat spent for heating a mixture is equal to the sum of the amounts of heat necessary for heating these system's parts separately (i.e., heating to the same temperature). For two gases 1 and 2 this statement has the following mathematical expression:

$$Q_{s,\text{mix}} m_{\text{mix}} \Delta T = (Q_{1,s} m_1 + Q_{2,s} m_2) \Delta T \quad (3.4.23)$$

or further

$$Q_{s,\text{mix}} = \frac{Q_{1,s} m_1 + Q_{2,s} m_2}{m_{\text{mix}}}. \quad (3.4.24)$$

The same is true for molar quantities.

### EXAMPLE E3.8

Calculate the specific heat capacity  $C_{v,\text{mix}}$  of a mixture of two gases:  $m_1 = 6$  g of helium and  $m_2 = 10$  g of nitrogen at constant volume.

**Solution:** The gas-specific heat capacity is determined by eq. (3.4.6). The heat capacity of a mixture of two gases can be found due to the additivity properties of specific heat capacity: this means that the heat required to warm each gas separately is equal to the heat required to warm the mixture to the same temperature  $m_1 C_{v1} \Delta t + m_2 C_{v2} \Delta t = C_{v,\text{mix}} (m_1 + m_2) \Delta t$ . Solving this equation relative to  $C_{v,\text{mix}}$  and reducing by  $\Delta t$  we arrive at the final expression

$$C_{v,\text{mix}} = \frac{m_1 C_{v,1} + m_2 C_{v,2}}{m_1 + m_2} = \frac{\frac{i_1}{2} \frac{m_1}{M_1} + \frac{i_2}{2} \frac{m_2}{M_2}}{m_1 + m_2} R.$$

Notice that the gases are different: helium is a monoatomic gas, but nitrogen is diatomic, therefore  $i_1$  is 3 ( $M_1 = 4 \times 10^{-3}$  kg/mole) and  $i_2$  is 5 ( $M_2 = 28 \times 10^{-3}$  kg/mole) (see Section 3.4.1). Executing all operations, we arrive at a numerical result:  $C_{v,\text{mix}} = 1.63$  kJ/(kg K)

### EXAMPLE E3.9

The degree of dissociation of a diatomic gas is equal to  $\alpha = 0.3$ . Determine the adiabatic rate  $\gamma$  (i.e.,  $C_p/C_v$ ) of such a partly dissociated gas.

**Solution:** The degree of dissociation shows the ratio of a number of decomposed molecules  $N_{\text{dis}}$  to the initial number of molecules  $N$ , i.e.  $\alpha = (N_{\text{dis}}/N)$ .

Multiplying both the numerator and denominator by the mass of a single molecule  $m_1$  we obtain

$$\alpha = \frac{m_1 N_{\text{dis}}}{m_1 N} = \frac{m_{\text{dis}}}{m},$$

i.e., we obtain the ratio of mass of dissociated molecules to the initial mass of molecules. Then, knowing the degree of dissociation, we can find the mass of dissociated  $m_{\text{dis}}$  ( $m_{\text{dis}} = \alpha \times m$ ) and mass of nondissociated  $m_{\text{nondis}}$  ( $m_{\text{nondis}} = m - \alpha m = m(1 - \alpha)$ ) molecules.

Therefore, we have in fact a mixture of two gases: monoatomic with  $i = 3$  and mole mass  $M/2$  ( $M$  is the mole mass of nondissociated diatomic gas) and the rest of the diatomic gas with  $i = 5$  and mole mass  $M$ . Taking into account the fact that the heat capacity is additive, we can write:

$$C_{v,\text{mix}} = \frac{m_{\text{dis}}}{(M/2)} \frac{i_1}{2} R + \frac{m_{\text{nondis}}}{M} \frac{i_2}{2} R.$$

Substituting in this expression all numbers we already know, we obtain

$$C_{v,\text{mix}} = \left( \frac{2\alpha m \times 3}{M} + \frac{(1-\alpha)m \times 5}{M} \right) \frac{R}{2} = \frac{m}{M} (5 + \alpha) \frac{R}{2}.$$

In an analogous way, we can find heat capacities at constant  $p$

$$C_{p,\text{mix}} = \frac{m_{\text{dis}}}{(M/2)} \frac{i_1 + 2}{2} R + \frac{m_{\text{nondis}}}{M} \frac{i_2 + 2}{2} R = \frac{m}{M} (7 + 3\alpha) \frac{R}{2}$$

Therefore, the adiabatic rate can be written

$$\gamma = \frac{C_{p,\text{mix}}}{C_{v,\text{mix}}} = \frac{7 + 3\alpha}{5 + \alpha} = \frac{7 + 3 \times 0.3}{5 + 0.3} = \frac{7.9}{5.3} = 1.49.$$

### EXAMPLE E3.10

Determine the heat amount absorbed by hydrogen  $m = 0.2$  g in mass on being heated from temperature  $T_1 = 0^\circ\text{C}$  to  $T_2 = 100^\circ\text{C}$ . Find the change of the gas external energy  $U$  and work done  $A$ .

**Solution:** For isobaric heating the amount of heat required is  $Q = mC_p\Delta T^*$  (see Section 3.4.2). Substitute the heat capacity  $C_p = ((i+2)/i)(R/M)$  into equation \*:  $Q = ((i+2)/i)(R/M)m\Delta T$ . Execute the calculations and arrive at the result  $Q = 291$  kJ.

The change of external energy can be found according to the formula  $\Delta U = (i/2)(m/M)R\Delta T$ . Calculations give  $\Delta U = 208$  kJ. The work done at the gas expansion is  $A = Q - \Delta U = 83$  kJ.

**EXAMPLE E3.11**

A uniform ideal gas is in a state which is characterized by parameters  $V_1 = 1$  L and  $p_1 = 2$  atm. At a rapid contraction to  $V_2 = 0.52$  L, the pressure rises to 5 atm. Determine: (1) the number of degrees of molecular freedom, (2) the change of internal energy  $\Delta U$ , and (3) the change of enthalpy  $\Delta H$ .

**Solution:** (1) It was mentioned that the process is rapid, therefore, it can be considered an adiabatic one. The equation for an adiabatic process (Poisson equation) is as follows:

$$p_1 V_1^\gamma = p_2 V_2^\gamma,$$

where  $\gamma$  is the adiabatic rate:

$$\gamma = \frac{C_p}{C_v} = \frac{\nu \frac{i+2}{2} R}{\nu \frac{i}{2} R} = \frac{i+2}{2},$$

(here  $\nu$  is an amount of substance, i.e., number of moles). From the last equation, it is possible to find  $i$ :  $i = 2/(\gamma - 1)$ . Rewrite the adiabatic equation and find  $\gamma$ :

$$\frac{p_2}{p_1} = \left( \frac{V_1}{V_2} \right)^\gamma,$$

therefore,

$$i = \frac{2}{\frac{\ln \frac{p_2}{p_1}}{\ln \frac{V_1}{V_2}} - 1} = \frac{2 \ln \left( \frac{V_1}{V_2} \right)}{\ln \frac{p_2 V_2}{p_1 V_1}}.$$

Execute calculations and arrive at:  $i = 4.99 \approx 5.0$ . This means that the gas is biatomic.

(2) The internal energy of an ideal gas is equal by equation:  $U = (m/M) C_{v,m} T$ . The internal energy change  $\Delta U = U_2 - U_1 = (m/M) C_{v,m} T_2 - (m/M) C_{v,m} T_1$ . That is  $\Delta U = (m/M) C_{v,m} (T_2 - T_1)$ . The temperatures  $T_1$  and  $T_2$  will be found from the ideal gas equation

$$T_1 = \frac{p_1 V_1}{\frac{m}{M} R} \text{ and } T_2 = \frac{p_2 V_2}{\frac{m}{M} R}.$$

$$\text{Then, } \Delta U = (m/M)(i/2)R \left( \frac{p_2 V_2 - p_1 V_1}{(m/M)R} \right).$$

After some simplifications, we arrive at  $\Delta U = (i/2)(p_2V_2 - p_1V_1)$  (the answer).

Using the SI system:  $p_1 = 2 \text{ atm} \approx 2.026 \times 10^5 \text{ Pa}$ ;  $V_1 = 1 \text{ L} \approx 10^{-3} \text{ m}^3$ ;  $p_2 = 5 \text{ atm} \approx 5.065 \times 10^5 \text{ Pa}$ ;  $V_2 = 0.52 \text{ L} \approx 0.52 \times 10^{-3} \text{ m}^3$ .

Execute calculations:  $\Delta U = (5/2)(5.065 \times 10^5 \times 0.52 \times 10^{-3} - 2.026 \times 10^5 \times 1 \times 10^{-3}) \text{ J} = 2.5 \times (2.634 - 2.026) \times 10^2 \text{ J} = 152 \text{ J}$

We have to carry out the calculations in SI.

$\Delta U = 2.5 \times (5.052 - 21) \text{ L atm} = 1.50 \text{ L atm}$ .

Since  $1 \text{ atm} = 101.3 \times 10^5 \text{ Pa}$ , then  $\Delta U = 1.50 \times 101.3 \text{ J} = 152 \text{ J}$ .

(3) Enthalpy  $H$  is  $H = U + pV$ . The change of enthalpy can be expressed as

$$H = (U_2 + p_2V_2) - (U_1 + p_1V_1) \text{ or } \Delta H = \Delta U + (p_2V_2 - p_1V_1).$$

Since  $\Delta U = (i/2)(p_2V_2 - p_1V_1)$  then,  $\Delta H = (i/2)(p_2V_2 - p_1V_1) + (p_2V_2 - p_1V_1)$  that is,  $\Delta H = (i+2)/2 (p_2V_2 - p_1V_1)$ .

Using the calculations for  $\Delta U$  presented above we arrive at

$\Delta H = 3.5 \times (2.634 - 2.026) \text{ J} = 213 \text{ J}$

### 3.4.4 Heat capacity: theory versus experiment

The expressions obtained earlier for average kinetic energy show that each degree of freedom can realize only the definite energy. Therefore, the heat capacity of gases significantly depends on several factors. Firstly, their properties depend on the degree to which they approach the state of ideal gases; i.e., the nearer the gas is to an ideal gas, the better the theory describes its thermodynamic properties. Secondly, the simple theory often only

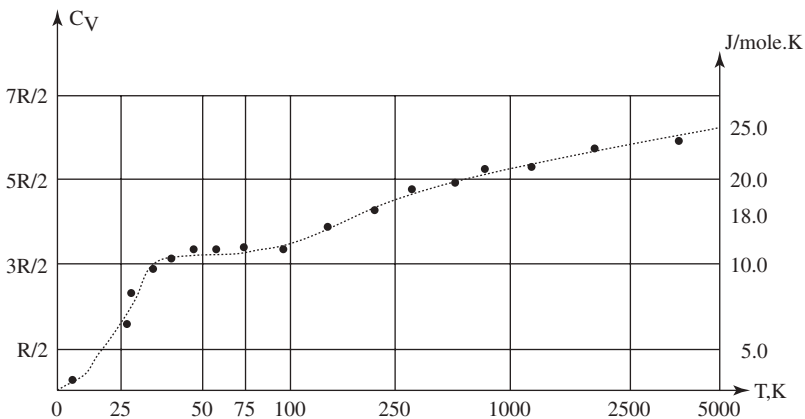


Figure 3.16 The experimental heat capacity values of hydrogen.

takes into account the molecular translational energy, though the molecules' rotation and vibration should also be accounted for. Thirdly, only quantum mechanics can explain the thermodynamic properties of complex gases. Therefore, comparison with experiment in the framework of used approximation gives only approximate agreement. We will return to this question in Chapters 7 and 9.

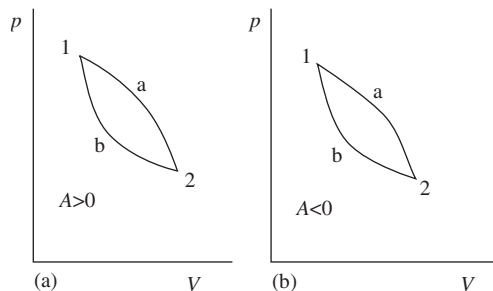
Figure 3.16 imagines the validity of the classic theory. At very low temperatures, quantum processes make the picture more complex. At 50–100 K, the  $(3/2)\kappa T$  law works relatively well. However, at higher temperatures, the heat capacity becomes temperature-dependent and, so far, no theory exists that explains this curve in detail.

### 3.5 THE SECOND LAW OF THERMODYNAMICS

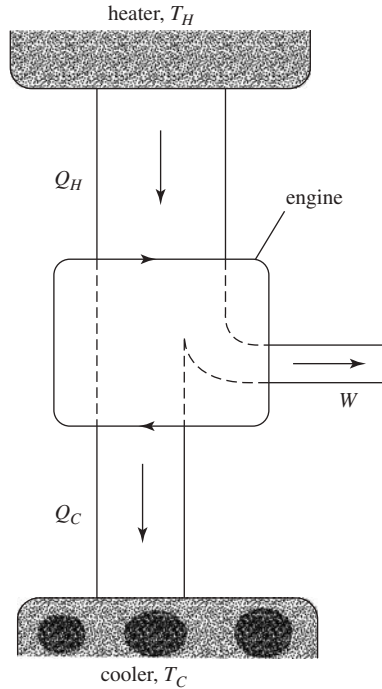
The second law of thermodynamics is a fundamental law of nature, covering numerous phenomena of the world around us and having deep practical and philosophical consequences. However, compared with the first law that has a simple and obvious physical sense as it is based on the well-known general law of conservation energy, the second law and its physical essence are less obvious and demand a more profound understanding of the physical processes occurring in nature. Before formulating the main ideas, it is necessary to make a number of remarks.

Any thermal machine works under a closed cycle creating a circular process. The process by which a thermodynamic system passes through a number of states and comes back to the initial point is referred to as circular process or a cycle. Figure 3.17 depicts the cycle made by an ideal gas in coordinates  $p$ - $V$ . Along line 1a2, the extending gas performs mechanical work  $A_{1a2} > 0$ .

At compression along a line 2b1, the work is taken over by external forces; therefore the mechanical work performed by the gas is  $A_{2b1} < 0$ . As the work performed by an ideal gas on the graph in coordinates  $p$ - $V$  is numerically equal to the area of a curvilinear trapeze, the difference between these areas, (the shaded area) is numerically equal to the work accomplished by the gas for a cycle. It is accepted that the cycle going clockwise is direct ( $A_{DC} = \oint pdV > 0$ ) and the cycle is reversed if it goes in the opposite direction (Figure 3.17), i.e.,  $A_{DC} = \oint_{1a2b1} pdV < 0$ .



**Figure 3.17** Thermal cycles: (a) represent a direct thermodynamic cycle 1-a-2-b, (b) the reversed cycle 1-b-2-a-1 is depicted.



**Figure 3.18** A heat engine. The engine is represented by arrows pointing in a clockwise direction around a central block: heat extracted from a heat reservoir is converted partly into work  $W$ .

The thermodynamic process is referred to as reversible if a thermodynamic system passes through the same intermediate equilibrium states in both the forward and in the opposite direction but in the reverse sequence; additionally, there will be no change in the surrounding bodies. It follows from this definition that any equilibrium process is reversible. Any process that does not meet these requirements is irreversible.

### 3.5.1 Heat engines

Heat engines (machines) are intended for the production of useful work due to the heat received from the combustion of fuel or other energy sources. A device that changes heat into work while operating in a cycle is referred to as a heat engine. The following components are necessary for the cyclic work of such an engine: a heater, a working body and a cooler (refrigerator). As a rule, one uses the environment as a cooler; in the design of a thermal engine a cooler as the component of the thermal machine is therefore absent. The basic scheme of a thermal engine is given in Figure 3.18.

The heater at temperature  $T_1$  transfers an amount of thermal energy  $Q_1$  to a working body; as a result, the temperature of the working body rises. Due to expansion, it carries

out mechanical work  $A$ , making any mechanical devices rotate (e.g., a turbine) or move (e.g., a piston in a cylinder). To return the system to its initial state, a cooler with temperature  $T_2$  is used to which the working body transfers an amount of heat  $Q_2$ . Notice that the presence of a cooler is an obligatory condition, otherwise the periodic (cyclic) work of the thermal engine is impossible: in fact, in this case the working body will eventually come into thermal balance with the heater and the thermal stream from the heater to the working body stops.

According to the first law of thermodynamics, after the return of the working body to its initial state, its internal energy  $U$  for a cycle does not change. Therefore the difference of amounts of heat  $Q_1$  and  $Q_2$  will be equal to useful mechanical work  $A$ , accomplished by the thermal engine for a cycle; this is the thermal efficiency  $e$ . The thermal efficiency of the engine cycle  $e$  is the ratio of useful work  $A$  to the amount of heat absorbed from a heater  $Q_1$ .

$$e = \frac{A}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

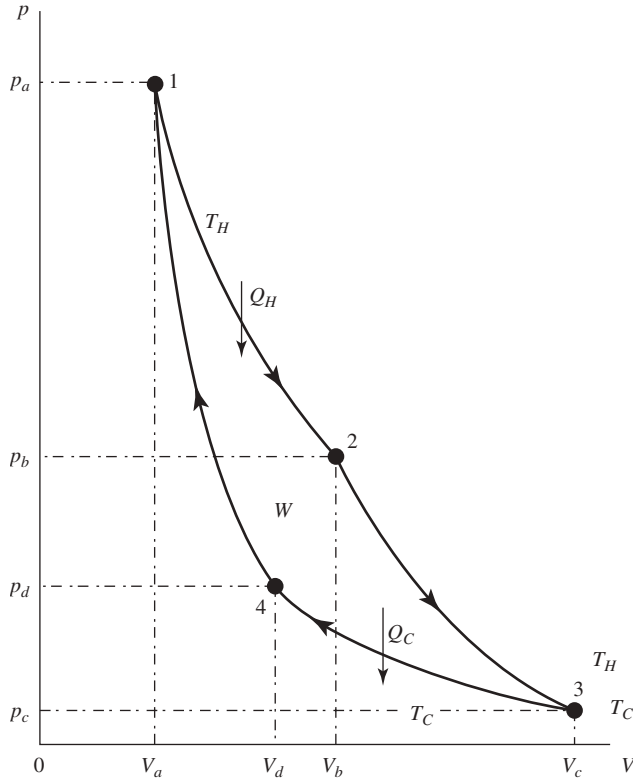
or

$$e = 1 - \frac{Q_2}{Q_1}. \quad (3.5.1)$$

As for all cyclically working thermal engines, quantity  $Q_2$  should necessarily be transferred to the cooler (otherwise the return of the working body to an initial state is impossible) so at  $Q_2 \neq 0$ , the thermal efficiency  $e$  is always less than unity.

### 3.5.2 The Carnot cycle

The development of thermodynamics is a direct result of the need for the description and calculation of thermal engines. The low thermal efficiency of the engines existing in *S. Carnot's* time prompted him to investigate the work of heat engines from a thermodynamic point of view. He aimed to find a thermal cycle, the efficiency of which would be maximal. It was obvious from this requirement that the cycle should consist only of reversible processes, excluding thermal losses. There can be only two processes: an isothermic process, which should be carried out infinitely slowly as only then will the working body (e.g., gas or vapor) pass a number of quasi-stationary states (without thermal losses since they are reversible); and an adiabatic process which, as a matter of fact, proceeds reversibly without heat exchange with the environment, i.e., it is carried out instantly. An ideal gas is used as a working body. Thus, in the search for the optimum process, the cycle should contain two isotherms corresponding to temperatures  $T_1$  (the temperature of the heater) and  $T_2$  (the temperature of the cooler). These two isotherms should be cut by two adiabatic curves. Such a cycle is represented in Figure 3.19. The line 1–2 corresponds to the isothermal gas expansion resulting from obtaining the heat  $Q_1$  from the heater. This is



**Figure 3.19** Carnot cycle.

in accordance with the first thermodynamic law  $Q_1 = \Delta U + A_{1,2}$  (where in our case  $\Delta U = 0$ ) and leads to the expression

$$Q_1 = A_{1,2} = \nu RT_1 \ln \frac{V_2}{V_1} \quad (3.5.2)$$

where  $\nu$  is the amount of gas moles.  $V_1$  and  $V_2$  are the initial and final gas volumes.

The line 2–3 corresponds to adiabatic gas expansion ( $Q = 0$ ) with no contact with the heat reservoir. Then  $\Delta U_{2-3} + A_{2-3} = 0$ . Therefore, the work done by gas along this line is

$$A_{2-3} = -\nu C_{vm}(T_2 - T_1) = \nu C_{vm}(T_1 - T_2) \quad (3.5.3)$$

When it reaches temperature  $T_2$  (at the end of the adiabatic expansion), the gas transfers to the refrigerator heat

$$Q_2 = A_{3-4} = \nu RT_2 \ln \frac{V_4}{V_3} = -\nu RT_2 \ln \frac{V_3}{V_4} \quad (3.5.4)$$



Then along the line 4–1, the gas is compressed so that its temperature acquires the initial temperature  $T_1$ . Since the heat exchange along this line is absent, the work of the external forces  $A'_{4-1}$  equals the increment of the internal energy  $\Delta U_{4-1} = \nu C_{Vm} (T_1 - T_2)$ . Then the work carried out by the gas is  $A_{4-1} = -A'_{4-1}$  or

$$A_{4-1} = -\nu C_{Vm} (T_1 - T_2). \quad (3.5.5)$$

The total work performed by gas in one cycle is the sum of work produced on each segment

$$A = A_{1-2} + A_{2-3} + A_{3-4} + A_{4-1}. \text{ or } A = \nu RT_1 \ln(V_2/V_1) + \nu C_{Vm} (T_1 - T_2) - \nu RT_2 \ln(V_3/V_4) - \nu C_{Vm} (T_1 - T_2).$$

After some transformation, the expression adopts the form:

$$A = \nu RT_1 \ln\left(\frac{V_2}{V_1}\right) - \nu RT_2 \ln\left(\frac{V_3}{V_4}\right) = \nu R \left( T_1 \ln \frac{V_2}{V_1} - T_2 \ln \frac{V_3}{V_4} \right). \quad (3.5.6)$$

This work is numerically equal to the  $W$  area in the graph.

We will execute some transformations that will be useful to us. Recall the equitable expression for adiabatic process  $TV^{\gamma-1} = \text{const}$ . Then some relationships for lines 2–3 and 4–1 can be written  $T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$  and  $T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$  or  $T_2 / T_1 = (V_2 / V_3)^{\gamma-1}$  and  $T_2 / T_1 = (V_1 / V_4)^{\gamma-1}$ . The volume relationships can be obtained from these expressions  $V_2/V_3 = V_1/V_4$  or  $V_2/V_1 = V_3/V_4$ . Therefore, in the expression (3.5.6), the transformation of the logarithmic terms as  $\ln(V_2/V_1) = \ln(V_3/V_4)$  allows us to write

$$A = \nu R (T_1 - T_2) \ln \frac{V_2}{V_1}. \quad (3.5.7)$$

Since  $Q_1 = \nu RT_1 \ln(V_2/V_1)$ , the maximum thermal efficiency of the ideal thermal engine is

$$e_{\text{id}} = \frac{A}{Q_1} = \frac{\nu R (T_1 - T_2) \ln(V_2 / V_1)}{\nu RT_1 \ln(V_2 / V_1)}, \quad (3.5.8)$$

that is,

$$e_{\text{id}} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}. \quad (3.5.9)$$

The results of these thermodynamic investigations of heat engine processing have resulted in Carnot's theorem (1850): the thermodynamic efficiency  $e$  of the ideal engine working on the Carnot cycle depends only on the heater  $T_1$  and cooler  $T_2$  temperatures and does not depend on the engine construction and on the kind of working body used.

Note that any real engine has an apparently smaller thermal efficiency  $e_{id}$  than the ideal one  $e_{real}$ :  $e_{real} < e_{id}$ :

Carnot's work permits problems to be approached from thermodynamic positions. It seems that there exist only two ways of increasing the thermal efficiency of engines: either increase the heater temperature  $T_1$  or lower the cooler temperature  $T_2$ . However, the second way is economically unjustified because of its complexity. Therefore, there is only one way of increasing engine thermal efficiency, i.e., raise the heater temperature. However, there are also difficulties inherent in method. For example, if water vapor is used as the working body the problem of corrosion arises which inevitably leads to the deterioration of the engine.

Thus, in a real heat engine the transformation of heat into work inevitably causes the transfer of a certain amount of heat to the environment. This results in the engine's thermal reservoir cooling and the cooler (i.e., the environment) heating; this is in agreement with the second law of thermodynamics.

At the same time, an infringement of this law would mean an opportunity to create a so-called perpetuum mobile of the second kind, i.e., one executing mechanical work due to the internal energy of the thermal reservoir but not changing the thermodynamic state of the environment. This allows us to suggest one more rule of the second law of thermodynamics: it is impossible to create a perpetuum mobile of the second kind.

### 3.5.3 Refrigerators and heat pumps

Another rule of the second law of thermodynamics is as follows: heat cannot flow from one body to another body at a higher temperature without other changes being involved. The transfer of heat from a cooler body to a warmer one can take place only because of work  $A'$  done under the action of external forces on the working body. The thermodynamic cycle initiated in the reverse direction is used in refrigerators and thermal pumps.

The removal of an amount of heat  $Q_2$  from a cool body and its transfer to a more heated one (the thermal reservoir) is the task of the refrigerating machine (refrigerator). The thermal coefficient of performance  $K$  is defined by the ratio of the amount of heat  $Q_2$  removed from a cool body and given to the warm body to the external mechanical forces work  $A'$

$$K = \frac{Q_2}{A'} = \frac{Q_2}{Q_1 - Q_2}. \quad (3.5.10)$$

Depending on the design of the refrigerator,  $K$  can be either less or more than unity. Notice that the refrigerator permits the cooling of bodies that are inside it, while simultaneously heating the surrounding air. The idea of using the heat machine's backwards cycle to carry an amount of heat from the cooler environmental air to heat the housing is achieved. Such a device is referred to as a thermal pump. The efficiency of the thermal pump is defined by the ratio of the amount of heat  $Q_1'$  received by the heated body to the mechanical work spent  $A'$  produced by external forces

$$K_{th.p.} = \frac{Q_1'}{A'} = \frac{Q_1'}{Q_1' - Q_2}, \quad (3.5.11)$$

where  $Q_2$  is the amount of heat taken from the cool body; it is always distinct from zero therefore, the efficiency of the thermal pump is always higher than unity.

The basic difference between a thermal pump and a refrigerator is that in the thermal pump the amount of heat  $Q_1'$  is given to the heated body, and in the refrigerator  $Q_2$  is removed from the cooled body. Heat pumps require less power expense for the work than electro-heating devices.

### 3.5.4 Reduced amount of heat: entropy

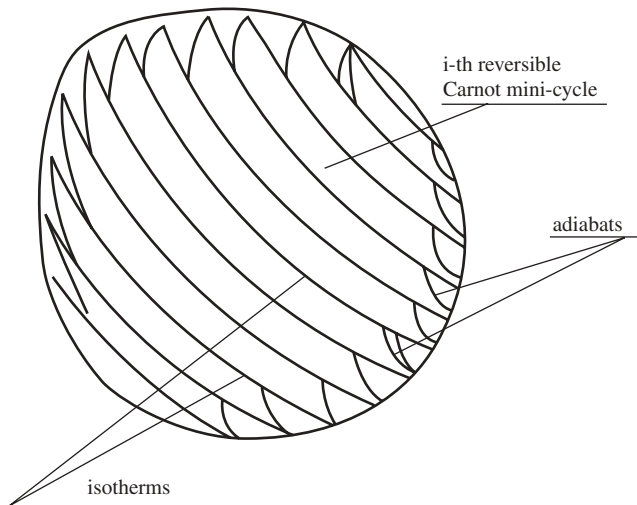
Write two expressions for the thermal efficiency of the ideal thermal engine  $e_{id}=1-(Q_1/Q_2)$  and  $e_{id} = 1 - (T_1/T_2)$ . Since these two equations are equal then,  $Q_1/Q_2 = T_1/T_2$  or  $Q_1/T_1 = Q_2/T_2$ .

Consider an amount of  $Q_1$  obtained by a working body from a heater positive ( $Q_1 > 0$ ) and the heat amount yielded by the working body to the cooler heat negative ( $Q_2 < 0$ ). Then the equation can be written as  $Q_1/T_1 = - (Q_2/T_2)$  or, for the Carnot cycle,

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0. \quad (3.5.12)$$

The ratio of the amount of heat to the temperature is referred to as the reduced amount of heat. So for the Carnot heat engine, the sum of the reduced amount of heat is zero.

Since the Carnot cycle is reversible, any reversible cycle can be presented as a sequence of elementary (Carnot) cycles. Ten such cycles consisting of isotherms crossed by adiabats are depicted in Figure 3.20.



**Figure 3.20** Carnot microcycles.

The larger the amount of such microcycles used, the better the degree of approximation. For each microcycle the eq. (3.5.12) is valid. Therefore, for any reversible cycle, we can write

$$\sum_{i=1}^N \left( \frac{\Delta Q_{1i}}{T_{1i}} + \frac{\Delta Q_{2i}}{T_{2i}} \right) \approx 0. \quad (3.5.13)$$

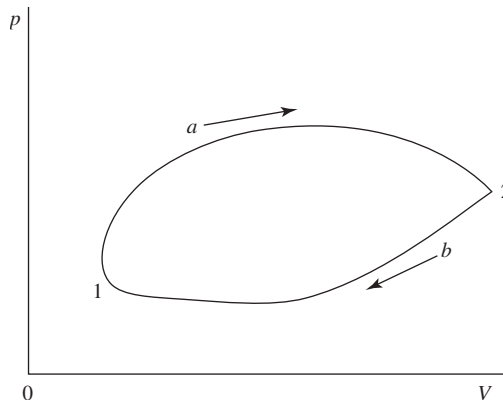
Notice that the amount of heat  $\Delta Q_{1i}$  obtained by a working body in the  $i$ th cycle is approximately equal to the amount of heat  $\Delta Q_{2,i}$ , which is yielded by a working body in the preceding cycle ( $i-1$ ). The precise equality can be reached at an infinitely large amount of cycles with infinitely thin Carnot microcycles. Therefore, all the heat flows into the system along the internal parts of cycles compensating each other; instead of a sum we can write an integral

$$\oint \frac{\delta Q}{T} = 0 \quad (3.5.14)$$

(for reversible cycles) where  $\delta Q$  is the small amount of heat obtained or given off by a working body. This equation is referred to as a Clausius equation. Since the integral is taken over a closed counter, it can be taken from any point and in any direction (since the cycle is reversible) (Figure 3.21).

This allows one to present it as a sum of two integrals  $\int_{1a2} \delta Q/T + \int_{2b1} \delta Q/T = 0$ . Thus the integral from  $\int_{12} \delta Q/T = 0$  between any two points of 1 and 2 equilibrium states does not depend on the form of a trajectory along which a thermodynamic reversible process is going on. As the choice of points 1 and 2 is arbitrary, we can assert that the integral describing the change of value (designated by the letter  $S$ ) is a function of a system's state. Suggested by Clausius, this value is referred to as entropy (measured in J/K units). For a reversible cycle  $\oint \delta S = 0$ .

From the expression obtained, it follows that for reversible processes  $\int_{12} \delta Q/T$  does not depend on the form of a line (trajectory) representing this process on the graph; it is



**Figure 3.21** The cycle and the work done; entropy.

defined only by the points describing initial and final equilibrium states. Thus, the elementary reduced amount of heat is the full differential of the  $S$ -function dependent only on the system's state, i.e.,

$$dS = \frac{\delta Q}{T} \quad (3.5.15)$$

Therefore, the entropy change  $\Delta S$  at the transition from the first equilibrium state (1) to another equilibrium state (2) at reversible process is determined by equality

$$\Delta S = S_2 - S_1 = \int_{1 \rightarrow 2} \frac{\delta Q}{T}. \quad (3.5.16)$$

Thus, entropy is only a function of an equilibrium state of a thermodynamic system. It does not depend, in this case, on particular processes leading the system into a given equilibrium state.

Entropy, as well as potential energy, can be defined only to some constant. This is a consequence of the fact that the formula (3.5.16) does not allow us to define the absolute entropy value but only its difference.

For the determination of entropy change at quasi-equilibrium, processes one can use a property of its additivity, i.e.,

$$\Delta S = \sum_{i=1}^N \Delta S_i \quad (3.5.17)$$

where  $\Delta S_i$  is the entropy change at the  $i$ -th quasi-equilibrium process.  $N$  is the number of such processes.

The entropy change will vary depending on the process if the initial and final positions of the thermodynamic system do not coincide. At quasi-equilibrium (sufficiently slow) heating of the system from temperature  $T_1$  to temperature  $T_2$ , we obtain the following.

(1) For an isochoric process:  $\delta Q = \nu C_{vm} dT$  (where  $C_{vm}$  is a molar heat capacity at constant volume):

$$\Delta S_v = \int_1^2 \frac{\delta Q}{T} = \nu C_{vm} \int_{T_1}^{T_2} \frac{dT}{T} = \nu C_{vm} \ln \frac{T_2}{T_1}.$$

(2) For an isobaric process:  $\delta Q = \nu C_{pm} dT$  (where  $C_{pm}$  is a molar heat capacity at constant pressure).  $\Delta S_p = \int_1^2 dQ/T = \nu \int_{T_1}^{T_2} dT/T = \nu C_{pm} \ln(T_2/T_1)$  (for reversible process). Since  $C_{pm} > C_{vm}$ , then  $\Delta S_p > \Delta S_v$ .

If the thermodynamic system is an ideal gas in which simultaneously the quasi-equilibrium changes of several parameters take place, we can use the first thermodynamic

law (3.4.3) in the form

$$\delta Q = \nu C_{vm} + p dV \text{ then, } \frac{\delta Q}{T} = \nu C_{vm} \frac{dT}{T} + \nu R \frac{dV}{V}.$$

Since for ideal gas

$$p dV = \nu R T \frac{dV}{V}$$

then,

$$\Delta S = \int_1^2 \frac{\delta Q}{T} = \nu C_{vm} \int_{T_1}^{T_2} \frac{dT}{T} + \nu R \int_{V_1}^{V_2} \frac{dV}{V}.$$

Executing the integration we obtain:

$$\Delta S = \nu C_{vm} \ln \frac{T_2}{T_1} + \nu R \ln \frac{V_2}{V_1}. \quad (3.5.18)$$

### 3.5.5 Clausius inequality and the change of entropy for nonequilibrium processes

Remember that the thermal efficiency of the thermal Carnot heat engine is given by equations

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

therefore,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}. \quad (3.5.19)$$

As noted earlier, the work of any heat engine is always accompanied by a thermal loss. Therefore, the thermodynamic cycles of real engines are irreversible and their thermal efficiency is less than that of ideal and reversible Carnot cycles

$$e_{\text{real (non-rev.)}} < e_{\text{ideal (rev.)}}$$

However, the mathematical equations  $e = (Q_1 - Q_2)/Q_1$  (real, irreversible) and  $e = (T_1 - T_2)/T_1$  (ideal, reversible) are still valid. That is,  $(Q_1 - Q_2)/Q_1 < (T_1 - T_2)/T_1$  or  $1 - Q_2/Q_1 < 1 - T_2/T_1$ . It follows then

$$\frac{Q_2}{Q_1} > \frac{T_2}{T_1} \quad (3.5.20)$$

or

$$\frac{Q_2}{T_2} > \frac{Q_1}{T_1}. \quad (3.5.21)$$

From comparison of these two equations, it follows

$$\frac{Q_2}{T_2} \geq \frac{Q_1}{T_1}. \quad (3.5.22)$$

The sign of equality relates to reversible processes whereas the sign of non-equality relates to irreversible processes.

Let us consider the heat obtained by a working body from a heater positive and the obtained from a working body to a cooler negative. Then the inequality will be

$$\frac{Q_2}{T_2} + \frac{Q_1}{T_1} \leq 0$$

and, in the more general form,

$$\sum_i \frac{Q_i}{T_i} \leq 0. \quad (3.5.23)$$

At the limit (for minicycles), the sum can be substituted by integral

$$\oint \frac{\delta Q}{T} \leq 0. \quad (3.5.24)$$

This expression is referred to as the Clausius inequality.

Let us change this inequality by incorporating the entropy notion. Use a cycle like that presented in Figure 3.21. Let us consider also that part of the cycle (1a2) is reversible and the other (1b2) is irreversible. From the Clausius inequality it then follows that  $\int_{\text{rever.,1a2}}(\delta Q/T) + \int_{\text{irrev.,1b2}}(\delta Q/T) < 0$ , and further,  $\int_{\text{rever.,1a2}}(\delta Q/T) > \int_{\text{irrev.,1b2}}(\delta Q/T)$ , i.e., the integral from  $(\delta Q/T)$  over the irreversible path is always lower than that over the irreversible path between the same states. Since the integral from the right is the change of the entropy  $\Delta S$ , therefore,  $\Delta S = S_2 - S_1 > \int_1^2 (\delta Q/T)$  for the irreversible cycle. Then for the irreversible cycle (approximately)  $\oint (\delta Q/T) < \Delta S$ . Applying this equation to a minicycle we obtain

$$dS > \frac{\delta Q}{T}. \quad (3.5.25)$$

Combining expressions (3.5.15) and (3.5.25) we obtain

$$dS \geq \frac{\delta Q}{T},$$

or

$$dS \geq 0. \quad (3.5.26)$$

The equality sign relates to reversible processes and the inequality sign to irreversible processes.

This form of the second law of thermodynamics possesses the greatest generality as microprocesses are practically elementary and on the basis of such mini-processes, other probable processes can be composed, both noncircular and circular (cyclic).

Thus, using the entropy concept, we can give one more rule of the second thermodynamic law: the entropy of an isolated thermodynamic system can only increase and, after reaching the maximum value, remain constant. This rule is also referred to as the law of entropy increase.

We can be convinced of this by a simple example. Let there be two bodies representing an isolated thermodynamic system. One body (hot) is at temperature  $T_1$  another (cold) at temperature  $T_2$ . We know that the first body cools down whereas the second is heated up; this process proceeds spontaneously. How then will entropy change? An amount of heat will be transferred from the hot body to the second body, warming it up. The entropy change of the first body will be equal to the reduced amount of heat ( $\delta Q/T_1$ ) taken with the negative sign:  $\Delta S_1 = -(\Delta Q/T_1)$ . This amount of heat is obtained by the second body. Therefore, the reduced amount of heat ( $\Delta Q/T_2$ ) is positive. The change of the second entropy can be similarly determined:

$$\Delta S_2 = \frac{\Delta Q}{T_2}.$$

We can find the entropy change of the whole system according to the additivity principle as the sum of  $\Delta S_1$  and  $\Delta S_2$ :  $\Delta S = \Delta S_1 + \Delta S_2$  or  $\Delta S = -(\Delta Q/T_1) + (\Delta Q/T_2) = \Delta Q ((T_1 - T_2) / T_1 T_2)$ . As  $T_1 > T_2$ , therefore the entropy at a spontaneous irreversible process increases: this is in accordance with the rule of the second law of thermodynamics given above.

Notice that in open systems entropy can decrease as well. In this case, however, there will always be changes in surrounding bodies so the total entropy of the system and the surrounding bodies will increase.

The first and second laws of thermodynamics can be combined. For this purpose, in the expression of the second law ( $dS \geq (\delta Q/T)$ ), a small amount of heat is presented as the sum  $dU + pdV$  as is required by the first law. Then  $dS \geq (dU + pdV) / T$  or

$$TdS \geq dU + pdV \quad (3.5.27)$$

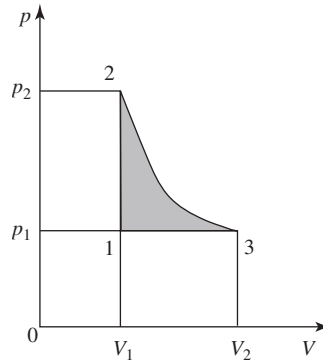
This expression is referred to as the basic thermodynamic equation. The equality sign relates to reversible processes; the inequality sign to irreversible processes.



**EXAMPLE E3.12**

An ideal diatomic gas in an amount of  $\nu = 1$  mole is under a pressure  $p_1 = 250$  kPa and occupies volume  $V_1 = 10$  L. The gas is heated to  $T_2 = 400$  K and further isothermally expanded to initial pressure. After that, the gas returns to its initial state by isobaric compression. Define the cycle thermal efficiency  $e$ .

**Solution:** For visualization, we shall draw the whole cycle in coordinates  $p$ - $V$  with characteristic points 1, 2, 3. The thermal efficiency of any cycle is given by expression (3.5.9) where  $Q_1$  is the amount of heat obtained by the gas from the heater,  $Q_2$  is the heat returned by the gas to a cooler. The heat difference is the work done by the gas in one cycle (marked  $W$  in Figure 3.19 in the graph). The working body obtains the heat  $Q_1$  at two lines: 1-2 (isochoric process) and 2-3 (isothermal process); therefore  $Q_1 = Q_{1-2} + Q_{2-3}$ . The amount of heat obtained at isochoric process is  $Q_{1-2} = C_{\nu} \nu (T_2 - T_1)$ .  $T_1$  can be found from the ideal gas equation



$$T_1 = \frac{p_1 V_1}{\nu R}.$$

Executing calculations we arrive at  $T_1 = 300$  K.

The amount of heat obtained by a gas in an isothermal process is  $Q_{2-3} \nu R T_2 \ln(V_2 / V_1)$ , where  $V_1$  is the volume at  $T_2$  and pressure  $p_1$  (point 3 in the graph). On the line 3-1, gas returned the heat  $Q_2$

$$Q_2 = Q_{3-1} = C_p \nu (T_2 - T_1).$$

Consequently the thermal efficiency is

$$E = 1 - \frac{\nu C_p (T_2 - T_1)}{\nu C_V (T_2 - T_1) + \nu R T_2 \ln \frac{V_2}{V_1}}.$$

We can change the ratio of volumes to that of temperatures  $V_2/V_1 = T_2/T_1$  and express the heat capacities according to their temperatures (see Section 3.4.2). Making substitutions we arrive at

$$e = 1 - \frac{(i+2)(T_2 - T_1)}{i(T_2 - T_1) + 2T_2 \ln \frac{T_2}{T_1}}.$$

Substituting corresponding values and executing calculations, we arrive at  $e = 0.041 = 4.1\%$ .

### EXAMPLE E3.13

There is cold ( $T_1 = 10^\circ\text{C}$ ) and hot ( $T_2 = 90^\circ\text{C}$ ) water in two vessels of masses  $m_1 = 7$  kg and  $m_2 = 3$  kg, respectively. Determine the entropy change  $\Delta S$  on mixing these portions of water. Ignore the thermal capacity of the vessels. Consider the specific thermal capacity of water to be independent of temperature and equal to  $C_s = 4.18$  kJ/kg K.

**Solution:** We must first find the temperature of the mixture produced. We shall take advantage of the equation of thermal balance  $Q_1 = Q_2$  where  $Q_1$  is the heat obtained by the cold portion of water and  $Q_2$  is the heat given by the hot water (we ignore the thermal capacity of the vessels.)

Therefore  $Cm_1(\Theta - T_1) = C m_2(T_2 - \Theta)$ . Wherefrom we can obtain

$$\Theta = \frac{m_1 T_1 + m_2 T_2}{m_1 + m_2}$$

In order to avoid complication, we calculate the value of  $\Theta$ :

$$\Theta = (7 \times 10 + 3 \times 90) / (7 + 3) = 34^\circ\text{C} \text{ or } 307 \text{ K.}$$

The entropy is additive. Its change  $\Delta S$  consists of two parts: part  $\Delta S_1$  describes the change of entropy as a result of heating the cold water from  $T_1$  to  $\Theta$  due to the cooling of the hot water, and  $\Delta S_2$  is equal to the change of entropy of hot water at its cooling from  $T_2$  to the average temperature  $\Theta$ . Hence  $\Delta S = \Delta S_1 - \Delta S_2$ . The change of entropy is determined by the integral  $\Delta S = \int_1^2 (dQ/T)$ .

Here limits 1 and 2 symbolize the initial and final states of the thermodynamic system. Apply to the given task

$$\Delta S_1 = \int_{T_1}^{\Theta} \frac{dQ_1}{T} \text{ and } \Delta S_2 = \int_{T_2}^{\Theta} \frac{dQ_2}{T}$$

where  $dQ_1 = C m_1 dT$  and  $dQ_2 = C m_2 dT$ . Substituting these equations into integrals and executing integrations, we obtain  $\Delta S_1 = C m_1 \ln(\Theta/T_1)$  and  $\Delta S_2 = C m_2 \ln(\Theta/T_2)$ . Therefore the entropy change is  $\Delta S = C(m_1 \ln(\Theta/T_1) - m_2 \ln(\Theta/T_2))$ . All values

required for calculation have already been mentioned. The final calculation is  $\Delta S = 4.18 \times 10^3 (7 \times \ln(307/283) + 3 \times \ln(307/363)) \text{ J/K} = 4.18 \times 10^3 (0.5698 - 0.5027) \text{ J/K} = 280 \text{ J/K}$ .

We know that the spontaneously running process goes with increasing of the entropy and our result corresponds to this regularity  $\Delta S > 0$ .

### 3.5.6 Statistical explanation of the second law of thermodynamics

The physical significance of entropy becomes clearer in a statistical interpretation offered by Boltzmann (1875). As already mentioned, thermodynamics does not consider the microscopic structure of a substance; it establishes a connection between the macroscopic properties of a thermodynamic system in various states of its existence. These states are defined by a small number of thermodynamic parameters ( $p$ ,  $T$ ,  $V$ , etc.). The states of a system characterized by such thermodynamic parameters are referred to as macrostates.

The microscopic structure of a substance is taken into account in molecular-kinetic theory using statistical descriptions. On the basis of the statistical laws of an ideal gas, the assumption of the independence of coordinate and speed of any single molecule from the speeds and coordinates of all other molecules was adopted. Therefore, the most detailed description of a gas state would be the enumeration of the six parameters for each particle (see Section 1.3.8); for a monoatomic gas consisting of  $N$  molecules there will be  $6N$  parameters. Such a representation of a system's state is referred to as a microstate approach.

As the gas molecules are in continuous motion accompanied by the exchange of energy at collisions, the microstates are changing almost continuously; however, the macrostate remains constant. This means that any macrostate can be realized through an enormous number of microstates. Assuming that all microstates are equiprobable (ergodic hypothesis), one can find the probability of any macrostate.

The so-called thermodynamic probability of a macrostate's statistical weights is used in statistical physics. The thermodynamic probability  $W$  of a system macrostate is determined by a number of various microstates that can assure the given macrostate.

Contrary to mathematical probability that cannot be more than a unit, thermodynamic probability is, as a rule, expressed by a giant number.

Boltzmann showed that a system's entropy is proportional to the natural logarithm of the number of possible microstates corresponding to the given macrostate, i.e., to the thermodynamic probability. The proportionality factor is  $\kappa$ , a value later called the Boltzmann constant. Therefore, entropy can be expressed as

$$S = \kappa \ln W \quad (3.5.28)$$

Notice that, under constant external conditions, the spontaneous transition of a system from one state to another is possible if the second state appears thermodynamically more probable. However, large entropy corresponds to a greater thermodynamic probability. As a transition is spontaneous, a system can pass only from a state of nonequilibrium state to a state of equilibrium; this means that entropy increases in irreversible processes. The equilibrium condition is achieved at the maximal value of thermodynamic probability and, hence, at the maximum entropy value compatible with the given external conditions. Thus

the Boltzmann formula explains entropy increase in irreversible processes, which follows from the second law of thermodynamics. Using the notion of entropy, the second law of thermodynamics can be interpreted as follows: any irreversible processes in a closed system occurs when the system's entropy increases.

Notice that the system should be closed because in an open system entropy can behave in any way, i.e., it can decrease, increase or remain constant. In closed systems entropy remains constant only in reversible processes. In irreversible processes entropy always increases.

### 3.5.7 Entropy and disorder

The energy of thermal motion is characterized by the irregular chaotic motion of molecules. It differs from the mechanical energy of a moving body where all molecules of the body participate both in the ordered motion together with the whole body, and also in chaotic motion. If the moving body were to stop sharply, it would heat up: the mechanical energy of the translational motion would transform to the kinetic energy of the thermal movement of the molecules, i.e., there would be a transformation of ordered into disordered motion. It is much more troublesome to carry out the return process.

Another example is shown in Figure 3.22. There are ordered balls, black and white, in a box (Figure 3.22a). When the box is shaken, the balls get mixed up (Figure 3.22b); this takes place almost spontaneously. However, all attempts to return the balls to their initial ordered state by shaking or stirring them will be unsuccessful.

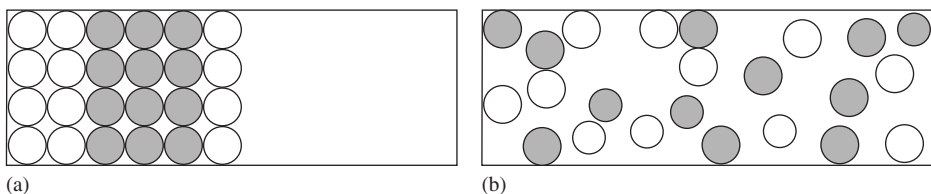
This simulated inconvertibility can be seen even more dramatically in any molecular system with an incommensurably large number of "balls".

One more example can be taken from a real problem of either the chemical or isotope separation of molecules. Let two different gases be divided by a partition. If the partition is removed, both gases will spontaneously become mixed. However, the return process of separation will not take place; separation demands a huge expenditure of energy and effort.

These examples show that any process aspires spontaneously to proceed to a state of greater disorder. This corresponds to the aspiration of a system to proceed to the state that has the greater entropy. The irreversibility of thermal processes corresponds to the irreversibility of order and disorder. Thus, entropy is a measure of the system's disorder.

Despite its generality, the second law of thermodynamics has no absolute character. Deviations from it due to fluctuations are quite natural; the fewer the number of particles, the greater the probability of deviations. Infringement of the second law is shown at small concentrations.

The first and second laws of thermodynamic allow us to judge the behavior of thermodynamic systems near to absolute zero (0 K). This problem was formulated by Nernst



**Figure 3.22** Irreversibility of the order (a) and disorder (b).

in 1906. On the basis of the generalization of experimental data, Nernst formulated a theorem which was subsequently referred to as the third law of thermodynamics: at the aspiration of any equilibrium thermodynamic system to absolute zero, the entropy aspires to some universal constant, the value of which does not depend on any thermodynamic parameters of the system and can be taken as equal to zero  $\lim_{T \rightarrow 0} S = 0$  and  $\lim_{T \rightarrow 0} \Delta S = 0$ . Simultaneously the following relation will also be fulfilled

$$\lim \left( \frac{\partial S}{\partial Z} \right)_T = 0, \quad (3.5.29)$$

where  $Z$  is any thermodynamic parameter (pressure, volume, etc.). Index  $T$  means that differentiation is executed at constant temperature.

Nernst's theorem is applicable only to equilibrium systems. From the third law of thermodynamics, it follows that absolute zero is unattainable because, according to eq. (3.5.27), if near a temperature of absolute zero, a small amount of heat is taken off a system ( $\Delta T \rightarrow 0$ ), a large enough (in a limit infinite) entropy change will take place; this contradicts Nernst's theorem.

Notice that at the aspiration of the temperature to absolute zero, the thermal heat capacities  $C_v$  and  $C_p$  will also aspire to zero.

### 3.6 A REAL GAS APPROXIMATION: VAN DER WAALS EQUATION

#### 3.6.1 An equation of state of a van der Waals gas

In order to come nearer to the state of an ideal gas, the conditions given in Section 3.1.3 must be satisfied: the volume of gas must be increased and the pressure reduced. In fact, these suggestions cannot be accepted by engineers. It is therefore important to improve the model (or make it more complex) by removing some of the restrictions and making them positively accounted.

Plenty of the equations aimed at developing an ideal gas model have been suggested (up to 150). Many of them, when applied in practice to certain classes of chemical substances and processes, give good agreement with experiment in limited intervals of temperatures and pressure.

The most successful approach has been worked out by van der Waals. The van der Waals equation contains two new parameters  $a$  and  $b$ , which takes into account intermolecular interactions ( $a$ ) and the total volume of molecules ( $b$ ). It supposes that the amount of interaction between molecules would affect the pressure value  $P$ , and that the amount of molecule volume will lead to a reduction of the volume accessible to free their movement. For one mole of van der Waals' gas, the following equation can be written:

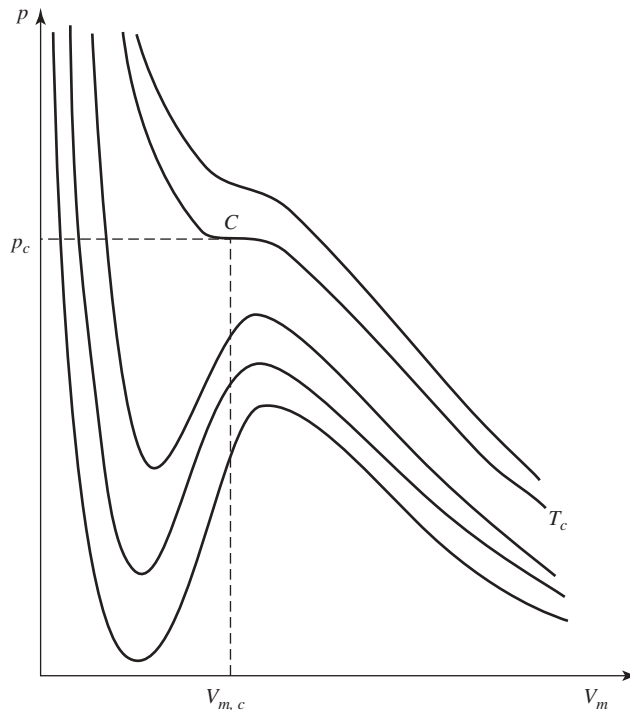
$$\left( \frac{p+a}{V_m^2} \right) (V_m - b) = RT. \quad (3.6.1)$$

Here, terms  $(a/V_m^2)$  and  $b$  describe the deviations of gas from ideality. The value  $(a/V_m^2)$  corresponds in its dimension to pressure; it results from the molecules' interaction and represents a so-called "internal (cohesive) pressure"  $p_i$ . The term  $b$  takes into account the total volume of all gas molecules. Therefore  $(V_m - b)$  is the volume free to molecular motion. Having removed the brackets the van der Waals equation can be rewritten as:

$$V_m^3 - V_m^2 \left( \frac{RT}{p} - b \right) + V_m \frac{a}{p} - \frac{ab}{p} = 0. \quad (3.6.2)$$

This equation is cubic relative to  $V_m$ ; at a definite set of temperatures, it should have either one real root or three roots, two of them being imaginary. (Further on, we shall omit index  $m$  so as not to block up the formula).

Solution of van der Waals by means of a mathematical treatment gives the isotherms depicted in Figure 3.23, from which it can be seen that there is a value of the  $T$  parameter ( $T = T_c$ ) that divides qualitatively various types of isotherms into two parts. At  $T > T_c$  curves  $p(V)$  monotonously falls down; this corresponds to the presence of one real equation root: only one value  $V$  corresponds to each value  $p$ . At  $T < T_c$ , the gas behaves approximately as ideal (exact conformity is absent only at  $T \rightarrow \infty$ , i.e., when it is possible to

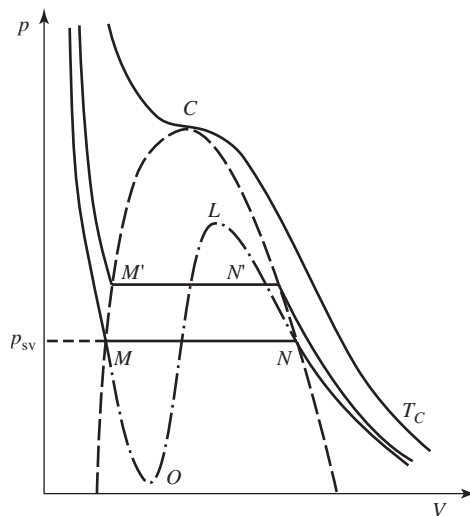


**Figure 3.23** Mathematical solution (isotherms) for a van der Waals gas.

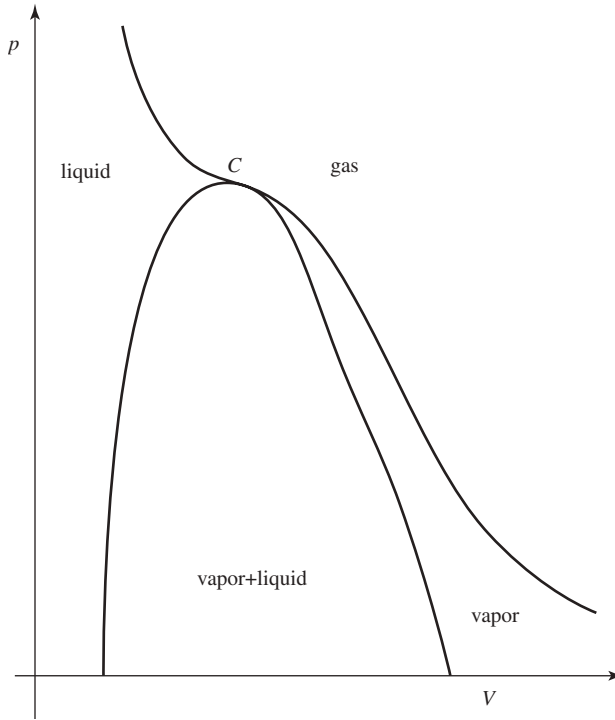
neglect the interaction between molecules and count them as MP). At lower temperatures ( $T < T_c$ ) one  $p$  value corresponds to three values  $V$ ; the form of isotherms essentially changes. At critical temperature  $T = T_c$ , the van der Waals's isotherm has one specified point (one solution). To this point corresponds  $p_c$  (critical pressure) and  $V_c$  (critical volume). This point  $C$  corresponds to the new substance state referred to as *critical*; as experiments show that in this state a substance is no longer either a gas or a liquid.

To obtain the real experimental isotherms, one can use the device presented in Figure 3.13. Reduction of volume  $V$  at  $T < T_c$  leads to the pressure increasing according to the theoretical curve (Figure 3.23). This occurs up to point  $N$ . Further reduction of the volume does not lead to an increase in pressure; part of the gas undergoes a transition from a vapor state to a liquid state (Figure 3.24). Reduction of the volume from point  $N$  to point  $M$  does not produce a pressure change but leads to a change in the amount of liquid and gaseous phases. The pressure, referred to as saturated vapor pressure, remains unchanged, whereas the amounts of the liquid and vapor phases change at this constant pressure (on Figure 3.24 this is marked by the letters svp—saturated vapor pressure). In a point of  $M$  all vapor volume liquefies. With a further reduction of volume, the isotherm sharply rises upwards; this corresponds to the sharp reduction in the compressibility of a liquid in comparison with vapor.

When temperature increases, the length of segment  $MN$  decreases; at  $T = T_c$ , it collapses into a critical point  $C$ . A locus of  $N$  and  $M$  points form a bell-like curve separating the diphasic area (under a bell-like curve) from single-phases—the vapor phase (at large  $V$ ) or the liquid phase (at small  $V$ ) (Figure 3.25). The gas cannot liquefy at any temperatures higher than  $T_c$ . (One can use this circumstance to distinguish gas and vapor—vapor can be compressed to liquid, but gas cannot be.)



**Figure 3.24** Real isotherms of a van der Waals gas.



**Figure 3.25** A phase diagram of a van der Waals gas.

In accurately adjusted experiments, metastable states characterized by segments MO and NL (Figure. 3.24) can be obtained. These states are supercooled vapor (line MO) and a superheated liquid (line NL). The supercooled vapor is in a state such that, according to the parameters it should be a liquid, but its properties continue to follow the behavior of a gaseous state—it aspires to extend, for example, as the volume increase. On the other hand, a superheated liquid is in a state such that, according to the parameters, it should be a vapor, but its properties remain liquid. Both these states are metastable: at small external influences they pass into a two-phase state. A line OL corresponds to a negative factor of compression; it is unstable and cannot be realized at all.

Constants  $a$  and  $b$  are independent of temperature and are different for different gases. The van der Waals equation can be modified; moreover being modified it describes the behavior of any gases provided that they are described by expression (3.6.1). For this purpose, we shall find the relation between constants  $a$  and  $b$ , as well as critical parameters:  $p_C$ ,  $V_C$  and  $T_C$ . Eq. (3.6.1) can be rewritten in another way:

$$p(V) = \frac{RT}{V-b} - \frac{a}{V^2}. \quad (3.6.3)$$



We can then use the property of the critical point; in this point value ( $dp/dV$ ) is zero since its tangent inherits a horizontal lines sv, and ( $d^2p/dV^2$ ) is zero because it is a point of inflection. For the critical point it is fair to say that

$$p_C = \frac{RT_C}{V_C - b} - \frac{a}{V_C^2} \quad (3.6.4)$$

$$\left(\frac{dp}{dV}\right)_C = -\frac{RT_C}{(V_C - b)^2} - \frac{2a}{V_C^3} = 0 \quad (3.6.5)$$

$$\left(\frac{d^2p}{dV^2}\right)_C = -\frac{2RT_C}{(V_C - b)^3} - \frac{6a}{V_C^4} = 0. \quad (3.6.6)$$

All these equations are valid for critical point  $C$ . The solution gives:

$$V_C = 3b, p_C = \frac{a}{(27b)^2}, T_C = \frac{8a}{27Rb}, \quad (3.6.5)$$

and consequently,

$$b = \frac{V_C}{3}, a = 3V_C^2 p_C, R = \frac{8p_C V_C}{3T_C}. \quad (3.6.7)$$

Let us now substitute these parameters into the initial equation:

$$\left(p + \frac{p_C V_C^2}{V_C}\right) \left(V - \frac{V_C}{3}\right) = \frac{8}{3} p_C V_C \frac{T}{T_C}.$$

After dividing the equation by  $p_C V_C$  and expressing the parameters in a reduced form ( $\pi = p/p_C$ ,  $\omega = V/V_C$ ,  $\tau = T/T_C$ ), eq. (3.5.1) became very simple:

$$\left(\pi + \frac{3}{\omega^2}\right) (3\omega^2 - 1) = 8\tau. \quad (3.6.8)$$

This is the van der Waals equation in *reduced parameters*, universal for all van der Waals gases (i.e., the gases submitting to eq. (3.6.1)).

Eq. (3.6.8) allows us to come to *the law of corresponding states*: if for two different gases, two of three ( $\pi$ ,  $\omega$ ,  $\tau$ ) reduced parameters coincide, the third parameter should also coincide. These substances are in *corresponding states*.

Writing the van der Waals equation in the form (3.6.3) allows us to apply the representations given to the case of any other gases that do not originally satisfy the van der Waals

equation. Notice that eq. (3.6.3) reminds us of a decomposition series of the function  $p(V)$  over a  $V^n$  term; it is only desirable to continue the series

$$p(V) = \frac{RT}{V} + \frac{A_1(T)}{V^2} + \frac{A_2(T)}{V^3} + \frac{A_3(T)}{V^4} + \dots \quad (3.6.9)$$

Factors  $A_n(T)$  are called *virial factors*. At an infinite number of terms in this decomposition, it could precisely describe the state of any gas.

Notice that factors  $A_n(T)$  are temperature-dependent functions. In different technological processes, various models for their calculation are used. There is also a theoretical estimation: what is the amount at which members of this decomposition term reach the desired accuracy.

### 3.6.2 Internal energy of the van der Waals gas

The internal energy of the van der Waals gas should contain the potential energy of the molecules' interaction as well as the kinetic energy part. Kinetic energy represents the total kinetic energy of all the gas's molecules; however, for calculating the potential energy, it is necessary to determine the work of the internal forces while carrying a system from a given state to a state with "zero" potential energy (see Section 1.4.5). It has been shown above (see Section 3.6.1) that the additional (internal) pressure appears because of intermolecular interactions in van der Waals gas; it is defined by the expression  $(a/V^2)$ . Then the elementary work of a gas expansion is equal to  $dA = (a/V^2)dV$ . An integration results:  $A = a \int_{V_0}^{\infty} (dV/V^2) = -a/V$ . Thus, the internal energy of one mole of a gas is  $U = (i/2)RT - a/V = C_V T - a/V$ . From this equation it follows that adiabatic expansion brings about gas cooling. In fact,  $dU = dQ = (i/2)RdT + (a/V^2)dV = 0$ . Therefore,  $-dT = (a/(C_V V^2))dV$  and  $dT \sim -dV$ . Indeed a volume increase leads to the decrease of the gas temperature since all factors in the equation are positive. However, this simple estimation becomes more complicated at a qualitative level.

#### EXAMPLE E3.14

Oxygen with density  $\rho = 120 \text{ kg/m}^3$  under a pressure of 10 MPa is in a pressure vessel. Considering oxygen under such pressure to be a van der Waals gas, find its temperature  $T$  and compare it with analogous calculations in the framework of an ideal gas. The van der Waals constants are:  $(a) = 0.136 \text{ N m}^4/\text{mole}^2$ ,  $(b) = 3.17 \cdot 10^{-5} \text{ m}^3/\text{mole}$ .

**Solution:** Write the van der Waals equation for any amount of the substance  $\nu$

$$\left( p + \nu \frac{a}{V^2} \right) \left( \frac{V}{\nu} - b \right) = RT_{vdW}^*$$

Here  $T_{vdW}$  is the temperature of the van der Waals gas. Making some apparent transformation ( $v = m/M$ ,  $m = \rho V$  and  $v = \rho(V/M)$ ) and substituting them in equation \*, we obtain

$$\left(p + \rho^2 \frac{a}{M^2}\right) \left(\frac{M}{\rho} - b\right) = RT_{vdW}.$$

Therefore,

$$T_{vdW} = \left(\frac{1}{R}\right) \left(p + \rho^2 \frac{a}{M^2}\right) \left(\frac{M}{\rho} - b\right).$$

Executing the calculations, we arrive at

$$T_{vdW} = \frac{1}{8.31} \left(10^7 + \frac{(120)^2 \times 0.136}{(32 \times 10^{-3})^2}\right) \left(\frac{32 \times 10^{-3}}{120} - 3.17 \times 10^{-5}\right) = 337 \text{ K}.$$

Considering the oxygen in the pressure vessel as an ideal gas, we can obtain from the ideal gas equation

$$T_{id} = \frac{pV}{\frac{m}{M}R} = \frac{MP}{\rho R}.$$

Thus,

$$T_{id} = \frac{32 \times 10^{-3} \times 10^7}{120 \times 8.31} = 321 \text{ K}.$$

Although the difference in temperatures is not so high (16 K), it can, nevertheless, be significant at precise experiments.

### 3.6.3 A Joule–Thomson effect

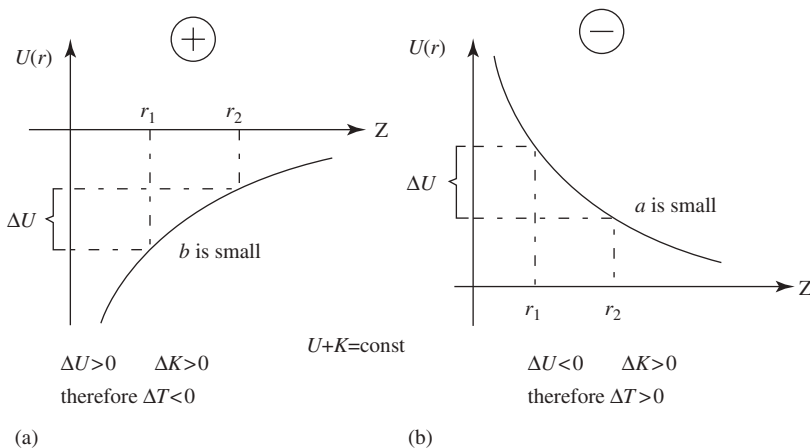
The potential energy of molecules interaction  $U$  depends on the average distance between molecules for the van der Waals gas and, consequently, it changes with the change in the volume occupied by gas. When there is no exchange of energy between the gas and its environment, the internal energy of gas should remain constant. Hence, if one part of the energy changes, there should be a respective alteration in the other part:  $dU = -dK$ . If we take into account only a molecule's attraction at the gas's expansion, its potential energy grows since the average distance between molecules increases. The increase in potential energy under these conditions causes reduction of the gas's average kinetic energy and, consequently, reduction of its absolute temperature. Therefore, if a real gas is allowed to extend adiabatically in vacuum (without producing any work against external forces) its temperature should go down. This phenomenon is called the *Joule–Thomson effect*. The

reduction in temperature at gas expansion is referred to as a positive Joule–Thomson effect. In some cases, heating of gas can occur and then the effect is referred to as being negative. For van der Waals gases the sign on the effect depends on which correction terms in the equation play the larger role.

The potential curves of molecule interaction are qualitatively presented in Figure 3.26.

Consider first the gas for which it is possible to neglect the first correction term in the equation with attraction forces between molecules. Then we should take into account only repulsion forces described by the second correction member  $b$  (Figure 3.26b). In this case, the average potential energy decreases with the increase in intermolecular distance. As with the reduction of pressure (expansion of gas in vacuum), the average distance between molecules is significantly enlarged; the average potential energy of the gas decreases. Reduction of the potential energy causes an increase in the gas's kinetic energy and, hence, leads to an increase in its temperature. Thus, gas in which one can neglect the action of the attraction forces, but in which the correction parameter  $b$  is essential, brings about gas heating at expansion—a negative Joule–Thomson effect occurs.

Now let us consider the gas for which forces of repulsion between molecules can be neglected. This case concerns a gas in which an inherent volume of molecules can be ignored (Figure 3.26a). We should then only account for attraction forces. Thus, the potential energy of molecule interaction is negative and its numerical value decreases with an increase in the intermolecular distance. Because with the reduction in the pressure of the gas the average distances between molecules increases, the change of its potential energy will be positive growing with the reduction of the gas pressure at its expansion in vacuum. Therefore, the average kinetic energy of the molecules of such a gas decreases and therefore its temperature goes down. Hence, in a gas in which attraction forces play an essential role and the coefficient  $b$  can be neglected, expansion brings about its cooling; the Joule–Thomson effect will be positive.

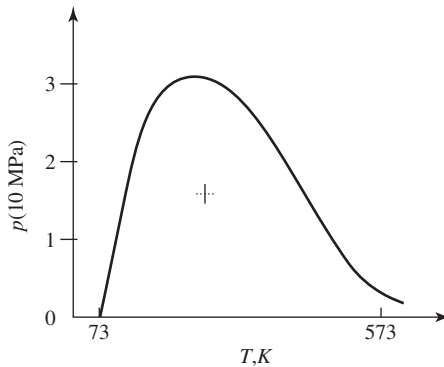


**Figure 3.26** (a) and (b) An explanation of the Joule–Thomson effect.

For any gas, the sign of the Joule–Thomson effect depends on temperature and pressure. The positive effect for each gas is observed only in the limited interval of temperatures and pressures. For each gas there are values of temperature and pressure at which the Joule–Thomson effect is equal to zero (no temperature changes occur at gas expansion in vacuum). These points  $(T_i, p_i)$  are called *points of inversion*. At these points, the influence of forces of attraction is completely compensated for by the influence of repulsion forces; consequently the gas temperature does not change. The set of inversion points forms an inversion curve in a  $p$ – $T$  diagram.

Figure 3.27 presents the inversion curve for nitrogen. It can be seen that, to a given value  $p$ , two points of inversion can occur. The curve of inversion outlines two points of inversion for which a positive Joule–Thomson effect is observed. Values for the upper and lower inversion points for some gases at various pressures are given in Table 3.2. For the majority of gases, the upper point of inversion lies above room temperature. Hydrogen and helium are an exception.

The Joule–Thomson effect finds important practical applications in the techniques of gas fluidization, when the gas is throttling over a wide range of pressures from  $2 \times 10^7$  to  $10^5$  Pa. Successive repetition results in reduction of the gas temperature down to its boiling point. If this procedure is applied to air, first oxygen gas is condensed (90 K) and then nitrogen (77 K). The boiling point of hydrogen is 20 K and helium 4.2 K. All these gases are widely used in various technical equipments, scientific explorations and in various crystallographic technologies.



**Figure 3.27** An inversion curve of the Joule–Thomson effect.

**Table 3.2**

Upper and lower temperature inversion points for some gases (in K)

Gas	$p$ (in $10^5$ Pa)	Upper	Lower
He	1	23.6	
H <sub>2</sub>	113	192.7	
Air	150	583	140
CO <sub>2</sub>	18–100	2050	249

### 3.7 ELEMENTS OF PHYSICAL KINETIC

#### 3.7.1 Introduction

In the previous sections we have considered ideal gases in a state of thermodynamic equilibrium. Such systems are stationary, i.e., their parameters do not change in time. In this section we shall consider macroscopic systems removed from an equilibrium state and aspiring to return to it. The area of physics that deals with this process is referred to as physical kinetics.

To describe quantitatively, such a process is possible only within the framework of the model of an ideal gas. The application of the results of this research to real gases and even to liquids can be provided on a qualitative or semiquantitative level. Although such analysis is carried out with such approximation, it can be usefully applied to nonideal systems.

In physical kinetics, there are two approaches to the study of physical phenomena: empirical phenomenological and microscopic at the molecular level. In the first of these, problems are investigated from a macroscopic point of view without considering the detailed atomic mechanism. In the second method the behavior of systems is investigated from microscopic standpoint on the basis of molecular representations. Both methods should yield the same results as the description of the same phenomena.

A system can be removed from a condition of thermodynamic equilibrium by external influence. For example, one can inject another gas into a certain point of the predominant gas and, due to thermal (chaotic) molecular movement the concentration of the second component will tend to spread over the whole volume. Sooner or later it will be equal. One can heat gas locally in one area of the volume and the gas temperature will also start to equalize over the whole volume due to molecular chaotic movement.

From the resulting examples it is clear that the thermal movement of molecules plays an active role in reaching equilibrium. We shall examine below the phenomena of alignment caused exclusively by this factor—chaotic movement of molecules, i.e., at a molecular level. This does not mean that there are no other mechanisms of alignment; however, we will avoid them at the moment.

#### 3.7.2 Transport processes: relaxation

Transport phenomena appear in different substances, mostly gases, because of chaotic molecular movement within them and permanent collisions with an interchange of their kinetic properties. During chaotic molecular movement and collisions, a transfer of energy and momentum and masses diffusion can take place and there is hence a gradual alignment. In this way a system can reach a state of equilibrium.

*The process of a system returning back to equilibrium is called relaxation.* Let us evaluate the speed of the relaxation process from a mathematical point of view. We shall suppose that the displacement rate ( $d\xi/dt$ ) of the return to equilibrium is proportional to the displacement itself  $\xi$  and is opposite to it in sign:  $(d\xi/dt) = -k\xi$ , where  $k$  is a coefficient of proportionality. Integration of this equation gives

$$\ln \xi(t) = -kt + \ln C \quad (3.7.1)$$

or,

$$\zeta(t) = C \exp(-kt). \quad (3.7.2)$$

Constant  $C$  can be found from the initial displacement. If at  $t = 0$  the maximum displacement  $\zeta_0$  is taking place  $C = \zeta_0$  and eq. (3.7.2) takes the final form:

$$\zeta(t) = \zeta_0 \exp(-kt). \quad (3.7.3)$$

The time  $\tau$  for which the displacement will decrease in  $e$  time is called the time of relaxation. This concept can be applied to a number of phenomena: radioactive fusion, damped oscillation, etc.

Let us find the physical sense of factor  $k$ . If we write eq. (3.7.3) for the time  $\tau$ , the displacement becomes:  $\zeta(\tau) = \zeta_0 \exp(-k\tau)$ . Therefore,  $(\zeta(\tau)/\zeta(0)) = \exp(-k\tau) = e^{-1}$ . Therefore,  $k\tau = 1$  or  $k = (1/\tau)$ . Hence,

$$\zeta(t) = \zeta_0 \exp\left(-\frac{\tau}{t}\right). \quad (3.7.4)$$

This equation is valid for many relaxation phenomena, not only for transport properties in gases.

We must emphasize that the transport phenomena can take place either in a closed system (where the system is removed from an equilibrium state and recovered coming back to it due to chaotic molecular movement), or in open stationary system where nonequilibrium can be induced permanently due to an external influence. In both cases, the relaxation consists of the redistribution of the uniformity over the whole system.

### 3.7.3 Transport phenomena in ideal gases

We define an ideal gas (see Section 3.1.3) as a gas whose molecules move from collision to collision without interaction. As a first rough approximation, we shall represent molecules as solid spheres with a certain diameter  $d$ . Enter an important characteristic of the gas, namely the free path length, i.e., the average distance  $\lambda$ , which a molecule moves freely from one collision to another. We can calculate the average time between molecule collisions as  $t = \lambda/v$ , where  $v$  is the average speed of the thermal movement of the molecules (to keep things simple in this section, we shall not write the sign on averages). The average number of collisions  $\nu$  of a molecule for 1 sec will be written as:

$$\nu = \frac{1}{t} = \frac{v}{\lambda}. \quad (3.7.5)$$

The shortest distance between the centers of the molecules on impact is referred to as the effective diameter of molecules  $d$  (see Section 1.5.4, Figure 1.34). During its

movement, a molecule (which we consider as a solid spheres) collides with those molecules whose centers lie at distances smaller than  $d$  from the line of its movement (Figure 3.28 inset). The value  $\sigma = \pi d^2$  is the target area in which the center of the molecule should lie in order to guarantee the collision. This area is called a *collision cross section*.

On collision, each molecule performs a zigzag path. If one rectifies the molecule's path one can assert that in the unit of time, the molecule describes the cylinder volume with a height equal to the speed of the molecule  $v$  and with a cross-section  $\pi d^2$ . The collision will take place with those molecules whose centers lie inside this cylinder. We shall consider that all molecules are at rest except those, which we follow up. Then the number of collisions in a unit of time  $v$  will make

$$v = \pi d^2 v n, \quad (3.7.6)$$

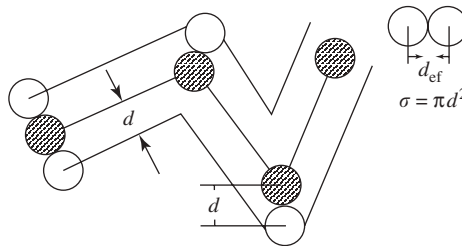
where  $n$  is the molecule concentration. Taking into account the movement of other molecules leads to an additional term  $\sqrt{2}$ . Then expression (3.6.6) will have the form:

$$v = \sqrt{2} \pi d^2 v n, \quad (3.7.7)$$

From comparison of eqs. (3.7.5) and (3.7.7) it can be deduced that

$$\lambda = \frac{1}{\sqrt{2} \sigma n} = \frac{1}{\sqrt{2} \pi d^2 n}. \quad (3.7.8)$$

Consider the relation of the free path length  $\lambda$  on the parameters of an ideal gas state. In an isothermal process  $p = nkT$  then  $\lambda \sim 1/p$ . So for nitrogen under normal conditions  $\lambda = 10^{-7}$  m, at pressure 1 Pa  $\lambda = 10^{-2}$  m, at pressure  $10^{-4}$  Pa a molecule on average runs a long distance without collision (about  $10^3$  m). If  $n = \text{const.}$ , (isochoric process)  $\lambda$  should



**Figure 3.28** A path traveled by a molecule.



not depend on temperature. However, practice shows that  $\lambda$  increases a little if the temperature rises; this dependence is described by empirical law:

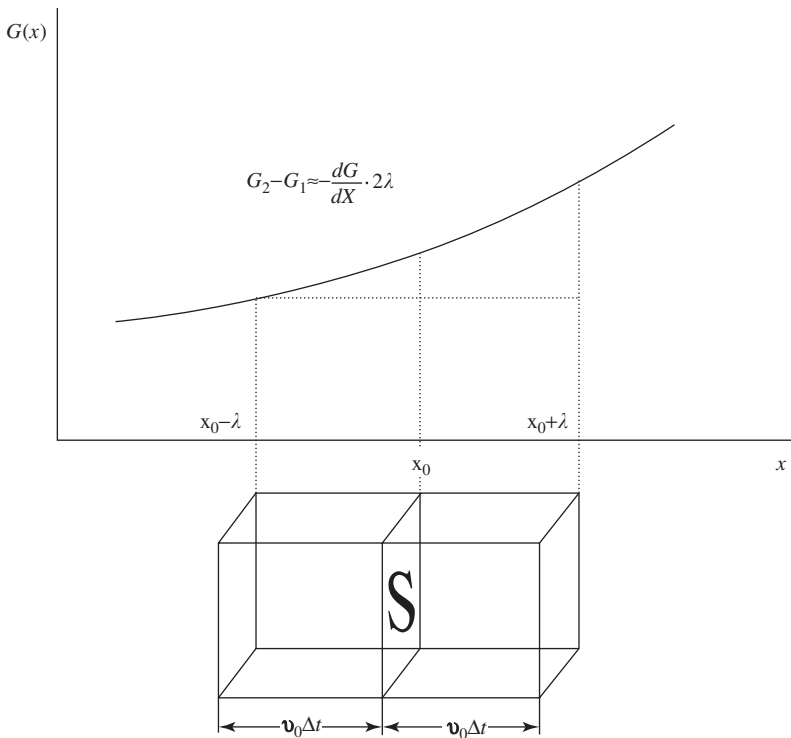
$$\lambda = \lambda_{\infty} \frac{T}{T+C} \quad (3.7.9)$$

where  $\lambda_{\infty}$  is the free path length at  $T \rightarrow \infty$ .

### 3.7.4 A macroscopic representation of a transport coefficient

Molecules in a closed volume can differ in their characteristics (mass, momentum, energy, etc.); assume that the spatial distribution of property values initially is nonuniform. Due to the thermal movement of the molecules and their collision, a process of restoration of uniformity in the volume can take place. We began a general analysis of these phenomena, then at particular processes: diffusion, heat conductivity and internal viscosity.

Denote  $G$  a transferable property and let it be distributed along an  $x$ -axis nonuniformly (Figure 3.29). We shall fix a point  $x_0$  on the  $x$ -axis and an area  $S$  normal to axis  $x$ . In time



**Figure 3.29** Macroscopic consideration of transport phenomena.

$\Delta t$ , due to thermal motion, a number of molecules will pass through this area from right to left and from left to right; both numbers being identical. However, each molecule will transfer that “quantity” of a property  $G$ , which corresponds to the last collision of the molecule. Due to nonuniformity of distribution  $G(x)$ , it will cause resulting transport  $G$  through the given area  $S$  which we shall designate  $\Delta q$ . We shall consider  $\Delta q > 0$  if the property  $G$  is transferred to the positive direction of the  $x$ -axis and vice versa. At the same time it is easy to understand that the sign  $\Delta q$  should be opposite to the sign on the gradient of the  $G$ -function, i.e., to the sign of derivative  $dG/dx$ . Thus, from the most general macroscopic consideration, it follows that

$$\Delta q \sim -\frac{dG(x)}{dx} S \Delta t.$$

Let us introduce a macroscopic (phenomenological) coefficient  $\alpha$ , which we denote as a transport coefficient. Then

$$\Delta q = -\alpha \frac{dG(x)}{dx} S \Delta t. \quad (3.7.10)$$

The expression  $(\Delta q/\Delta t)(1/S)$  is a flow of the  $G$  property.

Let us determine the microscopic meaning of coefficient  $\alpha$ . We will take two layers of the gas, parallel to the area  $S$  at distances  $\lambda$  from both sides of point  $x_0$ . Let  $G_1$  and  $G_2$  be the values of  $G$  in these layers. All molecules allocated in parallelepipeds (see Figure 3.29) and moving in the definite direction (to area  $S$ ) at a speed  $v$  and in time  $\Delta t$  will cross the area  $S$  in both directions. As the molecules move chaotically, the number of molecules moving in each side is 1/6 of their total number. Their number is equal, but they carry different amounts of property  $G$ . All molecules moving in a positive  $x$ -direction carry property  $G_1$  whereas in a negative direction they carry property  $G_2$ . The total transport of the  $G$ -value through the area  $S$  is

$$\frac{\Delta q}{\Delta t} \frac{1}{S} = \frac{1}{6} n v (G_1 - G_2). \quad (3.7.11)$$

Assuming that the gradient of the  $G$ -value is small, we can write  $(G_1 - G_2) = -(dG/dx)2\lambda$ . Hence,

$$\frac{\Delta q}{\Delta t} \frac{1}{S} = -\frac{1}{3} \frac{dG}{dx} n v \lambda. \quad (3.7.12)$$

Comparing eqs. (3.7.10) and (3.7.12) we arrive at

$$\alpha = \frac{1}{3} v \lambda n. \quad (3.7.13)$$

The significance of this coefficient consists of the fact that it connects the macroscopic (technical) value  $\alpha$  with microscopic one ( $\lambda$  and  $v$ ). Notice that this result is obtained from the comparison of macroscopic (phenomenological) and microscopic approaches.

### 3.7.5 Diffusion in gases

Imagine a gas in which a certain constant difference of concentration exists in the various fixed points (a nonequilibrium, but stationary system), whereas the temperature at any point in this system is the same and remains constant. Thus, there is a resulting flux of gas molecules referred to as stationary diffusion. We would like to emphasize that this flux is caused only by the chaotic movement of molecules and not for any other reasons. Another situation arises when the difference of concentration is not constant; the system aspires to equalize concentration; this will be nonstationary diffusion.

In any case, the driving force of molecular diffusion is the concentration gradient. We shall restrict ourselves to self-diffusion, i.e., diffusion of similar molecules distinguished by any insignificant (for diffusion) property (e.g., labeled by radioactive mark) in the environment of the same nonradioactive molecules. In fact, the diffusion of carbon oxide in nitrogen can be considered as self-diffusion because the molecules of these gases differ insignificantly with regard to their size and mass.

Our task is to find a relationship between the macroscopic and microscopic characteristics of diffusion. We shall consider a simple one-dimensional case: imagine a vessel in the form of a long thin cylinder (an  $x$ -axis is directed along one axis of the cylinder) containing a mixture of two gases; the concentration gradient of one of the gases is artificially maintained constant. Assume that the masses and the sizes of the molecules of both gases are identical: ( $m_1 = m_2 = m$ ). Therefore, the molecules can acquire identical average speed  $u$ ; free path length can be taken as equal to  $1/(\sqrt{2}\sigma n)$ , where  $n = n_1 + n_2$  is the total average concentration of molecules in the volume. A comparison of what we obtained from a macroscopic consideration and that of microscopic one looks like

$$j = \frac{\Delta q}{S \Delta t} = -D \frac{\Delta G}{\Delta x}, \quad (3.7.14)$$

where  $j$  is the mass diffusion flux and  $\alpha \equiv D$  is the *diffusion coefficient*. In this form, this equation is referred to as Fick's law. The transport value  $G(x)$  in this case is the relative concentration of the chosen molecules  $n_1$ , that is  $G(x) = (n_1(x))/n$ . Comparison with the eq. (3.7.13) shows that

$$j = \frac{\Delta q}{S \Delta t} = -\left(\frac{1}{3}\right)nv\lambda \frac{\Delta n_1(x)}{n}. \quad (3.7.15)$$

By comparing eqs. (3.7.13) and (3.7.14), we can further derive the microscopic expression for the macroscopic diffusion coefficient  $D$ :

$$D = \left(\frac{1}{3}\right)v\lambda. \tag{3.7.16}$$

It follows from this expression that the physical sense of the diffusion coefficient  $D$  consists of the fact that it shows the number of molecules that diffuse through a unit area in a unit time and at a unit gradient of relative concentration. Data on key parameters of diffusion as well as other transport phenomena, i.e., of heat conductivity and viscosity, are shown in Table 3.3.

If molecules differ considerably in their masses and the dimensions mentioned above, the calculations demand specification. More detailed examination shows that the process of diffusion is determined by the speed of the fastest (smallest) molecules, whereas for effective cross section determination, it is the larger molecules.

For the nonstationary diffusion, it is possible to estimate the time  $t$  for which there is an alignment of concentration (reduced in  $e$  times) from a dimension consideration. In fact,  $\tau$  is defined only by the character of distribution of molecular masses in the initial instant of time and gas property. The initial state is defined by the dimension of heterogeneity area  $L$ . There is only one combination from  $D$  and  $L$  that has a dimension of time, namely

**Table 3.3**

Transport phenomena characteristics

Phenomenon	Diffusion	Heat conductivity	Internal friction
Main laws	$\frac{\Delta q}{S \Delta t} = -D \frac{dc(x)}{dx}$	$\frac{\Delta q}{S \Delta t} = -\kappa \frac{dT(x)}{dx}$	$\frac{\Delta q}{S \Delta t} = -\eta \frac{du(x)}{dx}$
Transferred value	Fick's law Mass	Fourier's law Energy	Newton's law Momentum
Driving force	$\frac{dc(x)}{dx} = \frac{dn_1(x)}{dx}$ Concentration gradient	$\frac{dT(x)}{dx}$ Temperature gradient	$\frac{du(x)}{dx}$ Velocity gradient
Transfer coefficients	$D = \frac{1}{3} v\lambda$	$\kappa = \frac{1}{3} \rho v\lambda (C_v)_{sp}$	$\eta = \frac{1}{3} \rho v\lambda$  $v = \frac{\eta}{\rho} = \frac{1}{3} v\lambda$
Coefficient's value			
Units	m <sup>2</sup> /sec	W/(m×K)	N sec/m <sup>2</sup> * m <sup>2</sup> /sec**
Gases	10 <sup>-4</sup> ÷ 10 <sup>-6</sup>	10 <sup>-4</sup> ÷ 10 <sup>-5</sup>	10 <sup>-3</sup> ÷ 10 <sup>-5</sup>
Liquids	10 <sup>-9</sup> ÷ 10 <sup>-10</sup>		~10 <sup>-2</sup>
Resin, glass		100	~10 <sup>-6</sup>
Crystals	10 <sup>-16</sup> ÷ 10 <sup>-18</sup>	10 <sup>2</sup>	~10 <sup>-15</sup>

Non-SI units: \*Poise (P) = 0.1(N sec/m<sup>2</sup>); \*\*Stokes (St) = 10<sup>-4</sup>(m<sup>2</sup>/sec).

$\tau \sim L^2/D$ . The time  $\tau$  in gases can be estimated under the order of value: at  $D \sim 10^{-4} \text{ m}^2/\text{sec}$  and  $L \sim 0.1 \text{ m}$ , the order of  $\tau$  value is  $10^3 \text{ sec}$ , i.e., diffusion is a slow process even in gases and in liquids it is slower by some orders.

### 3.7.6 Heat transfer

If, at different points of any gas in a closed volume for a short time, a different temperature is created and the gas is then left to itself, the temperature at all gas points is equalized owing to the process of heat transfer. From a macroscopic point of view, the phenomenon of heat transfer in gases consists of temperature transport from hotter to colder places. Within the framework of the molecular kinetic theory, the process of heat transfer consists of the fact that molecules from a heated site of the gas, where they have large kinetic energy, transfer the energy to cooler areas via collisions; a flow of heat is thus created.

In reality, in gases and liquids this phenomenon is usually accompanied by heat transport by the steam of a gas or a liquid initiated by their density difference, i.e., so-called convection. However, we will now consider heat transfer exclusively from the point of view of molecular kinetics. By the way, it is very difficult to subdivide these two processes.

The transfer of heat caused by the thermal (chaotic) movement of microparticles is referred to as a *heat transfer* phenomenon. Thus, in the general transport formula (3.7.10),  $\Delta q$  is the flux of heat. The transferable value in this case is the amount of heat  $Q$  or  $G(x) = C_V T(x)$  where  $C_V$  is the heat capacity of a substance. This heat is produced by the total kinetic energy of the molecules. Hence the heat transport description can be given as:

$$\frac{dq}{dt} \cdot \frac{1}{S} = -\kappa \frac{dT(x)}{dx}, \quad (3.7.17)$$

where  $\kappa$  is the heat transfer coefficient. In this form, this equation is referred to as Fourier's law. The minus sign shows that the heat transfer is directed against the temperature increase (against the temperature gradient).

From a microscopic point of view, the driving force is the molecular averaged kinetic energy gradient:  $d\langle \varepsilon \rangle / dx$ . Taking into account that  $\langle \varepsilon \rangle = (i/2)\kappa T$ , we obtain:

$$\frac{d\langle \varepsilon \rangle}{dx} = \frac{i}{2}\kappa \frac{dT}{dx} = \frac{i}{2}\kappa \frac{dT}{dx} \frac{N_A}{N_A} = \frac{iRm}{2N_A m} \frac{dT}{dx} = (C_V)_{\text{sp}} m \frac{dT}{dx}. \quad (3.7.18)$$

where sp index specify the specific heat capacity.

From the other side a value of the particle's flux is equal to  $(dq/dt) \times (1/S) = -(1/3)nv\lambda (d\langle \varepsilon \rangle) / (dx)$ . Substituting here the value  $d\langle \varepsilon \rangle / (dx)$  from eq. (3.7.18), we obtain:  $(dq/dt) (1/S) = -(1/3)(C_V)_{\text{sp}} mnv\lambda (dT) / (dx)$ . From this equation the heat transfer coefficient  $\kappa$  is derived

$$\kappa = \frac{1}{3} \rho v \lambda (C_V)_{\text{sp}}, \quad (3.7.19)$$

where  $\rho = mn$  is the density of the substance. The physical meaning of the factor of heat transfer consists of the fact that it defines the amount of heat transferred in a unit of time through a unit of perpendicular area  $S_{\perp}$  and at a unit of temperature gradient.

Analyzing expression (3.7.19), we can see that the heat transfer coefficient depends on the structure of the gas's molecules (as  $\kappa$  depends on the molecules' number of degrees of freedom). In isothermal processes,  $\kappa$  does not depend on gas concentration and pressure ( $\rho \sim n$  and  $\lambda \sim 1/n$ ). In the isochoric process  $\kappa$  depends on temperature as  $\sqrt{T}$ .

The independence of  $\kappa$  on pressure seems strange at first sight: in fact it is well known that for manufacturing high quality Dewar vessels (thermoses), the presence of air in the space between the walls reduces the quality of the vessel (outflow of heat): the less pressure between the walls of the vessel, the higher the Dewar quality.

However, the result obtained seems to contradict this statement. In fact, there are no contradictions in the result, there is incorrectness in its interpretation: at low pressure when  $\lambda$  becomes commensurable with the space between the walls, dependence of  $\lambda$  on  $(1/n)$  disappears and  $\kappa$  becomes independent on  $n$  (and on  $p$ ) as will be shown in Section 3.7.8.

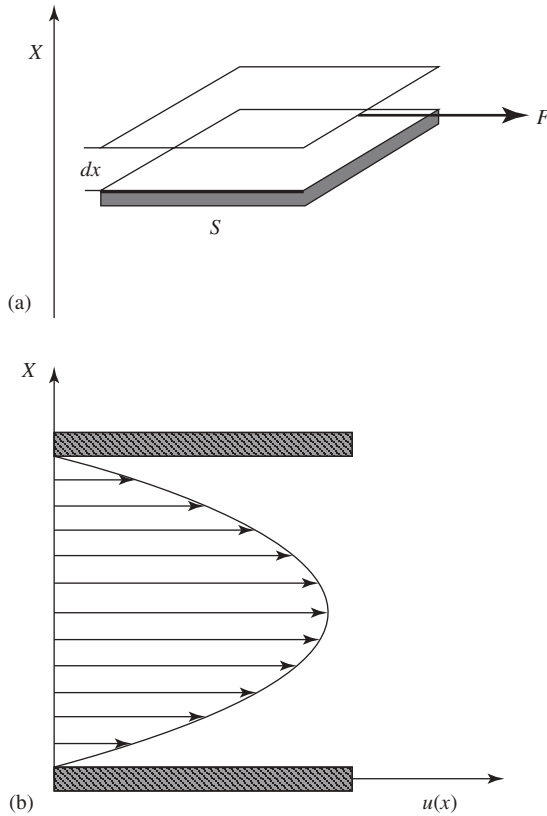
### 3.7.7 Viscosity or internal friction

Viscosity is a property of gases, liquids and solids to resist a flow under the action of external forces. We shall consider in more detail the viscosity of gases. In Figure 3.30, the laminar flow of gas or a liquid is schematically shown; the division of the overall flow into layers is also shown. Due to viscosity, the speed of movement of various gas layers is different: because of its interaction with the unmovable wall's border, the edge layer is zero and due to the external pressure increases to a central line.

The microscopic description of internal viscosity of gases is based on the fact that all molecules in the limit of its layer participate in the macroscopic motion with the momentum, where  $u$  is the macroscopic velocity of a molecule with the layer. However, owing to their chaotic movement, molecules jumping over one layer to another transfer the macroscopic momentum  $mu$ . Such jumping can influence the macroscopic speed of layers: molecules from faster layers accelerate slower layers and vice-versa. It looks like one layer renders a friction on its neighbor. Thus, viscosity in gases is the phenomenon of the chaotic momentum transfer of the macroscopic movement from layer to layer in a flowing gas.

Consider now the law to which the phenomenon of viscosity submits. For this purpose, we shall consider the behavior of a gas between two flat parallel plates (Figure 3.30b). Let one of the layer be resting and the other moves with a constant speed  $u$  parallel to the plane of the plates. If there is a viscous medium between the plates in order to move this plate with constant speed  $u$ , it is necessary to apply some constant force (directed along the speed) since the medium will exhibit resistance to such movement. Accordingly there appear tangent forces between the separate layers in the medium. Experience shows that this force  $F$  is proportional to the speed of plate  $u$  and to the area of plates  $S$  and is inversely proportional to the distance between the plates  $\Delta x$ . In a limit at  $\Delta x \rightarrow 0$

$$F = -\eta \left( \frac{du}{dx} \right) S, \quad (3.7.20)$$



**Figure 3.30** The viscous flow: (a) streamline motion of gases and liquids at a laminar flow, (b) friction between adjacent layers: the Newton's law of internal friction.

i.e., force  $F$ , which needs to be applied to move the two layers of gas over each other, is proportional to the area of contact of layers  $S$  and to the gradient of relative speed ( $du/dx$ ) perpendicular to the moving layers. This is Newton's law of internal friction,  $\eta$  is the coefficient of dynamic viscosity of the media in which the movement takes place. To clarify its physical meaning, we shall increase the left- and right-hand parts of eq. (3.7.20) by  $\Delta t$ . In this case, we have  $F\Delta t = -\eta(du/dx)S\Delta t$ . On the left-hand side we substitute  $F\Delta t$ , which is equal to  $\Delta p$  (eq. 1.3.12), i.e.,

$$\Delta p = -\eta \left( \frac{du}{dx} \right) S \Delta t, \tag{3.7.21}$$

where  $\Delta p$  is the change in momentum of a flux element due to the change in the speed of movement. The coefficient of dynamic viscosity  $\eta$  is numerically equal to the momentum of macroscopic movement, which is transferred in a time unit between adjacent layers of flux at a speed gradient along the  $x$ -direction equal to unity. In the phenomena of viscosity,

the transferred quantity is the momentum of the macroscopic movement of the molecules' layer  $G(x) = mu(x)$ . Substituting this value in eq. (3.7.10) we obtain:

$$\frac{\Delta q}{S \Delta t} = \frac{1}{3} n v \lambda m \frac{du(x)}{dx}, \quad (3.7.22)$$

therefore,

$$\eta = \left(\frac{1}{3}\right) \rho v \lambda. \quad (3.7.23)$$

For dynamic viscosity in SI units, the coefficient of viscosity of that media is that at a speed gradient equal to unity through area  $S$  in  $1 \text{ m}^2$ , the total molecule momentum  $1 \text{ N sec/m}^2 = \text{kg m/sec}$  is transferred.

Thus the unit of viscosity in SI units is  $\text{N sec/m}^2 = \text{kg/(m sec)}$ . Another widely used unit of viscosity is  $\text{g/(cm.sec)}$  (poiseuille or poise (P)) (in honor of J.L.M. Poiseuille). In tables, viscosity is usually expressed in centipoise (cP). The ratio between units is  $1 \text{ kg/(m sec)} = 10 \text{ P}$ .

Besides the coefficient of the dynamic viscosity  $\eta$ , the coefficient of the kinematical viscosity  $\nu$  is used in technology; there is a relation between the two coefficients: the kinematical coefficient is the ratio of the dynamic viscosity to the medium density  $\nu = \eta/\rho$ . The coefficient of the kinematical viscosity is measured in stokes (St):  $1 \text{ St} = 1 \text{ cm}^2/\text{sec}$ . In SI the unit of kinematical viscosity is  $\text{m}^2/\text{sec}$  ( $1 \text{ m}^2/\text{sec} = 10^4 \text{ Ct}$ ). Some viscosity factors are given in Table 3.3.

### EXAMPLE E3.15

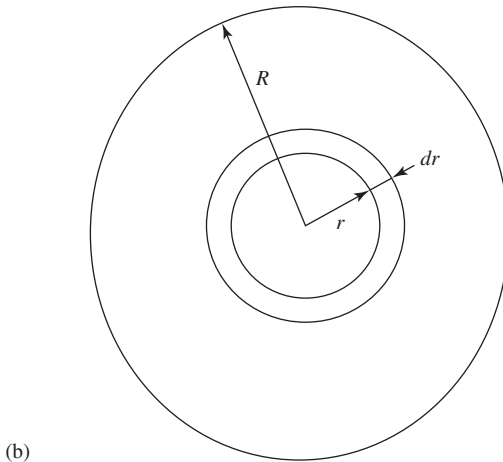
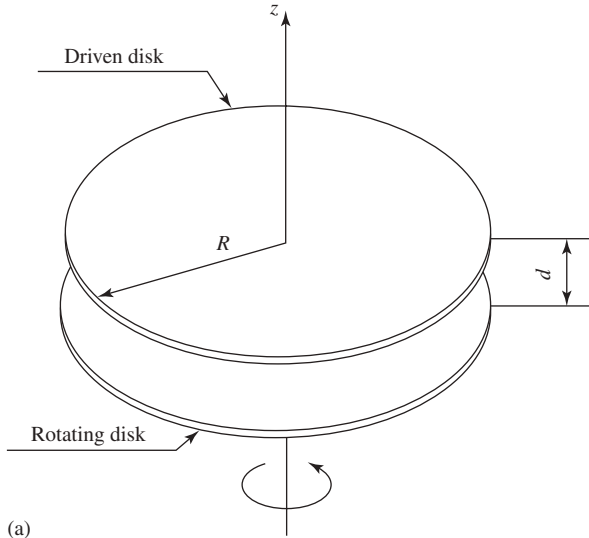
A free path flight  $\lambda$  of  $\text{CO}_2$  gas at normal conditions is  $\lambda = 40 \text{ nm}$ . Determine the molecule's average speed  $\langle v \rangle$  and the number of impacts  $z$  a molecule undergoes in 1 sec.

**Solution:** The average molecule speed can be found according to expression (3.3.7'). Substituting the known and given values we obtain  $\langle v \rangle = 362 \text{ m/sec}$ . The average number of impacts can be found according to equation  $z = v/\lambda$  (the averaging sign is omitted here). Substituting the given values in this equation, we arrive at  $z = 9.05 \times 10^9 \text{ sec}^{-1}$ .

### EXAMPLE E3.16

Two horizontal disks with identical radii  $R = 20 \text{ cm}$  settle one over another so that their  $z$ -axes coincide. The distance between the disks is  $d = 0.5 \text{ cm}$ . The lower disk rotates around the common axis (refer to Figures E3.16a and b) with frequency  $n = 10 \text{ cm}^{-1}$ , but the upper disk is kept motionless. Find the torque  $M$  working on the upper disk. Both disks are in air, the coefficient of the dynamical viscosity of air being  $\eta = 17.2 \mu\text{Pa sec}$ .





**Solution:** Due to the viscosity of the air that is between the disks, the rotational moment of forces is transferred from the bottom to the upper disk. Together with rotation of the bottom disk, the adjoining air layer comes in movement. In order to find the moment of friction forces working on the upper disk, we shall allocate an elementary thin layer of air with thickness  $dr$ . The bottom air layer rotates together with the bottom disk with angular velocity  $\omega$ . Accordingly, the linear speed of air particles is  $u = \omega r$ . We shall take advantage of Newton's law of external friction (see Section 3.6.4, eq. (3.7.20) and Figure 3.30) and make some simplifications (proceeding from a condition of the problem). We shall take the velocity gradient to be equal to  $(du/dz) \approx (\Delta u/d) = (u/d)$  (since  $u_2$  is equal to 0). We shall express the force of viscous friction by an elementary tangent force  $dF$  and the small area

of air layer touching as  $dS = 2\pi r dr$ . Accordingly, Newton's law for our particular problem will be

$$dF = \eta \frac{u}{d} 2\pi r dr.$$

We can find the elementary moment of friction forces relative to the z-axis working on the part of the allocated air layer having increased a tangent force  $dF$  on a shoulder  $r$ , i.e.,

$$dM = dF \times r = 4\pi^2 \eta \left(\frac{n}{d}\right) r^3 dr.$$

To find the total force moment, we have to integrate  $dM$  over the whole disk area, i.e., find the overall contributions from all elementary layers  $dr$ , that is to integrate the elementary force moment upon the radius in the limits from 0 to  $R$ . We obtain

$$M = 4\pi^2 \eta \left(\frac{n}{d}\right) \int_0^R r^3 dr = 4\pi^2 \eta \frac{n}{d} \frac{R^4}{4} = \pi \eta n \frac{R^4}{d}.$$

Checking the dimension of the result, we obtain  $\text{mN m}$ , which corresponds to the torque dimension. Let us express all values in SI units and execute calculations:

$$M_F = 3.14^2 \times 1.72 \times 10^{-5} (0.2)^4 / 5 \times 10^{-3} \text{ mN m} = 0.543 \text{ mN m (milli-Newton} \times \text{m)}.$$

### EXAMPLE E3.17

Define how many times the coefficient of diffusion of gaseous hydrogen differs from that of gaseous oxygen; both gases are under identical conditions. The effective diameters of the hydrogen and oxygen molecules are 0.27 and 0.36 nm, respectively; the molar masses  $M$  of oxygen and hydrogen molecules are 16 and 1, respectively.

**Solution:** The coefficient of diffusion  $D$  is expressed through physical characteristics of molecules by the formula (3.7.16):  $D = (1/3)\langle v \rangle \lambda$ , where  $\langle v \rangle$  is the average molecules speed (3.3.7') and  $\lambda$  the mean free path. Therefore, we can write the diffusion coefficients for oxygen and hydrogen (to an order of  $1/3$ ):

$$D_1 = \frac{1}{3} \sqrt{\frac{8RT}{\pi M_1}} \frac{1}{\sqrt{2}\pi d_1^2 n} \text{ and } D_2 = \frac{1}{3} \sqrt{\frac{8RT}{\pi M_2}} \frac{1}{\sqrt{2}\pi d_2^2 n}.$$

In the equations, we took into account that the conditions ( $n$  and  $T$ ) of both molecules are identical. Therefore the ratio of coefficients is as follows:

$$\frac{D_1}{D_2} = \sqrt{\frac{M_2}{M_1}} \left(\frac{d_2}{d_1}\right)^2.$$

Substituting the given values we arrive at:

$$\frac{D_1}{D_2} = \sqrt{\frac{32}{2} \left( \frac{0.36}{0.27} \right)^2} = 7.11$$

### 3.7.8 A transport phenomena in a vacuum condition

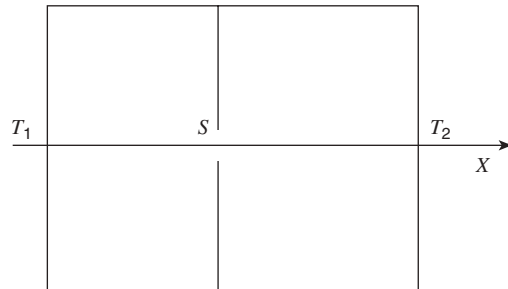
If the free path length of the gas molecules becomes commensurate (or more) with the linear size of the vessel, the condition of the gas is referred to as a *vacuum*. This means that the process of intermolecular collisions, which usually plays a predominant role in establishing a balance is no longer of any importance; the interaction between the molecules and the vessel's walls is more important in a vacuum. During its last collision with the surface of a hot wall, a molecule acquires additional kinetic energy and carries it, without sharing it with other molecules, to the surface of another wall to heat it. This kind of heat transfer is characterized by an absence of temperature gradient inside the gas (as molecules move the whole distance at the same speed); all occasions we have discussed so far have vanished.

In order to estimate heat transfer in a vacuum, we shall consider a simple experiment. Imagine a chamber divided in two by a partition wall with a hole of area  $S$  in this dividing wall (Figure 3.31). The temperature of the left wall is  $T_1$  and of the right is  $T_2$ .

Let  $T_1 > T_2$ . On impact with wall 1 a molecule obtains energy  $i\kappa T_1/2$ . Moving toward wall 2 along an axis  $x$  and reaching it the molecule gives the acquired energy to wall 2. The amount of energy will make:

$$\Delta q = \left( \frac{1}{6} \right) n v \left( \frac{i}{2} \right) \kappa (T_1 - T_2) S. \quad (3.7.24)$$

As the factor similar to the heat transfer coefficient  $\kappa$  in the given expression appears as  $(1/6)nv(i/2)$ ; it is proportional to concentration (and hence to pressure, contrary to what we obtained earlier in Section 3.7.6). This can be expected as this fact is well-known



**Figure 3.31** A scheme of vacuum experiments. Effusion.

from human experience. In fact, the quality of Dewar vessels (thermoses) depends significantly on the gas concentration between walls (residual molecule concentration): the less molecule concentration, the better the thermal protection. Notice that this phenomenon starts to operate only when  $\lambda$  becomes commensurate (or more) with the distance between the walls. At a distance of 1 cm, the pressure should be no higher than 0.10 Pa. A further reduction in pressure reduces the heat transfer between the walls under the linear law.

This distinction from the usual transport phenomena is not the only one for rarefied gases. The flow of molecules at outflow differs significantly too (it is referred to as Knudsen's flow.) Viscosity or internal friction in high vacuum is absent as there is no collision of molecules. In spite of the fact that pressure does not influence the individual molecular movement, it does influence the current.

Let us consider a gas outflow through an aperture under these conditions; i.e., molecular effusion (effusion is the slow outflow of gases through small apertures.) We shall restrict ourselves to the case of isothermal effusion. Refer to the scheme presented in Figure 3.31: two vessels where gas is at different pressures  $p_1$  and  $p_2$ . The effusion flow will take place through the aperture. If  $p_1 > p_2$ , the resulting flow will be directed from left to right. In the time unit the number of molecules crossing from left to right can be estimated as  $N_1 = n_1 v S / 6$ . The opposite stream is less as concentration is less:  $N_2 = n_2 v S / 6$ . Hence, the resulting stream is

$$\Delta N = N_1 - N_2 = \frac{vS(n_1 - n_2)}{6} = \left( \frac{1}{6\kappa T} \right) \sqrt{\frac{8\kappa T}{\pi m}} S \Delta p = \left( \frac{1}{3} \right) \sqrt{\frac{2}{\pi \kappa T m}} S \Delta p. \quad (3.7.25)$$

One can see from this equation that effusion depends on molecular mass. This circumstance is used for separation of gas isotope mixes. At transmission of a gas mix stream through a porous partition with fine pores, there is an enrichment of the mixture by molecules to lighter isotope. Repeating the process results in a mixture enriched mainly by a definite isotope.

With different temperatures in both chambers, the ratio of concentrations  $n_1/n_2$  will be other than at normal pressure. In fact, in normal conditions, it follows from the formula  $p = n\kappa T$  that  $n_1/n_2 = T_2/T_1$ . Another ratio is observed in vacuum. Equating the number of particles moving in the time unit in two sides, we can obtain:  $N_1 = N_2 = n_1 v_1 S = n_2 v_2 S$  and finally arrive at the ratio  $(n_1/n_2) = (v_2/v_1) = (\sqrt{T_2}/\sqrt{T_1})$ , which differs from normal conditions.

Notice that the laws marked in this section are relevant only to ideal gases. For gases that cannot be considered as ideal, or for liquids, the laws obtained should be used carefully.

The method of measuring small pressures is based on the effusion phenomenon ( $10^{-4}$ – $10^{-5}$  Hg mm or 0.1–0.01 Pa), if the diameter of the aperture is small in comparison with the free path length. Otherwise, the gas outflow in the unit time occurs under the laws of hydrodynamics; the gas volume that is penetrated in the time unit is  $\sim(1/\sqrt{\rho})$ , where  $\rho$  is the gas density. This allows one to determine the density of gases measuring time of outflow through small (0.1–0.01 mm) apertures.

### PROBLEMS/TASKS

- 3.1. How many atoms contain in 1 g weight each of gases (1) helium, (2) carbon, (3) fluorine, (4) polonium?
- 3.2. The cylinder contains gas at temperature  $t_1 = 100^\circ$ . To what temperature  $t_2$ , is it necessary to heat gas so that its pressure  $p$  has increased twice?
- 3.3. Assume that dry air consists only of oxygen and nitrogen. In this approximation air mass fractions of both gases are  $w_1=0.232$  and  $w_2=0.768$ , respectively. Define the relative molar weight  $M_r$  of air  $M(\text{air})_r=M/k$  ( $M$  is air molar weight;  $k=10^{-3}$  kg/mol).
- 3.4. A centrifuge rotor with a radius  $a = 0.2$  m is filled with atomic chlorine at  $T = 3000$  K. The chlorine consists of two isotopes  $^{37}\text{Cl}$  and  $^{35}\text{Cl}$ . The share of isotope  $^{37}\text{Cl}$  atoms make is  $w_1 = 0.25$ . Determine shares  $w_1'$  and  $w_2'$  of atoms of both isotopes near the centrifuge's rotor if it is rotated at an angular speed of  $\omega = 10^4$  rad/sec.
- 3.5. Knowing the Maxwell distribution of a molecule's speed (3.3.6) derive function  $f(u)$  where  $u$  is the molecule's relative speed  $u=(v/v_{\text{prob}})$ , i.e., expressed in dimensionless units. Apply this distribution to find that the particular molecule has the probability  $w$  of having a speed that differs from half the most probable speed  $v_{\text{prob}}/2$  by not more than 1%.
- 3.6. Determine the relative number  $\Delta N/N$  of ideal gas molecules that have a speed in the limits from zero to 0.1 of the most probable speed  $v_{\text{prob}}$
- 3.7. Find the relative number of ideal gas molecules whose kinetic energy  $\varepsilon$  differs from the average energy  $\langle \varepsilon \rangle$  by not more than 1%.
- 3.8. How many times will the maximum of the  $f(\varepsilon)$  function change if the gas temperature  $T$  increases two times? Illustrate the result graphically.
- 3.9. Find a number of all collisions  $N$  per  $t = 1$  sec between all hydrogen atoms in a volume of  $V = 1$  mm<sup>3</sup> at normal conditions.
- 3.10. Find the average time  $\langle \tau \rangle$  of the free path flight of oxygen molecules at  $T = 250$  K and pressure  $p = 100$  Pa.
- 3.11. Calculate the diffusion coefficient of an ideal gas at (1) normal conditions, (2)  $p = 100$  Pa and temperature  $T = 300$  K.
- 3.12. Calculate the dynamic viscosity coefficient  $\eta$  of oxygen at normal conditions.
- 3.13. Oxygen of mass  $m = 160$  g was heated for  $\Delta T = 12$  K, and expended an amount of heat  $Q = 1.76$  kJ. By which process did the heating take place: at constant  $V$  or at constant  $p$ ?
- 3.14. Water vapor is expanded at constant pressure  $p$ . Find the work of expansion  $A$ , if the amount of heat consumed is  $Q = 4$  kJ.
- 3.15. Nitrogen is heated at constant pressure by an amount of heat  $Q = 21$  kJ. Determine the gas work  $A$  and the change of its internal energy  $\Delta U$ .
- 3.16. An ideal gas performs a Carnot cycle. The cooler temperature  $T_2$  is 290 K. By how much is the cycle efficiency  $e$  increased if the heater temperature increases from  $T'_1 = 400$  K to  $T'_2 = 600$  K?
- 3.17. An ideal gas performs a Carnot cycle. The work of isothermal expansion of gas is  $A_1 = 5$  J. Define the work  $A_2$  of isothermal compression if thermal efficiency  $e$  is 0.2.

- 3.18. As a result of isochoric heating of hydrogen in weight  $m = 1$  d, the gas pressure increased by two times. Determine the change of gas entropy  $\Delta S$ .
- 3.19. A piece of ice  $m = 200$  g in weight taken at  $t_1 = -10^\circ\text{C}$  is heated to  $t_2 = 0^\circ\text{C}$  and fused; the water formed is heated to  $t = 10^\circ\text{C}$ . Define the entropy change at these processes.
- 3.20. Water in weight  $m = 36$  g is at boiling temperature at normal atmospheric pressure. Determine change  $\Delta U$  of the internal energy at its full evaporation. Specific heat of evaporation is  $L = 2.26$  J/kg. Ignore the volume of liquid water.
- 3.21. A gas mixture contains  $\nu_1 = 2$  mole of helium and  $\nu_2 = 3$  mole hydrogen. Determine the specific heat capacity  $C_{p,sp}$  of the mixture.  $M_1 = 4 \times 10^{-3}$  kg/mol and  $M_2 = 2 \times 10^{-3}$  kg/mol.
- 3.22. Determine the adiabatic index  $\gamma$  of partly dissociated nitrogen gas if its dissociation ratio is  $\alpha = 0.2$ .
- 3.23. A mixture of gases consists of argon of mass  $m_1 = 8$  g and nitrogen of mass  $m_2 = 4$  g. Determine the specific heat capacity  $C_{V,sp}$  of the mixture. ( $M_1 = 40 \times 10^{-3}$  kg/mole,  $M_2 = 28 \times 10^{-3}$  kg/mol).
- 3.24. Determine the dissociation rate  $\alpha$  of oxygen gas if its specific heat capacity is  $C_{V,sp} = 727$  J/(kg K). ( $M_{\text{oxg}} = 32 \times 10^{-3}$  kg/mol).
- 3.25. A gas mixture consists of equal masses of neon and oxygen. Determine the specific heat capacity of this mixture. ( $M_1 = 20 \times 10^{-3}$  kg/mol—neon,  $M_2 = 32 \times 10^{-3}$  kg/mol—oxygen).
- 3.26. A gas mixture consists of an equal number of moles of argon and oxygen. Determine the adiabatic index  $\gamma$ .
- 3.27. A gas mixture of helium and hydrogen are at equal conditions. Find the adiabatic index  $\gamma$  of the mixture consisting of  $V_1 = 4$  L of helium and  $V_2 = 3$  L of hydrogen.
- 3.28. Equal volumes of gas neon and oxygen are at equal conditions. Determine the specific heat capacity  $C_{pp}$  of the mixture. ( $M_1 = 20 \times 10^{-3}$  kg/mol,  $M_2 = 32 \times 10^{-3}$  kg/mol).
- 3.29. Determine the dissociation rate  $\alpha$  of the partly dissociated chlorine gas if the adiabatic index is  $\gamma = (C_p/C_V) = 1.48$ .
- 3.30. Identical particles of dust of mass  $m = 4 \times 10^{-19}$  g are in air as a suspension. The temperature of the air is  $T = 284$  K. Define the relative change of concentration ( $|\Delta n/n_o$ ) of particles of dust at levels with a height difference of  $h = 1$  m.
- 3.31. Air is in a uniform field of gravity. Assume that the temperature of the air is uniform and equals  $T = 290$  K. Define the relative change in air pressure ( $|\Delta p/p_o$ ) at levels with a height difference of  $h = 8.5$  km. Assume the molar mass of air to be  $29 \times 10^{-3}$  kg/mol.
- 3.32. Oxygen gas is in a uniform field of gravity. Assume the temperature of oxygen is identical in all layers and is  $T = 300$  K. Define the relative change in gas pressure ( $|\Delta p/p_o$ ) at levels with a height difference of  $h = 80$  m. Molar mass of the oxygen is  $\mu = 32 \times 10^{-3}$  kg/mol.
- 3.33. The rotor of a centrifuge is filled with air and finely dispersed particles of weight  $m = 10^{-19}$  g. The temperature of the air is  $T = 286$  K. Find the ratio of the concentration of particles ( $n/n_o$ ) at the walls of the rotor and in its center if the rotor revolves with a frequency  $\nu = 8$  sec $^{-1}$  and its radius is  $r = 25$  cm.
- 3.34. A concentration  $n_o$  of nitrogen molecules near to the ground surface is equal to  $2 \times 10^{19}$  cm $^{-3}$ . What is the change in concentration  $|\Delta n|$  of the molecules at height

- $h = 10$  m? The temperature of the air is  $T = 280$  K. The molar weight  $\mu$  of nitrogen is  $28 \times 10^{-3}$  kg/mole.
- 3.35. Identical particles of dust are suspended in air. The temperature of the air is  $T = 300$  K. Under the action of a gravitational force, the relative change of the concentration of suspension particles ( $|\Delta n|/n_o$ ) in levels with a height difference  $h = 3$  cm reaches a value of 0.01. Determine the particles' mass  $m$ .
- 3.36. Identical particles of dust of mass  $m = 1 \times 10^{-18}$  g are suspended in air. The temperature of the air is  $T = 300$  K. At what distance  $h$  are the layers in which the ratio ( $n_o/n$ ) of the concentration of the particles is equal to 4?
- 3.37. Carbonic acid is in a uniform field of gravity. The temperature of the gas is  $T = 300$  K. At what height  $h$  does the relative change of the molecule concentration ( $|\Delta n|/n_o$ ) of gas reach 1%? The molar weight of the carbonic gas  $\mu$  is  $44 \times 10^{-3}$  kg/mol.
- 3.38. The rotor of a centrifuge is filled with nitrogen at temperature  $T = 300$  K. The rotor radius  $r$  is 20 cm. At what frequency of the rotor rotation  $n$  ( $\text{sec}^{-1}$ ) will the gas pressure on its wall exceed the gas pressure in the center of the rotor by 2%? The molar weight of nitrogen is  $28 \times 10^{-3}$  kg/mol.
- 3.39. The rotor of an ultracentrifuge is filled with radon at temperature  $T = 305$  K. The radius of the rotor is  $r = 20$  cm. At what frequency of the rotor rotation  $n$  ( $\text{sec}^{-1}$ ) will the pressure on its walls be  $\varepsilon$  times higher than the pressure in the center of the rotor? The molar weight of radon is equal  $\mu = 0.222$  kg/mol.
- 3.40. Determine the molecular thermal conduction coefficient  $\kappa$  of saturated water vapor at temperature  $T = 373$  K ( $100^\circ\text{C}$ ). The effective molecular diameter  $d$  is 0.30 nm, molar mass  $M = 18 \times 10^{-3}$  kg/mol.
- 3.41. Find the dependence of the diffusion coefficient on molar mass  $M$  at  $p = \text{constant}$  and  $T = \text{constant}$ .
- 3.42. Find the average time  $\tau$  between oxygen molecule collisions at  $p = 1 \mu\text{Pa}$  and  $T = 300$  K. The effective diameter of oxygen molecule  $d$  is 0.36 nm, mole mass  $M = 32 \times 10^{-3}$  kg/mol.
- 3.43. Determine the ratio ( $\eta_1/\eta_2$ ) of the viscosity coefficients of oxygen and hydrogen at similar conditions if the ratio of effective diameters of their molecules is  $(d_1/d_2) = (4/3)$ .
- 3.44. Helium of mass  $m = 0.5$  g is in a high-pressure vessel with volume  $V = 20$  L. Find the average path length  $\lambda$  of the helium atoms. The effective diameter  $d$  of a helium atom is 0.22 nm, molar mass is  $M = 4.0 \times 10^{-3}$  kg/mole.
- 3.45. Oxygen is at a temperature of  $T = 300$  K. At what pressure  $p$  will the average molecule free path distance  $\lambda$  be  $N = 10^3$  times bigger than its effective diameter  $d = 0.36$  nm?

## ANSWERS

3.1. (1)  $1.50 \times 10^{23}$ ; (2)  $5.02 \times 10^{22}$ ; (3)  $3.17 \times 10^{22}$ ; (4)  $2.87 \times 10^{21}$ .

3.2.  $t_2 = \frac{p_2}{p_1}(t_1 + T_o) - T_o = 473^\circ\text{C} (T_o = 273^\circ\text{C})$ .

$$3.3. M_{\text{air}} = \frac{1}{\left(\frac{w_1}{M_1} + \frac{w_2}{M_2}\right)} = 28.9 \text{ kg/mol.}$$

3.4. 28% and 72%.

$$3.5. f(u) du = \frac{4}{\sqrt{\pi}} \exp(-u^2) u^2 du; w = 4.39 \times 10^{-3}.$$

$$3.6. \Delta N/N = 7.52 \times 10^{-7}.$$

$$3.7. w = \Delta N/N = 9.3 \times 10^{-3}.$$

3.8. Decreases three times.

$$3.9. N = 1.57 \times 10^{21}.$$

$$3.10. \langle \tau \rangle = 147 \text{ ns.}$$

$$3.11. (1) 90 \times 10^{-5} \text{ m}^2/\text{sec}, (2) 0.061 \text{ m}^2/\text{sec.}$$

$$3.12. \eta = 18 \mu\text{Pa sec.}$$

3.13. At  $p = \text{constant}$ .

$$3.14. A = 1 \text{ kJ.}$$

$$3.15. A = 6 \text{ kJ. } \Delta U = 15 \text{ kJ.}$$

$$3.16. e' = 1.88 e.$$

$$3.17. A_2 = 4 \text{ J.}$$

$$3.18. \Delta S = 7.2 \text{ J/K.}$$

$$3.19. \Delta S = 291 \text{ J/K.}$$

$$3.20. \Delta U = \frac{m}{M}(ML - RT_k) = 75.2 \text{ J.}$$

$$3.21. C_{p,sp} = \frac{5v_1 + 7v_2}{v_1M_1 + v_2M_2} \frac{R}{2} = 9.20 \text{ kJ/(kg K).}$$

$$3.22. \gamma = \frac{7 + 3\alpha}{5 + \alpha} = 1.46.$$

$$3.23. C_{V,sp} = \frac{3\frac{m_1}{M_1} + 5\frac{m_2}{M_2}}{m_1 + m_2} \frac{R}{2} = 455 \text{ J/(kg K).}$$

$$3.24. \alpha = \frac{2M}{R} C_{V,sp} - 5 = 0.6.$$

$$3.25. C_{V,sp} = \left(\frac{3}{M_1} + \frac{5}{M_2}\right) \frac{R}{4} = 636 \text{ J/(kg K).}$$

$$3.26. \gamma = \frac{(i_1 + 2) + (i_2 + 2)}{i_1 + i_2} = (12/8) = 1.5.$$



$$3.27. \gamma = \frac{5V_1 + 7V_2}{3V_1 + 5V_2} = 1.52.$$

$$3.28. C_{p,sp} = \frac{i_1 + i_2 + 4}{M_1 + M_2} \frac{R}{2} = \frac{6}{M_1 + M_2} R = 959 \text{ J / (kg K)}.$$

$$3.29. \alpha = \frac{5\gamma - 7}{3 - \gamma} = 0.263.$$

$$3.30. \frac{|\Delta n|}{n_o} = 1 - \exp(-\mu gh / \kappa T) = 1 - e^{-1} = 0.632.$$

$$3.31. \frac{|\Delta p|}{p_o} = 1 - \exp(-\mu gh / RT) = 1 - e^{-1} = 0.632.$$

$$3.32. \frac{|\Delta p|}{p_o} = (-\mu gh / RT) = 0.01.$$

$$3.33. \frac{n}{n_o} = \exp \frac{2\pi m v^2 r^2}{\kappa T} = e^2 = 7.39.$$

$$3.34. |\Delta n| = \frac{\mu gh}{RT} n_o = 2.36 \times 10^{16} \text{ cm}^{-3}.$$

$$3.35. m = (\kappa T / gh) \frac{|\Delta n|}{n_o} = 1.41 \times 10^{-22} \text{ kg}.$$

$$3.36. h = (\kappa T / mg) \ln(n_o / n) = 0.588 \text{ m}.$$

$$3.37. h = (RT / \mu g) \frac{|\Delta n|}{n_o} = 57.8 \text{ m}.$$

$$3.38. n = \frac{1}{\pi r} \sqrt{\frac{RT}{2\mu}} \cdot \sqrt{\frac{|\Delta p|}{p_o}} = 47.5 \text{ s}^{-1}.$$

$$3.39. n = \frac{1}{\pi r} \sqrt{\frac{RT}{2\mu}} \ln \varepsilon = 100 \text{ s}^{-1}.$$

$$3.40. \kappa = \frac{i\kappa}{3\pi d^2} \sqrt{\frac{RT}{\pi M}} = 22.9 \text{ mW / mK}.$$

$$3.41. D(M) \sim \frac{1}{\sqrt{M}}.$$

$$3.42. \tau = \frac{\sqrt{MRT}}{4\sqrt{\pi}d^2 pN_A} = 16.1 \text{ s.}$$

$$3.43. \frac{\eta_1}{\eta_2} = \frac{d_2^2}{d_1^2} \sqrt{\frac{M_1}{M_2}} = 2.25.$$

$$3.44. \lambda = \frac{MV}{\sqrt{2\pi}d^2 mN_A} = 1.24 \mu\text{m.}$$

$$3.45. p = \frac{\kappa T}{\sqrt{2\pi}d^3 N} = 20 \text{ kPa.}$$