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МІНІСТЕРСТВО ОСВІТИ І НАУКИ УКРАЇНИ
ОДЕСЬКА ДЕРЖАВНА АКАДЕМІЯ БУДІВНИЦТВА ТА АРХІТЕКТУРИ

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КУРС ФІЗИКИ

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The textbook discusses the basics of molecular kinetic theory, the thermodynamics of ideal gases and gases with intermolecular interactions. In addition, the theoretical material includes the features of transport processes and the thermodynamics of irreversible processes. Each theoretical section ends with self-examination questions. The textbook contains material that can be used in practical classes, namely: examples of problem solving, problem conditions for independent solutions, as well as reference data needed to solve them.

This textbook is intended for vocational training of students in the specialty 192 Construction and Civil Engineering for the Bachelor degree.

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PREFACE

Textbook “Physics course. Thermodynamics" is intended for students of higher educational institutions of specialty 192 "Construction and Civil Engineering". This study guide aims to provide an up-to-date and comprehensive coverage of the core curriculum in physics specified in the current Odessa State Academy of Civil Engineering and Architecture syllabus.

Molecular physics and thermodynamics study macroscopic processes in bodies, i.e. such phenomena that are associated with a very large number of atoms and molecules that are contained in these bodies.

Molecular physics proceeds from the idea of the atomic-molecular structure of matter and considers heat as the random movement of atoms and molecules. Molecular physics in the broad sense studies not only macroscopic phenomena. This science also considers the properties and structure of individual atoms and molecules.

Thermodynamics is an axiomatic science. Thermodynamics is based on general principles. These principles are a generalization of a large set of experimental facts. Thermodynamics considers heat as a type of some kind of internal movement, but does not try to specify this movement. Thermodynamics is one of the most important parts of physics. The conclusions of thermodynamics are as reliable as the axioms on which this science is built. The consequences of thermodynamics are used in all areas of macroscopic physics: hydrodynamics, elasticity theory, aerodynamics, electrical and magnetic phenomena, optics and other branches of physics. Physical chemistry and chemical physics are engaged in applications of thermodynamics to chemical phenomena.

The main content of modern physical thermodynamics is the study of the laws of the thermal form of motion of matter and related physical phenomena. Thermodynamic applications related to heat engines, refrigeration units and other heat engineering applications were allocated in an independent section. This section of thermodynamics is called technical thermodynamics.

Thermodynamics, as a rule, studies only the equilibrium states of bodies and slow processes, which can be considered as almost equilibrium states, continuously following each other. In addition, thermodynamics studies the general laws governing the transition of systems to states of thermodynamic equilibrium.

Molecular-kinetic theory studies a much wider range of phenomena associated with processes in bodies that occur at a finite speed. The section of molecular kinetic theory related to the properties of a substance in equilibrium is called statistical thermodynamics. The section of molecular kinetic theory that studies the processes in bodies that occur at a finite speed is called physical kinetics.

Molecular physics should be based on the laws that govern atoms and molecules. Such laws are the laws of quantum mechanics. A complete and rigorous study of molecular physics without knowledge of these laws is impossible. However, a wide range of macroscopic phenomena is caused not so much by the structural details of atoms and molecules as by a very large number of atoms in macroscopic systems. The knowledge of quantum mechanics in the study of this kind of phenomena is not mandatory, therefore molecular physics is usually studied by students after classical mechanics, but before quantum mechanics.

The quantum nature of atoms and molecules should be taken into account when studying thermodynamic processes associated, for example, with heat capacity near absolute zero temperature. In these cases, a little preliminary information from quantum physics is enough. This information can be mentioned during the study of the basic principles of thermodynamics.

The guide covers topics related to ideal gas model, Maxwell and Boltzmann distributions, gas laws, thermodynamics laws, effects in real gases and liquids, transport processes in gases and rarefied gases, thermodynamics of irreversible processes. Elements of the study guide include the following:

- fundamental concepts of molecular physics and thermodynamics
- test questions
- problem-solving examples
- problems
- appendices.

By the end of textbook "Physics course. Thermodynamics" students will be able to:

- apply principles and concepts of physics to explain various phenomena
- construct models and simulations to describe and explain natural phenomena
- use mathematics as a precise method for showing relationships
- solve problems by applying physics principles and laws
- select and use appropriate technological instruments to collect data,
- analyze data, check it for accuracy and construct reasonable conclusions
- use precise scientific language in oral and written communication.

It is well known that theoretical knowledge is useless without the ability to use it to solve practical problems. Therefore, the acquisition of problem solving skills is an integral part of studying the course of general physics. Currently, there are a sufficient number of collections of physical problems, but, unfortunately, there are practically no manuals intended for training in methods of solving problems. The material located at the end of each chapter of study guide is intended to remove the indicated disadvantage. This material is divided into three blocks. The first block contains test questions on the theoretical information that is present in the chapter. Examples of solving typical problems are included in the second block. The third block contains a number of problems for independent solution. These tasks are accompanied only by short answers. It is worth noting that in the theoretical part, the descriptions of experiments and in the methods of solving problems, the SI system is mainly used, which is convenient from a practical point of view.

The appendices placed at the end of the textbook are, on the one hand, an illustrative addition to the laws and phenomena that are described in the physics course, and on the other hand, have a reference character necessary for successful problem solving.

CHAPTER 1. MOLECULAR KINETIC THEORY

1.1. Basic Concepts

Molecular-kinetic theory is the doctrine that explains the structure and properties of bodies by the movement and interaction of atoms, molecules and ions of which the bodies are composed. The molecular-kinetic theory is based on three most important points (postulate), which are fully confirmed experimentally and theoretically:

1) all bodies are made up of particles: molecules, atoms or ions. The composition of atoms includes smaller elementary particles;
2) atoms, molecules and ions are in continuous chaotic motion;
3) there are interaction forces between the particles of any body, namely: attractive forces and repulsive forces.

These starting points are confirmed by the phenomena of diffusion, Brownian motion, structural features and properties of liquids and solids, as well as research in the field of particle physics.

An ***atom*** is the smallest particle of a given chemical element. Each chemical element corresponds to well-defined atoms that preserve the chemical properties of this element.

Each atom consists of a positively charged nucleus and negatively charged electrons moving in the electric field of the nucleus. The electric charge of the nucleus is equal to the absolute value of the total charge of all the electrons of the atom, so the atom is electrically neutral.

A ***molecule*** is the smallest stable particle of a given substance with its basic chemical properties. A molecule consists of one or more atoms of the same or different chemical elements.

An ***ion*** is an electrically charged particle of a substance that is formed from an atom or molecule when they lose or, conversely, attach one or more electrons.

Atoms combine into a molecule due to chemical bonds based on various interactions of external (valence) electrons. The number of atoms in the molecules varies widely: from two (CO, O_2, NO, H_2), three (CO_2, SO_2), four (NH_3) to hundreds of thousands (protein molecules). A molecule, like an atom, is electrically neutral. The molecule contains an equal amount of electrically charged particles of the opposite sign.

The ***quantity of a substance*** is the physical quantity determined by the number of specific structural elements: molecules, atoms or ions of which the substance is composed. Since the masses of individual structural elements (for example, molecules) differ from each other, the same amounts of different substances have different masses. For example, 10^{25} hydrogen molecules and 10^{25} oxygen molecules are considered the same amounts of matter, although they have different masses equal to 3.345×10^{-2} kg and 5.314×10^{-1} kg, respectively. Mass is not a measure of the amount of a substance. The unit of measurement for the amount of substance is mole. The ***mole*** (symbol mol) is a unit of the International System of Units defined as exactly $N_A = 6.02214076\times10^{23}$ particles. The integer N_A is called ***Avogadro number***. This number was named in honour of Amedeo Carlo Avogadro (9.08.1776 – 9.07.1856)

The volume of one mole is called the ***molar volume***.

$$V_\mu = \upsilon\mu = \frac{\mu}{\rho}, \tag{1.1.1}$$

where $\upsilon = 1/\rho$ is the specific volume; ρ is the density of the substance; μ is the mass of one mole.

Under normal conditions (***STP*** – standard temperature and pressure, temperature and pressure are equal t = 0°C, P = 101325 Pa, respectively), the molar volumes of all ideal gases (the concept of ideal gas is given in Section 1.2) are the same: $V_\mu = 2.241383\times10^{-2}$ m^3/mol.

Molar mass is

$$\mu = m_1 N_A, \tag{1.1.2}$$

where m_1 is the mass of one structural element (atom, molecule or ion).

The number of moles of substance with a mass of m is

$$\nu = \frac{m}{\mu}. \tag{1.1.3}$$

The dimensions of an atom are determined by those distances from the centre of the nucleus at which external valence electrons or external filled electron layers are located.

1.2. Ideal Gas Model

The density of a gas under normal conditions is a thousand times lower than its density in a liquid or solid state; therefore, the distance between gas molecules is tens of times greater than in other states.

The molecules in the gas move uniformly and rectilinearly at a very high speed (about 500 m/s). The forces of intermolecular interaction between collisions of molecules are negligible. The average distance a molecule travels without a collision is much larger than its size. During the collision itself, the molecules interact according to laws that differ little from the laws of elastic impact. Collision changes only the magnitude and direction of the velocity of the molecules.

In molecular physics, the **ideal gas model** is used, in which the interaction between the molecules is neglected. The collision of molecules can be described at zero potential energy $(W_p = 0)$. The total energy of molecules can be characterized by the sum of their kinetic energies. In this case, the interaction of molecules is reduced to a collision between them. These collisions occur with a high frequency (of the order of 10^{10} s^{-1}). However, most of the time, gas molecules move like free particles.

A real gas can be considered ideal if the average potential interaction energy of the molecules is much less than their average kinetic energy. This approximation can be used for rarefied gases. For example, helium under normal conditions with a good approximation can be considered an ideal gas.

The state of a given mass of gas can be characterized by pressure P, volume V, and temperature T. These values are not always equal in all parts of the system. If the temperature at different points of the body is different, then the body cannot be characterized by a certain value of the parameter T. Such a state, not subject to external influences, is called a non equilibrium state.

Consider the case of a system isolated from external influences. Over time, the temperature at different points of such a system equalizes. The state of the system becomes equilibrium.

An example of a non equilibrium state can be a gas coming from a small hole into a closed volume. At the initial time, the distribution of gas over such a volume is uneven. The pressure in different parts of the system is not the same. Now we will stop gas access to the system. The gas pressure at different points in the volume of the system will equalize, and the state will become equilibrium.

An ***equilibrium state*** is a state of the system in which all macroscopic parameters have a certain value, which remains unchanged under constant external conditions for an arbitrarily large time.

The transition of a system from one state to another is called a ***process***. If such a transition occurs through a sequence of non equilibrium states, then the transition is called a ***non equilibrium process***. If the transition occurs through a sequence of equilibrium states, then the transition is called the ***equilibrium process***. The equilibrium process should be slow enough (infinitely slow in the limit) so that the equilibrium state can be established at any time.

The thermodynamic system can be characterized by ***external*** and ***internal*** parameters. The volume of gas is an external parameter, since it depends on the location of bodies external to the system (gas), namely the walls of the vessel in which the gas is located. Pressure and temperature are internal parameters, since they depend on the coordinates, velocities of the gas molecules and its density.

When the gas is in equilibrium, there is a functional relationship between its parameters, which is called the ***equation of state***. The equation of state is often expressed as a dependency

$$F(P,V,T)=0, \tag{1.2.1}$$

where function F for ideal gases is determined theoretically using the relations of statistical physics.

Rudolf Julius Emanuel Clausius (2.01.1822 – 08.24.1888) substantiated the equation of an ideal gas state. An example of a state equation is the Mendeleev – Clapeyron equation for ideal gases and the van der Waals equation for real gases.

1.3. Maxwell Distribution

The result of each collision between molecules is a change in their velocities. After a large number of collisions, a stationary equilibrium state is established when the number of molecules in a given speed range is kept constant (accurate to fluctuations). The velocity distribution of molecules was first established by James Clerk Maxwell (13.06.1831 – 5.11.1879).

The most important macroscopic parameter characterizing the velocity distribution of molecules is the average kinetic energy of the molecules. Consider a mixture of gases enclosed in an isolated volume. Molecules of different varieties of this mixture have the same average kinetic energies. This means that the interaction of molecules of various varieties is equalization of these energies.

We prove this statement. Consider a mixture consisting of two types of molecules (indices 1 and 2, respectively). We calculate the relative velocities $\vec{v}_2 - \vec{v}_1$ and velocities of their centres of mass

$$\vec{v}_{cm} = \frac{m_1\vec{v}_1 + m_2\vec{v}_2}{m_1 + m_2}. \tag{1.3.1}$$

A consequence of the random nature of molecular collisions is that the two types of velocities indicated above cannot be in correlation. Consequently, the average of their scalar product, taken over all pairs of molecules, is zero

$$\langle(\vec{v}_{cm}, (\vec{v}_2 - \vec{v}_1))\rangle = 0$$

or

$$(\vec{v}_{cm}, (\vec{v}_2 - \vec{v}_1)) = \frac{(m_1 - m_2)\langle(\vec{v}_1, \vec{v}_2)\rangle + m_2\langle\vec{v}_2^2\rangle - m_1\langle\vec{v}_1^2\rangle}{m_1 + m_2} = 0 \tag{1.3.2}$$

Since the velocities of molecules of the first and second grades are not in correlation, there should be $\langle(\vec{v}_1, \vec{v}_2)\rangle = 0$. It follows that

$$\left\langle \frac{m_1 v_1^2}{2} \right\rangle = \left\langle \frac{m_2 v_2^2}{2} \right\rangle. \tag{1.3.3}$$

Consequently, a system of molecules capable of exchanging energy tends to a state in which the average kinetic energies of molecules of various sorts and the average kinetic energies of molecules in different spatial parts of the system have the same value.

This state of the system is called ***thermodynamic equilibrium***, and the average kinetic energy is characterized by a physical quantity called ***temperature***. Instead of talking about the constancy of the average kinetic energy of molecules, it can be argued that the temperature is constant throughout the volume of the system.

The temperature T is connected, by definition, with the average kinetic energy of the molecules by the formula

$$\left\langle \frac{mv^2}{2} \right\rangle = \frac{3}{2}kT . \tag{1.3.4}$$

where k = 1.380662×10^{-23} J/K is a proportionality coefficient (***Boltzmann constant***). Boltzmann constant named after its discoverer Ludwig Eduard Boltzmann (20.02.1844 – 5.09.1906).

The value T is the thermodynamic temperature. The ***kelvin*** (symbol: K) is the base unit of temperature in the International System of Units (SI). This base unit of temperature is named after William Thomson, Kelvin (26.06.1824 – 17.12.1907). Until 19 May 2019, the temperature of the triple point of water was defined as exactly 273.16 K or 0.01 °C (degree Celsius). This means that a temperature difference of one degree Celsius and that of one Kelvin are exactly the same.

Thermodynamic equilibrium is established as a result of a huge number of collisions between molecules. As a result of each collision, the projections of the velocity of the molecule change to a random values Δv_x, Δv_y, Δv_z. Variations of each velocity projection are independent of each other. Consider the motion of a molecule whose velocity at the initial moment of time is zero. The change in the projections of its velocity after a collision with index i is denoted by $\Delta v_{x,i}$, $\Delta v_{y,i}$, $\Delta v_{z,i}$. After a sufficiently large projection time, the velocities of the molecules are

$$v_x = \sum_i v_{x,i} \quad , \quad v_y = \sum_i v_{y,i} \quad , \quad v_z = \sum_i v_{z,i} \, . \tag{1.3.5}$$

Each of the velocity projections is the sum of a large number of random variables satisfying the condition for the implementation of the Gaussian distribution. Consequently, the velocity projections are distributed according to the law

$$\varphi\left(v_x^2\right) = A \exp\left(-\alpha v_x^2\right),$$

$$\varphi\left(v_y^2\right) = A \exp\left(-\alpha v_y^2\right),$$

$$\varphi\left(v_z^2\right) = A \exp\left(-\alpha v_z^2\right), \tag{1.3.6}$$

where constants A and α are the same for all three projections due to the complete equivalence of the coordinate axes and the independence of random variables v_x, v_y, v_z.

The probability that the projection of the velocity on the x axis is in the interval $[v_x, v_x + \Delta v_x]$ is equal to

$$dp(v_x) = \varphi\left(v_x^2\right)dv_x = A \exp\left(-\alpha v_x^2\right)dv_x . \tag{1.3.7}$$

Similar formulas are valid for other velocity projections. The probability that the molecule's speed is in the speed range [v_x, $v_x + \Delta v_x$; v_y, $v_y + \Delta v_y$; v_z, $v_z + \Delta v_z$] is expressed as

$$dp\left(v_x, v_y, v_z\right) = A^3 \exp\left(-\alpha\left(v_x^2 + v_y^2 + v_z^2\right)\right) dv_x dv_y dv_z \tag{1.3.8}$$

by the probability multiplication formula.

The constant value A is found from the normalization condition

$$\iiint\limits_{\infty} dp\left(v_x, v_y, v_z\right) = 1. \tag{1.3.9}$$

We use the following expression for further analysis

$$\int\limits_{-\infty}^{\infty} \exp\left(-\alpha v_x^2\right) dv_x = \sqrt{\frac{\pi}{\alpha}}. \tag{1.3.10}$$

In this case, from (1.3.9) and (1.3.10) we get

$$A = \sqrt{\frac{\alpha}{\pi}}. \tag{1.3.11}$$

We calculate the average value of the kinetic energy of the molecule

$$\left\langle \frac{mv^2}{2} \right\rangle = \left(\frac{m}{2}\right)\left\langle v_x^2 + v_y^2 + v_z^2 \right\rangle = \left(\frac{m}{2}\right) \iiint\limits_{\infty} \left(v_x^2 + v_y^2 + v_z^2\right) dp\left(v_x, v_y, v_z\right) =$$

$$= \left(\frac{m}{2}\right)\left(\frac{\alpha}{\pi}\right)^{3/2} \iiint\limits_{\infty} \left(v_x^2 + v_y^2 + v_z^2\right) \exp\left[-\alpha\left(v_x^2 + v_y^2 + v_z^2\right)\right] dv_x dv_y dv_z. \tag{1.3.12}$$

The calculation of the integrals (1.3.12) leads to the expression

$$\left\langle \frac{mv^2}{2} \right\rangle = \frac{3m}{4\alpha}. \tag{1.3.13}$$

Equating the right-hand sides of (1.3.4) and (1.3.13), we obtain

$$\alpha = \frac{m}{2kT}. \tag{1.3.14}$$

In this case, using formula (1.3.8), we can write

$$dp\left(v_x, v_y, v_z\right) = \left[\frac{m}{2\pi kT}\right]^{3/2} \exp\left[-\frac{m\left(v_x^2 + v_y^2 + v_z^2\right)}{2kT}\right] dv_x dv_y dv_z \tag{1.3.15}$$

The velocity distribution is isotropic. Therefore, from the distribution of velocity projections, we can proceed to the distribution of velocity modules. We consider the spherical coordinate system in the space of velocities in formula (1.3.15) and integrate (1.3.15) over the spherical layer dv thick, whose radius is $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$. As a result, we can write the formula

$$dv_x dv_y dv_z = v^2 d\Omega dv, \tag{1.3.16}$$

where $d\Omega$ is the solid angle at which the surface element of the spherical layer is visible from the origin.

The integral over the entire surface of the spherical layer is

$$\int_{\Omega=4\pi} v^2 d\Omega = v^2 \int_{\Omega=4\pi} d\Omega = 4\pi v^2. \tag{1.3.17}$$

Therefore, the integration of formula (1.3.15) over a spherical layer of thickness dv leads to the formula

$$dp(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mv^2}{2kT} \right) v^2 dv. \tag{1.3.18}$$

Formula (1.3.18) describes the probability that a molecule will have a velocity whose modulus is in the range of $[v, v + \Delta v]$.

Function

$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mv^2}{2kT} \right) v^2 \tag{1.3.19}$$

is called the ***Maxwell distribution***. The Maxwell distribution is the probability density that the molecule has a velocity modulus v. Maxwell in 1860 derived the statistical law of the distribution of velocities of gas molecules.

Formulas (1.3.18) and (1.3.19) allow you to find the relative number of molecules whose velocities are in a given interval $[v, v + \Delta v]$

$$\frac{dn(v)}{n} = dp(v) = f(v) dv. \tag{1.3.20}$$

An increase in the velocity of molecules leads to the fact that the maximum of the Maxwell distribution shifts toward higher velocities. The height of the curve corresponding to the Maxwell distribution for the maximum position decreases slightly.

The average value of a function $\varphi(v)$ depending on the velocity modulus is calculated by formula

$$\langle \varphi \rangle = \int_0^\infty \varphi(v) f(v) dv . \tag{1.3.21}$$

We determine by the formula (6.3.22) the ***average speed*** $\langle v \rangle$ and the ***root-mean-square speed*** $\sqrt{\langle v^2 \rangle}$

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}} \quad , \quad \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} . \tag{1.3.22}$$

The speed v_p that corresponds to the maximum of the Maxwell distribution curve is called ***most probable speed***. This speed is found from the condition of extremum $df(v)/dv = 0$ and is equal to

$$v_p = \sqrt{\frac{2kT}{m}} . \tag{1.3.23}$$

A comparison of formulas (1.3.22) and (1.3.23) leads to the following relation between the characteristic velocities for the Maxwell distribution

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3\pi}{8}} \langle v \rangle = \sqrt{\frac{3}{2}} v_p . \tag{1.3.24}$$

The characteristic velocities of oxygen and nitrogen molecules in air at room temperature are approximately (400 – 500) m/s. The speeds of hydrogen molecules are four times higher. The temperature dependence of the characteristic molecular velocities has the form $v \sim \sqrt{T}$.

We direct the x axis perpendicular to the wall of the vessel in which the gas is located. Denote the concentration of molecules by n_0. The density of the flow of molecules in the direction of the wall is

$$n' = n_0 f\left(v_x^{(+)}, v_y, v_z\right) v_x^{(+)} dv_x^{(+)} dv_y dv_z , \tag{1.3.25}$$

where $v_x^{(+)}$ is a component of speed in the direction of positive x axis values. The frequency of molecular impacts on the walls of the vessel per unit area is

$$\nu = n_0 \left(\frac{m}{2\pi kT} \right)^{3/2} \iint_{\infty} \exp\left[-\frac{m\left(v_y^2 + v_z^2\right)}{2kT} \right] dv_y dv_z \int_0^\infty \exp\left(-\frac{mv_x^2}{2kT} \right) v_x dv_x =$$

$$= n_0 \sqrt{\frac{kT}{2\pi m}} . \tag{1.3.26}$$

Taking into account formula (1.3.22), we obtain

$$\nu = \frac{n_0 \langle v \rangle}{4}. \tag{1.3.27}$$

The number $N(v_1,v_2)$ of molecules whose velocities are in the range $[v_1,v_2]$ is

$$N(v_1, v_2) = n_0 \int_{v_1}^{v_2} f(v) dv = n_0 \frac{4}{\sqrt{\pi}} \int_{v_1/v_p}^{v_2/v_p} \exp\left(-u^2\right) u^2 du. \tag{1.3.28}$$

There are integral tables

$$\varphi(x) = \frac{4}{\sqrt{\pi}} \int_x^\infty \exp\left(-u^2\right) u^2 du. \tag{1.3.29}$$

Using these tables, the value $N(v_1,v_2)$ in the formula (1.3.28) can be calculated as follows

$$N(v_1, v_2) = n_0 \left[\varphi\left(\frac{v_2}{v_p}\right) - \varphi\left(\frac{v_1}{v_p}\right) \right]. \tag{1.3.30}$$

The following ratios

$$N\left(v_p, \infty\right) = 0.5724 n_0, \quad N\left(0.5 v_p, 1.5 v_p\right) = 0.7053 n_0, \quad N\left(2 v_p, \infty\right) = 0.0460 n_0, \tag{1.3.31}$$

can be cited as examples of such calculations.

Thus, the largest part of all molecules has velocities in a relatively small interval near the most probable velocity.

The Maxwell distribution is an equilibrium and, therefore, also a stationary state that does not change over time. The ***principle of detailed equilibrium*** states that equilibrium is established in detail, i.e. between all pairs of volume elements. This means that each volume element per unit of time gives as many particles to any other volume element as it receives from it. The validity of the principle of detailed equilibrium is due there that the state of equilibrium is established as a result of the chaotic nature of collisions and the randomness of the movement of molecules. The principle of detailed equilibrium is valid not only for collisions, but also for other parameters in any systems whose equilibrium state is established as a result of chaotic processes.

The movement of a molecule in a gas is accompanied by collisions, as a result of which the molecule changes its direction of motion. All possible results of collisions in a specific situation can be predicted only probabilistically. The probability of a collision with a specific result is described using a cross section.

Suppose that the particle falls on the area S of the volume in which the target particles with a concentration of n_0 are located. In the layer of thickness dx there are target particles, the number of which is $n_0 S dx$. The sum of their cross sections, which, as it were, covers part of the area S, is equal to $dS = \sigma n_0 S dx$. It follows that the probability that the initial particle collides with one of the target particles in a layer of thickness dx is

$$dP = \frac{dS}{S} = \sigma n_0 dx. \qquad (1.3.32)$$

Formula (1.3.32) is the definition of the ***cross section*** σ of the process. Probability dP can usually be calculated based on the specific laws of the process or measured experimentally.

Values σ and n_0 are independent of x. Therefore, the probability of the event increases in proportion to the path travelled by the particle. The length of the path $\langle l \rangle$ at which this probability is equal to unity is called the ***mean free path***. Using formula (6.3.33) in this case leads to equality $\sigma n_0 \langle l \rangle = 1$, which implies that

$$\langle l \rangle = \frac{1}{\sigma n_0}. \qquad (1.3.33)$$

Suppose a particle beam moves in direction x. Particles of the beam, colliding with other particles, change the direction of their motion and drop out of the beam. Therefore, the particle flux $I(x)$ in the beam decreases as the substance passes, i.e. with an increase of x. The decrease in flux dI during the passage of the layer dx is proportional to the number of collisions of the beam particles with the target particles. The attenuation of the beam density is IdP. Therefore, we obtain the following equation for the particle flux density in the beam

$$dI = -I(x)\sigma n_0 dx. \qquad (1.3.34)$$

The minus sign in equation (1.3.34) takes into account that the particle flux density decreases with increasing x, i.e. as the beam advances in the substance. The solution of equation (1.3.34) has the form

$$I(x) = I(0)\exp(-\sigma n_0 x) = I(0)\exp\left(-\frac{x}{\langle l \rangle}\right). \qquad (1.3.35)$$

Measuring the flux density of incident particles at two distances: $x = 0$ and some other value of x, allows us to calculate the collision cross section

$$\sigma = \frac{1}{n_0 x}\ln\frac{I(0)}{I(x)}. \qquad (1.3.36)$$

A particle passing through a substance moves with an average speed of $\langle v \rangle$ and, therefore, passes the mean free path over a period of $\tau = \langle l \rangle / \langle v \rangle$. Therefore, the average collision frequency, i.e. the average number of collisions in a time equal to one second is

$$\nu' = \frac{1}{\tau} = \frac{\langle v \rangle}{\langle l \rangle} = \sigma n_0 \langle v \rangle . \tag{1.3.37}$$

Collisions of identical molecules in gases are most often represented as collisions of hard balls of the same radius r_0. In this case, the cross section and related quantities are easy to calculate.

The velocities of the colliding molecules and the mean free path taking into account the Maxwell distribution for the model of collisions of hard balls are

$$\nu' = 4\sqrt{2}\pi r_0^2 n_0 \langle v \rangle = 16 r_0^2 n_0 \sqrt{\frac{\pi R T}{\mu}} . \tag{1.3.38}$$

$$\langle l \rangle = \frac{1}{4\sqrt{2}\pi r_0^2 n_0} , \tag{1.3.39}$$

where $R = kN_A$ = 8.31446261815324 J/(mol·K) is ***gas constant***.

Normal conditions in air are characterized by the following values: $n_0 \approx 10^{25}$ m^{-3}, $r_0 \sim 10^{-10}$ m, $\langle v \rangle \sim 500$ m/s. Therefore, the mean free path and collision frequency are approximately equal to: $\langle l \rangle \approx 10^{-6}$ m, $\nu' \approx 10^9$ s^{-1}.

An analysis of formula (1.3.39) shows that, at a fixed temperature, relation $\langle l \rangle \sim 1/p$ holds, since pressure can be represented by formula

$$p = n_0 k T . \tag{1.3.40}$$

This makes it very easy to estimate the mean free path for various pressures.

1.4. Equation of State

Pressure arises as a result of the impact of molecules on the walls of the vessel. Each molecule during a collision transmits a certain momentum to the vessel wall. Let us direct the x axis perpendicular to the vessel wall. In this case, the momentum transferred to the wall is $2m_1 v_x^{(+)}$, where m_1 is the mass of the molecule. The pressure is equal to the total momentum transferred to a wall of 1 m^2 by molecules as a result of collisions in a time equal to 1 s.

The momentum flow towards the wall is

$$n' = n_0 f\left(v_x^{(+)}, v_y, v_z\right) v_x^{(+)} dv_x^{(+)} dv_y dv_z m_1 v_x^{(+)} . \tag{1.4.1}$$

The “+” index at speeds shows that this flow is created only by those molecules that move toward the wall (i.e., half the total number of molecules). Then

$$P_x = 2n_0 m_1 \int f\left(v_x^{(+)}, v_y, v_z\right) \cdot \left(v_x^{(+)}\right)^2 dv_x^{(+)} dv_y dv_z = n_0 kT. \quad (1.4.2)$$

A similar result can be obtained for the remaining pressure projections

$$P_x = P_y = P_z = n_0 kT. \quad (1.4.3)$$

Equation (1.4.3) shows that the pressure is isotropic and can be denoted by symbol P without indicating the direction to which it refers. If the mechanical properties of the medium are anisotropic, then the pressure at a given point in different directions can be different. Further analysis will be carried out under the assumption that the properties of an ideal gas are isotropic. We rewrite equation (1.4.3) using the dependence of temperature on the mean square velocity $\left\langle v^2 \right\rangle$ according to the formula (1.3.23)

$$P = \frac{2}{3}\left\langle \frac{m_1 v^2}{2} \right\rangle n_0. \quad (1.4.4)$$

Formula (1.4.4) is a mathematical expression of the basic equation of the kinetic theory of gases. When deriving equation (1.4.4), no assumptions were made about the law of the impact of molecules on the vessel wall. This process is very complex and depends on the properties of gas molecules, as well as on the properties of the wall material and its processing.

Denote the total number of molecules in the gas volume V by the symbol n. We rewrite equation (1.4.3), taking into account that $n_0 = n / V$

$$PV = nkT. \quad (1.4.5)$$

Since the value n is not directly measured for a given mass of gas, it is necessary to give equation (1.4.5) a more convenient form. For this, we use the concept of mol.

The total number of molecules in the volume containing ν moles of molecules is $n = \nu N_A$, therefore, equation (1.4.5) can be rewritten in the form

$$PV = \nu RT, \quad (1.4.6)$$

Values related to one mole of a substance are called molar quantities. Equality (1.4.6) is called the ***Mendeleev – Clapeyron equation***. Studies related to this equation were performed by Dmitri Ivanovich Mendeleev (8.02.1834 – 2.02.1907) and Benoît Paul Émile Clapeyron (26.01.1799 – 28.01.1864).

Molar volume refers to the volume of a substance assigned to one mole

$$V_\mu = \frac{V}{\nu}. \tag{1.4.7}$$

Then we can write

$$PV_\mu = RT. \tag{1.4.8}$$

In many cases, it is more advisable to write the Mendeleev – Clapeyron equation using the value of the gas mass in explicit form. We rewrite equation (1.4.6) using relation $\mu = m / \nu$, where μ is the molar mass; m is the mass of gas. Then equation (1.4.6) takes the form

$$PV = \frac{m}{\mu} RT. \tag{1.4.9}$$

The individual components of the gas mixture can be considered independent. Therefore, each component creates a pressure corresponding to equation (1.4.3). The total pressure is equal to the sum of the component pressures

$$P = n_{01}kT + n_{02}kT + ... + n_{0i}kT = P_1 + P_2 + ... + P_i. \tag{1.4.10}$$

where quantities P_i are called ***partial pressures***.

The law *expressed* by equation (1.4.10) is called the ***Dalton's law***. John Dalton (6.09.1766 – 27.07.1844) explained the law of partial pressures using the molecular theory. The molecules of each component of the mixture exert a pressure independent of the pressure exerted by the molecules of the other components. This is due to the fact that molecules do not interact in an ideal gas. Deviations from the Dalton law are observed at sufficiently high concentrations (pressures ~ 10^6 Pa) of gases. In this case, the interaction between the components of the mixture can no longer be neglected.

Each component of a gas mixture occupies a volume called a partial volume V_i. The volume of a mixture of ideal gases is equal to the sum of their partial volumes.

We denote the partial pressures, masses, and molar masses of the components of the gas mixture by symbols P_i, m_i, μ_i, respectively. Then, using equations (1.4.9) and (1.4.10), we can write

$$(P_1 + P_2 + ... + P_i)V = \left(\frac{m_1}{\mu_1} + \frac{m_2}{\mu_2} + ... + \frac{m_i}{\mu_i} \right) RT. \tag{1.4.11}$$

We introduce the following notation for the pressure of a mixture of gases, the mass of the mixture and the average molar mass

$$P = P_1 + P_2 + \ldots + P_i,$$

$$m = m_1 + m_2 + \ldots + m_i,$$

$$\frac{1}{\langle \mu \rangle} = \frac{1}{m}\left(\frac{m_1}{\mu_1} + \frac{m_2}{\mu_2} + \ldots + \frac{m_i}{\mu_i} \right). \quad (1.4.12)$$

Therefore, equation (1.4.11) can be written in a form similar to equation (1.4.9)

$$PV = \frac{m}{\langle \mu \rangle} RT. \quad (1.4.13)$$

An analysis of equation (1.4.5) shows that at the same pressures and temperatures in equal volumes of any gas contains the same number of molecules. This statement is called ***Avogadro's law***.

Therefore, a mole of any gas at fixed temperatures and pressures occupies the same volume. Under normal conditions, this volume is $V_\mu = 2.241383 \times 10^{-2}$ m^3/mol. The concentration of molecules under these conditions is determined by the ***Loschmidt constant*** $N_L = 2.686754 \cdot 10^{25}$ m^{-3}. This constant is named after Johann Josef Loschmidt (15.03.1821 – 8.07.1895).

Temperature is a quantitative measure of the body’s “heat”. The concept of "heating" is subjective and requires clarification. The body chosen to measure “heat” is called the ***thermometric body***. The quantity by which "heating" is measured is called the ***thermometric quantity***.

Denote the thermometric value by symbol l. For example, one can imagine a thermometric body in the form of a metal rod, and the thermometric quantity is the length l of the rod. The most easily defined and known are the values of “heating”, at which water boils at atmospheric pressure, and “heating”, at which water freezes. These reference points are called the ***boiling point*** of water and the ***freezing point***. The thermometric values at the boiling point of water and at the freezing point are l_1 and l_2, respectively. Temperature is the numerical value of a quantity by which the “heating” of a body is characterized.

Temperature t is expressed in degrees. The reference points can be associated with some arbitrary temperature. Let the freezing point correspond to a temperature of t_1, and the boiling point of water corresponds to a temperature of t_2. Then the value

$$1^\circ = \frac{l_2 - l_1}{t_2 - t_1} \quad (1.4.14)$$

is called the ***degree of temperature***.

The temperature of a thermometric body is a number, which is determined by the formula

$$t = t_1 + \frac{l_t - l_1}{1^\circ} = t_1 + \frac{l_t - l_1}{l_2 - l_1}(t_2 - t_1), \tag{1.4.15}$$

where l_t is a thermometric value that corresponds to a fixed value of "heat".

Formulas (1.4.14) and (1.4.15) characterize the empirical temperature scale. These formulas have a unique meaning only with a fixed choice of thermometric body and thermometric value. As an example of empirical temperature scales, celsius, reaumur, and fahrenheit shafts can be mentioned. Daniel Gabriel Fahrenheit (05.24.1686 – 09.16.1736), René Antoine Ferchault de Réaumur (28.02.1683 – 17.10.1757), and Anders Celsius (27.11.1701 – 25.04.1744) proposed a temperature scales named after them. These scales differ in temperature values corresponding to reference points: $t_2 = 100$, $t_1 = 0$ (Celsius scale, $t_{\circ\mathrm{C}}$); $t_2 = 80$, $t_1 = 0$ (Reaumur scale, t_{R}); $t_2 = 212$, $t_1 = 32$ (Fahrenheit scale, t_{F}). Therefore, the same "heating" is characterized in these scales by different temperatures $t_{\circ\mathrm{C}}$, t_{R}, t_{F}

$$t_{\circ C} = 100\frac{(l_t - l_1)}{l_2 - l_1},$$

$$t_R = 80\frac{(l_t - l_1)}{l_2 - l_1},$$

$$t_F = 32 + 180\frac{(l_t - l_1)}{l_2 - l_1}. \tag{1.4.16}$$

Formulas (1.4.16) allow a simple recalculation of temperature from one scale to another

$$t_{\mathrm{R}} = 0.8\, t_{\circ\mathrm{C}} \quad , \quad t_{\mathrm{F}} = 32 + 1.8\, t_{\circ\mathrm{C}}\,. \tag{1.4.17}$$

The boiling and freezing temperatures of water depend on pressure, and this pressure must be additionally recorded in determining the temperature. In addition, the boiling and freezing temperatures of water are recorded with insufficient accuracy. Therefore, in the International System of Units of SI, it was agreed to determine the temperature scale by one reference point, for which the triple point of water was taken. The temperature of the triple point of water is taken, by definition, equal to 273.16 K. The unit of temperature is defined as 1/273.16 part of the temperature interval between the triple point and the point of absolute zero temperature. The absolute zero point of temperatures is not a reference point, but a temperature 273.16 K below the temperature of the triple point of water.

Choosing the ideal gas as a thermometric body, one can determine the temperature by the formula

$$T = \frac{273.16}{P_0} P, \tag{1.4.18}$$

where P_0 is the gas pressure at the temperature of the triple point of water; P is the gas pressure at the measured temperature. The gas volume during measurement should be constant. The temperature scale defined in this way is called the ***absolute thermodynamic temperature scale***.

The Celsius scale is determined by the condition that the freezing temperature of water at a pressure of $1.013 \cdot 10^5$ Pa is 0 °C. One degree Celsius is equal to one Kelvin. The freezing temperature of water in the thermodynamic scale under these conditions is 273.15 K. Therefore, by definition, the temperature on the Celsius scale $t_{°C}$ is set by equality

$$t = T - 273.15, \tag{1.4.19}$$

where T is the value of temperature, expressed in absolute thermodynamic temperature scale.

1.5. Boltzmann Distribution

The total energy of a gas molecule located in an external potential field is $W = mv^2/2 + W_p$, where W_p is the potential energy of the molecule. In a state of thermodynamic equilibrium, the temperature at different points in the system in an external potential field has the same value. The external potential field has a significant effect on the distribution of the concentration of molecules.

Suppose that the system is in a condition of thermodynamic equilibrium. In this case, the potential force acting on a certain volume of gas is balanced by the forces of pressure on the surface of this volume. A force of $F = -\,\mathrm{grad}(W_p)$ acts on each molecule. Let us consider the balance of forces along the x axis. The force

$$dF_{1x} = -n_0 dx dy dz \frac{\partial W_p}{\partial x} \tag{1.5.1}$$

acts on the molecules in the volume of an infinitesimal cube with edges dx, dy, dz, where n_0 is the concentration of molecules.

The pressure difference between the bases of the cube along the x axis is $(\partial P / \partial x) dx$. Due to the pressure difference manifests force acting on the cube in the direction of the x axis

$$dF_{2x} = -\left(\frac{\partial P}{\partial x}\right) dx dy dz. \tag{1.5.2}$$

Under equilibrium, these forces must compensate each other, i.e. $dF_{1x} + dF_{2x} = 0$, or

$$\left(\frac{\partial P}{\partial x}\right)dx = -n_0 \frac{\partial W_p}{\partial x} dx. \tag{1.5.3}$$

Similar equalities hold for the other two coordinate axes. Adding the left and right sides of equalities (1.5.3) for all coordinate axes, we get

$$\left(\frac{\partial P}{\partial x}\right)dx + \left(\frac{\partial P}{\partial y}\right)dy + \left(\frac{\partial P}{\partial z}\right)dz = dP =$$

$$= -n_0\left(\frac{\partial W_p}{\partial x}dx + \frac{\partial W_p}{\partial y}dy + \frac{\partial W_p}{\partial z}dz\right) = -n_0 dW_p, \tag{1.5.4}$$

where dP, dW_p are complete differentials of pressure and potential energy changes.

From equation (1.3.41), taking into account the fact that $T = \text{const}$, we get

$$dP = kTdn_0, \tag{1.5.5}$$

and therefore

$$\frac{dn_0}{n_0} = -\frac{dW_p}{kT}. \tag{1.5.6}$$

We integrate this equation between points (x_0, y_0, z_0) and (x, y, z) along an arbitrary path. Then we can write the following relation

$$n_0(x,y,z) = n_0(x_0,y_0,z_0)\exp\left[-\frac{W_p(x,y,z) - W_p(x_0,y_0,z_0)}{kT}\right]. \tag{1.5.7}$$

Equation (1.5.7) is called the ***Boltzmann distribution***.

We normalize to zero potential energy at a point (x_0, y_0, z_0), those we assume that the relation $W_p(x_0, y_0, z_0) = 0$ is true. In this case, the Boltzmann distribution can be written in a simpler form

$$n_0 = n_{00}\exp\left(-\frac{W_p}{kT}\right), \tag{1.5.8}$$

where $n_0 = n_0(x, y, z)$; $n_{00} = n_0(x_0, y_0, z_0)$; $W_p = W_p(x, y, z)$.

Let us now consider the case when the concentration of molecules is unknown at any point, and the total number n of molecules in the system is known. Then the Boltzmann distribution must be represented as

$$n_0 = A\exp\left(-\frac{W_p}{kT}\right). \qquad (1.5.9)$$

The normalization constant A must be found from the normalization condition

$$\int_V n_0(x, y, z)dxdydz = n, \qquad (1.5.10)$$

where V is the volume of the system.

Combining formulas (1.5.9) and (1.5.10), we obtain the equation for determining the constant value A

$$\frac{n}{A} = \int_V \exp\left[-\frac{W_p(x, y, z)}{kT}\right]dxdydz. \qquad (1.5.11)$$

The ideal gas pressure can be unambiguously expressed in terms of temperature. Therefore, the Boltzmann distribution allows you to immediately write the pressure distribution in equilibrium (T = const). For a practically important case of pressure P distribution in an isothermal atmosphere with a change in height h, the following barometric formula can be written

$$P(h) = P_0 \exp\left(-\frac{\rho_0 gh}{P_0}\right), \qquad (1.5.12)$$

where $P_0 = P|_{h=0}, \rho_0 = \rho|_{h=0}$, is the pressure and density of the atmosphere at a height of h = 0.

Under conditions of statistical equilibrium, the same average energy falls on each degree of freedom of the system. This statement is called the energy equilibrium distribution among degrees of freedom. A consequence of applying this theorem to an ideal gas leads to the relations

$$\left\langle\frac{mv_x^2}{2}\right\rangle = \left\langle\frac{mv_y^2}{2}\right\rangle = \left\langle\frac{mv_z^2}{2}\right\rangle = \frac{kT}{2}. \qquad (1.5.13)$$

Rather small particles suspended in a liquid, when observed under a microscope, appear to be in continuous jitter. This type of movement is called ***Brownian motion***. This motion is named after Robert Brown (21.12.1773 – 10.06.1858). Energy $3kT/2$, attributable to the three translational degrees of freedom of the particle, leads to the movement of its centre of mass, which is observed under the microscope in the form of trembling. If the Brownian particle is sufficiently rigid, then an additional energy equal to $3kT/2$ falls on its rotational degrees of freedom.

Therefore, with its trembling, the particle also experiences constant changes in orientation in space.

Due to random collisions, Brownian motion occurs in chaotic jumps. The average square of particle removal from the beginning after n jumps is

$$\left\langle r_n^2 \right\rangle = \left\langle r_t^2 \right\rangle = \alpha^2 n = \frac{\alpha^2}{\Delta t} t = \alpha t, \tag{1.5.14}$$

where Δt is the time between jumps; $t = n\Delta t$.

Deviations of a Brownian particle in any direction are equally probable. From this assumption, we can obtain the following relation for a

$$\alpha = \frac{6kT}{b}, \tag{1.5.15}$$

where b is a quantity characterizing the force of liquid friction acting on a Brownian particle.

Therefore, formulas (1.5.14) and (1.5.15) solve the problem of the Brownian motion of particles suspended in a liquid

$$\left\langle r^2 \right\rangle = \frac{6kTt}{b}. \tag{1.5.16}$$

Suppose that particles in a thermodynamic system are distinguishable from each other. The behaviour of such particles obeys the ***Maxwell – Boltzmann distribution***

$$dn(x, y, z, v_x, v_y, v_z) = A \exp\left(\frac{\frac{mv^2}{2} + W_p}{kT} \right) dx dy dz dv_x dv_y dv_z. \tag{1.5.17}$$

The assumption of the distinguishability of particles (molecules, atoms of an ideal gas) is erroneous. However, in the most frequent situations of classical physics, the Fermi – Dirac distribution (distribution is named after Enrico Fermi (29.09.1901 – 28.11.1954) and Paul Adrien Maurice Dirac (8.08.1902 – 20.10.1984)) and Bose – Einstein distribution (distribution is named after Satyendra Nath Bose (1.01.1894 – 4.02.1974) and Einstein) for indistinguishable particles practically coincide with the Maxwell – Boltzmann distribution for distinguishable particles. Due to this, the Maxwell-Boltzmann distribution is the main distribution of classical statistical physics.

1.6. Gas Laws

We introduce the symbol $n = N / V = N_A / V_\mu$, which denotes the number of molecules per unit volume. Then, for the concentration and density of an ideal gas, we can write

$$n = \frac{PN_A}{RT} \quad , \quad \rho = \frac{\mu P}{RT} \,. \tag{1.6.1}$$

An ideal gas can be described by gas laws: the ***Boyle's law*** (law was named after Robert Boyle (25.01.1627 – 31.12.1691) and Edme Mariotte (1620 – 12.05.1684)), the Gay-Lussac's law (the law was made public by Joseph Louis Gay-Lussac (6.12.1778 – 9.05.1850)), and the Charles's law (law was named after Jacques Alexandre César Charles (12.11.1746 –7.04.1823)). According to the Boyle's law, at constant gas mass and constant temperature, the product of pressure and volume is a constant

$$PV = \text{const}, \quad \text{if} \quad T = \text{const} \quad m = \text{const} \,. \tag{1.6.2}$$

Equation (1.6.2) is called the ***isotherm equation***.

Dependence $P = P(V)$ for the isotherm has the form of a hyperbola, the position of which depends on the temperature of the gas. The process in which $T = \text{const}$ is called an ***isothermal process***. ***Internal energy*** U is equal to the sum of the energies of motion of all molecules and the energy of interaction of molecules with individual parts of the thermodynamic system. The internal energy U of the ideal gas depends on its temperature remains constant at $T = \text{const}$. All heat is converted to work by isothermal expansion of the gas. The work performed by the gas during isothermal expansion is equal to the amount of heat Q that must be supplied to the gas to perform this work

$$\delta A = dQ = PdV, \tag{1.6.3}$$

where δA is elementary work; dV is an elementary volume.

Consider the initial and final states of an ideal gas with the corresponding values of volume (V_1, V_2) and pressure (P_1, P_2). In this case, for the isothermal process, we can write

$$P_1 V_1 = P_2 V_2 \,. \tag{1.6.4}$$

Full work in the isothermal process is

$$A_{12} = \int_{V_1}^{V_2} PdV = \frac{m}{\mu} RT \ln \frac{V_2}{V_1} \,. \tag{1.6.5}$$

Gas compression and, accordingly, a negative value of work are observed at $V_1 > V_2$ or $P_1 < P_2$.

The property of a gas to change its volume when pressure changes is called ***compressibility***. The value

$$\chi = \frac{1}{V}\left(\frac{dV}{dP}\right)_T . \tag{1.6.6}$$

is called the ***isotremic compressibility coefficient***

The formulation of the ***Gay-Lussac's law*** has the form: at a constant gas pressure and constant mass, the ratio of the gas volume to its temperature is a constant

$$\frac{V}{T} = \text{const}, \quad \text{if} \quad P = \text{const}, \quad m = \text{const} . \tag{1.6.7}$$

Equation (1.6.7) is called the ***isobar equation***. The dependence $V = V(T)$ for the isotherm has the form of a half-line parallel to the axis V. The process in which $P = \text{const}$ is called the ***isobaric process***. Assume that V_1, T_1 and V_2, T_2 are the volume and temperature of the gas in the initial and final states, respectively. Then

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} . \tag{1.6.8}$$

Gas work performed during the expansion, is

$$A_{12} = P\Delta V = \frac{m}{\mu} R\Delta T , \tag{1.6.9}$$

where $\Delta V = V_2 - V_1$ is volume change; $\Delta T = T_2 - T_1$ is a change in temperature.

Gay-Lussac's law can be represented as

$$V = V_0(1 + \alpha_V t), \tag{1.6.10}$$

where V is the volume of an ideal gas at a temperature of t, counted from 0 °C; V_0 is the volume of an ideal gas at temperature T_0 = 273.16 K.

The value

$$\alpha_V = \frac{V}{V_0 T} \tag{1.6.11}$$

is called the ***coefficient of volume expansion***. In the general case of any substance, the coefficient of volume expansion at constant pressure is the quantity

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P , \tag{1.6.12}$$

where V is the initial volume.

The formulation of the ***Charles's law*** has the form: for a constant volume and constant mass of gas, the ratio of gas pressure to its temperature is a constant

$$\frac{P}{T} = \text{const}, \quad \text{if} \quad V = \text{const}, \quad m = \text{const}. \qquad (1.6.13)$$

Equation (1.6.13) is called the ***isochore equation***. Dependence $P = P(T)$ for isochore has the form of a half-line parallel to axis P. Dependence $P = P(T)$ for the isochore has the form of a half-line extending from the origin of the coordinate system. The process in which $V = \text{const}$ is called the ***isochoric process***. Gas does not perform work in an isochoric process. The thermal energy supplied to the gas is expended to increase its internal energy U.

Assume that P_1, T_1 and P_2, T_2 are the pressure and temperature of the gas in the initial and final states, respectively. Then

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}. \qquad (1.6.14)$$

The change in internal energy during the isochoric process is

$$\Delta U = \frac{m}{\mu} c_V \Delta T, \qquad (1.6.15)$$

where c_V is molar heat capacity at constant volume; $\Delta T = T_2 - T_1$.

Charles's law can be represented as

$$P = P_0(1 + \alpha_P t), \qquad (1.6.16)$$

where P is the pressure of an ideal gas at a temperature of t, counted from 0 °C; P_0 is the pressure of an ideal gas at a temperature of $T_0 = 273.16$ K.

The value

$$\alpha_P = \frac{P}{P_0 T} \qquad (1.6.17)$$

is called ***the thermal coefficient of pressure***.

It should be noted that $\alpha_P = \alpha_V$.

Test questions

1. Formulate the tasks that are studied by molecular kinetic theory.
2. List the postulates of molecular kinetic theory.
3. Give a determination of the amount of the substance.
4. Is the set of conditions: t = 0 °C and $P = 10^3$ Pa normal conditions?
5. What restrictions should be imposed on real gas so that it can be considered as an ideal gas?
6. Define the concept of a non equilibrium state of a thermodynamic system.
7. Explain why the gas volume can be considered as an external parameter, and the pressure and temperature of this gas can be considered as an internal parameter.
8. Give the definition of the gas equation of state.
9. Indicate the macroscopic parameter that characterizes the velocity distribution of the molecules.
10. Prove that the interaction of molecules of a mixture of two gases leads to a state in which the average kinetic energies of these gases are the same.
11. Give a definition of the temperature of the thermodynamic system.
12. Write down the Maxwell distribution.
13. Write down the formulas by which you can determine the characteristic speeds of the molecules: the average speed, the most probable speed and the root-mean-square speed.
14. Formulate the principle of detailed equilibrium.
15. What gas parameters affect the mean free path of a molecule?
16. Write down the basic equation of the kinetic theory of gases.
17. Is the statement true that the Mendeleev – Clapeyron equation is the equation of state of a real gas?
18. Write down the Boltzmann distribution.
19. Formulate the Boyle’s law.
20. Describe the formula by which the isothermal compressibility coefficient is determined.

Problem-solving examples

Problem 1.1

Problem description. An ideal gas contains a number of molecules equal to the Avogadro number. Determine the number ΔN of molecules whose speeds v are less than 0.001 of the most probable speed.

Known quantities: $N = N_A$.

Quantities to be calculated: ΔN.

Problem solution. Consider the distribution of molecules in relative velocities u $\left(u = \frac{v}{v_p}\right)$. The number $dN(u)$ of molecules whose relative velocities are in the range from u to $u + du$ is determined by the formula

$$dN(u) = \frac{4N}{\sqrt{\pi}} \exp\left(-u^2\right) u^2 du, \tag{P.1.1.1}$$

where N is the total number of molecules in volume.

According to the condition of the problem, the maximum molecular velocity is

$$v_m = 0.001 v_p. \tag{P.1.1.2}$$

Hence,

$$u_m = \frac{v_m}{v_p} = 0.001. \tag{P.1.1.3}$$

For such values of u, expression (P.1.1.1) can be significantly simplified. Considering the case of small values of u, we obtain

$$\exp\left(-u^2\right) \approx 1 - u^2, \qquad u << 1. \tag{P.1.1.4}$$

In addition, for small values of u, we can neglect the value $u^2 = u_m^2 = (0.001)^2 = 10^{-6}$ compared to unity. Then formula (P.1.1.1) can be written as

$$dN(u) = \frac{4N_A}{\sqrt{\pi}} u^2 du. \tag{P.1.1.5}$$

We integrate formula (P.1.1.5) by u in the range from 0 to u_m

$$\Delta N = \frac{4N_A}{\sqrt{\pi}} \int\limits_0^{u_m} u^2 du = \frac{4N_A}{\sqrt{\pi}} \left|\frac{u^3}{3}\right|_0^{u_m} = \frac{4N_A}{3\sqrt{\pi}} u_m^3 . \qquad \text{(P.1.1.6)}$$

We substitute the numerical values in the formula (6.1.6)

$$\Delta N = \frac{4 \times 6.02 \times 10^{23}}{3 \times \sqrt{\pi}} \times (0.001)^3 = 4.53 \times 10^{14} .$$

Answer. The number of molecules is ΔN = 4.53×10^{14}.

Problem 1.2

Problem description. The volume of the air bubble as it floated from the bottom of the lake to the surface increased three times. Determine the depth of the lake.

Known quantities: $V_2 = 3V_1$.

Quantities to be calculated: h.

Problem solution. Suppose that the temperature of the lake at any depth is constant. Then, according to the Boyle – Marriott law, we can write the following relation

$$P_1V_1 = P_2V_2 , \qquad \text{(P.1.2.1)}$$

where P_1, P_2 are air pressures in the bubble at the bottom and on the surface of the lake, respectively; V_1, V_2 are the volumes of the air bubble at the bottom and on the surface of the lake, respectively.

The air pressure P_2 in the bubble on the surface of the lake is equal to atmospheric pressure P_0, i.e.

$$P_1 = P_0 . \qquad \text{(P.1.2.2)}$$

We rewrite formula (P.1.2.1) taking into account the conditions of the problem ($V_2 = 3V_1$)

$$P_1V_1 = 3P_0V_1 . \qquad \text{(P.1.2.3)}$$

A consequence of formula (1.2.3) is the relation

$$P_1 = 3P_0 . \qquad \text{(P.1.2.4)}$$

Consequently, the increase in pressure at the bottom of the lake is

$$\Delta P = P_1 - P_0 = 2P_0 . \qquad \text{(P.1.2.5)}$$

The change in pressure, on the other hand, is equal to

$$\Delta P = \rho g h, \tag{P.1.2.6}$$

where ρ is the density of water; h is the depth of the lake; g is the acceleration of gravity.

We equate the right-hand sides of formulas (P.1.2.5) and (P.1.2.6)

$$2P_0 = \rho g h, \tag{P.1.2.7}$$

then

$$h = \frac{2P_0}{\rho g}. \tag{P.1.2.8}$$

Substitute the numerical values in the formula (P.1.2.8)

$$h = \frac{2 \times 1.01 \times 10^5}{10^3 \times 9.8} \approx 20.6\,\text{m}.$$

Answer. The depth of the lake is $h \approx 20.6$ m.

Problem 1.3

Problem description. The vessel has a volume of V = 10 l and is filled with dry air under normal conditions. Water of mass m = 3 g is added to the vessel and heated to a temperature of T = 373 K. Determine the pressure of moist air at this temperature.

Known quantities: V = 10 l, m = 3 g, T = 373 K.

Quantities to be calculated: P.

Problem solution. According to Dalton's law, the pressure in the vessel is

$$P = P_1 + P_2, \tag{P.1.3.1}$$

where P_1 is dry air pressure; P_2 is moist air pressure.

Air heating occurs at a constant volume. Therefore, the dry air pressure at temperature T = 373 K is determined by Charles law

$$\frac{P_0}{T_0} = \frac{P_1}{T}, \tag{P.1.3.2}$$

then

$$P_1 = \frac{P_0 T}{T_0}, \tag{P.1.3.3}$$

where P_0, P_1 are air pressures at temperatures $T_0 = 273$ K and $T = 373$ K, respectively.

We find the pressure of water vapour, considering it an ideal gas. The number n of moles of water vapour molecules in the vessel is

$$n = \frac{m}{\mu}, \tag{P.1.3.4}$$

where m is a mass of water; μ is the molar mass of water vapour.

In this case, the volume occupied by the vapour is

$$V_0' = V_0 n = \frac{V_0 m}{\mu}. \tag{P.1.3.5}$$

We write the combined law of the gas state

$$\frac{P_0 V_0'}{T_0} = \frac{P_2 V}{T}. \tag{P.1.3.6}$$

We determine from formula (P.1.3.6) the vapour pressure

$$P_2 = \frac{P_0 T V_0'}{T_0 V}. \tag{P.1.3.7}$$

We rewrite formula (P.1.3.7) taking into account formula (P.1.3.5)

$$P_2 = \frac{P_0 T m V_0}{T_0 V \mu}. \tag{P.1.3.8}$$

Therefore, the moist air pressure is

$$P = \frac{P_0 T}{T_0} + \frac{P_0 T m V_0}{T_0 V \mu} = \frac{P_0 T}{T_0}\left(1 + \frac{m V_0}{V \mu}\right). \tag{P.1.3.9}$$

We substitute the numerical values in the formula (P.1.3.9)

$$P = \frac{1.01 \times 10^5 \times 373}{273}\left(1 + \frac{3 \times 10^{-3} \times 22.4 \times 10^{-3}}{10^{-2} \times 18 \times 10^{-3}}\right) \approx 1.9 \times 10^5 \text{ Pa}.$$

Answer. Moist air pressure is $P \approx 1.9 \times 10^5$ Pa.

Problems

Problem A

Problem description. Calculate the probability ω that a given ideal gas molecule has a velocity other than $2v_p$ (v_p is the most probable speed) no more than 1%.

Answer. $\omega = 6.63\times10^{-3}$.

Problem B

Problem description. Determine the mean free path $\langle\tau\rangle$ of oxygen molecules at a temperature T = 250 K and a pressure P = 100 Pa.

Answer. $\langle\tau\rangle$ = 2.88 s.

Problem C

Problem description. Cylinders contain gas. The volumes of the cylinders are $V_1 = 20\ l$ and $V_2 = 44\ l$, respectively The pressure in the first cylinder is P_1 = 2.4 MPa. The pressure in the second cylinder is P_2 = 1.6 MPa. Determine the partial pressures P_1' and P_2' for the case when the gas temperature has remained unchanged.

Answer. $P_1' = 1.12\times10^6\ \text{Pa}$, $P_2' = 1.88\times10^6\ \text{Pa}$.

Problem D

Problem description. Determine the density ρ of the gas mixture of hydrogen and oxygen, if their mass fractions are equal, respectively $\omega_1 = 1/9$ and $\omega_2 = 8/9$. The pressure of the mixture is P = 100 kPa. The temperature of the mixture is T = 300 K.

Answer. ρ = 0.402 kg/m^3.

Problem E

Problem description. The volume of the flask is V = 240 cm^3. The flask contains gas at a temperature of T = 290 K and a pressure of P = 50 kPa. Determine the amount of gas substance ν and the number of its molecules N.

Answer. $\nu = 4.97\times10^3$ mol, $N = 2.99\times10^{21}$.

CHAPTER 2. BASICS OF THERMODYNAMICS

2.1. Thermodynamic Methods

The study of the states of macroscopic systems can be carried out not using model ideas about the molecular structure of matter, but based on experimentally established principles and laws. The branch of physics in which the general properties of matter associated with thermal motion in an equilibrium state and the transition process between these states are investigated are called ***thermodynamics***.

Thermodynamics is based on three principles, which are a generalization of experimental data. These principles are carried out regardless of the nature of the bodies forming the system and are accepted without evidence as axioms. The list of these principles is as follows: the energy principle (the first law of thermodynamics), the principle of entropy (the second law of thermodynamics) and the Nernst theorem (the third law of thermodynamics). Sometimes the principle of temperature is called the zero principle of thermodynamics.

Thermodynamics establishes relationships and patterns between physical quantities measured empirically in macroscopic systems. This approach to study is called the ***phenomenological approach***. Physical parameters characterizing the macroscopic state of bodies are called ***thermodynamic parameters***. As such parameters for gaseous substances can be called pressure, volume and temperature. The concepts of energy and volume also have a purely mechanical meaning. The concepts of temperature and entropy are generally not applicable to non-macroscopic systems.

Since the research method in thermodynamics is not connected with model representations, it can be general and often quite simple. Here, after formal mathematical transformations, we get the final result, which can be used to solve specific problems. However, the physical meaning of the phenomenon under consideration remains unrevealed. The study of molecular kinetic mechanisms is carried out by the methods of statistical physics, which makes it possible to clarify the limits of applicability of thermodynamic methods.

Consider the concept of thermodynamic equilibrium. An isolated system is in thermodynamic equilibrium if the thermodynamic parameters that determine its state remain constant for any length of time. Individual macroscopic parts of the equilibrium thermodynamic system are also in equilibrium. Bodies in contact for a sufficiently long time assume the same thermal state. Until equilibrium is established, bodies can be in a non equilibrium state. We note the following features of thermodynamic equilibrium.

1. Strictly speaking, the state parameters are not constant, but experience small fluctuations near their equilibrium average values. Such oscillations are called ***fluctuations***, which are neglected in thermodynamics, since they are negligible.
2. Thermodynamic equilibrium is possible only for a large number of particles forming a thermodynamic system.

The transition of a thermodynamic system from a non equilibrium state to an equilibrium state is called the ***relaxation process***. Moreover, each thermodynamic parameter has its own transition time, which is called the ***relaxation time***. The maximum time of all relaxation times for a given system is called the ***total relaxation time***. Determining the relaxation time for various processes is the task of physical kinetics.

The methods of thermodynamics and the results obtained with their help are used in the theory of phase equilibria, for example, equilibria between various aggregate states. In addition, thermodynamic methods are used in the theory of chemical equilibrium. In classical thermodynamics, quantitatively describe the equilibrium (reversible) processes, and for non equilibrium processes only possible directions for the development of these processes are established. The general theory of the macroscopic description of non equilibrium processes is called the thermodynamics of non equilibrium processes. The thermodynamics of non equilibrium processes describes small deviations from equilibrium states, in particular, determines the dependence of the rate of non equilibrium processes on external conditions. In addition, the thermodynamics of non equilibrium processes contains the formulations of the local first and second principles of thermodynamics and the analysis of transport equations.

Consider the concept of a thermostat and the principle of temperature. Suppose that the mass of a certain body is very large compared to another body. The state of the first body does not change when the bodies touch. In this case, the first body is called a ***thermostat***.

Numerous experimental experiments served as the basis for the formulation of the principle of temperature. The ***temperature principle*** is formulated as follows: there is a state parameter of the system, which is called temperature. This parameter remains unchanged for any process occurring in the thermostat. Since different thermal states correspond to different values of internal energy, the temperature is also associated with this energy. If two bodies are in thermodynamic equilibrium with a third body, then the first two bodies are in thermodynamic equilibrium with each other. This statement makes it possible to determine the temperature of different bodies.

Body temperature cannot be directly measured. The temperature can be measured by studying the change in the physical properties of the body, which depend on temperature (for example, volume, pressure, EMF, electrical resistance, radiation intensity, etc.). Temperature measurement methods can be contact and non-contact. Non-contact methods are also called ***radiation thermometry*** or pyrometry. These methods measure the intensity of thermal radiation. Contact methods are based on comparing the temperature of different bodies with the help of a special test body, which is called a thermometric body. Contact thermometers can be gas, liquid and solid state.

Consider the internal energy of a thermodynamic system. Internal energy can change due to the work that this system does (δA) or due to the work performed by external forces on the system ($\delta A'$).In addition, internal energy can vary due to thermal contact (heat exchange) of the system with a more or less heated body (heater or refrigerator).

The amount of energy that a thermodynamic system transfers to external bodies through force is called the work δA performed by the system

$$\delta A = \sum_i Q_i(T)\delta q_i(T), \tag{2.1.1}$$

where $q_i(T)$ are generalized coordinates (volume, strength of an external electric field, etc.); $Q_i(T)$ are generalized forces.

The amount of energy transferred (or received) by the thermodynamic system during heat exchange with external bodies (without changing external parameters) is called the ***heat*** δQ. Values δA and δQ can be either positive or negative. The system transfers part of the energy to external bodies if $\delta A > 0$.

In accordance with Newton’s third law, the work $\delta A'$ performed by external forces on the system is equal in magnitude and opposite in sign to the work δA that the system performs on the external body

$$\delta A = -\delta A'. \tag{2.1.2}$$

Work and the amount of heat characterize the change in the internal energy of the thermodynamic system and make sense only if there is a process that changes this energy. Therefore, the allegations that the system has a supply of work or a supply of heat are incorrect. Values δA and δQ are not complete differentials. The amount of heat transferred to the system and the work performed by the system depend on how the system passes from the initial state to the final one.

Between thermodynamic systems with different temperatures, a process of transferring a certain amount of heat from a warmer system to a less heated system can occur. The spontaneous irreversible process of heat transfer between systems with different temperatures is called ***heat transfer***. There are three types of heat transfer: thermal conductivity, heat transfer through radiation (radiant heat transfer) and convective heat transfer.

Thermal conductivity is associated with the transfer by contact of thermal energy from a part of the system with a higher temperature to that part of the system that has a lower temperature.

Radiant heat transfer is associated with the transfer of thermal energy between thermodynamic systems that are not in direct contact with each other. In this case, thermodynamic systems exchange thermal energy by means of electromagnetic radiation.

Convective heat transfer is associated with the transfer of thermal energy from one thermodynamic system to another system, which occurs when a stream of liquid, gas or bulk solids moves.

The unit of heat in the SI system is the joule (symbol J)

The amount of heat required to heat a substance by one degree (1 K) is called ***heat capacity***. The heat capacity per unit mass of a substance is called ***specific heat***

$$c = \frac{1}{m}\frac{\delta Q}{\Delta T}, \tag{2.1.3}$$

where δQ is the amount of heat transferred to the body; ΔT is a change in temperature; m is the mass of matter.

Molar heat capacity is the heat capacity referred to one mole of a substance

$$c_{\mu} = \mu c. \tag{2.1.4}$$

The heat capacity of a substance depends on the conditions of its heating. The state of the body is determined by temperature and physical parameters that are independent of temperature. Such parameters may be volume and pressure. Therefore, the heat capacity depends on changes in volume and pressure.

The heat capacity corresponding to processes at constant pressure is called the ***heat capacity at constant pressure*** (c_P). The heat capacity corresponding to processes at a constant volume is called the ***heat capacity at constant volume*** (c_V).

Condition $c_P > c_V$ is always satisfied, since when the thermodynamic system is heated at constant pressure, the internal energy of this system increases and work is performed. Heating a thermodynamic system at a constant volume is accompanied by an increase in only the internal energy of this system

2.2. First Law of Thermodynamics

The ***first law of thermodynamics*** is a generalized law of conservation and conversion of energy for those macroscopic systems in which thermal motion plays an important role. Let us first consider the physical meaning of such thermodynamic quantities as internal energy, work, and the amount of heat.

Thermodynamics and molecular physics mainly study physical processes in which there are no changes at the atomic and nuclear levels. Therefore, when calculating internal energy, atomic energy and nuclear energy are not taken into account. Internal energy is the sum of the kinetic energy of the thermal motion of molecules and atoms, and the potential energy of their interaction. Internal energy is an unambiguous function of the state of a physical system. The change in internal energy is zero $\Delta U = 0$ if the system returns to its original state in the thermodynamic process. Consider the equilibrium thermodynamic process that occurs along an arbitrary closed loop L. In this case, the following relation holds

$$\oint_L dU = 0. \tag{2.2.1}$$

Internal energy is a function of the macroscopic parameters of a thermodynamic system: $U = U(V,T)$, $U = U(P,V)$, $U = U(P,T)$.

Internal energy is an additive quantity: the internal energy of a composite system is equal to the sum of the internal energies of the components of this system

$$U = \sum_{i=1}^{n} U_i \,. \qquad (2.2.2.)$$

The internal energy of one mole of an ideal gas is equal to

$$U = \frac{3}{2} kTN_A = \frac{3}{2} RT \,. \qquad (2.2.3)$$

Molecular physics often considers atoms as material points. Consider a system of n material points (atoms) that do not interact with each other. An unambiguous description of the position of these points requires $i = 3n$ degrees of freedom. To calculate the internal energy of an ideal gas, we use the theorem on the equal distribution of energy over degrees of freedom. Suppose that the number of degrees of freedom of a molecule is i. In this case, the internal energy of the thermal motion of one mole of molecules of an ideal gas is

$$U = \frac{i}{2} RT \,. \qquad (2.2.4)$$

For polyatomic gas molecules at certain temperatures, it is necessary to take into account not only translational degrees of freedom i_t, but also rotational i_r and vibrational i_υ degrees of freedom

$$i = i_t + i_\upsilon + t_r \,. \qquad (2.2.5)$$

Each rotational degree of freedom corresponds to energy $kT/2$. Each vibrational degree of freedom corresponds to energy kT, which is the sum of the kinetic and potential energy of the vibrational motion.

Consider a gas in a cylindrical vessel. The gas is located under a weightless and movable piston with an area of S. The increase in gas volume corresponds to the gas doing work against external pressure forces P. The internal gas pressure is equal to the external pressure on the vessel in the case of a quasi-stationary process. Therefore, the pressure force is $F = PS$. Elementary work performed by gas is equal to

$$\delta A = Fdx = PSdx = PdV \,, \qquad (2.2.6)$$

where dx is an infinitesimal displacement of the piston; $dV = Sdx$ is an infinitely small change in volume. Formula (2.2.6) is written for the isobaric process P = const.

The complete work done by the gas upon the transition from state 1 to state 2 is

$$A = \int_{(1)}^{(2)} PdV \,. \qquad (2.2.7)$$

The amount of heat that the thermodynamic system receives, as well as the work, depends on how the system transitions from the initial state to the final state. However, there is a fundamental difference between the amount of heat and work.

Work is a macrophysical form of energy transfer of ordered movement. Heat is a combination of microphysical processes of energy transfer.

The first law of thermodynamics can be formulated as follows: A change in internal energy dU in thermal processes occurs due to a change in the amount of heat δQ and performing of work δA

$$dU = \delta Q - \delta A, \tag{2.2.8}$$

where δA is the work performed by external forces on the system.

The amount of heat is an important concept of thermodynamics, so the first law of thermodynamics is often formulated as follows

$$\delta Q = dU + \delta A. \tag{2.2.9}$$

The first law of thermodynamics can be formulated as the impossibility of the existence of a ***perpetual motion machine of the first kind***. In other words, it is impossible to build a periodically operating engine that did not receive energy from external sources.

Consider the internal energy as a function of volume and temperature. In this case, we can write the relation for molar heat capacities at a constant volume c_V and constant pressure c_P

$$c_P = c_V + R. \tag{2.2.10}$$

Formula (2.2.10) is called the ***Mayer's relation***. Julius Robert Mayer (25.11.1814 – 20.03.1878) derived this relation.

The thermodynamic process that occurs without heat exchange with the environment is called the ***adiabatic process***. The equation of the adiabatic process in coordinates (T,V) has the form

$$TV^{\gamma-1} = \text{const}, \tag{2.2.11}$$

where $\gamma = \dfrac{c_P}{c_V}$ called the ***adiabatic exponent*** or ***Poisson's ratio***. Equation (2.2.11) is called the ***Poisson's equation***.

The equation of the adiabatic process in coordinates (P,V) has the form

$$PV^{\gamma} = \text{const}. \tag{2.2.12}$$

The work performed by the gas during the adiabatic transition from state (V_1,T_1) to state (V_2,T_2) is

$$A=\frac{m}{\mu}\frac{R}{(\gamma-1)}(T_1-T_2)=\frac{m}{\mu}\frac{RT_1}{(\gamma-1)}\left[1-\left(\frac{V_1}{V_2}\right)^{\gamma-1}\right]. \qquad (2.2.13)$$

Consider the work done by an ideal gas in the processes described by gas laws. The work performed in the isochoric process is

$$A_V=\int_{V_1}^{V_1}PdV=0. \qquad (2.2.14)$$

The work performed in the isobaric process is

$$A_P=\int_{V_1}^{V_2}PdV=P(V_2-V_1)=\frac{m}{\mu}R(T_2-T_1). \qquad (2.2.15)$$

The work performed in the isothermal process is

$$A_T=\int_{V_1}^{V_2}PdV=\frac{m}{\mu}RT\ln\frac{V_2}{V_1}. \qquad (2.2.16)$$

The internal energy of an ideal gas is a function of temperature only. Therefore, for the heat capacities of gases, the behaviour of which is described by classical thermodynamics, the following relations can be written. The heat capacity of monatomic gases (i = 3) is expressed by the following formulas

$$c_V=\frac{3}{2}R \quad , \quad c_P=c_V+R=\frac{5}{2}R. \qquad (2.2.17)$$

The heat capacity of diatomic gases (i = 5) is equal to

$$c_V=\frac{5}{2}R, \quad c_P=\frac{7}{2}R. \qquad (2.2.18)$$

The heat capacity of polyatomic gases (i = 6) is equal to

$$c_V=3R, \quad c_P=4R. \qquad (2.2.19)$$

The classical theory of heat capacity does not completely take into account the energies associated with internal motion in gas molecules. The heat capacities of gases calculated in the framework of the classical theory of heat capacity (formulas (2.2.17) – (2.2.19)) do not always coincide with the experimental values of heat capacities. The correct values of heat capacity are obtained using quantum theory, which takes into account the discrete nature of the energy levels of the molecule.

2.3. Entropy

We write the first law of thermodynamics in the form

$$\delta Q = dU + PdV = c_V dT + PdV. \qquad (2.3.1)$$

Divide both sides of this equation by T

$$\frac{\delta Q}{T} = c_V \frac{dT}{T} + \frac{P}{T} dV. \qquad (2.3.2)$$

We take into account the following relations: $P/T = R/V$, $dT/T = d\ln T$, $dV/V = d\ln V$. We rewrite equation (2.3.2) with these relations

$$\frac{\delta Q}{T} = d\left(c_V \ln T + R\ln V\right). \qquad (2.3.3)$$

The right-hand side of equality (2.3.3) is the total differential. Therefore, the left side of this equality is also a full differential. The state function, whose differential is $\delta Q/T$, is called ***entropy*** and is denoted by the symbol S. Thus

$$dS = \frac{\delta Q}{T}. \qquad (2.3.4)$$

Dependence (2.3.4) is not satisfied for non equilibrium and irreversible processes. It should also be noted that formula (2.3.4) gives a definition of the difference in entropy, but not the absolute value of entropy.

The change in entropy in an isothermal process (T = const), for which the energy state of the gas remains constant, and possible changes in characteristics are caused only by a change in volume, is

$$dS = \frac{PdV}{T} = \frac{RT}{T}\frac{dV}{V} = Rd\ln V. \qquad (2.3.5)$$

Therefore, we can write the following relation

$$\int_{(1)}^{(2)} dS = R\int_{(1)}^{(2)} d\ln V. \qquad (2.3.6)$$

As a result of integration of formula (2.3.6), we obtain

$$S_2 - S_1 = R\left(\ln V_2 - \ln V_1\right) = R\ln\frac{V_2}{V_1}. \qquad (2.3.7)$$

We represent gas atoms in the form of identical spheres that can be inscribed in a cube with side $l = 10^{-10}$ m. The number of such cubes for volumes V_1 and V_2 is

$N_1 = V_1/l^3$ and $N_2 = V_2/l^3$, respectively. The number of atoms in a gas mole is equal to the Avogadro constant N_A. The number of spatial microstates for volumes V_1 and V_2 is

$$\Gamma_1 = \frac{N_1!}{(N_1 - N_A)!}, \quad \Gamma_2 = \frac{N_2!}{(N_2 - N_A)!} \tag{2.3.8}$$

Consider not too compressed gas when relations $N_1 >> N_A$ and $N_2 >> N_A$ is satisfied. In this case, we can write

$$\ln\frac{V_2}{V_1} = \frac{1}{N_A}\ln\frac{\Gamma_2}{\Gamma_1}. \tag{2.3.9}$$

Therefore, to change the entropy, we can write the formula

$$S_2 - S_1 = \frac{R}{N_A}\ln\frac{\Gamma_2}{\Gamma_1} = k\ln\Gamma_2 - k\ln\Gamma_1, \tag{2.3.10}$$

where $k = R/N_A$ is the Boltzmann constant.

A consequence of formula (2.3.10) is the equality

$$S = k\ln\Gamma. \tag{2.3.11}$$

It can be argued that entropy is determined by the logarithm of the number of microscopic states of the gas through which this macroscopic state of the gas is realized. Equality (2.3.11) is called the ***Boltzmann formula***.

Formula (2.3.11) allows you to give entropy a visual interpretation. An increase in the ordering of the system leads to a decrease in the number of microscopic states by which this macroscopic state of the gas is realized.

We generalize the previous statement. A system that is left to itself moves in the direction of an equilibrium state. Therefore, in a system that is left to itself, entropy does not decrease.

Consider the change in entropy in the processes of an ideal gas. We transform the formulas (2.3.3) and (2.3.4)

$$dS = d(c_V \ln T + R\ln V). \tag{2.3.12}$$

The change in entropy during an isothermal process is described by the formula (2.3.7).

The change in entropy during the isochoric process ($dV = 0$) is equal to

$$S_2 - S_1 = c_V \ln\frac{T_2}{T_1}, \tag{2.3.13}$$

therefore, entropy increases with increasing temperature. This result can be explained by the fact that the average particle energy increases with temperature, and therefore the number of possible energy states also increases.

The change in entropy in the adiabatic process ($\delta Q = 0$) is equal to $dS = \delta Q/T = 0$. Adiabatic expansion of gas is accompanied by an increase in entropy due to an increase in gas volume. On the other hand, entropy decreases due to a decrease in temperature with an increase in volume. These two trends completely cancel each other out, and entropy remains unchanged S = const.

A ***cyclic process*** is the process by which the system returns to its original state. The cyclic process is depicted on the process diagram of a closed curve.

Work done as a result of a cyclic process is

$$A = \int_{\substack{(1)\\L_1}}^{(2)} PdV + \int_{\substack{(1)\\L_2}}^{(2)} PdV, \tag{2.3.14}$$

where L_1 and L_2 are the parts that together make up a closed cycle curve in a process diagram.

We write the first law of thermodynamics for a cyclic process

$$\oint \delta Q = \oint dU + \oint PdV. \tag{2.3.15}$$

The closed-loop integral of the total differential is zero

$$\oint dU = U_1 - U_1 = 0. \tag{2.3.16}$$

Hence

$$\oint \delta Q = \oint PdV = A. \tag{2.3.17}$$

All work done in a cycle is done at the expense of the amount of heat that has entered the system.

By its significance, a system that performs a cyclic process is a heat engine that does work due to the amount of heat entering this machine from a thermostat. The efficiency of the heat engine is

$$\eta_h = 1 - \frac{Q_2}{Q_1}, \tag{2.3.18}$$

where Q_1 is the amount of heat that entered the heat engine; Q_2 is the amount of heat that leaves the heat engine.

The simplest in content, but important in principle, is the ***Carnot cycle***. The Carnot cycle (this model was proposed by Nicolas Léonard Sadi Carnot (1.06.1796 – 24.081832)) consists of two isotherms at temperatures T_1 and T_2 between states 1, 2 and 3, 4; as well as two adiabats between states 2, 3 and 4, 1. When performing the Carnot cycle, two thermostats are needed: a heat transmitter (heater) with a temperature of T_1 and a heat receiver (refrigerator) with a temperature of T_2.

The efficiency of the Carnot cycle is

$$\eta_C = 1 - \frac{T_2}{T_1}. \tag{2.3.19}$$

The efficiency factor of the Carnot cycle does not depend on the working substance and on the structural details of the design of the heat engine, but depends only on the ratio of the temperatures of the heat transmitter and heat receiver. The choice of an absolute thermodynamic temperature scale is based on this property.

2.4. Second Law of Thermodynamics

Consider the efficiency of the heat engine and the Carnot cycle. The following statement is true: the efficiency of an irreversible Carnot cycle machine cannot be greater than the efficiency of a reversible machine that has the same heat sink and heat transfer.

The coefficient of efficiency of a reversible Carnot cycle is greater than the coefficient of efficiency of any other reversible cycle in which the maximum and minimum temperatures are equal, respectively, to the temperature of the heat transmitter and the temperature of the heat receiver of the Carnot cycle.

Consider a system consisting of two series-connected heat engines. The system includes a thermostat with a temperature of T_1. The heat taken from the thermostat is transferred to a reversible machine 1 operating according to the Carnot cycle. This machine performs work δA_1 throughout its cycle and transfers heat δQ to heat engine 2. Transmission occurs at temperature T. The heat engine 2 may cycle in a reversible or irreversible manner. Temperature T is not constant and depends on the processes that occur in machine 2 and its environment. Thermal engine 2 performs work A_2 in its cycle. The cycle time of the heat engine 1 is much shorter than the cycle time of the heat engine 2. Therefore, during one cycle of operation of the heat engine 1, the temperature T can be considered constant.

The total work A performed by both heat engines during the cycle of operation of heat engine 2 is

$$A = \oint \delta A_1 + A_2 = \oint \left(\delta A_1 + \delta Q \right) = T_1 \oint \frac{\delta Q}{T}. \tag{2.4.1}$$

The only result of the cycle cannot be the production of work. Consequently, the only possibility for the functioning of this system is the entry of work into the system, or, in extreme cases, the equality to zero of the work produced by the system

$$A \le 0. \tag{2.4.2}$$

Based on formulas (2.4.1) and (2.4.2), we can write the following inequality

$$\oint \frac{\delta Q}{T} \leq 0, \tag{2.4.3}$$

insofar as T_1 = const > 0. Formula (2.4.3) is called the ***Clausius inequality*** and holds for any cycles.

Consider the case of a heat engine 2 operating in a reversible cycle. In this case, for the Clausius inequality, we can use the equal sign, i.e. $A < 0$. The heat engine 1 operates in a reversible cycle by definition. Consequently, the entire system of heat engines 1 and 2 also works in a reversible cycle. Therefore, a system of two heat engines can be reversed even then $A > 0$, which contradicts the first law of thermodynamics. Consequently, condition $A < 0$ cannot be used, and only the possibility of the equal sign $A = 0$ remains.

Summarizing the foregoing, it can be argued that for reversible processes in Clausius inequality (2.4.3) only the equal sign can be used, and for reversible processes both signs can be used.

Consider reversible cycles. In this case, inequality (2.4.3) has the form

$$\oint \frac{\delta Q}{T} = 0. \tag{2.4.4}$$

Therefore, under the sign of the integral is the full differential $\delta Q/T = dS$, where S is entropy. These considerations allow us to conclude that the formula for the entropy of an ideal gas is generalized to an arbitrary case. In addition, it can be argued that the Boltzmann formula is valid not only for an ideal gas, but also for arbitrary systems.

Consider a closed system, i.e. a system isolated from other systems. Suppose that in a certain process this system goes from state 1 to state 2. We return the system using a reversible process to state 1. In this case, of course, it is necessary to eliminate the isolation of the system. As a result of the system returning to a state, a cycle is formed to which the Clausius inequality can be applied

$$\oint \frac{\delta Q}{T} = \int\limits_{L_1}^{(2)} \frac{\delta Q}{T} + \int\limits_{L_2}^{(1)} \frac{\delta Q}{T} \leq 0. \tag{2.4.5}$$

The system remained isolated during the transition 1 → 2 along the path L_1. Therefore, the amount of heat δQ in the integral taken along the path L_1 is zero. All this integral is also equal to zero. On the other hand, in the reversible transition 2 → 1 in the integrand, we can assume that $\delta Q/T = dS$. Then formula (2.4.5) can be rewritten as follows

$$\underset{L_2}{\int_{(2)}^{(1)}} \frac{\delta Q}{T} = \underset{L_1}{\int_{(2)}^{(1)}} dS = S_1 - S_2 \le 0,$$

or

$$S_2 \ge S_1. \tag{2.4.6}$$

Upon the transition of a closed system from state 1 with entropy S_1 to state 2 with entropy S_2, the entropy either increases or remains unchanged. This statement, together with the statement on the existence of entropy (2.3.4), is the content of the ***second law of thermodynamics***.

More briefly, the second law of thermodynamics can be formulated as follows: <u>in the processes of an isolated system, the entropy does not decrease</u>. An essential feature of this statement is that it relates to isolated systems. In uninsulated systems, entropy can increase and decrease, and remain unchanged depending on the nature of the process.

It should be noted that in an isolated system, entropy remains unchanged only in reversible processes. Entropy does not decrease in irreversible processes.

Thermodynamic processes occur, as a rule, irreversibly in a system left to itself (isolated). This means that practically the entropy of an isolated system always grows. An increase in entropy means the system is approaching the state of thermodynamic equilibrium.

Thus, the first law of thermodynamics describes the quantitative relations between the quantities characterizing a system with various changes in the state of this system. But the first law of thermodynamics does not say anything about the direction of these changes. The second law of thermodynamics indicates the direction of changes in the system if these changes should occur or the absence of changes if these changes cannot occur.

Entropy is proportional to the number of microscopic states by which this macroscopic state is realized. An increase in entropy in an isolated system means a change in the characteristics of the system in the direction of the most probable, i.e. equilibrium state. However, in a system, in principle, fluctuations are possible, in which a change in the characteristics of the system occurs in the direction of less likely macroscopic states. At this time interval, the entropy of an isolated system does not increase, but decreases or remains unchanged.

Thus, the law of not decreasing entropy in an isolated system does not contain an absolute prohibition of decreasing entropy. The relative role of fluctuations increases for small systems, for example, systems with a small number of particles. Consequently, in systems with a relatively small number of particles, the probability of violating the ban on a decrease in entropy is much greater than in systems with a large number of particles.

However, in the practical case, the law of not decreasing entropy in isolated systems that have a sufficiently large number of particles can be considered as absolute.

The calculation of the entropy of irreversible processes is based on the fact that entropy is a function of the state. Suppose that a system has passed from one state to another through an irreversible process. It is logical to mentally transfer the system from the first state to the second using some reversible process and calculate the change in entropy that occurs in this case. This change is equal to the change in entropy in an irreversible process.

Consider an example of calculating the change in entropy in an irreversible process of equalizing the pressure in a gas. The gas is divided into two parts. These parts initially do not touch each other and have different pressures but the same temperature T. Suppose the system is thermally isolated. The density of gases is such that these gases can be considered ideal gases. This means that the internal energy of gases depends only on temperature and does not change after gas mixing, because gas temperatures were initially the same.

In this case, the equilibrium process, replacing the non equilibrium one, consists in the fact that each of the parts of the gas in the volumes V_1 and V_2 expands isothermally to the full volume $V_1 + V_2$. In this case, the change in entropy is

$$\Delta S = \int_{(1)}^{(2)} dS = \int_{V_1}^{V_1+V_2} \frac{PdV}{T} + \int_{V_2}^{V_1+V_2} \frac{PdV}{T}. \tag{2.4.7}$$

Formula (2.4.7) is written taking into account the fact that $TdS = dU + PdV$ ($dU = 0$). In addition, we take into account that $P/T = mR/\mu V$, where μ is the molar mass of gas. Then, as a result of integration for changing the entropy, we can write

$$\Delta S = \frac{m_1}{\mu} R \ln \frac{V_1 + V_2}{V_1} + \frac{m_2}{\mu} R \ln \frac{V_1 + V_2}{V_2}. \tag{2.4.8}$$

Pressure after gas mixing can be found according to Dalton's law

$$P_3 = \frac{P_1 V_1 + P_2 V_2}{V_1 + V_2}. \tag{2.4.9}$$

2.5. Thermodynamic Potentials

Thermodynamics includes consideration of the full differentials of various state functions. Different pairs of variables can be taken as independent variables of such differentials. Consider function F, which can be investigated as a function with arguments x, y, or as a function with arguments x, z. The total differentials of the function in these cases will have the form

$$dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy, \tag{2.5.1}$$

$$dF = \frac{\partial F}{\partial x}dx + \frac{\partial F}{\partial z}dz. \qquad (2.5.2)$$

Formulas (2.5.1) and (2.5.2) contain derivatives $\partial F/\partial x$, the meaning and meaning of which are different. For formula (2.5.1), the value $\partial F/\partial x$ is the derivative with a constant value of y, and for the formula (2.5.2), the value $\partial F/\partial x$ is the derivative with a constant value of z. Values y and z in order to avoid confusion put as an index with the corresponding derivatives

$$\left(\frac{\partial F}{\partial x}\right)_y \neq \left(\frac{\partial F}{\partial x}\right)_z. \qquad (2.5.3)$$

We consider the full differentials of functions $z = z(x,y)$, $y = y(x,z)$, $x = x(y,z)$ and take into account the formula (2.5.3). In this case, we can write the following equality

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \qquad (2.5.4)$$

Suppose that the value $d\Phi$ is a total differential and can be written as

$$d\Phi = Pdx + Qdy, \qquad (2.5.5)$$

where $P = P(x,y)$ and $Q = Q(x,y)$ are known functions.

Using the definition and properties of the total differential, we can write the equalities

$$P = \left(\frac{\partial \Phi}{\partial x}\right)_y, \quad Q = \left(\frac{\partial \Phi}{\partial y}\right)_x, \quad \left(\frac{\partial P}{\partial y}\right)_x = \left(\frac{\partial Q}{\partial x}\right)_y. \qquad (2.5.6)$$

The main functions of the state include: pressure P, volume V, temperature T, internal energy U, enthalpy H (***enthalpy*** can be determined as a function of the state of a thermodynamic system, which is equal to the sum of the internal energy and the product of pressure by volume: $H = U + PV$) and entropy S.

We consider the second law of thermodynamics for reversible processes in the form

$$TdS = dU + PdV, \qquad (2.5.7)$$

where it is taken into account that $\delta Q = TdS$.

We rewrite (2.5.7) in the form

$$\delta A = PdV = -dU + TdS. \qquad (2.5.8)$$

The work performed by the system in the isothermal process is

$$\delta A = -d(U - TS) = -dF. \tag{2.5.9}$$

Consequently, the infinitesimal work performed by the system in the isothermal process is a complete differential. Function F is called ***free energy*** (concept of free energy was developed by Hermann Ludwig Ferdinand von Helmholtz (31.08.1821 – 8.09.1894)) or the ***Helmholtz function***

$$F = U - TS. \tag{2.5.10}$$

Free energy is a function of state.

Consider a function G that is defined as follows

$$G = F + PV = H - TS. \tag{2.5.11}$$

Function G is called the ***Gibbs thermodynamic potential***. Thermodynamical potential was named after Josiah Willard Gibbs (11.02.1839 – 28.04.1903).

Each of the thermodynamic functions U, H, F, G can be represented as a function of any two independent variables taken from the following list P, V, T, S. The total differentials of these functions are equal

$$dU = TdS - PdV, \tag{2.5.12}$$

$$dH = TdS + VdP, \tag{2.5.13}$$

$$dF = -SdT - pdV, \tag{2.5.14}$$

$$dG = -SdT + VdP. \tag{2.5.15}$$

It follows from formula (2.5.12) that the quantities T and P play the role of generalized forces if internal energy is considered as potential energy expressed through the generalized coordinates S and V, i.e. $U = U(S,V)$. This gives reason to call function $U = U(S,V)$ the thermodynamic potential.

Arguing in this way, we can conclude that enthalpy $H = H(S,P)$ is the thermodynamic potential with respect to variables (S,P); free energy $F = F(T,V)$ is the thermodynamic potential with respect to variables (T,V); Gibbs thermodynamic potential $G = G(T,P)$ is the thermodynamic potential with respect to variables (T,P).

It can be shown that the heat capacities at constant values of pressure and volume are interconnected as follows

$$c_P - c_V = -T\frac{(\partial V / \partial T)_P^2}{(\partial V / \partial P)_T}. \tag{2.5.16}$$

Formula (2.5.16) in combination with the previously obtained formulas for dU, dH, and dS allows us to determine the values of U, H and S if the values of P, V, T and one of the heat capacities c_P or c_V are known. On the other hand, free energy F and the Gibbs function G are expressed in terms of U, H and S, therefore they can also be determined.

This fixes the properties of the substance, which must be measured in order to be able to describe all of its thermodynamic properties. In this case, only pure substances are meant.

Consider the criteria of thermodynamic stability. The main criterion for thermodynamic stability can be formulated as follows: the state of an adiabatic isolated system is stable at the maximum entropy of the system. Clausius inequality for an infinitely small irreversible process has the form

$$\delta Q < TdS. \tag{2.5.17}$$

We rewrite equation (2.5.17) taking into account the first law of thermodynamics

$$dU + PdV - TdS < 0. \tag{2.5.18}$$

We list several important particular cases of the stability criterion that follow from equation (2.5.18).

The stability criterion for a system with constant volume and entropy has the form

$$dU < 0. \tag{2.5.19}$$

Consequently, the state with a minimum of internal energy is stable U.

The stability criterion for a system with constant pressure and entropy has the form

$$d(U + PV) < 0. \tag{2.5.20}$$

Consequently, the state with a minimum value of enthalpy is stable H.

The stability criterion for a system with a constant volume and temperature has the form

$$d(U - TS) < 0. \tag{2.5.21}$$

Therefore, a stable state is at a minimum value of free energy F.

The stability criterion for a system with constant temperature and pressure has the form

$$dG < 0. \tag{2.5.22}$$

Consequently, the state is stable at the minimum value of the Gibbs thermodynamic potential G.

The stability of the state of a thermodynamic system is ensured by the fact that when a system is brought out of equilibrium, factors arise in it that tend to return this system to an equilibrium position. In thermodynamics, this statement is called the ***Le Chatelier's principle***. The principle was named after Henry Louis Le Chatelier (8.10.1850 – 17.09.1936) and Karl Ferdinand Braun (6.06.1850 – 20.04.1918).

The average energy of a thermodynamic system can be expressed as follows

$$<W> = -\frac{\partial \ln Z}{\partial \beta}. \qquad (2.5.23)$$

where $\beta = 1/(kT)$.

The value

$$Z = \sum_i \exp(-\beta W_i) \qquad (2.5.24)$$

is called the ***statistical sum***.

Free energy F is related to the partition function by the ratio

$$F = -kT \ln Z. \qquad (2.5.25)$$

The remaining thermodynamic potentials can be expressed in terms of free energy, which, in turn, is related to the partition function by the formula (2.5.24).

Thus, knowledge of the statistical sum allows a complete analysis of the thermodynamic state of the system.

2.6. Third Law of Thermodynamics

Entropy as a function of the state of the system in a reversible process is specified up to an arbitrary constant. Therefore, the second law of thermodynamics does not uniquely determine the difference in the entropies of two states related to different systems. The problem of determining entropy in such cases is solved by the fundamental ***Nernst theorem***, established experimentally. Nernst's theorem cannot be deduced from the first and second laws of thermodynamics. This theorem applies only to the thermodynamic equilibrium states of the system. Nernst theorem was named after Walther Hermann Nernst (25.06.1864 – 18.11.1941).

There are several formulations of the Nernst theorem, which are equivalent to each other.

1. The entropy S of any system at absolute zero temperature $T = 0$ is a universal constant S_0, which does not depend on any variable parameters (pressure, volume, etc.). Guillaume Amontons (08.31.1663 - 10.10.1705) concluded that there is an absolute zero temperature.
2. Entropy S tends to a certain finite limit S_0 as the temperature tends to zero $T \rightarrow 0$. The limit value S_0 does not depend on the final state of the system.

3. The increment of entropy ΔS does not depend on the specific values of the thermodynamic parameters of the state of the system and tends to a well-defined finite limit.
4. All processes at an absolute zero temperature $T = 0$, at which the system passes from one equilibrium state to another, occur without a change in entropy.

The choice of a universal constant S_0 equal to entropy at an absolute zero of temperature is arbitrary. Typically, the entropy of any equilibrium system at an absolute zero temperature is taken equal to zero $S_0 = 0$.

The validity of the Nernst theorem can only be proved by an experimental verification of the consequences of this theorem. Nernst's theorem is usually called the ***third law of thermodynamics***.

Consider the consequences of Nernst's theorem. The heat capacities of all substances should tend to zero while absolute thermodynamic temperature tends to zero

$$c(T) \to 0 \quad \text{at} \quad T \to 0, \tag{2.6.1}$$

where $c(T) = c_V$ at $V = \text{const}$ and $c(T) = c_P$ at $P = \text{const}$.

The relation (2.6.1) is confirmed experimentally for all studied systems.

Consider the case when the absolute thermodynamic temperature tends to zero. Then the isobaric coefficient of thermal expansion α_P and the isochoric thermal coefficient of pressure β_V also tend to zero

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{V}\left(\frac{\partial S}{\partial P}\right)_T \to 0 \quad \text{at} \quad T \to 0, \tag{2.6.2}$$

$$\beta_V = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V = -\frac{1}{P}\left(\frac{\partial S}{\partial V}\right)_T \to 0 \quad \text{at} \quad T \to 0. \tag{2.6.3}$$

For very low temperatures $T \approx 0$, the Mendeleev – Clapeyron equation is not satisfied even in those cases when the forces of interaction of the molecules are negligible.

A consequence of formula (2.6.3) is that near absolute zero the gas pressure is practically independent of temperature and is a function of only the density $P = P(\rho)$. Gases whose pressure depends on density are called ***degenerate gases***. The state of the gas in which the dependence is observed is called a ***degenerate state***. The internal energy U of a gas for a degenerate state is independent of temperature and is determined only by the density of the gas $U = U(\rho)$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \to -P(\rho) \quad \text{at} \quad T \to 0. \tag{2.6.4}$$

This property of internal energy is confirmed experimentally. In particular, it was found that the electron gas in metals even at ordinary temperatures does not make a noticeable contribution to the heat capacity. According to the definition of heat capacity, such a property can be observed if relation (2.6.4) holds and $U \neq U(T)$.

The system cannot be cooled to absolute zero using finite changes in thermodynamic parameters. From the relation

$$\frac{1}{T}\frac{dT}{dP} = \frac{V\alpha_P}{c_P} \to \text{const} \quad \text{at} \quad T \to 0 \tag{2.6.5}$$

it follows that the pressure change dP should increase unlimitedly for $T \to 0$ for the temperature to change by a finite value dT.

The third law of thermodynamics is a macroscopic manifestation of the quantum properties of thermodynamic systems. The third law of thermodynamics contradicts the notions of classical mechanics, according to which, even at an absolute zero of temperatures, the system must be in a continuous set of dynamic states.

In essence, it is more correct to consider the Nernst theorem simultaneously with the laws of ideal gases. The laws of ideal gases are also ultimate laws, namely, laws when pressure tends to zero $P \to 0$.

Thus, along with the first and second laws of thermodynamics, two more limit laws should be considered

$$\lim_{P \to 0} PV = RT \ \text{for gaseous systems,} \tag{2.6.6}$$

$$\lim_{T \to 0} S = 0 \ \text{for condensed systems.} \tag{2.6.7}$$

The indicated relations (2.6.6) and (2.6.7) are based on empirical data, i.e. in the framework of thermodynamics, they remain theoretically unprovable.

Test questions

1. List the three laws of thermodynamics.
2. Indicate the features of thermodynamic equilibrium.
3. Give a description of the three main types of heat transfer.
4. Write down the formula that determines the molar heat capacity of the substance.
5. Describe the types of energy that make up the internal energy of a substance.
6. Is the statement that the internal energy of one mole of an ideal gas depends on its volume true?

7. List the types of degrees of freedom that must be considered for polyatomic gas molecules.
8. Give the mathematical form for writing the first law of thermodynamics.
9. Write down the Mayer's relation.
10. Give the ratio for the work of an ideal gas, which is performed in an adiabatic process.
11. Draw a graph of the equation $U = f(P)$, where U is the internal energy and P is the pressure of an ideal gas.
12. Write down the Boltzmann formula.
13. Explain the immutability of entropy during adiabatic expansion of the gas.
14. Provide a detailed description of the Carnot cycle.
15. Write down Clausius inequality.
16. Formulate the second law of thermodynamics.
17. Is the statement true that the entropy of an isolated system is unchanged?
18. Write down the formula for the Helmholtz function.
19. Formulate a stability criterion for a system with constant volume and entropy.
20. What parameters affect the internal energy of a degenerate state of a gas?

Problem-solving examples

Problem 2.1

Problem description. Calculate the specific heat c_V and c_P of a mixture of neon and hydrogen. Mass fraction of gases, respectively, equal to $\omega_1 = 0.8$ and $\omega_2 = 0.2$. The specific heat of neon is equal to $c_{V1} = 624$ J/(kg·K), $c_{P1} = 1.04\times10^3$ J/(kg·K). The specific heat of hydrogen is equal to $c_{V2} = 1.04\times10^4$ J/(kg·K), $c_{P2} = 1.46\times10^4$ J/(kg·K).

Known quantities: $\omega_1 = 0.8$, $\omega_2 = 0.2$, $c_{V1} = 624$ J/(kg·K), $c_{P1} = 1.04\times10^3$ J/(kg·K), $c_{V2} = 1.04\times10^4$ J/(kg·K), $c_{P2} = 1.46\times10^4$ J/(kg·K).

Quantities to be calculated: c_V, c_P.

Problem solution. The heat required to heat the mixture to a temperature of ΔT is

$$Q = c_V(m_1 + m_2)\Delta T, \tag{P.2.1.1}$$

where c_V is the specific heat of the mixture calculated at a constant volume; m_1 is a mass of neon; m_2 is a mass of hydrogen.

Heat from formula (2.1.1) can be calculated in another way

$$Q = \left(c_{V1}m_1 + c_{V2}m_2\right)\Delta T\,, \tag{P.2.1.2}$$

where c_{V1} and c_{V2} are specific heat capacities at a constant volume for neon and hydrogen, respectively.

We equate the right-hand sides of formulas (2.1.1) and (2.1.2)

$$c_V\left(m_1 + m_2\right) = c_{V1}m_1 + c_{V2}m_2\,. \tag{P.2.1.3}$$

We express the heat capacity at a constant volume from the formula (P.2.1.3)

$$c_V = c_{V1}\frac{m_1}{m_1 + m_2} + c_{V2}\frac{m_2}{m_1 + m_2}\,. \tag{P.2.1.4}$$

Quantities

$$\omega_1 = \frac{m_1}{m_1 + m_2}\,, \tag{P.2.1.5}$$

$$\omega_2 = \frac{m_2}{m_1 + m_2} \tag{P.2.1.6}$$

determine the mass fraction of neon and hydrogen, respectively.

We rewrite formula (P.2.1.4), taking into account the notation in formulas (P.2.1.5) and (P.2.1.6)

$$c_V = c_{V1}\omega_1 + c_{V2}\omega_2\,. \tag{P.2.1.7}$$

We substitute the numerical values in the formula (P.2.1.7)

$$c_V = 624 \times 0.8 + 1.04 \times 10^4 \times 0.2 = 2.58 \times 10^3\ \text{J/}\left(\text{kg} \cdot \text{K}\right).$$

Arguing in this way, one can obtain a formula for calculating the specific heat of a mixture at constant pressure

$$c_P = c_{P1}\omega_1 + c_{P2}\omega_2\,, \tag{P.2.1.8}$$

where c_{P1} and c_{P2} are specific heat at constant pressure for neon and hydrogen, respectively.

We substitute the numerical values in the formula (P.2.1.8)

$$c_P = 1.04 \times 10^3 \times 0.8 + 1.46 \times 10^4 \times 0.2 = 3.75 \times 10^3\ \text{J/}\left(\text{kg} \cdot \text{K}\right).$$

Answer. The specific heat of the mixture at constant values of volume and pressure are c_V = 2.58×10^3 J/(kg·K) and c_P = 3.75×10^3 J/(kg·K), respectively.

Problem 2.2

Problem description. Oxygen occupies volume $V_1 = 1$ m^3 and is under pressure $P_1 = 200$ kPa. The gas was initially heated at constant pressure to a volume of $V_2 = 3$ m^3. Then the gas was heated at a constant volume to a pressure of $P_2 = 500$ kPa. Calculate the following values: 1) change in the internal energy of the gas ΔU; 2) the work that gas performed A; 3) the amount of heat Q transferred to the gas.

Known quantities: $V_1 = 1$ m^3, $P_1 = 200$ kPa, $V_2 = 3$ m^3, $P_2 = 500$ kPa.

Quantities to be calculated: ΔU, A, Q.

Problem solution. The state of the gas described in the condition is denoted by: (P_1,V_1,T_1), (P_2,V_2,T_2), (P_3,V_3,T_3) for state 1, 2 and 3, respectively.

The change in the internal energy of a gas during its transition from state 1 to state 3 is expressed by the formula

$$\Delta U = c_V m \Delta T, \tag{P.2.2.1}$$

where c_V is the specific heat of the gas at a constant volume; m is the mass of gas; ΔT is the temperature difference corresponding to the final (3) and initial (1) states: $\Delta T = T_3 = T_1$.

The heat capacity of gas at a constant volume is

$$c_V = \frac{i}{2}\frac{R}{\mu}, \tag{P.2.2.2}$$

where i is the number of degrees of freedom of gas; μ is the molar mass of gas; R is a gas constant.

The change in the internal energy of the gas is

$$\Delta U = \frac{i}{2}\frac{m}{\mu}R\left(T_3 - T_1\right). \tag{P.2.2.3}$$

The equation of state of an ideal gas (the Mendeleev-Clapeyron equation) has the form

$$PV = \frac{m}{\mu}RT, \tag{P.2.2.4}$$

where P is gas pressure; V is the volume of gas.

The initial and final temperatures are equal

$$T_1 = \frac{\mu P_1 V_1}{mR}, \tag{P.2.2.5}$$

$$T_3 = \frac{\mu P_2 V_2}{mR}. \tag{P.2.2.6}$$

In this case, formula (P.2.2.3) can be rewritten as follows

$$\Delta U = \frac{i}{2}\left(P_2 V_2 - P_1 V_1\right). \tag{P.2.2.7}$$

We substitute the numerical values in the formula (P.2.2.7)

$$\Delta U = \frac{5}{2}\left(5\times10^5 \times 3 - 2\times10^5 \times 1\right) = 3.25\times10^6 \text{ J}.$$

The total work done by gas is

$$A = A_1 + A_2, \tag{P.2.2.9}$$

where A_1 is the work done in the section 1-2; A_2 is the work done in the section 2-3.

In section 1-2, the pressure is constant. Работа в этом случае равна

$$A_1 = P_1\left(V_2 - V_1\right). \tag{P.2.2.10}$$

In section 2-3, the gas volume does not change and, therefore, the gas operation in this section is zero ($A_2 = 0$).In this way

$$A = A_1 = P_1\left(V_2 - V_1\right). \tag{P.2.2.11}$$

We substitute the numerical values in the formula (P.2.2.11)

$$A = 2\times10^5 \times (3-1) = 4\times10^5 \text{ J}.$$

According to the first law of thermodynamics, the amount of heat transferred to a gas is equal to the sum of the work A done by the gas and the change in internal energy ΔU

$$Q = \Delta U + A. \tag{P.2.2.12}$$

We substitute the numerical values in the formula (P.2.2.12)

$$Q = 3.25\times10^6 + 4\times10^5 = 3.65\times10^6 \text{ J}.$$

Answer. The change in the internal energy of the gas is ΔU = 3.25×10^6 J. Work done by gas is A = 4×10^5 J. The amount of heat transferred to the gas is Q = 3.65×10^6 J.

Problem 2.3

Problem description. Calculate the change in entropy ΔS when heating water of mass m = 100 g from temperature t_1 = 0°C to temperature t_2 = 0°C and the subsequent conversion of water into vapour at the same temperature.

Known quantities: m = 100 g, t_1 = 0°C, t_2 = 0°C.

Quantities to be calculated: ΔS.

Problem solution. The total change in entropy for this problem is

$$\Delta S = \Delta S' + \Delta S'', \tag{P.2.3.1}$$

where $\Delta S'$ is a change in entropy when water is heated; $\Delta S''$ is a change in entropy when water is converted into vapour.

The change in entropy is generally equal

$$\Delta S = S_2 - S_1 = \int_0^2 \frac{dQ}{T}, \tag{P.2.3.2}$$

where dQ is the amount of heat transferred to the system in a thermodynamic process of 0-2; T is the system temperature.

With an infinitely small change in the temperature dT of the heated body, the amount of heat is expended

$$dQ = mcdT, \tag{P.2.3.3}$$

where m is body mass; c is the specific heat of the body.

Substituting the expression for the amount of heat dQ from the formula (P.2.3.3) into the formula (P.2.3.2), we find the change in entropy when the water is heated

$$\Delta S' = \int_{T_1}^{T_2} \frac{mcdT}{T}. \tag{P.2.3.4}$$

We transform the formula (P.2.3.4)

$$\Delta S' = mc \ln\left(\frac{T_2}{T_1}\right). \tag{P.2.3.5}$$

We substitute the numerical values in the formula (P.2.3.5)

$$\Delta S' = 0.1 \times 4.18 \times 10^3 \times \ln\left(\frac{373}{273}\right) = 1.3 \times 10^2 \text{ J/K}.$$

The change in entropy during the conversion of water into vapour (T_2 = const) is

$$\Delta S'' = \frac{1}{T_2}\int_1^2 dQ = \frac{Q}{T_2}. \qquad \text{(P.2.3.6)}$$

The amount of heat associated with the phase transition is

$$Q = \lambda m, \qquad \text{(P.2.3.7)}$$

where λ is the specific heat of vaporization.

Therefore, we can write formula (P.2.3.6) in the following form

$$\Delta S'' = \frac{\lambda m}{T_2}. \qquad \text{(P.2.3.8)}$$

We substitute the numerical values in the formula (P.2.3.8)

$$\Delta S'' = \frac{2.3\times10^6\times0.1}{373} = 6.17\times10^2 \text{ J/K}.$$

The total change in entropy upon heating of water and its subsequent transformation into steam, according to formulas (P.2.3.1), (P.2.3.5), and (P.2.3.8), is

$$\Delta S = 1.3\times10^2 + 6.17\times10^2 = 7.47\times10^2 \text{ J/K}.$$

Answer. The total change in entropy is ΔS = 7.47×10^2 J/K.

Problems

Problem A

Problem description. The difference in specific heat capacities $c_P - c_V$ of a certain diatomic gas is 260 J/(kg·K). Find the molar mass μ of the gas and its specific heats c_V and c_P.

Answer. μ = 0.032 kg/mol, c_V = 650 J/(kg·K), c_P = 910 J/(kg·K).

Problem B

Problem description. Oxygen was heated at constant pressure P = 80 kPa. Oxygen volume increased from V_1 = 1 m^3 to V_2 = 3 m^3. Calculate the following values: 1) change in internal energy ΔU of oxygen; 2) work A done by oxygen during expansion; 3) the amount of heat Q transferred to oxygen.

Answer. ΔU = 4×10^5 J, A = 1.6×10^5 J, Q = 5.6×10^5 J.

Problem C

Problem description. Calculate the work A, which is accomplished by isothermal expansion of hydrogen with a mass of 5 g, having a temperature of T = 290 K, if the volume of gas has increased three times.

Answer. A = 6.62×10^3 J.

Problem D

Problem description. Carbon dioxide under pressure P_1 = 100 kPa and having a temperature of T_1 = 290 K was compressed in an adiabatic process to a pressure of P_2 = 100 kPa. Determine the temperature T_2 of the gas after compression.

Answer. T_2 = 345 K.

Problem E

Problem description. The ideal gas completes the Carnot cycle. Heater temperature is T_1 = 470 K. Cooler temperature is T_2 = 280 K. Gas performs the work A = 100 J of isothermal expansion. Determine the thermal efficiency η of the cycle, as well as the amount of heat Q_2 that gives gas to the cooler during isothermal compression.

Answer. η = 0.404, Q_2 = 59.6 J.

CHAPTER 3. REAL GASES AND LIQUIDS

3.1. Interaction Forces

The electrons near the nucleus in the atom are held by the Coulomb forces of attraction of unlike charges. The atom as a whole is electrically neutral. Molecules are made up of atoms. The forces that hold together atoms in a molecule are also electric in nature. However, the appearance of these forces has a more complex nature in comparison with the Coulomb forces. There are basically two types of atomic bonds in a molecule, namely an ionic bond and a covalent bond.

Consider the ***ionic bond***. The bonding strength of various electrons in an atom with an atom as a whole is different. This force depends on the structure of the atom. In some atoms there is an electron or several electrons that are very weakly bound to the atom as a whole. These electrons are easily lost by the atom, resulting in the formation of a positively charged ion.

In other cases, on the contrary, not only all electrons are tightly bound to the atom, but under favourable conditions, the atom captures an electron or two electrons and turns into a negatively charged ion.

Between the ions there are Coulomb forces of attraction, which provide the formation of the molecule. Among these molecules is, for example, a molecule of sodium chloride $NaCl$. The structure of this molecule in the form of ions can be written as $Na^{+}Cl^{-}$. Therefore, the molecule of sodium chloride consists of a positive ion Na^{+} and a negative ion Cl^{-}.

The potential energy of attraction of ions Na^{+} and Cl^{-} is

$$W_p(r) = -\frac{e^2}{4\pi\varepsilon_0 r_0}, \tag{3.1.1}$$

where e is an electron charge; ε_0 is an electric constant; r_0 is the equilibrium distance between the ions.

Along with potential energy W_p, there is a positive energy associated with the repulsive forces between the ions when they are very close together, since the ions cannot penetrate each other. These forces are large only at small distances between ions and quickly decrease with distance. The contribution of these forces to the total ion interaction energy is small and does not exceed about 10%.

From a physical point of view, an ionic bond is characterized by a complete charge exchange between ions. The amount of charge exchanged by ions is a multiple of the charge of an electron. Partial charge exchange between ions is characteristic of a covalent bond.

Consider a covalent bond. The ionic bond is not able to explain the existence of molecules consisting of two identical atoms, such as, for example, H_2, O_2, N_2, etc. Two atoms enter the molecule on an equal footing, and there is no reason for one of them to become a positive ion, and for the other atom there is no reason to become a negative ion. The bond existing in such molecules is called a ***covalent bond***.

A full understanding of the essence of covalent bonds is possible only within the framework of quantum mechanics, but the physical essence of the matter can be clearly explained in the framework of classical concepts.

We place a negative ion in the middle between positively charged ions. The charge of a negatively charged ion is equal in magnitude to the charge of a positive ion. In this case, from the side of a negatively charged ion, an attractive force acts on positive charges. This force is four times greater than the force of repulsion of positive charges from each other. As a result, a force acts on positive charges, which tends to bring them closer, i.e. force of gravity. The forces acting on a negative charge from the side of positive charges are mutually balanced. This is the process of the emergence of covalent bonds. However, such a static equilibrium is not possible. Quantum mechanics explains how the movement of electrons occurs, in which, on average, some electrons spend most of their time between positively charged nuclei during their motion. Consequently, these electrons form an effective negative charge between the positively charged nuclei of the interacting atoms. In this case, two electrons are considered, the motion of which is socialized, and it cannot be said which of the atoms of the molecule these electrons belong to. Therefore, the bond resulting from this is called the covalent bond.

A solid state arises when the binding energy of molecules is much greater than the kinetic energy of their thermal motion. As a result of this, an ordered structure arises corresponding to a minimum of free energy.

Ionic and covalent bonds are important for retaining not only atoms in a molecule, but also molecules and atoms in a solid.

As a result of these processes, the crystalline structure of a solid forms. If the crystalline structure arises due to covalent bonding, then the crystals are called covalent. If the crystalline structure arises due to ionic bonding, then the crystals are called ***ionic crystals***.

The next type of crystals are molecular crystals with molecules located in the nodes of the crystal lattices. In this case, very weak forces act between the molecules, which are called ***van der Waals forces*** (named after Johannes Diderik van der Waals (23.11.1837 – 8.03.1923)). These forces arise due to the fact that with a small shift of negative and positive charges in a neutral molecule, it ceases to be neutral, turning into a dipole. The phenomenon of the formation of a dipole moment in a molecule is called ***polarization***.

The approach of molecules leads to their mutual polarization. The sides of the polarized molecules facing each other have charges of the opposite sign. Such mutually polarized molecules attract each other. These attractive forces are called dispersion forces.

At small distances between the molecules, repulsive forces act. These forces are found in a very small region, on the order of the size of the atom. This interaction can be characterized by a distance of r_0. The value of r_0 depends on the type of molecule. At distances $r > r_0$ between the molecules, attractive forces act. At distances $r < r_0$ between the molecules, repulsive forces act. The potential energy of interaction of molecules is approximated by a formula of the type

$$W_p(r) = \frac{a_1}{r^n} - \frac{a_2}{r^m}. \tag{3.1.2}$$

In the formula (3.1.2), the constant values of a_1, a_2, n, m are selected from the requirements of the best approximation of the real interaction potential of the molecules.

In most cases, a good approximation is the following selection of parameters $n = 12$, $m = 6$. The interaction potential obtained in this case can be written as

$$W_p(r) = 4\varepsilon_0 \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right], \tag{3.1.3}$$

where ε_0 is the minimum potential interaction energy for $r = r_0$; σ is the distance between the molecules when the potential interaction energy is zero $W_p = 0$.

The interaction potential described by formula (3.1.3) is called the ***Lennard-Jones potential*** (potential was first proposed by John Edward Lennard-Jones (27.10.1894 – 1.11.1954)). This potential is widely used in the theory of liquids and gases.

Let us estimate the dependence of the van der Waals forces on the distance. Consider two polarized molecules whose centres are at a distance of r from each other. The dipole moments of the molecules are directed along one straight line. The distances between the polarization charges q and q' molecules are $2l$ and $2l'$, respectively. In this case, the electric field at a distance of r from the centre of one molecule is

$$E(r) = \frac{q}{4\pi\varepsilon_0} \left[\frac{1}{(r-l)^2} - \frac{1}{(r+l)^2} \right], \tag{3.1.4}$$

where $q = |q| = |q'|$.

The following relation is valid

$$\frac{1}{(1 \mp l/r)^2} \approx 1 \pm \frac{2l}{r} \pm \ldots \tag{3.1.5}$$

In this case, one can limit oneself to first-order quantities of l/r, since $l << r$. In this case, the formula (3.1.4) takes the form

$$E(r) = \frac{ql}{\pi\varepsilon_0 r^3}. \tag{3.1.6}$$

Now we calculate the force with which the electric field created by the first molecule acts on the second molecule

$$F(r) = q'E(r+l') - q'E(r-l') = \frac{qq'l}{\pi\varepsilon_0}\left[(r+l')^{-3} - (r-l')^{-3}\right]. \qquad (3.1.7)$$

Using the relation $l' << r$, we can assume that $(1 \pm l'/r)^{-3} \approx 1 \mp 3l'/r$. In this case, the formula can be written as

$$F(r) = -\frac{6qlq'l'}{\pi\varepsilon_0 r^4}. \qquad (3.1.8)$$

The polarizability of molecules depends on the electric field strength. Therefore, in formula (3.1.8) it must be assumed that $l' \sim E \sim r^{-3}$. Then the force can be expressed by the relation

$$F(r) \sim r^{-7}. \qquad (3.1.9)$$

Consequently, the forces of van der Waals very quickly decrease with distance. It follows from formula (3.1.9), that the potential energy varies in proportion to the sixth power of the distance between the molecules

$$W_p(r) \sim r^{-6}. \qquad (3.1.10).$$

Van der Waals forces arise in the complete absence of charge exchange. Therefore, in comparison with the forces of ionic bonding, they represent another extreme case. The covalent bond arises as a result of a partial charge exchange and is an intermediate case between the ionic bond and the van der Waals forces.

Covalent bonding is enhanced in metals or metal crystals. Such amplification leads to the fact that the electron density between the nodes of the crystal lattice reaches appreciable values. Electrons that bond between ions practically lose all bond with ions and can be considered as common electrons for the entire crystal. An electron gas is formed in the crystal. The resulting bond is called a ***metal bond***.

The considered types of bonds do not exhaust the entire variety of bonds existing in crystals. Substances with a rather complex crystalline structure often cannot be attributed to any specific types of bonds.

An important role in the formation of bonds in solids is played by the ***hydrogen bond***. By its physical nature, it is not a separate type of connection. But according to its role, it is advisable to separate it into a separate category. This is due to the structural features of the hydrogen atom. First, a proton ion is a hydrogen atom whose size is approximately 10^5 times smaller than other ions. Therefore, the entire ion can practically be considered a material point. Secondly, the electron in the hydrogen atom is very strongly attached to the proton, which serves as the nucleus of the hydrogen atom. The ionization potential of atomic hydrogen is approximately 13.5 eV. This value is several times greater than the ionization potential for other atoms. The essence of the hydrogen bond is that the electron and proton move in such a way that bonds arise in the crystal due to their motion, called hydrogen bonds. It is important when hydrogen bonds arise that the first filled electron shell in the Coulomb field is a shell with two electrons. Therefore, a hydrogen atom can form only one covalent bond, which is very important for characterizing the structure of the corresponding covalent crystals.

The potential energy of attraction between the molecules is negative. If the sum of the kinetic and potential energies of the considered system of molecules is positive, then the molecules, left to themselves, tend to disperse over an infinitely large distance. This corresponds to the tendency of the gas to expand.

When a gas is compressed, its density increases, and the average distance between molecules decreases. This leads to a decrease in potential energy.

If the average kinetic energy of the molecules is not too large, then there comes a moment when the sum of the kinetic and potential energies of the system becomes negative. Such a system of molecules can no longer spontaneously disperse in a large volume. In this case, the situation of the bound state is realized. This state of the molecules is either liquid or solid.

3.2. Two-Phase States

Consider the experience of studying the isotherm of real gas. Gas compression occurs at a temperature T. When gas is compressed to a volume V_1, its pressure will increase to value P. With a further decrease in the volume of gas, part of it turns into liquid, but the pressure remains equal to P. Therefore, in this section of the isotherm in the vessel there are simultaneously gas and liquid, separated by a boundary, which is the surface of the liquid.

The physically homogeneous parts into which the system has broken up are called ***phases***. Thus, the system in this section of the isotherm consists of liquid and gaseous phases. At a certain volume V_2, the gas is completely converted into liquid and only the liquid phase is present in the system. A further decrease in volume leads to compression of only the liquid. This liquid has a very high resistance to compression.

An increase in temperature leads to a decrease in the portion of the isotherm corresponding to a two-phase system. At a critical temperature, this section of the isotherm becomes a point.

The difference between the liquid and gas disappears at this point, in other words, the liquid and gas have the same properties. This state is called a ***critical state***, and T_c, P_c, V_c is called the ***critical temperature***, ***critical pressure***, and ***critical volume***, respectively.

Gas cannot be converted to liquid at any pressure if $T > T_c$. The isotherm T_c at a pressure of $P > P_c$ separates the gaseous and liquid state of the substance so that at the points of this isotherm the phase properties are the same.

The transition from the gaseous state to the liquid state can be accomplished both through the region of two-phase states and bypassing this region. At neighbouring points on different sides of the isotherm, the properties of the system are different. On one side of the isotherm, the substance is a gas, and strives to expand. On the other hand, the isothermal substance is a liquid and seeks to maintain its volume.

In a two-phase system, liquid and vapour are in ***dynamic equilibrium*** and at a given temperature have well-defined values of density and pressure. Pressure is called saturated vapour pressure at temperature. Saturated vapour pressure increases with increasing temperature. Steam is called saturated because it cannot be "condensed" at the same temperature. Part of the saturated vapour is converted to liquid upon attempt to compact.

At a temperature of T, the entire volume V_1 is filled with saturated steam, since with the slightest decrease in this volume, part of the vapour passes into the liquid. Therefore, the density of saturated vapour at this temperature is equal $\rho_\upsilon = m/V_1$. At a temperature of T', the density of saturated steam is

$$\rho'_\upsilon = \frac{m}{V'_1} > \rho_\upsilon \,. \tag{3.2.1}$$

Near the vapour-liquid interface at a point on the liquid side, the entire volume V_2 is filled with liquid. Therefore, the density of the liquid at a temperature of T is

$$\rho_l = \frac{m}{V_2} \,. \tag{3.2.2}$$

It is obvious that the density of a liquid at a temperature of T is higher than the density of saturated vapours at the same temperature. The density of the liquid at a temperature of T' is $\rho'_l = m/V'_2 < \rho_l$. This means that with increasing temperature, the density of the liquid decreases.

The difference in the liquid and gas phases density decreases as the temperature approaches the critical temperature. At the critical point, the density of the liquid phase is equal to the density of the gaseous phase

$$\rho_c = \frac{m}{V_c} \,. \tag{3.2.3}$$

Consider the state of a two-phase system, characterized by some intermediate point. Denote the total volume occupied by the system by symbol V. The volumes and densities of the liquid and gaseous phases are V_l, V_υ, ρ_l, ρ_υ. We write down the law of conservation of matter

$$V_l\rho_l + V_\upsilon\rho_\upsilon = m \,. \tag{3.2.4}$$

Using the relation $V_l, + V_\upsilon = V$, we obtain

$$V_l(\rho_l - \rho_\upsilon) = m - V\rho_\upsilon. \tag{3.2.5}$$

Hence,

$$V_l = \frac{1 - V/V_1}{(1/V_2 - 1/V)} = V_2 \frac{V_1 - V}{V_2 - V_1}, \tag{3.2.6}$$

where $\rho_\upsilon = m/V_1, \quad \rho_l = m/V_2$.

We transform the formula (3.2.6) taking into account relations $\rho_l V_l = m_l$, $\rho_l V_2 = m$. In this case, the mass of the liquid phase can be expressed as follows

$$m_l = \frac{m(V_1 - V)}{V_2 - V_1}. \tag{3.2.7}$$

A similar expression can be obtained for the mass of the gaseous phase

$$m_\upsilon = \frac{m(V - V_2)}{V_2 - V_1}. \tag{3.2.8}$$

We express the mass ratio of the liquid and gaseous phases from formulas (3.2.7) and (3.2.8)

$$\frac{m_l}{m_\upsilon} = \frac{V_1 - V}{V - V_2}. \tag{3.2.9}$$

Formula (3.2.9) is called the ***lever arm rule***.

Isotherms of real matter cannot always be depicted in the drawing. For example, the density of water and its saturated steam at 50°C are equal, respectively, to 988.0 kg/m^3 and 8.3×10^{-2} kg/m^3. Saturated vapour pressure is 122×10^3 Pa. This means that the ratio of abscissa V_1/V_2 should be 10^4. We use the fact that the critical pressure of water is $P_c = 220.53\times10^5$ Pa. In this case, the ratio of ordinates P_c/P_1 in the drawing should be approximately 2000. It is clear that such a curve cannot be represented on a linear scale.

The isotherm has a horizontal direction at the critical point, i.e. a relation of $(\partial P/\partial V)_T = 0$ holds. Therefore, pressure (density) is independent of volume. This means that if in a certain region the particle density increases, then there are no pressure forces that would try to reduce this density, and vice versa. As a result of this, in a critical state, density fluctuations become very large. This leads to the appearance of a phenomenon called ***critical opalescence***. The essence of the phenomenon is that density fluctuations lead to significant fluctuations in the refractive index and absorption of the medium. This leads to the fact that light is strongly scattered and absorbed in the medium.

The phases in a two-phase system are in equilibrium at the same temperature. The increase in volume leads to the fact that some of the liquid turns into steam. In order to maintain a constant temperature, it is necessary to transfer a certain amount of heat to the system.

Thus, in order to make the transition from the liquid phase to the gaseous system, heat must be obtained without changing the temperature. This heat is expended in changing the phase state of a substance and is called the ***heat of phase transformation*** or the latent heat of transition. Phase transitions that occur with the absorption or release of latent heat of transition are called ***phase transitions of the first kind***.

Saturated vapour pressure increases with temperature. Define a quantitative relationship between these phenomena.

We consider an infinitesimal reversible Carnot cycle, in which the isotherms are the states of a two-phase system at temperatures T and $T - dT$. The work performed in this cycle is

$$A = (V_1 - V_2)dP. \tag{3.2.10}$$

The efficiency of this Carnot cycle is

$$\eta = \frac{A}{Q_1} = \frac{(V_1 - V_2)dP}{L}, \tag{3.2.11}$$

where L is the latent heat of transition of a given mass of substance.

On the other hand, the efficiency of the Carnot cycle is

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{T - dT}{T} = \frac{dT}{T}. \tag{3.2.12}$$

Equating the right-hand sides of equations (3.2.11) and (3.2.12), we get

$$\frac{dP}{dT} = \frac{L}{T(V_1 - V_2)}. \tag{3.2.13}$$

Equation (3.2.13) is called the ***Clapeyron – Clausius equation***. This equation relates the pressure at which a two-phase system is in equilibrium to temperature. If the latent heat of transition L and the dependence of the volumes of the liquid V_l and gaseous V_υ phases on the temperature are known, then the solution of the differential equation (3.2.13) allows us to find the dependence of pressure on temperature.

3.3. Van der Waals Equation

Experimental studies of gases carried out in a wide range of pressures that the product of pressure on the volume is not constant at $T = \text{const}$, as it should be according to the equation of state of an ideal gas. Product PV changes with pressure as if at low pressures the gas is more readily compressed than an ideal gas. At high pressures, the gas resists compression more than an ideal gas. In other words, at low gas densities, additional attractive forces act in it, and at high densities in the gas, additional repulsive forces act.

These factors can be described using the concept of compressibility. ***Isothermal compressibility*** κ is the coefficient of proportionality between the relative change in volume $\Delta V/V$ and the change in pressure ΔP at $T = \text{const}$

$$\left(\frac{\Delta V}{V}\right)_T = -\kappa \Delta P, \tag{3.3.1}$$

hence

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T. \tag{3.3.2}$$

The state of an ideal gas is characterized by the ratio

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{V}{P}. \tag{3.3.3}$$

Therefore, $\kappa = 1/P$. The experiment shows that, at low pressure, the compressibility of real gas is greater than ideal.

The compressibility of liquids is very small, since the molecules in the liquid are packed densely enough. Therefore, very high pressures are required to slightly change the volume of liquid. For example, the compressibility of water and gasoline is 0.47×10^{-9} Pa^{-1} and 0.82×10^{-9} Pa^{-1}, respectively. The compressibility of liquids is thousands of times less than the compressibility of gases.

The equation of state depends on the law of interaction between the molecules. Therefore, each sort of molecule has its own equation of state.

The exact equation of state can be represented as a virial equation of state

$$PV_\mu = RT + A_1(T)V_\mu + A_1(T)V_\mu^2 + \ldots, \tag{3.3.4}$$

where $A_i(T)$ are virial coefficients.

This equation is an infinite series in inverse powers of the molar volume and requires knowledge of an infinite number of virial coefficients. In this sense, it has only theoretical significance. In the study of specific substances, a very large number of different approximate equations of state were used. Among the approximate equations, the van der Waals equation is most widely known.

Consider the features of this equation. The equation of state $PV = (m/\mu)RT$ of an ideal gas does not take into account the presence of attractive forces between molecules when the molecules are removed from each other, and also does not take into account the presence of repulsive forces when the molecules are close to each other.

The action of repulsion is reduced to the fact that the molecule does not allow penetration of other molecules into the volume occupied by it. Therefore, repulsive forces are characterized by an effective volume of molecules. We denote the total effective volume of molecules proportional to the mass of the gas by mb'. Then, taking into account the final volume of molecules reduces to the fact that in the equation of state of an ideal gas, not all of the volume, but only part of it, is accessible for change $V - mb'$.

The presence of attractive forces leads to the appearance of additional internal pressure on the gas. The force with which each molecule is attracted by other molecules is proportional to the concentration of gas molecules n_0. The number of these molecules is also proportional to n_0. Therefore, the additional internal pressure on the gas due to the attractive forces is proportional to n_0^2, i.e. inversely proportional to the square of the specific volume m^2/μ^2. The presence of additional internal pressure on the gas leads to a decrease in the external pressure, which must be applied to the gas to keep it in a given volume.

Therefore, taking into account the two corrections considered, the equation of state of an ideal gas is modified into the ***van der Waals equation***

$$\left(P + \frac{m^2 a'}{V^2}\right)(V - mb') = \frac{m}{\mu} RT, \tag{3.3.5}$$

where a' and b' are constant values that have different meanings for different gases. These quantities are called ***van der Waals constants***.

Instead of the constant values a' and b', the values $a = a'\mu^2$ and $b = b'\mu^2$ are often used. In this case, equation (3.3.5) can be rewritten in the form

$$\left(P + \frac{a}{V_\mu^2}\right)(V_\mu - b) = RT. \tag{3.3.6}$$

Equation (3.3.6) is written taking into account the notation $V_\mu = V/\nu$, where ν is the number of moles.

For the analysis of isotherms, it is more convenient to present equation (3.3.6) in a different form

$$V_\mu^3 - \left(b + \frac{RT}{P}\right)V_\mu^2 + \frac{aV_\mu}{P} - \frac{ab}{P} = 0. \tag{3.3.7}$$

Equation (3.3.7) is an equation of the third degree with respect to V_μ. Consider the case of constant temperature. Then, according to the properties of polynomials of the third degree, the gas volume at different pressure values will have either one or three real values.

This means that the isotherm of the van der Waals equation in plane (P,V) is intersected by a straight line $P = \text{const}$ either at one point or at three points. In this case, the gas states are not absolutely stable. With a small external impact on the system, a quick transition to the nearest stable state occurs. Such states are called ***metastable states***.

The van der Waals equation at temperature $T > T_c$ always has only one real root. The van der Waals equation at temperature $T < T_c$ has three real roots in a certain pressure range. Obviously, with increasing temperature, the values of these three material roots approach each other and, at a critical temperature T_c, all three roots become equal. Therefore, for a critical state, equation (3.3.7) has the form

$$(V - V_c)^3 = V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0. \tag{3.3.8}$$

A comparison of equations (3.3.7) and (3.3.8) leads to the statement that the following relation is valid

$$3V_c = b + \frac{RT_c}{P_c}, \quad 3V_c^2 = \frac{a}{P_c}, \quad V_c^3 = \frac{ab}{P_c}. \tag{3.3.9}$$

Equalities (3.3.9) are a system of three equations with three unknown quantities V_c, P_c, T_c. The solution to this system has the form

$$V_c = 3b,$$

$$P_c = \frac{a}{27b^2},$$

$$T_c = \frac{8a}{27Rb}. \tag{3.3.10}$$

Thus, there are three equations for the two van der Waals constants. Solving equations (3.3.10) with respect to a, b, and R, we obtain

$$a = 3P_c V_c^2, \quad b = \frac{V_c}{3}, \quad R = \frac{8P_c V_c}{3T_c}. \tag{3.3.11}$$

Relations (3.3.11) show that for each real gas it is necessary to calculate its individual gas constant R, which differs from the molar gas constant kN_A. An individual gas constant is less than a molar gas constant.

Since the gas constant is proportional to the number of molecules in the mole, it can be argued that in the critical state there is a decrease in the number of structural units forming the gas constant. Consequently, real gas molecules are combined into complexes. When moving away from the critical state, these complexes decompose, and the individual gas constant becomes equal to the molar gas constant.

The van der Waals equation is conveniently presented in a dimensionless form. We introduce the following notation

$$V_r = \frac{V}{V_c}, \quad P_r = \frac{P}{P_c}, \quad T_r = \frac{T}{T_c}. \qquad (3.3.12)$$

The van der Waals equation, taking into account dimensionless parameters V_r, P_r, and T_r, can be written in the following form

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r. \qquad (3.3.13)$$

The equation of state written in the form (3.3.13) is the same for all substances.

3.4. Joule-Thomson Effect

Gas does work when expanded. If the gas is isolated, the source of work is internal energy. If all internal energy were reduced to the kinetic energy of particles, then the gas temperature would have to decrease. If this expansion of gas were carried out without performing work, the gas temperature would not change.

The internal energy of a real gas includes the potential energy of interaction of molecules. In fact, the molecules are in rapid motion and we can talk about some average distance and average potential energy. The average distance depends on density and temperature. An increase in density leads to a decrease in average distance. The kinetic energy of molecules increases with increasing temperature. Consequently, molecules in collisions approach each other at a shorter distance.

The above considerations indicate that the expansion of a real gas without heat transfer should be accompanied by a change in its temperature. With a small increase in volume and, consequently, with a small decrease in pressure, the gas temperature should increase. If the density and temperature of the gas are such that the average distance between the molecules is greater than a certain characteristic value r_0, then with a small increase in volume and, therefore, with a small decrease in pressure, the gas temperature decreases. It should be noted that for distances $r > r_0$ between the molecules, attractive forces act, and for distances $r < r_0$ between the molecules, repulsive forces act.

The change in temperature of a real gas described here with a very small adiabatic change in its volume and pressure is called the ***Joule-Thomson differential effect***. The effect is named after James Prescott Joule (24.12.1818 – 11.10.1889) and Thomson. With a significant change in pressure (or volume), it is necessary to summarize small changes in temperature. This cumulative effect is called the ***Joule-Thomson integral effect***. The Joule-Thomson integral effect may consist in increasing the gas temperature when the contribution of differential effects with $\Delta T > 0$ exceeds the contribution of differential effects with $\Delta T < 0$. The opposite relation for these contributions leads to the fact that the Joule-Thomson integral effect consists in a decrease in temperature.

We calculate the differential Joule-Thomson effect. Consider gases whose volumes are V_1 and V_2. There is a partition made of a material with low thermal conductivity between the gases. Direct heat exchange between gases is absent. The two-gas system is thermally insulated.

A certain amount of gas with a volume of ΔV_1 and an internal energy of ΔU_1 is located on one side of the partition. After passing through the partition, the gas began to occupy volume ΔV_2 and have internal energy ΔU_2. We write down the law of conservation of energy for this process

$$\Delta U_1 + P_1 \Delta V_1 = \Delta U_2 + P_2 \Delta V_2 . \tag{3.4.1}$$

The values located on the left and right side of equation (3.4.1) are the enthalpy of the amount of gas under consideration. Therefore, equality (3.4.1) means that the Joule-Thomson effect occurs with constant enthalpy. For a certain mass of gas, equality (3.4.1) can be written in the form

$$H = U + PV = \text{const} . \tag{3.4.2}$$

We choose T and P as independent variables. In this case, from equation (3.4.2) we can obtain

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP = 0 . \tag{3.4.3}$$

We use the relations for the functional dependences between the enthalpy and heat capacity at constant pressure

$$\left(\frac{\partial H}{\partial T} \right)_P = c_P , \quad \left(\frac{\partial H}{\partial P} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P . \tag{3.4.4}$$

Therefore, using formulas (3.4.3) and (3.4.4), we can obtain

$$\left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{c_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] . \tag{3.4.5}$$

This formula describes the differential Joule-Thomson effect.

For an ideal gas $(\partial V / \partial T)_P = R / P = V / T$ and therefore $(\partial T / \partial P)_H = 0$, that is, the Joule-Thomson effect is absent.

Consider the Joule-Thomson integral effect. Assume that the gas pressures P_1 and P_2 on opposite sides of the septum differ by a final value. In this case, the Joule-Thomson effect can be represented as a sequence of quasistatic Joule-Thomson processes, in each of which the pressure changes to an infinitely small value dP. For this sequence of processes, we can write

$$T_2 - T_1 = \int_{P_1}^{P_2} \left(\frac{\partial T}{\partial P} \right)_H dP = \int_{P_1}^{P_2} \frac{1}{c_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] dP. \tag{3.4.6}$$

The sequence of Joule-Thomson quasistatic processes transfers the system from the same initial state to the same final state. Therefore, formula (3.4.6) describes the complete change in temperature in a real process. Formula (3.4.6) is a mathematical description of the integral Joule-Thomson effect.

Consider the Joule-Thomson effect in a van der Waals gas. The calculation of the derivative $(\partial V / \partial T)_P$ is generally complicated, since the van der Waals equation is an equation of the third degree with respect to V. Therefore, we consider only the case of a sufficiently rarefied van der Waals gas. We represent the van der Waals equation in virial form

$$PV_\mu = RT + \frac{RTb - a}{V_\mu} + RT \sum_{n=2}^{\infty} \frac{b^n}{V_\mu^2}. \tag{3.4.7}$$

The case of a rarefied gas corresponds to the presence in equation (3.4.7) of terms linear with respect to a and b. Under these conditions, equation (3.4.7) takes the form

$$V = \frac{RT}{P} + \frac{1}{PV}(RTb - a) = \frac{RT}{P} + \frac{1}{RT}(RTb - a) = \frac{RT}{P} + b - \frac{a}{RT}. \tag{3.4.8}$$

It follows from equation (3.4.8) that

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P} + \frac{a}{RT^2}. \tag{3.4.9}$$

Therefore, the formula (3.4.5) for the differential Joule – Thomson effect takes the form

$$\left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{c_p} \left(\frac{TR}{P} + \frac{Ta}{RT^2} - \frac{RT}{P} - b + \frac{a}{RT} \right) = \frac{1}{c_P} \left(\frac{2a}{RT} - b \right). \tag{3.4.10}$$

An analysis of formula (3.4.10) leads to the following conclusions. At a sufficiently low temperature, a ratio of $(\partial T / \partial P)_H > 0$ is satisfied. Consequently, the gas cools during expansion. At a sufficiently high temperature, a ratio of $(\partial T / \partial P)_H < 0$ is satisfied; the gas is heated during expansion. This behaviour of the gas is in complete agreement with the physical nature of the Joule-Thomson effect.

The temperature at which relation $(\partial T / \partial P)_H < 0$ is satisfied, i.e. there is a change in sign of the Joule-Thomson effect, called the ***inversion temperature***

$$T_i = \frac{2a}{Rb}. \tag{3.4.11}$$

The inversion temperature of a sufficiently rarefied gas is $2a/(Rb)$. With increasing gas density, the inversion temperature decreases. For most gases, the inversion temperature is much higher than room temperature, so they are cooled in the Joule – Thomson process.

Such gases include, for example, oxygen and nitrogen. For some other gases, such as hydrogen and helium, the inversion temperature lies well below room temperature, which is why these gases are heated during the Joule – Thomson process.

The conversion of gases to a liquid state is often associated with great technical difficulties. If the gas temperature is below the critical temperature, then it can be converted into a liquid state by simple compression. However, the critical temperature of many gases is very low. For example, the critical temperatures of helium, hydrogen, nitrogen, and oxygen are 5.3 K, 33 K, 126.1 K, and 154.4 K, respectively. Reaching such low temperatures is not an easy problem. The temperature reduction is achieved by cooling the gas in the Joule-Thomson process and adiabatic expansion.

3.5. Surface Tension

A liquid state arises when the potential energy of attraction of molecules exceeds in absolute value their kinetic energy. The forces of attraction between the molecules in the liquid are large in magnitude and ensure the retention of molecules in the volume of the liquid. Thus, a surface forms on the liquid that limits its volume. The surface limiting this volume depends on the shape. For a given volume, the ball has a minimal surface.

Particles in a thin layer near the surface of the liquid are acted upon by other molecules of the liquid, forces whose resultant is directed inside the liquid, normal to its surface. As the surface of the liquid increases, a certain number of molecules from the volume of the liquid must be lifted into the surface layer. In this case, it is necessary to do the work

For the case when the surface formation process is isothermal, the potential surface energy is equal with the opposite sign of the energy spent on the formation of this surface.

On the other hand, in isothermal processes, the role of potential energy is played by free energy F, for which the following relation holds true

$$dF = -dA, \tag{3.5.1}$$

where dA is the work associated with the emergence of free energy dF.

As a result of the surface uniformity property, it is obvious that free surface energy is proportional to the surface area. Therefore, taking into account formula (3.5.1), we can write

$$F=\sigma S, \tag{3.5.2}$$

where σ is the specific free energy density of surface.

The mechanical system seeks to reach the state with the least potential energy. The state with the least potential energy is stable. The thermodynamic system strives to achieve the state with the least free energy. Therefore, the surface of the liquid tends to contract. Due to this, forces called ***surface tension forces*** act along the surface of the liquid.

In this regard, the liquid is similar to a thin rubber film stretched isotropically in all directions in the plane of the surface.

The presence of surface tension is very effectively demonstrated with the help of soap films formed on a wire frame removed from a soap solution. In order to increase the area of the soap film, it is necessary to apply force to the wire f. When the wire section is shifted by dx, work equal to $dA = fdx$ is performed. The area of the soap film in this case changes by a value of $dS = ldx$, where l is the length of the portion of wire to which the force is applied. The change in free energy is

$$dF=2\sigma dS=-fdx=-\frac{fdS}{l}, \tag{3.5.3}$$

where factor 2 takes into account that the soap film has two surfaces; the value $-f/(2l)$ is numerically equal to the force related to the perimeter portion of each of the film surfaces.

This force is numerically equal to the surface free energy density, since 1 J/m^2 = 1 N/m. Therefore, the value of σ is called surface tension.

Surface tension depends on the properties of the fluid and varies widely. In most liquids, the surface tension at a temperature of 20 °C is on the order of 10^{-2} to 10^{-1} N/m. For example, in ether, acetone, benzene, glycerol and water, it is equal to 1.71×10^{-2}; 2.33×10^{-2}; 2.89×10^{-2}; 6.57×10^{-2}; 7.27×10^{-2} N/m, respectively.

The specific gravity of the surface's free energy, characterized by a value of σ, is localized in a small surface layer of the liquid. Therefore, surface tension forces act only in a thin surface layer. In this regard, a thin surface layer acts like a rubber sheath, which surrounds a volume of liquid. The only difference with the rubber sheath is that it has a constant tension, regardless of how the surface of the liquid changes as a result of the change in the shape of the volume occupied by this liquid.

In addition to the tensile forces on the molecules of the surface layer, other forces also act that prevent these molecules from moving inside the liquid. The resultant of these forces and provides the occurrence of surface tension.

Surface tension depends on the properties of the substance with which the surface of the liquid is in contact.

The value of σ can be interpreted as the density of free energy. In this regard, the substance at the surface of the liquid also acts on the molecules of the surface layer of the liquid and, therefore, changes the forces that draw them into the liquid. This means that the surface tension is changing. Therefore, when the surface tension is studied, it is necessary to indicate not only the liquid that is meant, but also the substance with which the surface of the liquid is in contact. Therefore, the symbol σ, denoting surface tension, must be provided with two indices that indicate two substances adjacent to each other.

The surface tension on the interface between two liquids should be less than on the free surface. For example, at the water-ether interface, the surface tension is 0.0122 N/m.

At the interface between a solid and a liquid, surface tension also decreases. For example, the value of σ on the free surface of mercury is 0.465 N/m, and on the interface between mercury and water, the surface tension is 0.427 N/m. Values shown are for room temperature.

If a drop of the third liquid is placed on the interface of two liquids, then two results are possible, depending on the ratio of surface tension. Let symbol dl denote the length element directed along the line of contact of the three media 1, 2, 3. The surface tension forces acting on this element are $\sigma_{12}dl$, $\sigma_{23}dl$, $\sigma_{13}dl$. Consider the case when $\sigma_{13} < (\sigma_{23} + \sigma_{12})$. Then the equilibrium condition is the vanishing of the resultant of all the forces acting on element dl

$$\sigma_{13} = \sigma_{23}\cos\theta_1 + \sigma_{12}\cos\theta_2,$$

$$\sigma_{23}\sin\theta_1 = \sigma_{12}\sin\theta_2. \qquad (3.5.4)$$

The system of equations (3.5.4) makes it possible to determine angles θ_1 and θ_2. These angles are formed by the tangent plane to the surface of the droplet in the region of the interface and the plane of the interface. Angles θ_1 and θ_2 are called ***edge angles***.

Consider the case when $\sigma_{13} > (\sigma_{23} + \sigma_{12})$. Equilibrium is not possible in this case, and a drop of the third liquid spreads over the entire interface between the first two liquids.

Consider the equilibrium conditions at the liquid – solid interface. In this case, there is only one contact angle θ. The equilibrium conditions can be written in the following form

$$\sigma_{13} = \sigma_{23}\cos\theta + \sigma_{12},$$

$$\sigma_{23}\cos\theta + \sigma_{13} = \sigma_{12}. \qquad (3.5.5)$$

If condition $\sigma_{13} > (\sigma_{23} + \sigma_{12})$ is satisfied, then the liquid spreads over the surface of the solid with a molecular layer. In this case, the liquid wets the boundary of the solid.

Swimming bodies in a liquid is accompanied by the effects of wetting or not wetting. Because of this, additional forces arise that either increase the lifting force or reduce it.

The presence of surface tension forces leads to a curvature of the surface of the liquid. In this case, pressure arises from the surface layer on the underlying layers. For example, the overpressure for a spherical soap bubble is

$$P = \frac{4\sigma}{r}, \tag{3.5.6}$$

where r is the radius of the soap bubble.

Formula (3.5.6) takes into account that overpressure is created by two curved surfaces of the soap bubble (internal and external). One surface creates pressure $P' = P/2$.

In the general case, the surface curvature is determined by the two principal radii of curvature r_1 and r_2. In this case, the overpressure is

$$P = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right). \tag{3.5.7}$$

Equation (3.5.7) is called the ***Laplace formula***.

When interacting with the vessel wall, surface tension forces tend to either raise the liquid level or lower this level. The surface of the liquid rises if the walls of the vessel are wetted by the liquid, and decreases if the walls of the vessel are not wetted by the liquid.

If the liquid wets the walls of the vessel in the form of a tube, a column with a height of h is formed in the vessel. The pressure of the liquid column is compensated by the pressure created by the surface tension of the curved surface. In this case, we can write the following relation

$$\rho g h = \frac{2\sigma}{R} = \frac{2\sigma\cos\theta}{r}, \tag{3.5.8}$$

where ρ is the density of the liquid; R is the radius of curvature of the liquid surface; r is the radius of the tube ($r = R\cos\theta$).

The phenomena caused by the interaction of the fluid with the walls of the tubes by means of surface tension forces are called ***capillary phenomena***. The phenomenon of capillarity was discovered and studied by Leonardo da Vinci (14.04.1452 – 2.05.1519).

Surface energy strives to reach its minimum value. This is possible due to a decrease in both surface area and surface tension σ. Consider the case of adding the first fluid to the second fluid with lower surface tension. In this case, the second liquid will be adsorbed mainly in the surface layer, as a result of which the surface tension will decrease. Such a substance is called a surfactant. Examples of surfactants include soap (reduces surface tension) and sugar solution (increases surface tension).

3.6. Evaporation and Boiling

In the surface layer and near the surface of the liquid, forces act that ensure the existence of the surface and prevent the molecules from leaving the volume of the liquid. Due to thermal motion, some of the molecules have sufficiently high speeds to overcome the forces that hold the molecules in the liquid and leave the liquid. This phenomenon is called ***evaporation***. Evaporation of a liquid is observed at any temperature, but the evaporation rate increases with increasing temperature.

Molecules that have left the liquid form steam. Steam molecules that fall into the area near the surface of the liquid are drawn into the liquid by attractive forces. Thus, the evaporation rate decreases.

With a further increase in vapour density, a situation is achieved when the number of molecules leaving the liquid for some time is equal to the number of molecules returning to the liquid at the same time. A state of dynamic equilibrium sets in. Vapour in a state of dynamic equilibrium with a liquid is called saturated vapour.

The density and pressure of saturated steam increase with increasing temperature. As the density of saturated vapours increases, the surface tension of the liquid decreases, since the forces directed inside the liquid decrease due to the growth of oppositely directed forces from the side of saturated vapour. It follows from this that the latent heat of vaporization decreases with increasing temperature. At a critical temperature, the density of saturated vapours becomes equal to the density of the liquid, and the difference between them disappears.

Vapour is not a gas in the strict sense of the word. Gas is the state of matter at a given temperature and pressure. Vapour is not an aggregate state of a substance, because the aggregate state of a substance at a given temperature and pressure is a liquid state. In this regard, the behaviour of vapour differs from the behaviour of gas.

The ideal gas pressure is exactly inversely proportional to the volume. The pressure of a real gas is only approximately inversely proportional to the volume. Vapour pressure close to saturation varies slightly with volume. Saturated vapour pressure does not change with volume. Gas laws can only be applied to unsaturated vapours in a rough approximation.

Near a curved surface, the pressure of saturated vapours differs from their pressure near a flat surface. The conditions of dynamic equilibrium near a curved surface are identical in physical content to those near a flat surface. The physical content in this case is that the intensities of the transition of molecules from liquid to gas and vice versa are the same. However, in the case of a curved surface, the intensity of the exchange of molecules depends on the curvature of the surface.

Taking this dependence into account allows us to conclude that the saturated vapour pressure in the case of a concave surface of the liquid is less than in the case of a flat surface. In the case of a convex surface, the pressure of saturated vapours increases compared to the pressure above a flat surface.

We define a quantitative criterion for the change in the pressure ΔP of saturated vapours arising due to the curvature of the surface of the liquid. Consider an experiment in which a liquid and a capillary tube partially lowered into this liquid are in a closed vessel. Saturated steam is located in the space above the liquid. The height h of the liquid column in the capillary and the radius R of curvature of the liquid surface in the capillary tube depend on the surface tension, the density of the liquid, and the characteristics of the saturated vapour. The pressure P_0 at the liquid surface level is the same both inside the capillary and outside the capillary

$$P_0 = P_h + \rho_\upsilon gh, \tag{3.6.1}$$

$$P_0 = P_h - \frac{2\sigma}{R} + \rho_l gh, \tag{3.6.2}$$

where P_h is the vapour pressure at a height of h; ρ_l and ρ_υ is the density of the liquid and saturated vapour.

Equality (3.6.1) expresses the change in pressure between levels 0 and h in a pair, and equality (3.6.2) expresses the pressure difference between the same levels in a liquid. Term $2\sigma/R$ takes into account the pressure difference on opposite sides of the curved surface of the liquid. Equating the right-hand sides of equations (3.6.1) and (3.6.2), we obtain

$$gh = \frac{2\sigma}{R(\rho_l - \rho_\upsilon)}. \tag{3.6.3}$$

The joint solution of equations (3.6.1) and (3.6.3) allows us to write the expression for the pressure difference

$$\Delta P = P_0 - P_h = \rho_\upsilon gh = \frac{2\sigma\rho_\upsilon}{R(\rho_l - \rho_\upsilon)}. \tag{3.6.4}$$

Equation (3.6.4) is called the ***Thomson's formula***. In the formula (3.6.1) it is assumed that the density of saturated vapours does not change with a change in height. This ratio is satisfied in most real cases. If necessary, you can take into account the effect of changing the density of saturated vapours with a change in height using the barometric formula.

When, when heating a liquid, a temperature is reached at which the saturated vapour pressure is equal to the external pressure, equilibrium is established between the liquid and its saturated vapour. When fluid is supplied with additional heat, the corresponding mass of liquid is immediately converted to steam. The lowest pressure in the liquid theoretically falls on its upper layers. Consequently, the conversion to steam should occur in the upper layers. But, in reality, the pressure difference between the different layers of the liquid is negligible compared to the pressure itself, since the atmospheric pressure of 10^5 Pa corresponds approximately to the pressure of a column of water 10 m high. These circumstances lead to the fact that the conversion of liquid into steam occurs throughout the volume of the liquid. This process is called ***boiling***.

The boiling point is the temperature at which the saturated vapour pressure becomes equal to the external pressure. With increasing pressure, the boiling point increases. A decrease in pressure leads to a decrease in the boiling point.

Water in a hermetically sealed vessel can be heated to a temperature well above 100 °C, without the water boiling. This technique is used, for example, in everyday life to accelerate the cooking of products in a hermetically sealed vessel. On the other hand, by sufficiently lowering the pressure above the surface of the water, for example, by pumping air from the vessel in which the liquid is located, boiling of the liquid at room temperature can be caused.

If the liquid is devoid of impurities and does not contain a vapour bubble, then upon reaching the boiling point vapour bubbles tend to form in it. Inside the bubble, steam forms which is saturated with respect to the flat surface of the liquid. The same vapour is oversaturated with respect to the concave surface of the liquid to which this bubble is limited. Therefore, the vapour of the bubble immediately condenses into liquid and the vapour disappears.

Boiling will begin if some substance is introduced into the liquid that makes it possible to form vapour bubbles having a sufficiently large radius from the very beginning so that the vapour in the bubble is not too supersaturated and the pressure from the side of the bubble walls is not too great.

Such a substance may be, for example, chalk powder. The individual powder particles are those “nuclei” around which vapour bubbles form. Therefore, when a pinch of chalk is thrown into superheated water, a boiling boil resembles an explosion.

We estimate the maximum allowable overheating of the liquid. Saturated vapour pressure can be estimated using formula (3.6.4). We take into account that the density of saturated vapours at the boiling point is much lower than the density of the liquid. In this case, formula (3.6.4) can be rewritten as

$$\Delta P = \frac{2\sigma\rho_\upsilon}{R\rho_l}. \tag{3.6.5}$$

Permissible overheating of the liquid can be found by the Clapeyron-Clausius formula, taking into account the ratio between the volumes of the liquid V_2 and gaseous V_1 phases $(V_2 << V_1)$

$$\Delta T = \frac{TV_1\Delta P}{L} = \frac{T\Delta P}{\rho_\upsilon l_0}, \quad l_0 = \frac{L}{m}, \tag{3.6.6}$$

where L is the latent heat of transition of mass m of liquid.

Substituting tabular values of quantities into this formula, we find that $\Delta T \approx 0.5$ K for $R = 0.5\times10^{-7}$ m.

Similarly, we can estimate the increase in the boiling point of a liquid with a change in depth by Δh

$$\Delta T = \frac{TV_1\Delta P}{L} = \frac{TV_1\rho_l g\Delta h}{L} = \frac{T\rho_l g\Delta h}{\rho_\upsilon l_0}. \tag{3.6.7}$$

It follows that $\Delta T/\Delta h \approx 0.03$ K/cm. Therefore, in a teapot at a depth of 10 cm from the surface of the water, the boiling point is greater by about 0.3 K than on the surface.

If a charged particle flies through an overheated liquid, then it in its path ionizes the atoms of the liquid and imparts some energy to the liquid. This energy is converted into heat and causes the liquid to boil, i.e. the formation of bubbles. In other words, the superheated liquid boils along the trajectory of the charged particle, due to the scratch, the trajectory is clearly visible and can be photographed. In experimental studies of elementary particles, liquid hydrogen is usually used. Devices that use the stated principle are called ***bubble chambers***.

A charged particle in its path in a supercooled vapor ionizes the vapor molecules. Ions become condensation centers around which droplets of liquid form. Due to this, fog forms along the particle's trajectory, and the trajectory becomes visible. This allows the study of charged particles. Devices that use the stated principle in their work are called ***cloud chambers***.

3.7. Chemical Potential. Phase Balance

There are systems consisting not only of two components and two phases, but also of a large number of components, and their composition varies depending on temperature, pressure and other thermodynamic parameters. If the system has several components, then the internal energy of the system depends on the number n_i of particles of each of the components.

It is convenient to take volume V and entropy S as independent components on which internal energy depends

$$U = U(S, V, n_1, n_2, ..., n_i). \tag{3.7.1}$$

Then

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} dV + \sum_i \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_j} dn_i, \tag{3.7.2}$$

where $n_j \neq n_i$.

Comparing formula (3.7.2) and formula $dU = TdS - PdV$, we can write

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n_i}, \quad -P = \left(\frac{\partial U}{\partial V}\right)_{S,n_i}. \tag{3.7.3}$$

Therefore, the expression (3.7.2) takes the form

$$dU = TdS - PdV + \sum_i \mu_i dn_i\,, \tag{3.7.4}$$

where

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_j}, \quad n_j \neq n_i\,. \tag{3.7.5}$$

Similarly, taking into account the variable number of particles, the remaining thermodynamic potentials can be modified. Consider the Gibbs potential. The Gibbs potential is conveniently regarded as a potential that depends on the pressure P, temperature T, and number of particles of various components of the system

$$G = G(T, P, n_1, n_2, \ldots, n_i). \tag{3.7.6}$$

Then the equality

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_i \tag{3.7.7}$$

taking into account the formulas for thermodynamic potentials T, S, V, and P takes the form

$$dG = -SdT + VdP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_i} dn_i\,. \tag{3.7.8}$$

Taking into account formulas (3.7.4) and (3.7.8), we can write

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}, \quad n_j \neq n_i\,. \tag{3.7.9}$$

Therefore, the formula (3.7.8) finally takes the form

$$dG = -SdT + VdP + \sum_i \mu_i dn_i\,. \tag{3.7.10}$$

Performing similar transformations for enthalpy and free energy, we obtain

$$dH = TdS + VdP + \sum_i \mu_i dn_i\,, \tag{3.7.11}$$

$$dF = -SdT - PdV + \sum_i \mu_i dn_i\,. \tag{3.7.12}$$

The following notation is used in formulas (3.7.11) and (3.7.12)

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j}, \quad \mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j}, \quad n_j \neq n_i . \tag{3.7.13}$$

The value of μ is called the ***chemical potential***. Formulas (3.7.5), (3.7.9), and (3.7.13) contain a representation of the chemical potential for various variables, which are taken as independent values.

An analysis of formula $dG = -SdT + VdP$ shows that the equilibrium condition at a constant pressure and temperature should be equal

$$(dG)_{T,P} = 0 . \tag{3.7.14}$$

A system can consist of many components, but the number of phases in most practically important cases is two or three. Suppose for definiteness that there are two phases 1 and 2 and two components a and b in the system. The Gibbs function of a complete system is equal to the sum of the Gibbs functions of its phases. The phases will be considered homogeneous. For a complete system, from the condition of conservation of the total number of particles, we get

$$n_{a1} + n_{a2} = \text{const}, \quad n_{b1} + n_{b2} = \text{const} . \tag{3.7.15}$$

Then we can write

$$dn_{a1} + dn_{a2} = 0, \quad dn_{b1} + dn_{b2} = 0 . \tag{3.7.16}$$

For the Gibbs function of the first and second phases, we can obtain the following relation

$$dG_1 = -SdT + VdP + \mu_{a1} dn_{a1} + \mu_{b1} dn_{b1},$$

$$dG_2 = -SdT + VdP + \mu_{a2} dn_{a2} + \mu_{b2} dn_{b2} . \tag{3.7.17}$$

For the equilibrium state at constant values of T and P it is necessary to fulfil the following condition

$$(dG)_{T,P} = (dG_1)_{T,P} + (dG_2)_{T,P} = 0 . \tag{3.7.18}$$

Solving equations (3.7.16), (3.7.17), and (3.7.18) together, we obtain

$$(\mu_{a1} - \mu_{a2}) dn_{a1} + (\mu_{b1} - \mu_{b2}) dn_{b1} = 0 . \tag{3.7.19}$$

Hence, in view of the independence of n_a and n_b, it follows that

$$\mu_{a1} = \mu_{a2}, \quad \mu_{b1} = \mu_{b2} . \tag{3.7.20}$$

Assume that μ_{ij} is the chemical potential of the component with symbol i, which is present in the system in phase with symbol j. Then, a generalization of formula (3.7.20) for a large number of components is equalities

$$\mu_{i1} = \mu_{i2} = \ldots = \mu_{ij}, \quad i = 1, 2, \ldots \tag{3.7.21}$$

Therefore, the chemical potential of each component of the system has the same value for all phases under equilibrium at constant pressure and temperature.

Consider a system consisting of several components. There is a simple connection between the number of f degrees of freedom of a thermodynamic system, the number of r phases coexisting in equilibrium, and the number of n components of the system

$$f = 2 + n - r, \quad r \leq n + 2. \tag{3.7.22}$$

Equation (3.7.22) is called the ***Gibbs phase rule***.

Let us consider particular cases of the Gibbs phase rule.

1. One component system (n = 1). For such a system, you can write

$$f = 3 - r, \quad r \leq 3. \tag{3.7.23}$$

For r = 1 (single-phase state), we have f = 2. The free parameters are temperature T and pressure P. For r = 2 (equilibrium state of two phases), we have f = 1, and only one of the variables T or P can be set arbitrarily: $P = P(T)$ or $T = T(P)$. Three phases are in equilibrium at the triple point if the condition r = 3 is fulfilled: $T = T_{tr}$, $P = P_{tr}$ and here f = 0.

2. Two-component system (n = 2). For such a system, you can write

$$f = 4 - r, \quad r \leq 4. \tag{3.7.24}$$

For r = 1, we have f = 3, and three parameters will be independent variables T, P, and x. Symbol x indicates concentration (e.g., the concentration of salt in water). For r = 2, we have f = 2, and only two of the three parameters are independent. The following relations can be written: $P_s = f_1(T,x)$ – ***Raoult's law*** (law was established by François-Marie Raoult (10.05.1830 – 1.04.1901)) steam and solution are in equilibrium; $T_m = f_2(P,x)$ (solution and ice crystals are in equilibrium); $x_s = f_3(T,P)$ (solution and salt crystals are in equilibrium). The following notation is used here: P_s is saturated vapour pressure; T_m is the melting point; x_s is the concentration of the saturated solution.

The equilibrium state of the five phases (r = 5) is forbidden by the Gibbs phase rule.

Test questions

1. Describe the ionic bond of atoms in the molecule.
2. Explain the existence of a covalent bond in a molecule consisting of two identical atoms.
3. Write down the formula for the Lennard–Jones potential.
4. Give the relationship between the forces of van der Waals and the distance between the atoms in the molecule.
5. Is the hydrogen bond between atoms a separate type of bond?
6. Give a definition of the phase of the thermodynamic system.
7. Describe the critical pressure, critical volume, and critical gas temperature.
8. Formulate the lever arm rule for a two-phase thermodynamic system.
9. Describe the phenomenon of critical opalescence.
10. Write down the Clapeyron – Clausius equation.
11. Formulate the van der Waals equation for the molar volume of gas.
12. Write down formulas that describe the relationship between critical parameters and Van der Waals constants.
13. Indicate the features of the integral Joule – Thomson effect.
14. Give a mathematical formulation of the differential Joule – Thomson effect.
15. Indicate the nature of the inversion temperature change with increasing gas density.
16. Describe the physical factors that cause surface tension.
17. Write down the Laplace formula.
18. Indicate the restrictions imposed on the application of the Thomson’s formula.
19. Give a definition of chemical potential.
20. Formulate the Gibbs phase rule.

Problem-solving examples

Problem 3.1

Problem description. In a cylinder with a volume of V = 8 *l* is oxygen with mass m = 0.3 kg. Oxygen has a temperature of T = 300 K. Determine the part of the volume k that makes up the intrinsic volume of gas molecules. Calculate the ratio k_1 of internal pressure P' to gas pressure P on the walls of the vessel.

Known quantities: V = 8 *l*, m = 0.3 kg, T = 300 K.

Quantities to be calculated: k, k_1.

Problem solution. The ratio of the intrinsic volume of gas molecules to the volume of the vessel is determined by the formula

$$k = \frac{V'}{V}100\%, \tag{P.3.1.1}$$

where V is the volume of the cylinder; V' is the intrinsic volume of gas molecules.

We write the van der Waals equation

$$\left(P + \frac{\nu^2 a}{V^2}\right)\cdot\left(V - \nu b\right) = \nu RT, \tag{P.3.1.2}$$

where $\nu = \frac{m}{\mu}$ is the amount of substance; μ is the molar mass of the substance; R is a gas constant; P is the pressure of the gas on the walls of the vessel; a and b are van der Waals constants for one mole of gas.

The value of νb in the van der Waals equation is equal to the quadruple volume of gas molecules, i.e.

$$\nu b = 4V'. \tag{P.3.1.3}$$

Then

$$V' = \frac{\nu b}{4} \tag{P.3.1.4}$$

or

$$V' = \frac{mb}{4\mu}. \tag{P.3.1.5}$$

Substitute the found value V' into the formula (P.3.1.1)

$$k = \frac{mb}{4\mu V}. \tag{P.3.1.6}$$

We substitute the numerical values in the formula (P.3.1.6)

$$k=\frac{0.3\times 3.17\times 10^{-5}}{4\times 32\times 10^{-3}\times 8\times 10^{-3}}\times 100=0.93\%.$$

The ratio of internal pressure P' to pressure P is determined by the formula

$$k_1=\frac{P'}{P}100\%. \qquad \text{(P.3.1.7)}$$

The internal pressure P' according to the van der Waals equation (P.3.1.2) is determined by the following relation

$$P'=\frac{\nu^2 a}{V^2} \qquad \text{(P.3.1.8)}$$

or

$$P'=\frac{m^2 a}{\mu^2 V^2}. \qquad \text{(P.3.1.9)}$$

We substitute the numerical values in the formula (3.1.9)

$$P'=\frac{0.3^2\times 0.136}{\left(32\times 10^{-3}\right)^2\left(8\times 10^{-3}\right)^2}=1.87\times 10^5\ \text{Pa}.$$

Gas pressure P on the vessel walls can be found from formula (P.3.1.2)

$$P=\frac{\nu RT}{V-\nu b}-\nu^2\frac{a}{V^2}. \qquad \text{(P.3.1.10)}$$

We substitute the numerical values in the formula (P.3.1.10)

$$P=\frac{9.38\times 8.31\times 300}{8\times 10^{-3}-9.38\times 3.17\times 10^{-5}}-9.38^2\frac{0.136}{\left(8\times 10^{-3}\right)^2}=1.54\times 10^6\ \text{Pa}$$

Substituting the obtained numerical values in the formula (P.3.1.7), we obtain

$$k_1=\frac{1.87\times 10^5}{1.54\times 10^6}100=12.1\%.$$

Answer. The ratio of the intrinsic volume of gas molecules to the volume of the vessel is k = 0.93 %. The ratio of internal pressure to gas pressure on the walls of the vessel is k_1 = 12.1 %.

Problem 3.2

Problem description. In the cylinder under the piston is chlorine of mass m = 20 g. Determine the change in the internal energy of ΔU chlorine during its isothermal expansion from volume V_1 = 200 cm^3 to volume V_2 = 500 cm^3.

Known quantities: m = 20 g, V_1 = 200 cm^3, V_2 = 500 cm^3.

Quantities to be calculated: ΔU.

Problem solution. The internal energy U of the real gas is determined by the ratio

$$U = \nu\left(c_V T - \frac{a}{V_m}\right), \tag{P.3.2.1}$$

where ν is the amount of substance; c_V is the specific heat of chlorine at a constant volume; T is the temperature of chlorine; a is the van der Waals constant assigned to one mole of chlorine; V_m is the molar volume of chlorine.

For further analysis, it is necessary to take into account the following relations

$$\nu = \frac{m}{\mu} \tag{P.3.2.2}$$

and

$$V_m = \frac{V}{\mu}, \tag{P.3.2.3}$$

where V is the volume occupied by the gas; m is a mass of chlorine; μ is the molar mass of chlorine.

We rewrite equation (P.3.2.1) taking into account relations (P.3.2.2) and (P.3.2.3)

$$U = \frac{m}{\mu}\left(c_V T - \frac{ma}{\mu V}\right). \tag{P.3.2.4}$$

The change in internal energy ΔU as a result of isothermal expansion can be defined as the difference between the two values of internal energy U_2 and U_1

$$\Delta U = U_2 - U_1 = \frac{m^2 a (V_2 - V_1)}{\mu^2 V_1 V_2}, \tag{P.3.2.5}$$

where V_1 and V_2 are the values of chlorine volumes before and after expansion, respectively.

We substitute the numerical values in the formula (P.3.2.5)

$$\Delta U = \frac{\left(2\times10^{-2}\right)^2 \times 0.650 \times \left(5\times10^{-4} - 2\times10^{-4}\right)}{0.071^2 \times 2\times10^{-4} \times 5\times10^{-4}} = 154\,\mathrm{J}$$

Answer. The change in the internal energy of chlorine is ΔU = 154 J.

Problem 3.3

Problem description. Determine the change in the free energy ΔF of the surface of the soap bubble with an isothermal increase in its volume from V_1 = 10 cm^3 to $V_2 = 2V_1$.

Known quantities: V_1 = 10 cm^3, $V_2 = 2V_1$.

Quantities to be calculated: ΔF.

Problem solution. The free energy F of the surface of the liquid is proportional to the area S of this surface

$$F = \sigma S, \tag{P.3.3.1}$$

where σ is the surface tension coefficient.

The soap bubble has two surfaces (internal and external), the areas of which are almost equal due to the small thickness of the soap film. Therefore, the total free energy of the inner and outer surfaces of the soap bubble is

$$F = 2\sigma S. \tag{P.3.3.2}$$

The process described in the problem statement is isothermal. The surface tension coefficient for a given liquid is a function of temperature only. Therefore, the surface tension coefficient is a constant.

The change in free energy is

$$\Delta F = 2\sigma \Delta S, \tag{P.3.3.3}$$

where ΔS is a change in only one surface of the soap bubble (internal or external).

Suppose a soap bubble has the shape of a sphere. In this case, the change in surface area is

$$\Delta S = 4\pi r_2^2 - 4\pi r_1^2, \tag{P.3.3.4}$$

where r_1 and r_2 are the radii of the spheres corresponding to the initial V_1 and final V_2 volumes.

The radii of the spheres and volumes are related by the relations

$$r_1 = \left(\frac{3V_1}{4\pi}\right)^{1/3}, \tag{P.3.3.5}$$

$$r_2 = \left(\frac{3V_2}{4\pi}\right)^{1/3}. \tag{P.3.3.6}$$

Rewrite formula (P.3.3.4)

$$\Delta S = 4\pi\left[\left(\frac{3V_2}{4\pi}\right)^{2/3} - \left(\frac{3V_1}{4\pi}\right)^{2/3}\right] \tag{P.3.3.7}$$

or, given that $V_2 = 2V_1$

$$\Delta S = 4\pi\left(\frac{3V_1}{4\pi}\right)^{2/3} \cdot \left(2^{2/3} - 1\right). \tag{P.3.3.8}$$

We substitute the expression for changing the surface ΔS in the formula (P.3.3.3)

$$\Delta F = 8\pi\sigma\left(\frac{3V_1}{4\pi}\right)^{2/3} \cdot \left(2^{2/3} - 1\right). \tag{P.3.3.9}$$

We substitute the numerical values in the formula (P.3.3.9)

$$\Delta F = 8\times3.14\times4\times10^{-2}\times\left(\frac{3\times10^{-5}}{4\times3.14}\right)^{2/3} \cdot \left(2^{2/3} - 1\right) = 1.05\times10^{-4}\ \text{J}$$

Answer. The change in the free energy of the surface of the soap bubble is $\Delta F = 1.05\times10^{-4}$ J.

Problems

Problem A

Problem description. The quartz flask is partially filled with liquid pentane C_5H_{12}. The flask was sealed so that only saturated steam was located above the pentane. The density of pentane is considered equal to 626 kg/m^3. Determine the fraction ε of the internal volume of the flask that pentane should occupy, so that when heated, it is possible to observe the transition of a substance through a critical point. The van der Waals constant for pentane is $b = 14.5\times10^{-5}$ m^3/mol.

Answer. $\varepsilon = 0.264$.

Problem B

Problem description. The volume V and pressure P of nitric oxide are three times higher than the corresponding critical values V_c and P_c. The critical temperature of nitric oxide is $T_c = 180$ K. Determine the temperature T of nitric oxide.

Answer. $T = 600$ K.

Problem C

Problem description. The oxygen temperature is $T = 350$ K. Oxygen contains an amount of a substance equal to $\nu = 1$ mol. Determine the relative error ε in the calculation of the internal energy of oxygen, if this gas is considered as ideal. Calculations are performed for two volume values: 1) $V_1 = 2\ l$; 2) $V_2 = 0.2\ l$.

Answer. $\varepsilon_1 = 9.43\times10^{-3}$; $\varepsilon_2 = 0.103$.

Problem D

Problem description. Gaseous chlorine of mass $m = 7.1$ g is in a vessel of volume $V_1 = 0.1\ l$. Calculate the amount of heat Q that needs to be brought to chlorine, so that when the chlorine expands into a void to volume $V_2 = 1\ l$, the gas temperature remains unchanged

Answer. $Q = 58.5$ J.

Problem E

Problem description. Two vertical capillary tubes are lowered by the lower ends into the liquid. The inner diameters of the tubes are $d_1 = 0.05$ cm and $d_2 = 0.1$ cm, respectively. The difference in fluid levels in the tubes is $\Delta h = 11.6$ mm. The density of the liquid is $\rho = 0.8$ g/cm^3. Calculate the surface tension coefficient σ of a fluid.

Answer. $\sigma = 2.2\times10^{-3}$ N/m.

CHAPTER 4. TRANSPORT PROCESSES

4.1. Transport Processes in Gases

If the system is in a non equilibrium state, then left to itself, it will gradually move to an equilibrium state. The time during which the system reaches an equilibrium state is called the relaxation time. The relaxation time is different with respect to different parameters by which the system can deviate from the equilibrium state.

In equilibrium, the temperature at all points in the system is the same. When the temperature deviates from the equilibrium value in a certain region, the system moves heat in such directions to make the temperature of all parts of the system the same. The heat transfer associated with this movement is called thermal conductivity.

The density of each component at all points of the phase is the same in equilibrium. When the density deviates from the equilibrium value in a certain region, the system moves the components of the substance in such directions to make the density of each component constant over the entire volume of the system. The transport of matter of the components that make up the phase associated with this movement is called diffusion.

Various phases are stationary relative to each other in equilibrium. With relative phase motion, factors arise that tend to reduce the relative velocity. Consequently, braking forces or viscosity arise. The mechanism of these forces in gases is reduced to the exchange of momentum by various layers of gas, i.e. to the transfer of momentum of ordered movement.

We denote by a symbol G some physical property that is assigned to one molecule. This property can be energy, momentum, concentration, electric charge, etc. If in equilibrium the quantity G is constant in volume, then in the presence of a gradient there is a movement of this quantity in the direction of decreasing gradient G.

Let us direct the x axis along the gradient of G. The average distance travelled by molecules crossing the area dS after the last collision is $2\langle l\rangle/3$, where $\langle l\rangle$ is the average mean free path. This value in most cases is quite small, and the value of G at a distance of $2\langle l\rangle/3$ from the site can be represented as

$$G\left(x\pm\frac{2}{3}\langle l\rangle\right)=G(x)\pm\frac{2}{3}\langle l\rangle\frac{\partial G(x)}{\partial x}. \tag{4.1.1}$$

We limited ourselves to the first term in the expansion of the value G in the Taylor series at point x.

The flux of the number of molecules in the direction of the x axis is $n_0\langle v\rangle/4$, where n_0 is the concentration of molecules, $\langle v\rangle$ is the average speed. Therefore, the flux of G through the area dS in the direction of the negative x axis values is

$$I_G^{(-)} = -\frac{1}{4} n_0 \langle v \rangle \left\{ G(x) + \frac{2}{3} \langle l \rangle \frac{\partial G(x)}{\partial x} \right\}. \tag{4.1.2}$$

The flux of G in the direction of positive values of x axis is

$$I_G^{(+)} = \frac{1}{4} n_0 \langle v \rangle \left\{ G(x) - \frac{2}{3} \langle l \rangle \frac{\partial G(x)}{\partial x} \right\}. \tag{4.1.3}$$

Therefore, the total flow in the positive direction of the x axis at point x is

$$I_G = I_G^{(+)} + I_G^{(-)} = -\frac{1}{3} n_0 \langle v \rangle \langle l \rangle \frac{\partial G}{\partial x}. \tag{4.1.4}$$

Equation (4.1.4) is the basic equation for the transfer processes of a physical quantity G.

Consider the process of thermal conductivity. In this case, the value G is the average energy of thermal motion per one molecule. The value of G is a variable in the case when the temperature at different points of the system changes. The value of I_G in this case is the heat flux, which we will denote by the symbol I_q. From the theorem on the equal distribution of energy over degrees of freedom we have

$$G = \frac{i}{2} kT = \frac{i}{2} \frac{kN_A}{N_A} T = \frac{i}{2} \frac{R}{N_A} T = \frac{c_V}{N_A} T. \tag{4.1.5}$$

Then the basic transport equation (4.1.4) takes the form

$$I_q = -\frac{1}{3} n_0 \langle v \rangle \langle l \rangle \frac{c_V}{N_A} \frac{\partial T}{\partial x} = -\lambda \frac{\partial T}{\partial x}, \tag{4.1.6}$$

$$\lambda = \frac{1}{3} n_0 \langle v \rangle \langle l \rangle \frac{c_V}{N_A} = \frac{1}{3} \rho \langle v \rangle \langle l \rangle c_V. \tag{4.1.7}$$

The value of λ, defined by equation (4.1.7), is called the ***coefficient of thermal conductivity***. The following notation is used in equations (4.1.6) and (4.1.7): $\rho = n_0 m$ is density; $c_V = C_V/(N_A m)$ is the specific heat of the gas at a constant volume. Equation (4.1.6) is called the Fourier equation for thermal conductivity or the ***Fourier's law*** (law was named after Jean-Baptiste Joseph Fourier (21.03.1768 – 16.05.1830)).

Since the radii of all molecules are approximately the same, the values also differ little for different gases. The main change in thermal conductivity at a fixed concentration n_0 of gas particles occurs due to differences in the average velocity $\langle v \rangle$. Due to this, light gases have significantly higher thermal conductivity than heavy gases.

This is confirmed by experience. For example, oxygen and hydrogen have a thermal conductivity of 0.024 W/(m·K) and 0.176 W/(m·K) under normal conditions, respectively.

The value of $n_0\langle l\rangle = 1/\sigma$ is independent of pressure. The value $\langle v\rangle \sim \sqrt{T}$ is also independent of pressure. Therefore, thermal conductivity is independent of pressure. Thermal conductivity is approximately directly proportional to the square root of temperature.

Consider the viscosity process. Viscosity, or internal friction in gases, is caused by the transfer of momentum of the molecules across the direction of motion of the gas layers, which have different speeds.

As a result of thermal motion, molecules pass from one layer to another, transferring momentum mu. Between the layers moving at different speeds, there is an exchange of molecules. Momentum faster than a moving layer decreases, and momentum slower than a moving layer increases.

The friction force τ, referred to the area of the rubbing surfaces of the gas, is equal to the flow of the momentum of the ordered movement in the direction perpendicular to the velocity. In this case, the value of G is

$$G = mu. \tag{4.1.8}$$

Therefore, equation (4.1.4) takes the form

$$I_{mu} = -\frac{1}{3} n_0 \langle v\rangle \langle l\rangle m \frac{\partial u}{\partial x} = -\eta \frac{\partial u}{\partial x} = \tau, \tag{4.1.9}$$

and

$$\eta = \frac{1}{3} n_0 \langle v\rangle \langle l\rangle m = \frac{1}{3} \rho \langle v\rangle \langle l\rangle. \tag{4.1.10}$$

The value of η described by equation (4.1.10) is called ***dynamic viscosity***. The sign of magnitude τ takes into account that the friction force acting on more rapidly moving layers is directed against speed.

Since $n_0\langle l\rangle = 1/\sigma$ and $\langle v\rangle \sim \sqrt{T}$, it can be concluded that the dynamic viscosity is independent of pressure and varies mainly in proportion to the square root of temperature.

Together with dynamic viscosity, kinematic viscosity ν is also used, defined as dynamic viscosity, referred to density

$$\nu = \frac{\eta}{\rho}. \tag{4.1.11}$$

Consider the diffusion process. With a non-uniform distribution of gas in the system, equalization of concentrations begins as a result of collisions between molecules. The tolerated amount in this case is the concentration of the species in question. Suppose that the concentration of the first sort of molecules is $n_1(x)$. For value G, we can write the relation

$$G = \frac{n_1}{n_0}, \tag{4.1.12}$$

where n_0 is an equilibrium concentration.

Equation (4.1.4) takes the form

$$I_{n_1} = -\frac{1}{3} n_0 \langle v \rangle \langle l \rangle \frac{\partial}{\partial x}\left(\frac{n_1}{n_0}\right) = -D \frac{\partial n_1}{\partial x}, \tag{4.1.13}$$

where

$$D = \frac{1}{3} \langle v \rangle \langle l \rangle. \tag{4.1.14}$$

The value D described by equation (4.1.14) is called the ***diffusion coefficient***. Equation (4.1.14) is called the ***Fick's law*** (law was derived by Adolf Eugen Fick (3.09.1829 – 21.08.1901)).

At a fixed temperature, the value $\langle v \rangle$ is constant, and $\langle l \rangle \sim 1/P$. Therefore, at a constant temperature $D \sim 1/P$. On the other hand, at a fixed pressure $\langle l \rangle \sim T$ and $\langle v \rangle \sim \sqrt{T}$. Therefore, at constant pressure for the diffusion coefficient, we can write $D \sim T^{3/2}$.

The relationship between the coefficients characterizing the transfer processes has the form

$$\lambda = \frac{\eta C_V}{m N_A} = \eta c_V, \quad D = \frac{\eta}{\rho} = \frac{\lambda}{c_V \rho}, \tag{4.1.15}$$

4.2. Relaxation Time

As a result of transport phenomena, temperature and concentration are equalized, i.e. temperature and concentration change over time. The time during which this occurs is called the relaxation time of the system. An analysis of the change in thermodynamic quantities in time requires the explicit recording of unsteady heat conduction and diffusion equations.

Consider the diffusion, the flow of which can be described using equation (4.1.13). Consider the volume V in the form of a cylinder, the base area of which is ΔS, and the height directed along the x axis is Δx. By the definition of flow, the change in the number of particles in the volume of the cylinder over time Δt is

$$\Delta N_1 = \left[I_{n_1}\left(x - \frac{\Delta x}{2}\right) - I_{n_1}\left(x + \frac{\Delta x}{2}\right) \right] \Delta S \Delta t. \tag{4.2.1}$$

We expand flux I_{n_1} in a Taylor series and restrict ourselves to a term linear in Δx. In this case, we can write

$$I_{n_1}\left(x \pm \frac{\Delta x}{2}\right) = I_{n_1}(x) \pm \frac{\Delta x}{2}\frac{\partial I_{n_1}(x)}{\partial x}. \tag{4.2.2}$$

Therefore, formula (4.2.1) takes the form

$$\Delta N_1 = -\frac{\partial I_{n_1}}{\partial x}\Delta x \Delta S \Delta t. \tag{4.2.3}$$

Then

$$\lim_{\substack{\Delta V \to 0 \\ \Delta t \to 0}} \frac{\Delta N_1}{\Delta V \Delta t} = \frac{\partial n_1}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial n_1}{\partial x}\right), \tag{4.2.4}$$

where $\Delta V = \Delta S \Delta x$ is the test volume.

Since the quantity D is independent of the coordinates, instead of equation (4.2.4), we can write

$$\frac{\partial n_1}{\partial t} = D\frac{\partial^2 n_1}{\partial x^2}. \tag{4.2.5}$$

Formula (4.2.5) is a non-stationary equation of diffusion. Consider the case when the direction of diffusion does not coincide with the x axis, but has an arbitrary direction. Then the value ΔN_1 in the formula (4.2.1) can be expressed as the sum of the contributions along each of the coordinate axes. In the general case, instead of equation (4.2.5), we can write the following relation

$$\frac{\partial n_1}{\partial t} = D\left(\frac{\partial^2 n_1}{\partial x^2} + \frac{\partial^2 n_1}{\partial y^2} + \frac{\partial^2 n_1}{\partial z^2}\right) = D\nabla^2 n_1, \tag{4.2.6}$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{4.2.7}$$

is the Laplace operator.

Using equation (4.2.6), we can study the change in the concentration n_1 of molecules at all points of the volume for a given concentration distribution at the initial time and under certain conditions at the boundary of the volume.

Consider the case of non-stationary thermal conductivity. Analysis of non-stationary thermal conductivity can be carried out similarly to the analysis of non-stationary diffusion. Instead of particle flux I_{n_1}, it is necessary to take heat flux Q, which is described by equation (4.1.6). Then, instead of equation (4.2.4), we can write the following relation

$$\lim_{\substack{\Delta V \to 0 \\ \Delta t \to 0}} \frac{\Delta Q}{\Delta V \Delta t} = \lim \frac{c_V \Delta m \Delta T}{\Delta V \Delta t} == c_V \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x} \right) \qquad (4.2.8)$$

where $\Delta Q = c_V \Delta m \Delta T$ is a change in the amount of heat in volume ΔV over time Δt; c_V is the specific heat at a constant volume; $\rho = \Delta m / \Delta V$ is the density of the gas.

Thermal conductivity λ can be described using formula (4.1.7). Taking into account the formula (4.1.15), the non-stationary heat equation (4.2.8) can be written as

$$\frac{\partial T}{\partial t} = a^2 \frac{\partial^2 T}{\partial x^2}, \qquad (4.2.9)$$

where

$$a = \left(\frac{\lambda}{\rho c_V} \right)^{1/2} \qquad (4.2.10)$$

is the ***coefficient of thermal diffusivity***.

When a certain value deviates from the equilibrium value, some factors arise that tend to return the value to this value.

The rate at which the quantity approaches the equilibrium value is considered proportional to its deviation from the equilibrium value. The inverse of the coefficient of proportionality is the relaxation time.

Consider the value q, the equilibrium value of which is q_0. Then the statement formulated earlier can be written as follows

$$\frac{dq}{dt} = \frac{q_0 - q}{\tau}. \qquad (4.2.11)$$

The solution to this equation has the form

$$q - q_0 = \left(q - q_0 \right)\Big|_{t=0} \exp\left(-\frac{t}{\tau} \right), \qquad (4.2.12)$$

where $\left(q - q_0 \right)\Big|_{t=0}$ is a deviation from the equilibrium value at the initial moment of time $t = 0$.

In accordance with the general condition on exponentially changing quantities, the value τ has the meaning of the time when the value q reaches its equilibrium value. Therefore, the value τ is the relaxation time.

Consider a volume whose linear dimensions are of the order of L with an average value of $\langle L \rangle$. Suppose that $\langle \Delta n \rangle$ is the average deviation of the particle concentration from the equilibrium value in the volume $V \sim L^3$. Let symbol $V \langle \Delta n \rangle$ denote the excess number of particles in the volume as compared with the number of particles corresponding to the equilibrium value. The change in the number of particles inside the volume over time dt is

$$d\left(V\langle\Delta n\rangle\right)=-\langle I_n\rangle S dt, \tag{4.2.13}$$

where S is the surface area limiting the volume; $\langle I_n\rangle$ is the average particle flux through the surface.

Using relation $\partial n/\partial x \sim \Delta n/L$, we rewrite equation (4.2.13)

$$\langle I_n\rangle = D\frac{\langle\Delta n\rangle}{\langle L\rangle}. \tag{4.2.14}$$

Solving equations (4.2.13) and (4.2.14) together, we obtain

$$\frac{d\langle\Delta n\rangle}{dt}=\left[-\frac{SD}{V\langle L\rangle}\right]\langle\Delta n\rangle. \tag{4.2.15}$$

The solution of equation (4.2.15) has the form

$$\langle\Delta n\rangle = \left(\langle\Delta n\rangle\right)_0 \exp\left(-\frac{t}{\tau_n}\right), \tag{4.2.16}$$

where

$$\tau_n = \frac{V\langle L\rangle}{SD}. \tag{4.2.17}$$

The value τ_n determined from equation (4.2.17) is the relaxation time to the equilibrium concentration distribution.

The calculation of the relaxation time for temperature is similar to the calculation just made. The relaxation time for temperature can be expressed by the following formula

$$\tau_T = \frac{\rho c_V V\langle L\rangle}{\lambda S}. \tag{4.2.18}$$

4.3. Rarefied Gas Transport

Let us consider transport processes in media with a low concentration of molecules and, accordingly, low pressure. The mean free path increases with decreasing pressure. Suppose that the mean free path has become equal to the linear geometric dimensions of the vessel in which the gas is located. In this case, the molecules collide only with the walls of the vessel and practically do not collide with each other.

This state of gas is called vacuum. The concept of vacuum is relative. The larger the linear dimensions of the vessel, the lower the vacuum. Under normal atmospheric conditions, the mean free path is approximately $\langle l \rangle \sim 10^{-8}$ m. Consequently, the vacuum conditions are observed only in very small volumes with linear dimensions of d orders of the mean free path $d \sim \langle l \rangle$.

Since there are practically no collisions between molecules under vacuum conditions, the transfer processes considered earlier cease to be valid.

Molecules in straight lines fly from one wall to another. When they collide with the walls, the molecules exchange energy with them. Thus, molecules are carriers of energy from hotter walls to colder ones. Therefore, it is more correct to speak not about the thermal conductivity of the gas, but about heat transfer, since there is no temperature gradient in the volume of the vessel.

The dependence of heat transfer ability on gas pressure is different than the dependence of heat conductivity on pressure at a higher pressure. At high pressure, thermal conductivity is independent of pressure. Heat transfer at low pressure increases with increasing pressure, since the frequency of impact of molecules on the walls of the vessel increases. Conversely, heat transfer decreases with decreasing pressure to arbitrarily small values. An example of the practical use of this effect is a ***cryogenic storage dewar*** (named after James Dewar (20.09.1842 – 27.03.1923)). In the hollow walls of the Dewar vessel, vacuum conditions are created with a sufficiently low heat transfer.

Consider the features of diffusion at low pressures. Since there are practically no collisions between molecules in the volume, the transfer of molecular traits occurs with the speed of movement of the molecules, i.e. very fast. The concentration equalization time, even in very large volumes, is short. This time depends on the shape of the vessel.

Consider two solid surfaces moving relative to each other. Between the surfaces there is gas in a vacuum. In this case, friction forces arise between the surfaces, which tend to slow down the more rapidly moving surface and accelerate the less rapidly moving surface. This phenomenon is similar in appearance to the appearance of similar friction forces at a fairly high air pressure between moving surfaces, but the mechanism is completely different.

Under vacuum conditions, there are no gas layers between moving surfaces that move translationally relative to each other, as a result of which an internal friction force would be transmitted from layer to layer.

In a collision with a moving surface, the molecule acquires the corresponding impulse of ordered motion and, flying without collisions the space between the surfaces, exchanges the impulse of its ordered motion with another surface. The momentum transmitted to the surface by molecules in every second is numerically equal to the friction force.

Thus, under vacuum, there is no internal friction in the gas in the sense in which it exists at a higher pressure. However, we can observe the mutual friction of surfaces moving relative to each other.

Consider a system that consists of two vessels communicating through a porous septum. The pore sizes in the porous septum can be arbitrarily small.

However, in these pores the vacuum conditions are observed even at normal atmospheric pressure.

Suppose that the same gas is located on different sides of the partition, but at different temperatures. In this case, an equilibrium state is established in the gas, in which the pressure on different sides of the partition is different. Denote the quantities related to volumes on opposite sides of the partition by indices 1 and 2.

Under equilibrium, the number of molecules passing through the porous septum from one half of the vessel to the other half is equal to the number of molecules passing through the same septum in the opposite direction. The frequency of molecular impacts on the wall is $n_0\langle v\rangle/4$. Since the pores of the molecule themselves pass without collisions, the condition for the equality of the number of molecules for both directions can be formulated as

$$\frac{n_{01}\langle \upsilon_1\rangle S_e}{4}=\frac{n_{02}\langle \upsilon_2\rangle S_e}{4}, \tag{4.3.1}$$

where S_e is the effective total pore area in the septum.

Using the relation, which can be written for concentration $n_0 = P/(kT)$ and for average velocity $\langle v\rangle = const\sqrt{T}$, from equation (4.3.1) we can obtain

$$\frac{P_1}{\sqrt{T_1}}=\frac{P_2}{\sqrt{T_2}}. \tag{4.3.2}$$

Therefore, the pressure is increased in those areas of the vessel where an increased temperature value is observed.

Such a situation is impossible under normal conditions, since the hydrodynamic flows arising from the pressure difference quickly equalize the pressure. Formula (4.3.2) was experimentally confirmed by Reynolds.

Consider the exchange of molecules of various varieties through a porous septum. Imagine that at some point in time the volumes on opposite sides of the porous septum of the vessel are filled with two different gases at the same pressure and temperature. Such a state is not equilibrium. The density of molecules on both sides of the septum is the same, but the average speeds of the molecules are different. Lighter molecules move faster. Therefore, the frequency of impacts of light molecules on the septum is greater than heavy. Accordingly, the number of light molecules penetrating the septum is greater than heavy.

The pressure in the volume of the vessel occupied by heavy molecules begins to increase, and the pressure in the volume of the vessel occupied by light molecules begins to decrease. As the molecules mix, the pressure growth slows down and then stops. The number of molecules penetrating the septum on both sides is leveled. However, the concentration of molecules of each variety on opposite sides of the septum is not equal. Only after some time does the pressure and concentration of molecules of each sort become equalized.

When a molecule hits a surface, it interacts with only a small number of atoms or molecules near the surface. In this type of interaction, the angle of reflection in the general case is not equal to the angle of incidence and depends on the specific conditions of interaction with surface molecules. Such a surface is called a rough surface.

For molecules coming from a given direction, the reflection angle is on average less than the angle of incidence. As a result of this, not only the pressure force acts on the surface, but also the tangential force in the direction of the tangential component of the velocity of the molecules incident on the surface.

For the case when the flows to the surface from all directions are the same, the tangential forces are mutually compensated, and only the pressure of the molecules on the surface remains.

The reflection of molecules from the surface leads to a change in their energy. If the temperature of the flows of molecules incident on the surface is equal to the temperature of the surface, then the temperature of the reflected flows is equal to the temperature of the incident flows. In other cases, as a result of interaction with the surface, the flow temperature changes and becomes equal to the surface temperature.

Consider the interaction of molecules with the surface in a deep vacuum. The flow of molecules in this case is isotropic and has the same temperature in all directions. If the surface temperature is constant, then no tangential forces arise and the pressure at all points on the surface is the same.

If the surface temperature changes from point to point, it is obvious that there are still no tangential forces, because the incident stream of molecules is still isotropic, but the pressure at different points on the surface is different. The pressure is greater on the surface area with a higher temperature, since when the molecules are reflected, the normal component of their momentum not only reverses direction, but also increases in absolute value.

As a result of these processes, forces acting on a body with a temperature varying along its surface under vacuum conditions cause its centre of mass to move and create a moment of rotation about an axis passing through the centre of mass. These forces are called ***radiometric forces***.

Consider the case of a not very deep vacuum. The nature of the interaction of molecules with the wall will remain as it was analyzed previously. However, now the surface temperature affects the temperature of the gas in a layer near the surface. Collisions between molecules occur in this layer.

Due to collisions, the properties of the flow of molecules falling on the surface change. If the surface is heated uniformly, then, as in the previous case, tangential forces do not arise, and the pressure at all points on the surface is the same. If the temperature at different points on the surface is different, then the situation changes.

Suppose, for definiteness, that the surface temperature rises along some positive axis direction. Then the falling molecules have an average tangential component of the force in the direction of the negative values of the axis. This force is applied to the surface of the body.

The momentum change of the molecules that interact with the surface should be directed in the opposite direction, i.e. towards positive x axis values. This means that in the near-wall layer there is a flow along the surface, directed from less heated parts of the surface to more heated parts of the surface.

The described phenomenon is called ***thermal slip***. Thermal glide occurs when the vacuum is not too deep.

With increasing pressure between regions with different pressures, hydrodynamic flows arise, which equalize the pressure. As a result of an increase in temperature near the warmer sections of the surface, gas pressure rises and gas flows occur along the surface from the warmer sections to the less heated sections.

These flows compensate for thermal slip and equalize pressure at various surface areas. Therefore, both radiometric forces and forces due to thermal slip are eliminated.

4.4. Transport Phenomena in Solids and Liquids

Transport phenomena also occur in liquids and solids. The transport mechanism in liquids and solids is different from the transport mechanism in gases. In liquids and solids, the notion of mean free path loses its meaning. In addition, the forces of interaction between the molecules of solids and liquids are very large and have a constant effect on the movement of molecules.

In solids, both diffusion and mutual diffusion are observed. This is most clearly demonstrated by the fact of the interpenetration of the matter of two bodies that have been in close contact with each other for a rather long time. Diffusion in solids is carried out using three main mechanisms.

1. If there is a vacancy in the site of the crystal lattice, then one of the neighbouring atoms can make a transition from its site to the vacant site. This transition is equivalent to the movement of a vacancy. In order for the diffusion process to take place, it is necessary that an uneven distribution of vacancies be present in the lattice. The uneven distribution of vacancies can be described using the gradient of vacancies. For diffusion through the movement of vacancies, the simultaneous presence of two conditions is necessary: the existence of a vacancy and the formation of a sufficiently large vibrational energy in one of the neighbouring atoms so that it can leave its area.
2. Atom leaves the node if it has sufficiently high energy oscillations. If there are no vacancies in the neighbourhood, then atom is located between nodes and then moves in internodes.
3. In a solid, an exchange of atoms is possible at neighbouring lattice nodes. This diffusion mechanism is not related to the motion of defects in the crystal lattice.

Diffusion in a solid is described by the Fick's law, but the diffusion coefficient D is determined by other factors. The main role in diffusion is played by the movement of vacancies. We introduce the following notation: $\langle \tau \rangle$ is the average lifetime of an atom in the nodes of the crystal lattice; $\langle d \rangle$ is the displacement of the atom during the jump. The value of $\langle d\rangle$ is approximately equal to the main periods of the crystal lattice. The average velocity of the atoms at jumps equals

$$\langle \upsilon\rangle = \frac{\langle d\rangle}{\langle \tau\rangle}. \tag{4.4.1}$$

An atom can equally likely jump $\langle d\rangle$ in six independent directions. Further analysis is similar to that which was carried out in deriving equations (4.1.4) and (4.1.13). As a result, for the diffusion coefficient we can write

$$D = \frac{\langle \upsilon\rangle\langle d\rangle}{6} = \frac{(\langle d\rangle)^2}{6\langle \tau\rangle}. \tag{4.4.2}$$

We denote by symbol E_υ the energy upon acquisition of which the atom leaves its node. As a result of this process, a vacancy is formed. In accordance with the Gibbs distribution, the probability of vacancy formation is

$$P_\upsilon = A_\upsilon \exp\left(-\frac{E_\upsilon}{kT}\right). \tag{4.4.3}$$

We denote by symbol E_j the energy that an atom must have in order to jump into an existing vacancy. Then for the hopping probability we can write the relation

$$P_j = A_j \exp\left(-\frac{E_j}{kT}\right). \tag{4.4.4}$$

The probability of the formation of a vacancy of a simultaneous atomic jump into this vacancy is

$$P = P_\upsilon P_j = A\exp\left(-\frac{E_\upsilon + E_j}{kT}\right) = A\exp\left(-\frac{E_a}{kT}\right). \tag{4.4.5}$$

where $A = A_\upsilon A_j = \text{const}$; $E_a = E_\upsilon + E_j$ is the ***activation energy of diffusion***, determined by the properties of the substance.

The jumping frequency is directly proportional to the hopping probability, i.e. $1/\langle \tau\rangle \sim P$. Substituting this expression for $\langle \tau\rangle$ into the formula (4.4.2), we get

$$D = D_0 \exp\left(-\frac{E_a}{kT}\right), \tag{4.4.6}$$

where $D_0 = A(\langle d\rangle)^2/6$ is a constant determined by the properties of the substance.

The diffusion coefficient in solids is very small compared with the diffusion coefficient in gases. For example, for gold and oxygen, the diffusion coefficients are 10^{-35} m^2 / s and 10^{-5} m^2 / s, respectively.

Thermal conductivity in solids is carried out not by the movement of molecules, as in gases, but through the interaction of molecules, as a result of which the movement of molecules becomes collective. As a result, the motion of molecules in a solid is described as an ideal phonon gas.

The thermal conductivity in solids can be described by the ratio

$$\lambda = \frac{\rho v_s \langle l_{ph} \rangle c_V}{3}, \tag{4.4.7}$$

where v_s is the speed of sound in a solid; $\langle l_{ph} \rangle$ is the mean free path of phonons: $\langle l_{ph} \rangle \sim T^{-1}$.

The thermal conductivity of solids is many times greater than the thermal conductivity of gases. The thermal conductivity of gases under normal conditions is of the order of 1 mW/(m·K), while the thermal conductivity of solids is of the order of 1 kW/(m·K).

If a solid body is surrounded by a medium with a temperature different from that of the body, then a stream of heat flows through the surface of the body. The temperature on the surface of the body experiences a jump from body temperature T to the temperature T_0 of the environment. As experience shows, at small temperature differences $T - T_0$, the normal component of the heat flux is proportional to this temperature difference

$$I_{qn} = \alpha(T - T_0), \tag{4.4.8}$$

where α is the ***coefficient of external thermal conductivity***.

Consider diffusion in liquids. The mechanism of diffusion in liquids is similar to the mechanism of diffusion in a solid. A molecule in a liquid abruptly changes its environment and moves to another point. If the average lifetime of the molecule between the jumps is denoted by the symbol $\langle \tau \rangle$, then for the diffusion coefficient in the liquid we can obtain the expression

$$D = \frac{(\langle \Delta \rangle)^2}{6\langle \tau \rangle}, \tag{4.4.9}$$

where $\langle \Delta \rangle$ is the average distance that a molecule jumps from its environment.

The time $\langle \tau \rangle$ in the fluid is also determined through the probability of a jump. In determining the probability of a jump, one needs to take into account the required energy and the probability that the molecule has this energy. In addition, it is necessary to take into account the probability that there are conditions for hopping in the environment of the molecule. As a result, for the diffusion coefficient, we can obtain a ratio similar to that presented in formula (4.4.6). In this case, the activation energy E_a is determined by the properties of the liquid. The diffusion coefficient of liquids is much less than that of gases, but much more than that of solids. A typical diffusion coefficient order for liquids is 10^{-9} m^2 / s.

As in solids, thermal conductivity in liquids is carried out by the transfer of thermal motion from one molecule to another as a result of interaction. However, a simple picture in the form of phonon motion in the case of liquids does not work out and the whole theory becomes complicated.

The mechanism of the appearance of viscosity in liquids cannot be presented as simply as in rarefied gases, when the picture is reduced to the transfer of momentum of the ordered motion of gas layers during the transition of molecules from one layer to another. Using the mechanism of molecular jumps to describe viscosity leads to the following relation $\eta \sim \exp(-b/T)$. However, in experimental studies revealed a dependence of $\eta \sim \exp(+b/T)$.

The pattern of molecule jumps from one position to another can be used, but it is necessary to consider these jumps in the direction of action of the force, i.e. perpendicular to the speed gradient. In this case, the process turns out to depend on the specific features of intermolecular forces. The molecule has to break its ties with its immediate environment in order to advance in the direction of the force. The bonds between the molecules that have to be overcome in this case are similar to those that are overcome during evaporation.

The calculation of the considered process is extremely complicated. It turns out that the dynamic viscosity depends on an external force, although this dependence is not always significant. In particular, for ordinary liquids with not very large values of external forces, this dependence is not significant.

The dynamic viscosity of most liquids is well described by the formula

$$\eta \approx A \exp\left(\frac{b}{T}\right), \tag{4.4.10}$$

where coefficients A and b are determined by the properties of the liquid.

The dynamic viscosity of a liquid decreases significantly with increasing temperature. This behaviour of the dynamic viscosity of a liquid is the opposite of the behaviour of the dynamic viscosity of gases. The dynamic viscosity of gases increases with temperature.

The dynamic viscosity of ordinary, not very viscous liquids is of the order of 1 mPa·s. In viscous fluids, the dynamic viscosity increases thousands of times. For example, the dynamic viscosity of water at a temperature of 20 ^{0}C is equal to 1.002×10^{-3} Pa·s.

4.5. Thermodynamics of Irreversible Processes

Transfer processes are irreversible. A description of their general appearance is phenomenological in nature. The transfer mechanism must be considered only to calculate the corresponding transfer coefficient.

The task of the thermodynamics of irreversible processes is to study the phenomenological laws of irreversible processes, in which they do not go into the discussion of the internal mechanisms of these processes.

The phenomenological equations describing transport processes have the form

$$I_q = -\lambda \frac{\partial T}{\partial x}, \tag{4.5.1}$$

$$I_n = -D \frac{\partial n}{\partial x}, \tag{4.5.2}$$

$$I_{mu} = -\eta \frac{\partial u}{\partial x}. \tag{4.5.3}$$

It is advisable to add Ohm's law in differential form to these equations for further applications

$$j = -\gamma \frac{\partial \varphi}{\partial x}, \tag{4.5.4}$$

where j is the current density; γ is the electrical conductivity; φ is the potential of the electric field; $-\partial\varphi/\partial x$ is the electric field strength.

Equations (4.5.1) - (4.5.4) can be written similarly for the y axis and z axis.

The peculiarity of these equations is that they describe the flow of a certain quantity standing on the left side of the equality, which arises due to the corresponding driving force standing on the right side of the equality. This force is a gradient of some magnitude. All equations for flow have the form

$$I = LX, \tag{4.5.5}$$

where I is a flux of magnitude; X is a generalized force creating a flux; L is a coefficient of proportionality.

In the cases that were considered earlier, each flux was determined by only one driving force. However, even in thermal diffusion, the flow of molecules was determined by two driving forces: a density gradient and a temperature gradient. Therefore, in the general case, the expression for the flux I_i has the form

$$I_i = L_{i1}X_1 + L_{i2}X_2 + \ldots = \sum_j L_{ij}X_j, \tag{4.5.6}$$

where index i numbers the types of flows, and index j numbers the types of driving forces. The number of equations of type (4.5.6) is equal to the number of fluxes.

Equations (4.5.6) are called linear phenomenological equations of the thermodynamics of irreversible processes. The coefficients L_{ij} in these equations are called ***Onsager coefficients*** (was named after Lars Onsager (27.11.1903 – 5.10.1976)).

Statistical thermodynamics proves that the coefficients L_{ij} are not completely independent. There are relations between these coefficients

$$L_{ij} = L_{ji}. \qquad (4.5.7)$$

Equations (4.5.7) are called ***Onsager relations***.

Another important point of the thermodynamics of irreversible processes is the formula for the production of entropy

$$\left(\frac{dS}{dt}\right)_{pr} = I_1 X_1 + I_2 X_2 + \ldots = \sum I_i X_i, \qquad (4.5.8)$$

where $(dS/dt)_{pr}$ is the rate of production of entropy related to volume, i.e. entropy density production rate.

Thus, fluxes I_i and forces X_i cannot be arbitrarily selected. They must be such that equality (4.5.8) holds.

The selection of flows and driving forces must be carried out in such a way as to ensure uniformity of dimension in both sides of equality (4.5.8). For example, if heat flux I_q is selected as the flux, then the value $X_q = -\left(1/T^2\right)\cdot\left(\partial T/\partial x\right)$ should be taken as the driving force. Similarly, we can conclude that if we take the density of electric current j as the flow, then we must take $X = (1/T)\cdot(\partial\varphi/\partial x)$ as the driving force.

Based on the foregoing, we can conclude that in the heat flux entropy is formed according to the law

$$\left(\frac{dS}{dt}\right)_{pr} = I_q\left(-\frac{1}{T^2}\frac{\partial T}{\partial x}\right) = -\frac{I_q}{T^2}\frac{\partial T}{\partial x}. \qquad (4.5.9)$$

The rate of production of the entropy density during the passage of electric current can be calculated using the formula

$$\left(\frac{dS}{dt}\right)_{pr} = -\frac{j}{T}\frac{\partial\varphi}{\partial x}. \qquad (4.5.10)$$

Consider the thermodynamic phenomena in the presence of coupled flows. Let us analyze the density of electric current and heat flux, which are interconnected. In accordance with equation (4.5.6), we write the electron flux and heat flux in the form

$$I_q = -L_{qq}\frac{1}{T^2}\frac{\partial T}{\partial x} - L_{qe}\frac{1}{T}\frac{\partial\varphi}{\partial x}, \qquad (4.5.11)$$

$$j=-L_{eq}\frac{1}{T^2}\frac{\partial T}{\partial x}-L_{ee}\frac{1}{T}\frac{\partial \varphi}{\partial x}. \tag{4.5.12}$$

For the case of unconnected flows of heat and electrical conductivity, these equations take the form

$$I_q=-L_{qq}\frac{1}{T^2}\frac{\partial T}{\partial x}. \tag{4.5.13}$$

$$j=-L_{ee}\frac{1}{T}\frac{\partial \varphi}{\partial x}. \tag{4.5.14}$$

Comparing equations (4.5.13) and (4.5.14) with equations (4.5.1) and (4.5.4), we obtain

$$\lambda=\frac{L_{qq}}{T^2}. \tag{4.5.15}$$

$$\gamma=\frac{L_{ee}}{T}. \tag{4.5.16}$$

Consider the case when there is no electric current ($j=0$). Then equation (4.5.12) takes the form

$$0=-L_{eq}\frac{1}{T^2}\left(\frac{\partial T}{\partial x}\right)_{j=0}-L_{ee}\frac{1}{T}\left(\frac{\partial \varphi}{\partial x}\right)_{j=0}. \tag{4.5.17}$$

In this case, we can write

$$\frac{(\partial\varphi/\partial x)_{j=0}}{(\partial T/\partial x)_{j=0}}=\left(\frac{\partial\varphi/\partial x}{\partial T/\partial x}\right)_{j=0}=\left(\frac{\partial\varphi}{\partial T}\right)=-\frac{L_{eq}}{L_{ee}T}. \tag{4.5.18}$$

Equation (4.5.18) means that the presence of a temperature gradient in the absence of an electric current causes a potential difference. In other words, a temperature gradient leads to an electric field. This phenomenon is called the ***Seebeck effect*** (was named after Thomas Johann Seebeck (4.04.1770 – 10.12.1831)). The value

$$E_T=-\left(\frac{\partial\varphi}{\partial T}\right)_{j=0}=\frac{L_{eq}}{L_{ee}T} \tag{4.5.19}$$

is called the ***thermoelectromotive force***.

Consider the processes at the transition between two different conductors a and b under isothermal conditions. When an electric current passes through the boundary of two conductors, either cooling or heating of this boundary occurs. This phenomenon is called the ***Peltier effect***. (was named after Jean Charles Athanase Peltier (22.02.1785 – 27.10.1845))

The power of heat that is released or absorbed at the boundary of the conductors is

$$I_{qab} = A\left(I_{qb} - I_{qa}\right) = AT\left(E_{Tb} - E_{Ta}\right)j = A\pi_{ab}j, \tag{4.5.20}$$

where

$$\pi_{ab} = T\left(E_{Tb} - E_{Ta}\right) \tag{4.5.21}$$

the ***Peltier coefficient***.

Test questions

1. Give a definition of the physical phenomenon of diffusion.
2. Write down the basic equation of the processes of transfer of a physical quantity.
3. What physical parameters of the system affect the coefficient of thermal conductivity?
4. Write down the Fourier’s law for thermal conductivity.
5. Draw a graph of the thermal conductivity versus temperature.
6. Describe in detail the physical viscosity process.
7. What physical parameters affect the dynamic viscosity coefficient?
8. Is the statement that dynamic viscosity coefficient depends on pressure true?
9. Give the formula by which the diffusion coefficient is determined.
10. Write down the Fick’s law.
11. Give the equations describing the relationship between the coefficients characterizing the transfer processes.
12. Write down the unsteady diffusion equation.
13. Give the formula by which the coefficient of thermal diffusivity is determined.
14. Indicate the nature of the change in the relaxation time for the concentration with a decrease in the diffusion coefficient.
15. Is the statement that the state of vacuum implies the absolute absence of gas molecules in the vessel true?
16. Explain the nature of the physical processes that give rise to radiometric forces.
17. Write down the formula for the diffusion activation energy.
18. Compare the diffusion coefficients in solids and gases.
19. Write down the Onsager relations.
20. Consider the physical background for the Seebeck effect.

Problem-solving examples

Problem 4.1

Problem description. The average mean free path of a carbon dioxide molecule under normal conditions is $\langle l \rangle = 40\,\mathrm{nm}$. Determine the average speed $\langle v \rangle$ of molecules and the average number $\langle z \rangle$ of collisions that the molecule experiences in time $t = 1$ s.

Known quantities: $\langle l \rangle = 40\,\mathrm{nm}$, $t = 1$ s.

Quantities to be calculated: $\langle v \rangle, \langle z \rangle$.

Problem solution. The average speed of molecules is determined by the formula

$$\langle v \rangle = \sqrt{\frac{8RT}{\pi\mu}}, \tag{P.4.1.1}$$

where R is the gas constant; T is the temperature of carbon dioxide; μ is the molar mass of carbon dioxide.

Substitute the numerical values in the formula (P.4.1.1)

$$\langle \upsilon \rangle = \sqrt{\frac{8 \times 8.31 \times 273}{3.14 \times 44 \times 10^{-3}}} = 3.62 \times 10^{2}\ \mathrm{m/s}.$$

The average number $\langle z \rangle$ of collisions of a molecule over time $t = 1$ s is determined by the ratio of the average speed $\langle v \rangle$ of the molecule to the average mean free path $\langle l \rangle$

$$\langle z \rangle = \frac{\langle v \rangle}{\langle l \rangle}. \tag{P.4.1.2}$$

We substitute numerical values in the formula (P.4.1.2)

$$\langle z \rangle = \frac{3.62 \times 10^{2}}{40 \times 10^{-9}} = 9.06 \times 10^{9}\ \mathrm{s}^{-1}$$

Answer. The average speed of molecules is $\langle v \rangle = 3.62 \times 10^{2}\ \mathrm{m/s}$. The average number of collisions of a molecule in one second is $\langle z \rangle = 9.06 \times 10^{9}\ \mathrm{s}^{-1}$.

Problem 4.2

Problem description. Two thin-walled coaxial cylinders of length $l = 10$ cm can freely rotate around their common axis z. The radius of the large cylinder is $R = 5$ cm. Between the cylinders there is a gap of size $d = 2$ mm. Both cylinders are in the air under normal conditions. The inner cylinder is rotated at a constant frequency of $n_1 = 20$ s^{-1}. The outer cylinder is inhibited and does not rotate. Determine after what period of time Δt from the moment the external cylinder is released, it will rotate with a frequency of $n_2 = 1$ s^{-1}. Neglect the change in the relative speed of the cylinders. The mass of the outer cylinder is $m = 100$ g.

Known quantities: $l = 10$ cm, $R = 5$ cm, $d = 2$ mm, $n_1 = 20$ s^{-1}, $n_2 = 1$ s^{-1}, $m = 100$ g.

Quantities to be calculated: Δt.

Problem solution. The layer of air between the cylinders begins to rotate when the inner cylinder rotates. Near the surface of the inner cylinder, the air layer with time acquires almost the same linear velocity as the speed of the points on the surface of the inner cylinder. Therefore, the speed v of the air layer is

$$v = 2\pi n_1 (R - d), \tag{P.4.2.1}$$

where n_1 is the rotational speed of the inner cylinder; R is the radius of the outer cylinder; d are the dimensions of the gap between the inner and outer cylinders.

Since $d << R$, then we can approximately assume that

$$v \approx 2\pi n_1 R. \tag{P.4.2.2}$$

Due to internal friction, the angular momentum is transmitted to adjacent gas layers and, ultimately, to the external cylinder. The external cylinder acquires a moment of impulse L for a time interval of Δt

$$L = pR, \tag{P.4.2.3}$$

where p is the momentum that the outer cylinder received in time Δt.

Consequently, the momentum of the points on the surface of the outer cylinder is

$$p = \frac{L}{R}. \tag{P.4.2.4}$$

On the other hand, for the momentum p, we can write the following relation

$$p = \eta \frac{dv}{dz} S \Delta t, \qquad \text{(P.4.2.5)}$$

where η is the coefficient of dynamic viscosity; $\frac{dv}{dz}$ is the speed gradient in air; S is the area of the outer cylinder.

We define the time interval Δt from formulas (P.4.2.4) and (P.4.2.5)

$$\Delta t = \frac{L}{\left(\eta R \frac{d\upsilon}{dz} S\right)}. \qquad \text{(P.4.2.6)}$$

The angular momentum of the outer cylinder is

$$L = J\omega_2 = mR^2\omega_2 = mR^2 2\pi n_2, \qquad \text{(P.4.2.7)}$$

where J is the moment of inertia of the outer cylinder about z axis; ω_2 is the angular velocity of the outer cylinder; m is the mass of the outer cylinder; n_2 is the rotational speed of the outer cylinder.

The gradient of speed is

$$\frac{dv}{dz} = \frac{v}{z} = \frac{v}{d}. \qquad \text{(P.4.2.8)}$$

The area of the outer cylinder is

$$S = 2\pi R l, \qquad \text{(P.4.2.9)}$$

where l is the length of the coaxial cylinders.

Substituting formulas (P.4.2.7), (P.4.2.8), (P.4.2.9) into formula (P.4.2.6), we obtain

$$\Delta t = \frac{mdn_2}{\eta v l}. \qquad \text{(P.4.2.10)}$$

We rewrite the formula (P.4.2.10) taking into account the expression for speed from the formula (P.4.2.1)

$$\Delta t = \frac{mdn_2}{2\pi l \eta R n_1}. \qquad \text{(P.4.2.11)}$$

Substitute the numerical values in the formula (P.4.2.11)

$$\Delta t = \frac{0.1 \times 2 \times 10^{-3} \times 1}{2 \times 3.14 \times 0.1 \times 1.72 \times 10^{-5} \times 5 \times 10^{-2} \times 20} = 18.5\,\text{s}.$$

Answer. Time interval is equal Δt = 18.5 s.

Problem 4.3

Problem description. The vessel has a volume $V = 10^{-3}$ m^3. There is a vacuum inside the vessel. A small hole with an area of $S = 10^{-10}$ m^2 is opened in the vessel. Calculate the time τ after which the pressure in the vessel becomes equal to half the atmospheric pressure. The temperature of the air in the vessel is equal to the temperature of the outside air.

Known quantities: $V = 10^{-3}$ m^3, $S = 10^{-10}$ m^2.

Quantities to be calculated: τ.

Problem solution. The number of molecules in a volume of 1 cm^3 that enter the vessel during the time interval from t to $t + dt$ is

$$dn' = \frac{n_0 \langle v \rangle}{4} S dt, \tag{P.4.3.1}$$

where n_0 is the number of molecules in a volume of 1 cm^3 of external air at atmospheric pressure; $\langle \upsilon \rangle$ is the average velocity of the molecules of external air; S is the area of the hole.

The number of molecules in a volume of 1 cm^3 that emitting the vessel during the time interval from t to $t + dt$ is

$$dn'' = \frac{n \langle v \rangle}{4} S dt, \tag{P.4.3.2}$$

where n is the number of molecules in the volume of 1 cm^3 of the vessel at time t.

The total balance equation has the form

$$dn = \frac{dn' - dn''}{V} = \frac{\langle \upsilon \rangle S}{4V} (n_0 - n) dt, \tag{P.4.3.3}$$

where V is the volume of the vessel; dn is an increase in the number of molecules in the volume of 1 cm^3 of the vessel over time dt.

We write one of the forms of the equation of state of an ideal gas

$$P = nkT, \tag{P.4.3.4}$$

where P is the air pressure in the vessel after a time of $t + dt$; k is the Boltzmann constant; T is the thermodynamic temperature of the air in the vessel.

We transform the formula (P.4.3.4)

$$dn = \frac{dP}{kT}. \qquad \text{(P.4.3.5)}$$

In this case, the balance equation has the form

$$dP = \frac{\langle v \rangle S}{4V}(P_0 - P)dt, \qquad \text{(P.4.3.6)}$$

where P_0 is atmospheric pressure.

We integrate equation (P.4.3.6)

$$\int_0^{P_0/2} \frac{dP}{P_0 - P} = \frac{\langle v \rangle S}{4V}\int_0^{\tau} dt, \qquad \text{(P.4.3.7)}$$

where τ is the time interval during which the pressure in the vessel increases to a value of $P_0 / 2$.

Formula (P.4.3.7) allows you to determine the time interval τ

$$\tau = \frac{4V}{\langle v \rangle S}. \qquad \text{(P.4.3.8)}$$

We substitute numerical values in the formula (P.4.3.8)

$$\tau = \frac{4 \times 10^{-3}}{4.63 \times 10^{2} \times 10^{-10}} = 8.64 \times 10^{4}\,\text{s}.$$

Answer. Time interval is equal $\tau = 8.64 \times 10^{4}$ s.

Problems

Problem A

Problem description. Calculate the diffusion coefficient of nitrogen for the following cases: 1) under normal conditions; 2) at pressure $P = 100$ Pa and temperature $T = 300$ K.

Answer. $D_1 = 9 \times 10^{-5}$ m^2/s, $D_2 = 0.061$ m^2/s.

Problem B

Problem description. Determine how many times the diffusion coefficient D_1 of gaseous hydrogen differs from the diffusion coefficient D_2 of gaseous oxygen if both gases are under the same conditions.

Answer. $k = 7.1$.

Problem C

Problem description. Two horizontal disks of radius $R = 20$ cm are located in the air one above the other so that their axes coincide. The distance between the planes of the disks is $d = 0.5$ cm. The upper disk is stationary, and the lower disk rotates at a frequency of $n = 10$ s^{-1}. Calculate the torque acting on the upper disc. The coefficient of dynamic viscosity of air is $\eta = 1.72$ μPa·s.

Answer. $M = 5.8\times10^{-4}$ N·m.

Problem D

Problem description. Determine the coefficient of dynamic viscosity of helium under normal conditions, if the diffusion coefficient under the same conditions is $D = 1.06\times10^{-4}$ m^2/s.

Answer. $\eta = 1.9\times10^{-5}$ Pa·s.

Problem E

Problem description. The space between two large parallel plates is filled with helium. The distance between the plates is $d = 5$ mm. The temperature of one of the plates is $T_1 = 290$ K. The temperature of the second plate is $T_2 = 310$ K. Helium pressure is $P = 0.1$ MPa. Calculate the heat flux density between these plates.

Answer. $q = 196$ W/m^2.

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APPENDICES

Table A1. Greek alphabet

Name	Capital	Lower-case	Name	Capital	Lower-case
Alpha	A	α	Nu	N	ν
Beta	B	β	Xi	Ξ	ξ
Gamma	Γ	γ	Omicron	O	o
Delta	Δ	δ	Pi	Π	π
Epsilon	E	ε	Rho	P	ρ
Zeta	Z	ζ	Sigma	Σ	σ
Eta	H	η	Tau	T	τ
Theta	Θ	θ	Upsilon	Υ	υ
Iota	I	ι	Phi	Φ	ϕ
Kappa	K	κ	Chi	X	χ
Lambda	Λ	λ	Psi	Ψ	ψ
Mu	M	μ	Omega	Ω	ω

Table A2. SI prefixes

Prefix		Representation	Prefix		Representation
Name	***Symbol***	***Base 10***	***Name***	***Symbol***	***Base 10***
yotta	Y	10^{24}	deci	d	10^{-1}
zeta	Z	10^{21}	centi	c	10^{-2}
exa	E	10^{18}	milli	m	10^{-3}
peta	P	10^{15}	micro	μ or u	10^{-6}
tera	T	10^{12}	nano	n	10^{-9}
giga	G	10^{9}	pico	p	10^{-12}
mega	M	10^{6}	femto	f	10^{-15}
kilo	k	10^{3}	atto	a	10^{-18}
hecto	h	10^{2}	zepto	z	10^{-21}
deca	da	10^{1}	yocto	y	10^{-24}

Table A3. SI base units

Unit name	**Unit symbol**	**Quantity name**	**Definition**
metre	m	length	The distance travelled by light in vacuum in 1/299792458 second.
kilogram	kg	mass	The kilogram is defined by taking the fixed numerical value of the Plank constant h to be 6.62607015×10^{-34} when expressed in the unit J×s, which is equal to $kg\times m^2\times s^{-1}$, where the metre and the second are defined in terms of c and $\Delta\nu_{Cs}$.
second	s	time	The second is define by taking the fixed numerical value of the caesium frequency $\Delta\nu_{Cs}$, the unperturbed ground-state hyperfine transition frequency of the ^{133}C atom, to be 9192631770 when expressed in the unit Hz, which is equal to s^{-1}.
ampere	A	electric current	The ampere is defined by taking the fixed numerical value of the elementary charge e to be $1.602176634\times10^{-19}$ when expressed in unit C, which is equal to A×s, where the second is defined in terms of $\Delta\nu_{Cs}$.
kelvin	K	thermodynamic temperature	The kelvin is defined by taking the fixed numerical value of the Boltzmann constant k to be 1.380649×10^{-23} $J\times K^{-1}$ ($J=kg\times m^2\times s^{-2}$), given the definition of the kilogram, the metre, and the second.
mole	mol	amount of substance	The amount of substance of exactly 6.02214076×10^{23} elementary entities. This number is the fixed numerical value of the Avogadro constant, N_A, when expressed in the unit mol^{-1} and is called the Avogadro number.
candela	cd	luminous intensity	The luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 5.4×10^{14} Hz and that has a radiant intensity in that direction of 1/683 watt per steradian.

Table A4. SI derived units

Unit name	Unit symbol	Unit Equivalents	Quantity name
hertz	Hz	s^{-1}	frequency
radian	rad	One radian is the angle subtended at the center of a circle by an arc that is equal in length to the radius of the circle.	angle
steradian	sr	The solid angle subtended at the center of a unit sphere by a unit area on its surface	solid angle
newton	N	$kg \times m \times s^{-2}$	force, weight
pascal	Pa	$N/m^2 = kg \times m^{-1} \times s^{-2}$	pressure, stress
joule	J	$N \times m = kg \times m^2 \times s^{-2}$	energy, work, heat
watt	W	$J/s = kg \times m^2 \times s^{-3}$	power, radiant flux
coulomb	C	$A \times s$	electric charge
volt	V	$J/C = kg \times m^2 \times s^{-3} \times A^{-1}$	voltage, electromotive force
farad	F	$C/V = A^2 \times s^4 \times kg^{-1} \times m^{-2}$	electrical capacitance
ohm	Ω or Ohm	$V/A = kg \times m^2 \times s^{-3} \times A^{-2}$	electrical resistance, impedance
siemens	S	$1/Ohm = A^2 \times s^3 \times kg^{-1} \times m^{-2}$	electrical conductance
weber	Wb	$V \times s = kg \times m^2 \times s^{-2} \times A^{-1}$	magnetic flux
tesla	T	$Wb/m^2 = kg \times s^{-2} \times A^{-1}$	magnetic field strength
henry	H	$Wb/A = kg \times m^2 \times s^{-2} \times A^{-2}$	electrical inductance
degree Celsius	°C	K	temperature relative to 273.15 K
lumen	lm	$cd \times sr = cd$	luminous flux
lux	lx	$lm/m^2 = cd \times m^{-2}$	illuminance
becquerel	Bq	s^{-1}	radioactivity
gray	Gy	$J/kg = m^2 \times s^{-2}$	absorbed dose
sievert	Sv	$J/kg = m^2 \times s^{-2}$	equivalent dose
katal	kat	$mol/s = mol \times s^{-1}$	catalytic activity

Table A5. Physical constants

Quantity	**Symbol**	**Value**
Avogadro constant	N_A	$6.0221415(10)\times10^{23}$ mol^{-1}
Boltzmann constant	k	$1.3806505(24)\times10^{-23}$ J / K
Electric constant	ε_0	$8.854187817\times10^{-12}$ F×m^{-1}
Faraday constant	F	96485.3383(83) C×mol^{-1}
Fine-structure constant	α	$7.297352568(24)\times10^{-3}$
Gravitational constant	G	$6.6742(10)\times10^{-11}$ N×m^2 / kg^2
Magnetic constant	μ_0	$4\pi\times10^{-7}$ T×m /A (exact)
Molar gas constant	R	8.314472(15) J/(mol×K)
Planck constant	h	$6.6260693(11)\times10^{-34}$ J×s
Rydberg constant	R_H	$1.0973731568525(73)\times10^{7}$ m^{-1}
Stefan-Boltzmann constant	σ	$5.670400(40)\times10^{-8}$ W×m^{-2}×K^{-4}
Wien displacement law constant	b	$2.8977685(51)\times10^{-3}$ m×K
Atomic mass unit	u	$1.66053886(28)\times10^{-27}$ kg
Electron mass	m_e	$9.1093826(16)\times10^{-31}$ kg
Neutron mass	m_n	$1.67492728(29)\times10^{-27}$ kg
Proton mass	m_p	$1.67262171(29)\times10^{-27}$ kg
Elementary charge	e	$1.60217653(14)\times10^{-19}$ C
Speed of light in vacuum	c	2.99792458×10^{8} m /s
Bohr magnetron	μ_B	$9.27400949(80)\times10^{-24}$ J/T
Bohr radius	a_0	$5.291772108(18)\times10^{-11}$ m
Compton wavelength	λ_C	$2.426310238(16)\times10^{-12}$ m

Table A6. Periodic table of elements

Name	${}_{AN}$**Symbol** (*AN – atomic number*)	**Standard atomic weight**	**Name**	${}_{AN}$**Symbol** (*AN – atomic number*)	**Standard atomic weight**
1	***2***	***3***	***1***	***2***	***3***
Actinium	${}_{89}\mathrm{Ac}$	227	Einsteinium	${}_{99}\mathrm{Es}$	252
Aluminium	${}_{13}\mathrm{Al}$	26.9815384	Erbium	${}_{68}\mathrm{Er}$	167.259
Americium	${}_{95}\mathrm{Am}$	243	Europium	${}_{63}\mathrm{Eu}$	151.964
Antimony	${}_{51}\mathrm{Sb}$	121.760	Fermium	${}_{100}\mathrm{Fm}$	257
Argon	${}_{18}\mathrm{Ar}$	39.948	Flerovium	${}_{114}\mathrm{Fl}$	289
Arsenic	${}_{33}\mathrm{As}$	74.921595	Fluorine	${}_{9}\mathrm{F}$	18.9984032
Astatine	${}_{85}\mathrm{At}$	210	Francium	${}_{87}\mathrm{Fr}$	223
Barium	${}_{56}\mathrm{Ba}$	137.327	Gadolinium	${}_{64}\mathrm{Gd}$	157.25
Berkelium	${}_{97}\mathrm{Bk}$	247	Gallium	${}_{31}\mathrm{Ga}$	69.723
Beryllium	${}_{4}\mathrm{Be}$	9.0121831	Germanium	${}_{32}\mathrm{Ge}$	72.630
Bismuth	${}_{83}\mathrm{Bi}$	208.98040	Gold	${}_{79}\mathrm{Au}$	196.966570
Bohrium	${}_{107}\mathrm{Bh}$	270	Hafnium	${}_{72}\mathrm{Hf}$	178.49
Boron	${}_{5}\mathrm{B}$	10.81	Hassium	${}_{108}\mathrm{Hs}$	270
Bromine	${}_{35}\mathrm{Br}$	79.904	Helium	${}_{2}\mathrm{He}$	4.002602
Cadmium	${}_{48}\mathrm{Cd}$	112.414	Holmium	${}_{67}\mathrm{Ho}$	164.930328
Calcium	${}_{20}\mathrm{Ca}$	40.078	Hydrogen	${}_{1}\mathrm{H}$	1.008
Californium	${}_{98}\mathrm{Cf}$	251	Indium	${}_{49}\mathrm{In}$	114.818
Carbon	${}_{6}\mathrm{C}$	12.011	Iodine	${}_{53}\mathrm{I}$	126.90447
Caesium	${}_{55}\mathrm{Cs}$	132.905452	Iridium	${}_{77}\mathrm{Ir}$	192.217
Cerium	${}_{58}\mathrm{Ce}$	140.116	Iron	${}_{26}\mathrm{Fe}$	55.845
Chlorine	${}_{17}\mathrm{Cl}$	35.45	Krypton	${}_{36}\mathrm{Kr}$	83.798
Chromium	${}_{24}\mathrm{Cr}$	51.9961	Lanthanum	${}_{57}\mathrm{La}$	138.90547
Cobalt	${}_{27}\mathrm{Co}$	58.933194	Lawrencium	${}_{103}\mathrm{Lr}$	266
Copernicium	${}_{112}\mathrm{Cn}$	285	Lead	${}_{82}\mathrm{Pb}$	207.2
Copper	${}_{29}\mathrm{Cu}$	63.546	Lithium	${}_{3}\mathrm{Li}$	6.94
Curium	${}_{96}\mathrm{Cm}$	247	Livermorium	${}_{116}\mathrm{Lv}$	293
Darmstadtium	${}_{110}\mathrm{Ds}$	281	Lutetium	${}_{71}\mathrm{Lu}$	174.9668
Dubnium	${}_{105}\mathrm{Db}$	268	Magnesium	${}_{12}\mathrm{Mg}$	24.305
Dysprosium	${}_{66}\mathrm{Dy}$	162.500	Manganese	${}_{25}\mathrm{Mn}$	54.938043

1	***2***	***3***	***1***	***2***	***3***
Meitnerium	$_{109}$Mt	278	Rubidium	$_{37}$Rb	85.4678
Mendelevium	$_{101}$Md	258	Ruthenium	$_{44}$Ru	101.07
Mercury	$_{80}$Hg	200.592	Rutherfordium	$_{104}$Rf	267
Molybdenum	$_{42}$Mo	95.95	Samarium	$_{62}$Sm	150.36
Moscovium	$_{115}$Mc	290	Scandium	$_{21}$Sc	44.955908
Neodymium	$_{60}$Nd	144.242	Seaborgium	$_{106}$Sg	269
Neon	$_{10}$Ne	20.1797	Selenium	$_{34}$Se	78.971
Neptunium	$_{93}$Np	237	Silicon	$_{14}$Si	28.085
Nickel	$_{28}$Ni	58.6934	Silver	$_{47}$Ag	107.8682
Nihonium	$_{113}$Nh	286	Sodium	$_{11}$Na	22.9897693
Niobium	$_{41}$Nb	92.90637	Strontium	$_{38}$Sr	87.62
Nitrogen	$_{7}$N	14.007	Sulfur	$_{16}$S	32.06
Nobelium	$_{102}$No	259	Tantalum	$_{73}$Ta	180.94788
Oganesson	$_{118}$Og	294	Technetium	$_{43}$Tc	98
Osmium	$_{76}$Os	190.23	Tellurium	$_{52}$Te	127.60
Oxygen	$_{8}$O	15.999	Tennessine	$_{117}$Ts	294
Palladium	$_{46}$Pd	106.42	Terbium	$_{65}$Tb	158.925354
Phosphorus	$_{15}$P	30.9737620	Thallium	$_{81}$Tl	204.38
Platinum	$_{78}$Pt	195.084	Thorium	$_{90}$Th	232.0377
Plutonium	$_{94}$Pu	244	Thulium	$_{69}$Tm	168.934218
Polonium	$_{84}$Po	209	Tin	$_{50}$Sn	118.710
Potassium	$_{19}$K	39.0983	Titanium	$_{22}$Ti	47.867
Praseodymium	$_{59}$Pr	140.90766	Tungsten	$_{74}$W	183.84
Promethium	$_{61}$Pm	145	Uranium	$_{92}$U	238.02891
Protactinium	$_{91}$Pa	231.03588	Vanadium	$_{23}$V	50.9415
Radium	$_{88}$Ra	226	Xenon	$_{54}$Xe	131.293
Radon	$_{86}$Rn	222	Ytterbium	$_{70}$Yb	173.045
Rhenium	$_{75}$Re	186.207	Yttrium	$_{39}$Y	88.90584
Rhodium	$_{45}$Rh	102.90549	Zinc	$_{30}$Zn	65.38
Roentgenuim	$_{111}$Rg	282	Zirconium	$_{40}$Zr	91.224

SUBJECT INDEX

NAME INDEX