



**MINISTRY OF EDUCATION AND SCIENCE OF  
UKRAINE**

**State Biotechnological University**

**Faculty of Mechatronics and Engineering  
Department of Physics and Mathematics**

**EDUCATIONAL AND METHODOLOGICAL LITERATURE**

**SUMMARY OF LECTURES**

**FROM EDUCATIONAL DISCIPLINE**

**PHYSICS**

**PART II**

for acquirers

level of higher education first (bachelor) full-time (part-time) study in specialty 133  
"Industrial mechanical engineering"

Kharkiv

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Educational and methodical literature. The synopsis of lectures on the academic discipline "PHYSICS" was developed in accordance with the initial program. The history of the development of physics, the scientific path of outstanding scientists, the main laws and formulas from the discipline of physics, examples of experimental research are given, the physical foundations of the mechanics of translational motion, the mechanics of rotational motion, molecular physics and thermodynamics are discussed.

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## *Lecture 11*

### **CONTENT MODULE 2.**

### **MOLECULAR PHYSICS AND THERMODYNAMICS**

#### **Topic 1**

#### **MOLECULAR-KINETIC THEORY OF IDEAL GASES. PHENOMENA OF TRANSFER**

##### Plan

1. General concepts of molecular physics and thermodynamics.
2. Experimental ideal gas laws.
3. Equation of state of an ideal gas.
4. The basic equation of the molecular kinetic theory.
5. Maxwell's law on the distribution of gas molecules according to the speeds and energies of thermal motion.
6. Barometric formula. Boltzmann distribution.
7. Average length of free path and average number of collisions of molecules.
8. Transfer phenomena.

#### **1. General concepts of molecular physics and thermodynamics**

**Molecular physics and thermodynamics** are branches of physics that study macroscopic processes in bodies that are related to the huge number of atoms and molecules that make up the body.

*The molecular-kinetic* method is based on the molecular-kinetic theory of the structure of matter. *The molecular kinetic theory is based on two statements:*

- 1) any body (substance) consists of atoms;
- 2) in the gaseous state, the atoms of the substance move continuously chaotically.

It is based on the fact that the properties of the macroscopic system are determined by the properties of the particles of the system, the peculiarities of their movement and the averaged values of the dynamic characteristics of the particles (for example, temperature; we cannot talk about the temperature of a single molecule). This method uses the laws of probability theory and mathematical statistics. The relevant section of physics is called statistical physics.

*The thermodynamic method* is based on the analysis of energy conversion and conservation processes in the considered systems. Thermodynamics does not study the microscopic structure of matter, the mechanisms of phenomena, but only establishes connections between the macroscopic properties of matter. Thermodynamics deals with thermodynamic systems.

*A thermodynamic system* is any macroscopic body or collection of bodies in a solid, liquid, or gaseous state.

*Thermodynamic parameters* are physical quantities that characterize a thermodynamic system (describe its state): *V - volume, T - temperature, P - pressure*, concentration *n* and others.

*Temperature* is a measure of the average kinetic energy of the chaotic movement of molecules of a substance. At thermal equilibrium, the temperature in all parts of the body or system of bodies is the same.

A change in the temperature of a substance leads to a change in the parameters characterizing its state - pressure, volume, as well as physical properties of the substance - optical, electromagnetic, etc. Observing the change in these parameters and properties allows you to measure the change in temperature. A thermometer is used for this. The thermometer is brought into a state of thermal equilibrium with the substance whose temperature is measured. In practice, mercury and alcohol thermometers are most often used. In this case, the dependence of the volume of liquid (mercury, alcohol) on temperature is used.

In the Celsius scale, zero temperature  $t = 0^{\circ}\text{C}$  is taken to be the temperature of melting ice, and the temperature of boiling water at normal pressure ( $P = 101325 \text{ Pa}$ ) is taken to be  $100^{\circ}\text{C}$ . 1 degree Celsius is one hundredth of the difference between these two temperatures.

The disadvantage of liquid thermometers is that the dependence of the volume of different liquids on temperature is not the same, so the readings of thermometers with different working liquids at temperatures different from  $0^{\circ}\text{C}$  and  $100^{\circ}\text{C}$  do not match. A more perfect way of measuring temperature is based on the fact that for any gases that are in thermal equilibrium, the ratio of the product of pressure  $P$  per volume  $V$  to the number of molecules  $N$  is the same:

$$\frac{PV}{N} = \text{const} .$$

This allows us to express the average kinetic energy of the chaotic movement of molecules through the temperature  $T$ . The temperature  $T$  introduced in this way is called *the absolute temperature, or the temperature on the Kelvin scale*. One degree of absolute temperature scale 1 K (1 kelvin) is equal to  $1^{\circ}\text{C}$ . The temperature on the Kelvin scale is related to the temperature on the Celsius scale by the equality:

$$T = 273,15 + t . \tag{1.1}$$

Absolute zero corresponds approximately to ( $-273^{\circ}\text{C}$ ). At absolute zero, translational movement of molecules stops; other types of motion (oscillatory and rotational) remain even at 0 K. The state of matter at absolute zero is unattainable, but it can be approached as close as you like.

**Gas pressure**  $P$  is a physical quantity equal to the ratio of the normal force with which the gas acts on a certain plane to the surface area of this plane

$$P = \frac{\Delta F}{\Delta S}. \quad (1.2)$$

The unit of pressure is *pascal* (Pa). Non-system pressure unit of 1 mm Hg.

## 2. Experimental ideal gas laws

The properties of matter in the gaseous state can be explained using the ideal gas model. **An ideal gas** is called a gas whose molecules have a negligibly small volume (the linear dimensions of the molecules  $d$  are much smaller than the distance  $r$  between them,  $d \ll r$ ) and do not interact with each other and the walls of the vessel at a distance. When the molecules collide with each other and with the walls of the vessel, they behave like elastic balls.

Real gases, under conditions that do not differ too much from normal ones, are close in their properties to ideal gases.

**The sizes of the molecules** are extremely small, they cannot be seen with the naked eye. The diameter of a hydrogen molecule consisting of two atoms is  $2,3 \cdot 10^{-10}\text{m}$ , the diameters of more complex molecules, for example, protein, reach  $43 \cdot 10^{-10}\text{m}$ . The dimensions of large molecules can be determined by their image obtained using an electron microscope.

The number of molecules in each of the bodies surrounding us is extremely large.  $1\text{ cm}^3$  of water contains  $3,7 \cdot 10^{22}$  molecules. It is customary to measure the amount of a substance not by the number of molecules, but in other units - moles. **A mole** ( $\nu$ ) is the amount of a substance that contains as many particles as there are atoms in 0.012 kg of carbon  $^{12}\text{C}$ .

One mole of any substance contains the same number of particles. This number is called **Avogadro's constant (or Avogadro's number)**  $N_A$ , which is equal to  $6,022 \cdot 10^{23}\text{ mol}^{-1}$ .

**Avogadro's law**: moles of different gases at the same temperature and pressure occupy the same volumes. Under normal conditions, this volume is equal to  $22,4 \cdot 10^{-3}\text{ m}^3/\text{mol}$ .

**Normal conditions**:  $T = 273\text{ K}$ ;  $P = 1,013 \cdot 10^5\text{ Pa}$ ;  $V = 22,4 \cdot 10^{-3}\text{ m}^3/\text{mol}$ .

The mass of one mole is called **the molar mass**  $M$ . The molar mass is easily determined by Mendeleev's table of elements.

The unit of molar mass is *kilogram per mole* (kg/mol).

The mass of a molecule  $m_0$  can be determined by the formula

$$m_0 = \frac{M}{N_A}. \quad (1.3)$$

Let's estimate, for example, the mass of the H<sub>2</sub>O water molecule. Substituting the molar mass of water,  $M = 2 \times 1 + 16 = 18 \text{ г/моль} = 0,018 \text{ кг/моль}$  we get

$$m_0 = \frac{0,018}{6,022 \cdot 10^{23}} \text{ кг} \approx 3 \cdot 10^{-26} \text{ кг}$$

The number of moles of gas  $\nu$ , as well as the number of molecules in the vessel  $N$ , can be determined using the ratio

$$\nu = \frac{N}{N_A} = \frac{m}{M}.$$

### Isoprocesses in gases.

Processes in which, in addition to the amount of matter, one of the three parameters - pressure, volume or temperature - remain unchanged in physics and technology. Such processes are called isoprocesses.

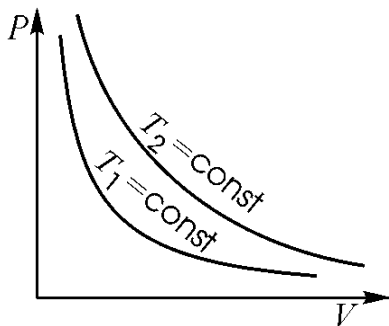


Fig. 1.1

$$P_1 V_1 = P_2 V_2. \quad (1.4)$$

The law expressed by **Marriott law**. A hyperbola on volume at  $T = \text{const}$  is isotherms corresponding to

**An isothermal process** is a process that occurs at a constant temperature  $T = \text{const}$ . The equation of the isothermal process has the form

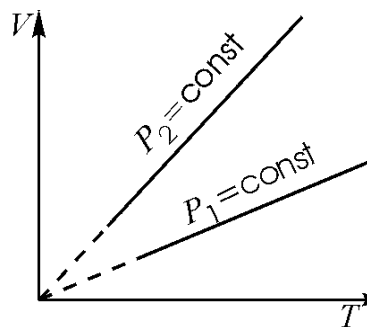


Fig. 1.2

$$PV = \text{const}, \quad \text{або}$$

this equation is called **the Boyle-**depicting the dependence of pressure called an **isotherm**. In fig. 1.1 are the two temperatures  $T_1$  and  $T_2 > T_1$ .



**An isobaric process** is a process that occurs at a constant pressure  $P = \text{const}$ . Its equation has the form

$$V = \text{const} \cdot T, \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}. \quad (1.5)$$

The law expressed by equation (1.5) is called the **Gay-Lussac law**. A straight line depicting the dependence of volume on temperature at constant pressure is called an **isobar**. In fig. 1.2 shows two isobars corresponding to different gas pressures  $P_1$  and  $P_2 < P_1$ .

**An isochoric process** is a process that occurs at a constant volume  $V = \text{const}$ . The equation of the isochoric process has the form

$$P = \text{const} \cdot T, \quad \text{or} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}. \quad (1.6)$$

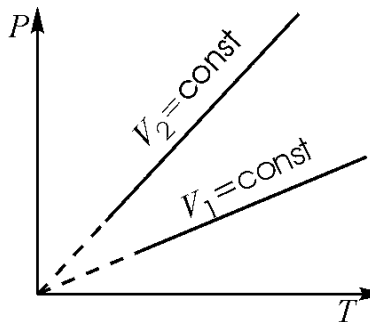


Fig. 1.3

The law expressed by equation (1.6) is called **Charles' law**. A straight line depicting the dependence of pressure on temperature at constant volume is called an **isochore**. In fig. 1.3 shows isochores for two gas volumes  $V_1$  and  $V_2 < V_1$ .

Isochores and isobars cannot be extrapolated to the point  $T = 0$  (dashed lines in Figs. 1.2 and 1.3), because the properties of the substance are very different from the properties of an ideal gas at great cooling.

**Dalton's law**: the pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the gases included in it, i.e.:

$$P = P_1 + P_2 + \dots + P_n, \quad (1.7)$$

where  $P_1, P_2, \dots, P_n$  - **partial pressures** - pressures of the gases that make up the mixture, if each of them occupied the volume of the mixture at the same temperature.

### 3. Equation of state of an ideal gas

The equation of state of an ideal gas (**Mendeleev-Clapeyron equation**) relates the volume  $V$ , the pressure  $P$  and the absolute temperature  $T$  of the gas:

$$PV = \frac{m}{M}RT = \nu RT . \quad (1.8)$$

where  $m$  is the gas mass;

$$\frac{m}{M} = \nu - \text{amount of substance.}$$

The constant value  $R$  is called the **universal gas constant**,  $R = 8.31 \text{ J}/(\text{K}\cdot\text{mol})$ . Along with the universal gas table, the **Boltzmann table** is also used  $k = 1.38 \cdot 10^{-23} \text{ J/K}$ . The universal gas constant is related to Avogadro's number and Boltzmann's constant:

$$R = kN_A . \quad (1.9)$$

Taking into account the equation of state of an ideal gas and the relationship between  $k$  and  $R$  and performing the following transformations,  $PV = \nu \cdot N_A kT$ ,  $\nu \cdot N_A = N$  is the number of molecules in a given volume of gas,  $PV = NkT$ ,  $P = \frac{N}{V}kT = nkT$ ,  $n$  is the concentration of molecules (the number of molecules per unit volume), we arrive at the equation of state of a gas in the form

$$P = nkT . \quad (1.10)$$

At the same pressure and temperature, all gases have the same number of molecules per unit volume. Under normal conditions  $N_L = 2.68 \cdot 10^{25} \text{ m}^{-3}$  – **Loschmidt number**.

## Lecture 12

### MOLECULAR-KINETIC THEORY OF IDEAL GASES. TRANSFER PHENOMENA (CONTINUED)

#### 4. The basic equation of the molecular kinetic theory

This is an equation that links the macroparameters of the system, which include gas pressure  $P$ , its temperature,  $T$  and the average kinetic energy  $\langle E \rangle$  of molecules.

Consider a monatomic gas. Let's select an elementary platform on the wall of the vessel  $\Delta S$  and find the pressure that the gas exerts on the platform:

$$P = \frac{F}{\Delta S} = \frac{\Delta p}{\Delta t \Delta S}. \quad (1.11)$$

At each collision, one molecule, moving perpendicular to the platform, imparts momentum  $\Delta p = m_0 v - (-m_0 v) = 2m_0 v$  to it, where  $m_0$  is the mass of the molecule and  $v$  is its speed. In time  $\Delta t$ , the molecules at a distance will reach the site  $v \Delta t$ . The number of these molecules  $n v \Delta t \Delta S$  is, where  $n$  is the concentration of molecules. For simplicity of calculations, the chaotic motion of molecules will be replaced by motion along mutually perpendicular directions. It follows that only 1/6 of all molecules move to the site. Then the number of collisions of molecules on the platform is equal to  $\frac{1}{6} n v \Delta t \Delta S$ . Impulse transferred to the site  $\Delta p = 2m_0 v \frac{1}{6} n v \Delta t \Delta S = \frac{1}{6} n m_0 v^2 \Delta t \Delta S$ . Substitute this expression in (1.11) and get the pressure on the walls of the vessel

$$P = \frac{1}{3} n m_0 v^2. \quad (1.12)$$

In this equation  $v$  is the *mean square speed*  $\langle v_{\text{KB}} \rangle$ ,  $\langle v_{\text{KB}} \rangle = \sqrt{\frac{\sum v_i^2}{N}}$ . Taking into account this equation (1.12) takes the form

$$P = \frac{1}{3} n m_0 \langle v_{\text{KB}}^2 \rangle \quad (1.13)$$

Expression (1.13) is called the *basic equation of molecular kinetic theory*. Taking into account that  $n = N/V$ , we will get

$$PV = \frac{1}{3}Nm_0\langle v_{\text{KB}}^2 \rangle = \frac{2}{3}N \frac{m_0\langle v_{\text{KB}}^2 \rangle}{2} = \frac{2}{3}E, \quad (1.14)$$

where  $E$  is the total kinetic energy of gas molecules.

Let us rewrite equation (1.14) in the form  $PV = \frac{1}{3}Nm_0\langle v_{\text{KB}}^2 \rangle$ , compare it with the Mendeleev-Clapeyron equation  $PV = \frac{m}{M}RT$ , taking  $m_0N = m$  into account that we will obtain the expression of the *mean square velocity*

$$v_{\text{KB}} = \sqrt{\frac{3RT}{M}}. \quad (1.15)$$

Since  $M = m_0N_A$ ,  $R = kN_A$ , the expression (1.15) can be rewritten in the form

$$v_{\text{KB}} = \sqrt{\frac{3kT}{m_0}} = \sqrt{\frac{3RT}{m_0N_A}}$$

***The average kinetic energy of translational movement of one molecule:***

$$\langle \varepsilon \rangle = \frac{E}{N} = \frac{m_0 v_{\text{KB}}^2}{2} = \frac{3}{2}kT, \quad (1.16)$$

The higher the temperature of the gas, the higher the average speed, which means that as the temperature increases, the number of molecules increases with a higher speed and decreases with a lower speed.

## **5. Maxwell's law on the distribution of gas molecules by speed and energy of thermal motion**

The chaotic thermal movement of gas molecules, which are in a state of thermodynamic equilibrium, leads to the distribution of molecules according to their velocities. This distribution is described by a statistical law, which was theoretically derived by Maxwell (1931-1879). Maxwell's law allows you to determine how many molecules  $dN$  out of their total number  $N$  at a certain temperature  $T$  are in the range of speeds  $d\nu$  from  $\nu$  to  $\nu + d\nu$ . It is assumed that the gas is chemically homogeneous. This distribution is expressed by the formula

$$dN = N \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m\nu^2}{2kT}} \cdot 4\pi\nu^2 d\nu = f(\nu) d\nu. \quad (1.17)$$

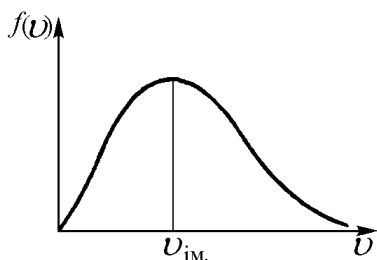


Fig. 1.4

In fig. 1.4 shows the Maxwell distribution graphically. The value  $dN/Nd\nu$ , which is a function of Maxwell's distribution, is plotted on the ordinate axis. The speed at which the distribution function  $f(\nu)$  is maximal is called the **most probable speed**  $\nu_{im}$ . This speed is equal to

$$\nu_{im} = \sqrt{\frac{2kT}{m_0}} = \sqrt{\frac{2RT}{M}} \quad (1.18)$$

**The average arithmetic speed of a molecule**  $\langle \nu \rangle$  is determined by the formula  $\langle \nu \rangle =$

$$\frac{1}{N} \int_0^{\infty} \nu dN(\nu) = \int_0^{\infty} \nu f(\nu) d\nu, \text{ whence}$$

$$\langle \nu \rangle = \sqrt{\frac{8kT}{\pi m_0}} = \sqrt{\frac{8RT}{\pi M}}. \quad (1.19)$$

Comparing formulas (1.15), (1.17) and (1.19), we get:

$$\langle \nu \rangle = 1,13\nu_{im}; \quad \nu_{KB} = 1,22\nu_{im}.$$

For a long time, it was possible to estimate the speed of molecules only with the help of indirect calculations. The first experimental determination of the speeds of molecules was carried out by Stern in 1920. A thin platinum wire covered with a layer of silver was stretched along the axis of

two concentric cylinders that rotated with the same angular speed. When a current was passed through the wire, the silver evaporated, passed through the gap made in the inner cylinder and settled on the outer cylinder. By measuring the time of rotation and knowing the radii of the cylinders and the angular velocity, Stern calculated the speed of the silver atoms. Molecules with a higher speed condense closer to the place opposite the slit. By measuring the thickness of the silver layer according to the velocities of the molecules, one can find their distribution, which, as it turned out, coincides with Maxwell's distribution at a certain temperature.

Table 1 shows data on the number of nitrogen molecules at a temperature of 421 K in certain speed intervals. The most likely speed under these conditions is 500 m/s.

Table 1.

$v$ , m/s	0-100	100-300	300-500	500-700	700-1000	1000
$dN/N, \%$	0,6	12	30	29	23	5,4

From the distribution of gas molecules by velocities (1.17), it is possible to proceed to their distribution by energies  $E$  by  $\frac{mv^2}{2}$  substituting  $E$ . Substituting in (1.17)  $v = \sqrt{\frac{2E}{m}}$  and  $dv = (2mE)^{-\frac{1}{2}} dE$ , we get

$$dN(E) = \frac{2N}{\sqrt{\pi}} (kT)^{-3/2} E^{1/2} e^{-E/kT} dE = N \cdot f(E) dE, \quad (1.20)$$

where  $dN(E)$  is the number of molecules in which the kinetic energy of translational motion lies in the interval from  $E$  to  $E + dE$ .

In order to obtain the distribution of molecules in space, it is necessary to replace kinetic energy  $\frac{mv^2}{2}$  with potential energy  $E_n(x, y, z)$ .

## 6. Barometric formula. Boltzmann distribution

Molecules of any gas are in the field of the Earth's gravitational forces. The force of gravity, on the one hand, and the thermal motion of molecules, on the other, lead to the distribution of molecules with height. Gas pressure decreases with height according to the barometric formula:

$$P = P_0 e^{-\frac{Mgh}{RT}} = P_0 e^{-\frac{m_0gh}{kT}}, \quad (1.21)$$

where  $P$  is air pressure at height  $h$ ;

$P_0$  – air pressure at altitude  $h_0 = 0$ ;

$m_0$  – mass of the molecule;

$T$  is the absolute temperature, which is considered constant;

$M$  is the molar mass of the gas.

Zero height can be any level on the surface of the Earth or above it. From the barometric formula, formulas  $P = nkT$  and  $P_0 = n_0kT$  we get

$$n = n_0 e^{-\frac{m_0gh}{kT}} = n_0 e^{-\frac{E_n}{kT}}. \quad (1.22)$$

This formula expresses the potential energy distribution of molecules, or the ***Boltzmann distribution***. The Boltzmann distribution (1844-1906) takes place not only in the field of gravitational forces, but also in any potential field.

## 7. Average free run length and the average number of molecular collisions

Molecules in the process of chaotic movement collide. The number of their collisions is greater per unit of time, the greater their size and concentration, as well as speed. The average number of molecule collisions per second  $\langle Z \rangle$  is equal to:

$$\langle Z \rangle = \sqrt{2}\pi d^2 n \langle v \rangle, \quad (1.23)$$

where  $d$  is the ***effective diameter of the molecule*** - the minimum distance by which the centers of two molecules converge upon collision;

$n$  – concentration of molecules;

$\langle v \rangle$  – average arithmetic speed.

Між послідовними зіткненнями молекула пробігає деяку відстань. Середнє значення довжин шляхів, пройдених молекулою між двома послідовними зіткненнями, називається

*середньою довжиною вільного пробігу*. Беручи до уваги, що, знаходимо

Between successive collisions, the molecule travels some distance. The average value of the lengths of paths traveled by a molecule between two consecutive collisions is called the *mean free path*  $\langle \lambda \rangle$ . Taking into account that  $\langle \lambda \rangle = \frac{\langle v \rangle}{\langle Z \rangle}$ , we find

$$\langle \lambda \rangle = \frac{1}{\sqrt{2}\pi d^2 n} . \quad (1.24)$$

## 8. Transfer phenomena

Transport phenomena are associated with certain inhomogeneities in the system, such as inhomogeneity of density, temperature, and speed of directional movement of individual layers of the system. Involuntary alignment of these inhomogeneities takes place, flows of matter, energy, and momentum of directed movement of particles occur. Transport phenomena include diffusion, heat conduction, and internal friction (viscosity).

*Diffusion* is the spontaneous mutual penetration and mixing of molecules of gaseous, liquid and solid bodies in contact. Diffusion is associated with the non-uniformity of the substance density. *Mass is transferred as a result of diffusion*  $\Delta m$ . According to Fick's law

$$\Delta m = -D \frac{\Delta \rho}{\Delta x} \Delta S \Delta t , \quad (1.25)$$

where  $\Delta \rho / \Delta x$  is the density gradient along the direction of substance transport  $x$ ;

$\Delta S$  – cross-sectional area through which diffusion occurs;

$\Delta t$  – the time period for which diffusion is considered;

$D = \frac{1}{3} \langle v \rangle \langle \lambda \rangle$  is the diffusion coefficient.

The "-" sign in Fick's law indicates that matter is transported in the direction of decreasing density. As a result of diffusion, the density of the substance is equalized.

*Internal friction* occurs when there is inhomogeneity of the directional (not chaotic) velocity, and hence the momentum of molecules in adjacent layers of liquids or gas (perhaps solid bodies). *As a result of internal friction, impulses are transferred from one layer of matter to another*, thus the impulses are equalized. The transmitted momentum is determined by Newton's law:



$$\Delta p = -\eta \frac{\Delta v}{\Delta x} \Delta S \Delta t, \quad (1.26)$$

where  $\Delta v / \Delta x$  is the velocity gradient along the  $x$  direction;

$\Delta S$  – area of collision of layers;

$\Delta t$  – time;

$\eta = \frac{1}{3} \langle \lambda \rangle \langle v \rangle \rho$  is the **dynamic viscosity** of the substance.

The sign “–“ in Newton's law indicates that momentum is transferred in the direction of decreasing velocity. Given that  $\Delta p / \Delta t = F$ , the law (1.26) can be rewritten as follows:

$$F = -\eta \frac{\Delta v}{\Delta x} \Delta S, \quad (1.27)$$

where  $F$  is the force of internal friction that acts on the area  $\Delta S$  of collision of layers.

The value  $\nu = \eta / \rho$  is called **kinematic viscosity**. The viscosity of oils is an important characteristic required when operating car engines. The technical condition of the engine can be judged by the change in viscosity. The instrument used to measure viscosity is called a viscometer.

**Теплопровідність** пов’язана з неоднорідністю температури. **При теплопровідності переноситься енергія у вигляді тепла**, внаслідок чого температура вирівнюється. Кількість перенесеної енергії  $\Delta Q$  визначається за законом Фур’є:

Thermal conductivity is related to temperature heterogeneity. With thermal conductivity, energy is transferred in the form of heat, as a result of which the temperature is equalized. The amount of transferred energy is determined by Fourier's law:

$$\Delta Q = -K \frac{\Delta T}{\Delta x} \Delta S \Delta t, \quad (1.28)$$

where  $\Delta T / \Delta x$  is the temperature gradient;

$K = \frac{1}{3} \langle v \rangle \langle \lambda \rangle \rho \cdot C_v^\rho$  – thermal conductivity coefficient;

$C_v^\rho$  is the specific heat capacity of the substance in the isochoric process.



## Lecture 13

### Topic 2

# FUNDAMENTALS OF THERMODYNAMICS

## Plan

1. Internal energy of the system.
2. Gas operation.
3. The first law of thermodynamics. Heat capacity of an ideal gas.
4. Adiabatic and polytropic processes.
5. Circular processes.
6. Reversible and irreversible processes. The second law of thermodynamics.
7. Heat engines. Carnot cycle. K.k.d. cycle
8. Entropy.

### 1. Internal energy of the system

*The number of degrees of freedom of a molecule  $i$*  is the smallest number of coordinates necessary to fully determine its position in space.

A monatomic molecule can be considered as a material point that has three degrees of freedom associated with translational motion,  $i = 3$ .

A diatomic molecule can be considered as a thin rod that has three degrees of freedom translational (coordinates of the center of gravity) and two rotational (angles of rotation) in total  $i = 5$ .

Molecules with three or more atoms that do not change their position relative to each other can be considered a solid. For such molecules,  $i = 6$ , of which 3 are translational and 3 are rotational degrees of freedom.

A molecule of an ideal gas is a material point, for which  $i = 3$ . For such a molecule, the kinetic energy is  $\varepsilon = \frac{3}{2}kT$ . From this it can be seen that one degree of freedom of the molecule requires an energy of  $1/2 kT$ . This is also true for complex molecules. We arrive at a statement known as the **law of uniform distribution of molecular energy by degrees of freedom**: for each translational or rotational degree of freedom of a molecule, on average, there is the same kinetic energy equal to  $1/2 kT$ .

One vibrational degree of freedom has energy  $kT$ .

Thus, the average energy of the molecule

$$\varepsilon = \frac{i}{2}kT, \quad (2.1)$$

where  $i = i_{\text{пост}} + i_{\text{об}} + 2i_{\text{кол}}$  is the sum of translational, rotational and doubled number of vibrational degrees of freedom.

The internal energy of the system consists of the kinetic energy of molecules and the potential energy of their interaction. The *internal energy  $U$  of an ideal gas* containing  $N$  molecules is determined only by the average kinetic energy of the molecules  $\varepsilon$ :  $U = N\varepsilon$ . Taking into account (2.1), we obtain for one mole of gas  $N = N_A$

$$U_M = \frac{i}{2}kTN_A = \frac{i}{2}RT. \quad (2.2)$$

Internal energy of an arbitrary mass  $m$  of gas

$$U = \frac{i}{2} \frac{m}{M} RT. \quad (2.3)$$

The internal energy of a system is a function of the state of this system, and it has a very definite value in each state of the system.

In real gases, as well as in liquids and solids, it is necessary to take into account the potential energy of interaction between molecules, which depends on the distance between them.

The internal energy of the system can change, for example, when work is performed by the system or on the system, when heat is transferred to the system.

When gas is compressed (for example, in the cylinders of a diesel engine), its temperature increases, that is, its internal energy also increases.

The second way of changing the internal energy of the system is heat transfer. For example, when a system is cooled, no work is done, and its internal energy decreases. At the same time, the surrounding bodies heat up, that is, they increase their internal energy. Such a process, in which energy is transferred from one body to another without performing work, is called heat exchange (or heat transfer).

## 2. Gas operation

Consider the work of a gas during expansion. The gas in the cylinder under the piston due to expansion moves the piston a distance  $dx$ . The gas presses on the piston  $S$  with a force of  $F = PS$ . At the same time elementary work is performed

$$\delta A = Fdx = PSdx = PdV . \quad (2.4)$$

With a finite change in volume from  $V_1$  to  $V_2$ , the work is expressed by a definite integral

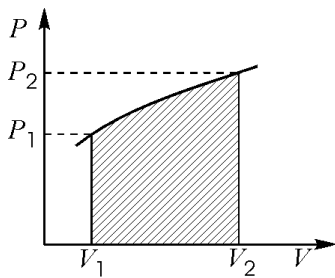


Fig. 2.1

$$A = \int_{V_1}^{V_2} PdV . \quad (2.5)$$

Graphically, the work in any process is determined by the area of the figure bounded by the pressure-volume dependence curve  $P(V)$ , the  $V$  axis, and the ordinate segments corresponding to the initial  $P_1$  and final  $P_2$  pressures (shaded figure in Fig. 2.1).

Positive work is performed during gas expansion, and negative work during compression, i.e., in the latter case, work is performed by external forces on the system.

## 3. The first law of thermodynamics. Heat capacity of an ideal gas

Work, the amount of heat and the internal energy of the system are interconnected. This relationship is expressed by the law of conservation and transformation of energy in relation to thermal processes - *the first law (or principle) of thermodynamics*: the amount of heat  $\delta Q$  transferred to the system is spent on changing the internal energy  $dU$  of this system and on the work  $\delta A$  of the system against external forces:

$$\delta Q = dU + \delta A . \quad (2.6)$$

Internal energy is a function of the state of the system  $dU$  is therefore a complete differential, while heat and work are not functions of the state of the system  $\delta Q$  and  $\delta A$  therefore are not complete differentials.

*The heat capacity of an ideal gas* is a physical value numerically equal to the amount of heat required to heat a given amount of gas by 1 K:

$$C = \frac{\delta Q}{dT}. \quad (2.7)$$

**Specific heat capacity** is a physical quantity that is numerically equal to the amount of heat required to heat a unit of mass (1 kg) by 1 K:

$$C^p = \frac{\delta Q}{mdT}. \quad (2.8)$$

Одиниця виміру питомої теплоємності – Дж/(кг·К).

The unit of specific heat capacity is J/(kg·K).

**Molar heat capacity** is a physical quantity that is numerically equal to the amount of heat required to heat a unit amount of a substance (1 mole) per 1 K:

$$C^M = \frac{\delta Q}{\nu dT}. \quad (2.9)$$

The unit of molar heat capacity is J/(mol·K). There is an obvious connection between molar and specific heat capacities:

$$C^M = MC^p. \quad (2.10)$$

Heat capacities at **constant volume**  $C_V^M$  and at **constant pressure** are distinguished  $C_p^M$ .

Let's write the equation of the first law of thermodynamics (2.6) for 1 mole of gas, taking into account formulas (2.2) and (2.4):

$$C^M dT = dU_M + PdV_M. \quad (2.11)$$

If the gas is heated at a constant volume, then the work of external forces is zero, and the heat supplied to the gas from the outside goes only to increase its energy  $C_V^M = \frac{dU_M}{dT}$ , that is, the molar heat capacity of the gas at a constant volume is equal to the change in the internal energy of 1 mole of gas when its temperature is increased by 1 K. According to formula (2.2)

$$C_V^M = \frac{i}{2} R. \quad (2.12)$$

If the gas is heated at a constant pressure, then the expression (2.11) can be written in the form  $C_P^M = \frac{dU_M}{dT} + \frac{PdV_M}{dT}$ . Taking into account that  $\frac{dU_M}{dT}$  does not depend on the type of process (the internal energy of the gas is determined only by temperature) and is always equal to  $C_V^M$ , by differentiating the Mendeleev-Clapeyron equation with respect to  $T$ , we obtain the **Mayer ratio**:

$$C_P^M = C_V^M + R. \quad (2.13)$$

Considering (2.12), equation (2.13) can be written in the form

$$C_P^M = \frac{i+2}{2} R. \quad (2.14)$$

### **Application of the first law of thermodynamics to isoprocesses.**

**Isochoric process.** In this process, as can be seen from (2.4), the gas work is zero. The change in the internal energy of the system according to (2.6) is equal to the amount of transferred heat:

$$dU = \delta Q = \frac{m}{M} C_V^M dT = \frac{m}{M} \frac{i}{2} R dT. \quad (2.15)$$

When the gas is heated  $\delta Q > 0$ , the internal energy increases, when it is cooled, it decreases.

**Isobaric process.** In an isobaric process, the transferred heat goes both to perform work and to change the internal energy of the gas. When heated, the gas expands and performs positive work. At the same time, its internal energy increases. During cooling, the volume of the gas decreases, the work performed by it is negative, and the internal energy decreases. In this process

$$\delta Q = dU + \delta A. \quad (2.16)$$

In an isobaric process, when the amount of heat is given to the gas  $\delta Q = \frac{m}{M} C_P^M dT$ , its internal energy increases by the amount of  $dU = \frac{m}{M} C_V^M dT$ . At the same time, the gas performs work

$$A = \int_{V_1}^{V_2} P dV = P(V_2 - V_1), \text{ or, taking into account the Mendeleev-Clapeyron equation, } A = \frac{m}{M} R(T_2 - T_1).$$

The physical meaning of the **universal gas constant  $R$**  follows from this expression: the universal gas constant is a physical quantity that is numerically equal to the work done by one mole of gas upon isobaric heating of it by 1 K, i.e.

$$R = \frac{A}{\frac{m}{M}(T_2 - T_1)}. \quad (2.17)$$

**Isothermal process.** In an isothermal process, the internal energy does not change  $dU = 0$ , therefore

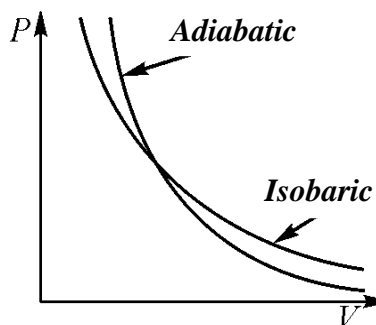
$$\delta Q = \delta A, \quad (2.18)$$

that is, all the transferred heat is spent on performing work by the gas. When heated, the gas performs positive work, when cooled - negative (positive work is performed by external forces on the gas). Let's find the work of isothermal expansion, taking into account the fact that the pressure depends in this process on the volume according to the Mendeleev-Clapeyron equation  $P = \frac{m}{M} \frac{RT}{V}$ :

$$A = \int_{V_1}^{V_2} \frac{m}{M} RT \frac{dV}{V} = \frac{m}{M} RT \ln \frac{V_2}{V_1} = \frac{m}{M} RT \ln \frac{P_1}{P_2}. \quad (2.19)$$

#### 4. Adiabatic and polytropic processes

**An adiabatic process** is a process that occurs in the system without heat exchange with the external environment,  $\delta Q = 0$ . In this case, according to the first law of thermodynamics, work is performed by the gas only due to a decrease in its internal energy:



$$\delta A = -dU, \quad (2.20)$$

the gas temperature decreases at the same time. This happens during the adiabatic expansion of the gas. During adiabatic compression of

Fig. 2.2



the gas by external forces, the work of the gas is  $\delta A < 0$ ,  $\Delta U > 0$  - in this case, the temperature of the gas rises. Therefore, the work of a gas in an adiabatic process is determined by the change in internal energy:

$$A = \frac{m}{M} C_v^M (T_1 - T_2). \quad (2.21)$$

To carry out the adiabatic process, the gas must be completely thermally insulated, which is practically impossible. However, if the process proceeds very quickly, then the heat exchange between the system and the environment can be neglected, and such a process can be considered adiabatic.

Let's find the relationship between the system parameters during an adiabatic process, that is, find the equation of this process. For this, we write down the system of equations:  $\frac{m}{M} C_v^M dT = -PdV$  ;

$C_p^M = C_v^M + R$  ;  $PV = \frac{m}{M} RT$  . By excluding one parameter, we will find the relationship between the other two. Thus, excluding the temperature, we find the **adiabatic equation** in the form

$$PV^\gamma = const, \quad (2.22)$$

**This is Poisson's equation.** The ratio  $\gamma$  is **Poisson's ratio**, which by definition

$$\gamma = C_p / C_v = \frac{i+2}{i}. \quad (2.23)$$

For **monatomic**  $\gamma = 5/3$ , **diatomic**  $\gamma = 7/5$ , and **polyatomic**  $\gamma = 4/3$  gases.

The adiabatic equation can be written in another form:

$$TV^{\gamma-1} = const ; \quad PT^{\frac{\gamma}{1-\gamma}} = const . \quad (2.24)$$

During adiabatic expansion, the temperature of the gas decreases, so the pressure of the gas decreases faster with increasing volume than in an isothermal process. When gas is compressed, the opposite happens: the pressure in an adiabatic process grows faster than in an isothermal process. Therefore, the curve graphically depicting the adiabatic process (adiabatic) is steeper than the isotherm (Fig. 2.2).

A **polytropic process** is a process that takes place at a constant heat capacity. The processes considered above are separate cases of the polytropic process. The **equation of a polytropic process** for an ideal gas has the form

$$PV^n = \text{const}, \quad (2.25)$$

where  $n = \frac{C_{np} - C_P^M}{C_{np} - C_V^M}$  is the polytropy index.

For an isochoric process  $C_{np} = C_V^M$ ,  $n = \pm\infty$ ; for the isobaric process  $C_{np} = C_P^M$ ,  $n = 0$ ; for an isothermal process  $C_{np} = \infty$ ,  $n = 1$ ; for the adiabatic process  $C_{np} = 0$ ,  $n = \frac{C_P^M}{C_V^M}$ .

## Lecture 14

### FUNDAMENTALS OF THERMODYNAMICS (CONTINUED)

#### 5. Circular processes

A **circular process (or cycle)** is a process in which the thermodynamic system returns to its original state. On the graphs, such processes are depicted by closed curves (Fig. 2.3). Circular processes are the

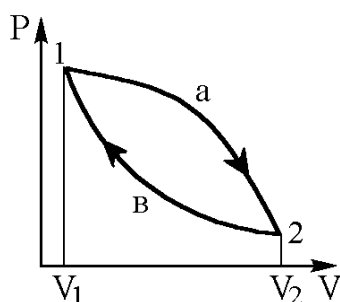


Fig. 2.3

basis of all heat engines: internal combustion engines, steam engines, diesel engines, steam and gas turbines, refrigerating machines.

The circular process consists of two parts: the process of gas expansion from state 1 to state 2 (1a2) and gas compression from state 2 to state 1 (2B1). In the first case, the work performed is positive, in the second - negative. In general, the work will be positive and numerically equal to the area of the closed figure 1a2v1

$A = A_{V_1 1a2V_2} - |A_{V_2 1b2V_2}|$ . A cycle in which the work is positive is called **direct**. If the cycle occurred in the opposite direction, then the work would be the same in magnitude, but negative is the **reverse cycle**. The total change in the internal energy of the system in a circular cycle is zero,  $dU = 0$ , because the system returns to its initial state. Therefore, according to the first law of thermodynamics, in a circular cycle, the total amount of heat supplied to the system is equal to the work done  $\delta Q = \delta A$ .

#### 6. Reversible and irreversible processes. The second law of thermodynamics

A thermodynamic process is called **reversible** if it allows the system to return to its previous state without any changes in the environment. This means that when the system performs it first in the forward direction, and then in the reverse direction, both the system itself and all the external bodies with which the system interacts return to the initial state. An example of a reversible process is undamped oscillations of a spring pendulum.

A process that does not meet these conditions is called **irreversible**. The process with friction is irreversible, where the energy of directed movement of bodies is transformed into the energy of chaotic (thermal) movement of molecules of bodies and the environment. All real processes are irreversible.

Experience shows that many processes, the course of which is completely allowed by the first law of thermodynamics, do not actually occur. So, a heated body, which is in thermal contact with a cold one, cools down, transferring its energy to the cold one. The reverse process of heat transfer from

a cold body to a heated body and an increase due to this temperature of a heated body with a further decrease in the temperature of a cold body is never observed, although this would not contradict the first law of thermodynamics. When a stone falls from a certain height to the ground, its mechanical energy is transformed into thermal energy: the stone and the part of the earth in contact with it are heated. The reverse process - raising the stone to a height due to the thermal movement of molecules, which is allowed by the law of conservation of energy, does not occur. The considered cases are typical examples of irreversible processes. Many such examples can be cited. All of them testify to a certain orientation of the processes taking place in nature, which is not reflected in the first law of thermodynamics, namely: in nature, all processes (not only thermal ones) occur in such a way that a directed, orderly movement turns into an undirected, chaotic one. The reverse transition can occur only when the state of the surrounding bodies changes. Thus, the transfer of heat from a cold body to a body heated in a refrigerator is connected with the consumption of electricity and the heating of the surrounding air.

The first principle of thermodynamics does not exclude the possibility of such a process, the only result of which would be the transformation of heat received from some body into equivalent work. Based on this, one could try to build a periodically operating engine that would perform work by cooling one body (for example, ocean water). Such an engine is called a perpetual motion machine of the second kind. Generalization of a large amount of material led to the conclusion about the impossibility of a perpetual motion machine of the second kind. This conclusion was called the **second law of thermodynamics**. There are several different wordings of this law:

1. According to Kelvin: an impossible process, the only result of which is the conversion of the heat received from the heater into work equivalent to it.
2. According to Clausius: an impossible process, the only result of which is the transfer of energy in the form of heat from a cold body to a hot one.

## 7. Heat engines. Carnot cycle. K.k.d. cycle

A **heat engine** is a device that converts the internal energy of fuel into the energy of mechanical movement. The heat engine consists of three main parts: a heater, a working body and a refrigerator (Fig. 2.4). The working medium is gas. The fuel serves as a heater, during the burning of which heat  $Q_1$  is transferred to the working body, as a result of which its temperature rises, the pressure increases, and it performs useful work  $A$ . At the same time, part of the heat  $Q_2$  is necessarily transferred to the

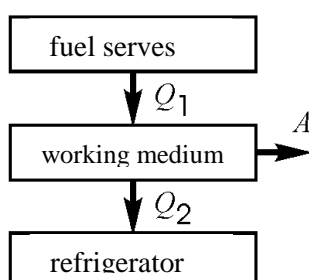


Fig. 2.4

refrigerator, that is, the amount of heat due to which useful work is performed per cycle is equal to

$$Q = Q_1 - Q_2. \quad (2.26)$$

After that, the engine returns to its initial state, having completed one operating cycle. Then such cycles are repeated many times. Heat  $Q$ , in accordance with the first law of thermodynamics, is completely converted into work,

$$A = Q_1 - Q_2. \quad (2.27)$$

The work done by  $A$  is always less than the heat  $Q_1$ . The impossibility of complete conversion of internal fuel energy into work in heat engines is due to the irreversibility of thermal processes in nature.

The **thermal efficiency of a heat engine** is equal to the ratio of the mechanical work performed by the engine to the energy consumed:

$$\eta = \frac{A}{Q_1} = \frac{Q_1 - Q_2}{Q_1}. \quad (2.28)$$

An example of the most economical circular process is the **Carnot cycle**, which is widely used in practice. This cycle (Fig. 2.5) consists of two isotherms 1-2 and 3-4 and two adiabats 2-3 and 4-1.

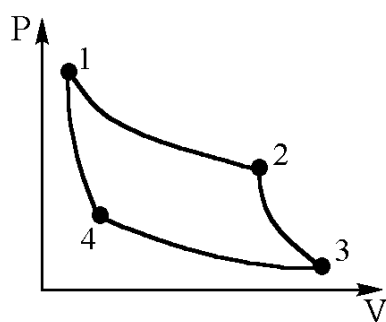


Fig. 2.5

In the process of isothermal expansion 1-2, the working body (for example, gas in a cylinder with a moving piston) is in thermal contact with a heater, the temperature of which is  $T_1$ . In an isothermal process  $dU = 0$ , therefore, the amount of heat  $Q_1$  received by the gas from the heater is equal to the work of expansion performed  $A_{1-2}$  by the gas during the transition from state 1 to state 2

$$A_{1-2} = \frac{m}{M} RT \ln \frac{V_2}{V_1} = Q_1. \quad (2.29)$$

With adiabatic expansion 2-3, the working body is completely thermally insulated from the external environment. The work of expansion  $A_{2-3}$  is performed due to the change in internal energy:

$$A_{2-3} = \frac{m}{M} C_V^M (T_1 - T_2) = -\frac{m}{M} C_V^M (T_2 - T_1).$$

In section 3-4, isothermal compression of the working fluid occurs due to contact with the refrigerator, the temperature of  $T_2$  which is  $T_2 < T_1$ . The amount of heat  $Q_2$  given to the refrigerator is equal to the work of compression  $A_{3-4}$ :

$$A_{3-4} = \frac{m}{M} RT \ln \frac{V_4}{V_3} = -Q_2. \quad (2.30)$$

Work of adiabatic compression

$$A_{4-1} = -\frac{m}{M} C_V^M (T_1 - T_2) = \frac{m}{M} C_V^M (T_2 - T_1) = -A_{2-3}.$$

Work done per cycle,

$$A = A_{1-2} + A_{2-3} + A_{3-4} + A_{4-1} = Q_1 + A_{2-3} - Q_2 - A_{2-3} = Q_1 - Q_2.$$

Let's write down the adiabatic equations 2-3 and 4-1, we get  $T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$ ;  $T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$ , from where  $\frac{V_2}{V_1} = \frac{V_3}{V_4}$ . Taking this into account, we substitute (2.29) and (2.30) into (2.28), and we get

$$\eta = \frac{\frac{m}{M} RT_1 \ln \frac{V_2}{V_1} - \frac{m}{M} RT_2 \ln \frac{V_2}{V_1}}{\frac{m}{M} RT_1 \ln \frac{V_2}{V_1}}, \quad \eta = \frac{T_1 - T_2}{T_1}. \quad (2.31)$$

We obtained a very important statement of thermodynamics, which is called **Carnot's theorem**: thermal k.k.d. of the Carnot cycle does not depend on the nature of the working medium and is determined only by the temperatures of the heater and refrigerator.

Increase efficiency possible by lowering the temperature of the refrigerator and increasing the temperature of the heater. The maximum value of k.k.d. of modern heat engines is 65%, but its real value due to various energy losses is about 40%. K.k.d. of modern steam power plants with a steam engine equals 10-15%, with a steam turbine 20-30%.

Reverse cycles are used to cool bodies. With the help of refrigerating machines, heat is transferred from a colder body to a warmer one due to the work done on the working body by external forces. In the reverse Carnot cycle, the working body takes heat from a colder body with a temperature  $T_2$  of  $Q_2$ , and transfers heat  $T_1$  to a body with a hotter temperature  $Q_1$ . The general work is negative.

Most of the engines used on Earth are heat engines. In our country, a significant part of electricity is produced at thermal power plants, where heat engines are used mainly in the form of powerful steam turbines. Heat engines are widely used in transport and agricultural machines. The use of heat engines for the production of convenient energy increases the possibility of satisfying human needs, but it is associated with the growth of coal, oil and gas consumption. More than half of air pollution is caused by motor vehicles, especially in cities. Therefore, the problem of significant improvement of the environment is directly related to the improvement of the automobile engine, the use of hydrogen as fuel, and the use of electric motors. More attention should be paid to the use of ecologically clean sources of energy - wind, solar, energy of sea tides. Reasonable limitation of consumption of energy resources, economical use of them, application of energy-saving technologies, along with economic benefits, will also bring environmental benefits.

## 8. Entropy

The *total amount of heat*  $Q^*$  is the ratio of the heat received by the body in an isothermal process  $Q$  to the temperature of the  $T$  "heat source", i.e.

$$Q^* = \frac{Q}{T}. \quad (2.32)$$

An arbitrary process can be divided into a number of infinitely small sections. The total amount of heat is elementary in such a section -  $\frac{\delta Q}{T}$ . If the process proceeds from state 1 to state 2, then the total amount of heat

$$Q^*_{1,2} = \int_1^2 \frac{\delta Q}{T}. \quad (2.33)$$

For any reversible circular process, the total amount of heat is zero:

$$Q^* = \int_{ob.} \frac{\delta Q}{T} = 0. \quad (2.34)$$

This means that the expression  $\frac{\delta Q}{T}$  is the complete differential of some state function  $S$ ,

$$\frac{\delta Q}{T} = dS . \quad (2.35)$$

This state function is called *entropy*.

In thermodynamics, it is proved that the entropy of an isolated system cannot decrease during any processes taking place in it:

$$dS \geq 0 . \quad (2.36)$$

The equal sign corresponds to reversible processes, the inequality sign corresponds to irreversible processes.

Analysis of the concept of entropy shows that entropy characterizes the degree of disordered movement in the system, the measure of "disorder" in it. More entropy means more chaotic, thermal motion. The entropy of the system and the thermodynamic probability  $W$  are related by the Boltzmann formula:

$$S = k \cdot \ln W , \quad (2.37)$$

where  $k$  is the Boltzmann constant;

$W$  is the number of ways in which this state of the macroscopic system can be realized (according to the definition  $W \geq 1$ ).

The value  $W$  is maximum in the equilibrium state, which is the most disordered state.



## **Lecture 15**

### **Topic 3**

## **REAL GASES, LIQUIDS AND SOLIDS**

### Plan

1. Forces of intermolecular interaction.
2. Van der Waals equation.
3. Liquids. Characteristics of liquid structure Surface tension. Wetting Edge angle. Capillary effect.
4. Solid and amorphous bodies.

### **1. Forces of intermolecular interaction**

Dilute ideal gases obey the ideal gas laws with a sufficient degree of accuracy. In other cases, real gases differ in their properties from ideal gases. This is due to the fact that the behavior of the molecules of real gases differs from that attributed to the particles of an ideal gas. Firstly, molecules have finite dimensions, secondly, there are forces of interaction between them.

The forces of interaction between molecules are of a complex nature, they depend on the distance between molecules. Interaction forces are mainly of electromagnetic and quantum origin. At very close distances, forces of repulsion prevail, at greater distances - forces of mutual attraction. Repulsive forces are considered positive.  $r_0$  is the equilibrium distance at which the force of interaction is zero. Molecules would be at this distance if thermal motion did not disturb this equilibrium,  $10^{-10} \leq r_0 \leq 10^{-9}$  m. Experiments show that at  $r \geq 10^{-9}$  m the intermolecular interaction can be neglected (molecule sizes  $\sim 10^{-10}$  m). At  $r \leq 10^{-10}$  m, a special quantum interaction occurs, which leads either to the emergence of significant forces of repulsion, or to the forceful attraction of neighboring atoms and the establishment of new chemical bonds between them, that is, to the occurrence of a chemical reaction and the formation of new molecules.

### **2. Van der Waals equation**

The Dutch physicist Van der Waals (1837-1923) assumed that the molecules of a real gas are absolutely solid spheres with a diameter  $d$  between which the forces of mutual attraction act. Repulsive forces are taken into account by assigning certain sizes to the molecules. The entered diameter is actually the effective size of the molecule, which depends, in particular, on the average kinetic energy of the molecules (gas temperature): the higher the energy, the smaller the distance of the smallest

approach of the molecules, that is, the smaller the effective diameter of the molecule.

The molecules of a real gas, having finite dimensions, do not move as freely as if they had no dimensions; they come into contact with the walls of the vessel more often, so they exert a greater pressure on them than molecules of an ideal gas at the same temperature. On the other hand, thanks to the forces of mutual attraction of the molecules, the force of their impact on the wall is softened. Taking into account these factors, as well as other, more complex ones, Van der Waals obtained the *equation of state of the gas* that bears his name:

$$\left(P + \frac{A}{V^2}\right)(V - B) = \frac{m}{M} RT. \quad (3.1)$$

Amendments A and B to the Mendeleev-Clapeyron equation take these factors into account. For a given amount of gas, correction A depends on the chemical nature of the gas, B – takes into account their sizes.

For rare gases A and B are small, they can be neglected, and equation (3.1) turns into the Mendeleev-Clapeyron equation.

### **3. Liquids. Characteristics of the liquid structure. Surface tension. Wetting Edge angle. Capillary effect.**

In gases, the distances between molecules are many times greater than the size of the molecules themselves, so gases are easily compressed. The forces of interaction between gas molecules are small, and the molecules move throughout the vessel. In liquids, molecules are located almost close to each other. Therefore, when trying to change the volume of the liquid, the molecules themselves are deformed. Liquid molecules oscillate near the mean equilibrium positions. Particles of liquid after very small intervals of time move in a jump-like manner in space, which can explain the fluidity of liquids. A liquid has a short-range order, that is, it consists of many microscopic regions in which there is an orderliness of adjacent particles that changes in time and space.

***Surface tension of a liquid.*** Let's compare the liquid molecule located on its surface with the molecule inside the liquid. A molecule inside a liquid is surrounded by other molecules from all sides, so the attraction of "internal" molecules is mutually balanced. A molecule placed on the surface is surrounded by liquid only on one side, and on the gas side there are very few molecules. Therefore, adding up all the forces acting on the molecule near the surface gives a uniform force directed inward of the liquid. In the absence of other forces, this leads to the reduction of the liquid surface to a minimum. For a given volume of matter, a sphere has the minimum surface area. This explains the

spherical shape of dew drops. The surface layer of the drop behaves like an elastic film stretched over it. This phenomenon is called **surface tension**. It is characteristic not only for spherical drops, but also for any liquid surface.

The force  $F$  arising from surface tension acts along the tangent to the liquid surface perpendicular to the line bounding this surface and is called the **surface tension force**. At the length of the limiting line  $\ell$

$$F = \alpha \ell, \quad (3.2)$$

where  $\alpha$  is the coefficient of surface tension of the liquid, which depends on the nature of the liquid and the environment bordering its surface, as well as on the temperature of the liquid. The coefficient of surface tension is measured in *newtons per meter* (N/m).

Surface tension coefficients of liquids bordering on air are usually given in the tables.

As the temperature increases, the adhesion forces in the liquid decrease, which means that the surface tension also decreases. At a temperature of 20°C, the coefficient of surface tension of water is 0.073 N/m, mercury is 0.47 N/m.

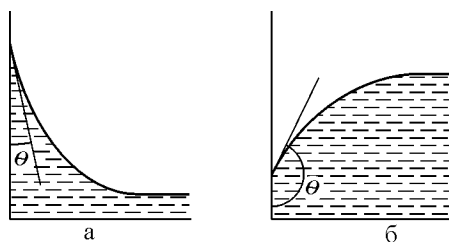


Fig. 3.1

**Wetting.** At the boundary of the collision of a liquid with a solid body, for example, the walls of a vessel, interaction forces arise between the molecules of the liquid and the solid body, which cause the curvature of the liquid surface. This phenomenon is called **wetting**. If the forces of interaction between liquid molecules are smaller than the forces of interaction between molecules of a liquid and a solid body,

then the liquid wets the surface of the solid body (for example, mercury-zinc, water-glass). The angle  $\theta$  between the plane touching the surface of the liquid and the wall, which is called the **edge angle**, is sharp in this case (Fig. 3.1a). In the opposite case, the edge angle is obtuse, the liquid does **not wet** the surface of a solid (for example, mercury-glass, water-paraffin) (Fig. 3.1b). With complete wetting, the edge angle is equal to 0, with complete non-wetting – 180°.

**Capillary phenomena** consist in the rise or fall of liquid in small-diameter tubes (capillaries) compared to the liquid level in a wide vessel. The cause of capillary phenomena is the interaction of liquid with wettable or non-wetting capillary surfaces. A wetting liquid, for example, water in a glass capillary, rises (Fig. 3.2a), and a non-wetting liquid, for example, mercury in the same capillary, falls (Fig. 3.2b).

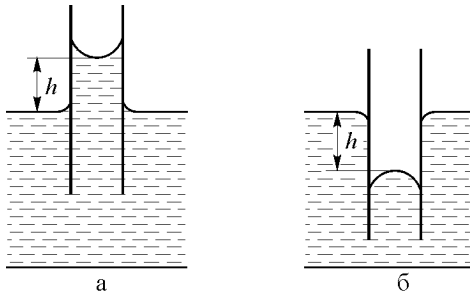


Fig. 3.2

The height  $h$  of the rise or fall of the liquid *density*  $\rho$  in the radius  $r$  capillary in comparison with the liquid level in the wide vessel is determined by the formula

$$h = \frac{2\alpha}{\rho g r}, \quad (3.3)$$

where  $\alpha$  is the surface tension coefficient of the liquid;  
 $g$  is the acceleration of free fall.

Capillary phenomena play an important role in nature. Thanks to numerous capillaries in the soil, water rises from the deep layers of the soil to the surface, which contributes to the drying out of the soil. This is prevented by such an agrotechnical measure as destruction of the crust formed after rain on the surface of the soil, loosening of the soil. On the other hand, to improve the germination conditions of the seeds of some agricultural crops (for example, millet), an increased concentration of moisture in the upper layer of the soil is required, for which the soil is compacted with special rollers.

#### 4. Solid and amorphous bodies

Solids retain not only their volume, like liquids, but also their shape. Solids exist in two essentially different states, different in their internal structure, which leads to the difference in many of their properties - these are *crystalline and amorphous states*.

In *amorphous* bodies, the arrangement of atoms or molecules is disordered. These bodies are isotropic - their physical properties are the same in all directions. Amorphous bodies include glass (an amorphous alloy of silicates), ebonite, resins. In amorphous bodies, similarly to liquids, atoms oscillate near randomly arranged nodes. The movement of particles of an amorphous body takes place in such long intervals of time that amorphous bodies can be considered solid.

In modern physics, only crystalline bodies are called solids. *Crystals* are solid bodies in which atoms or molecules form an ordered structure. In solids, the forces of interaction between molecules are large. Molecules oscillate near constant equilibrium positions - nodes. In a solid body, the arrangement of nodes is defined correctly, it is called a crystal lattice. A distinctive property of crystalline bodies is their anisotropy, which consists in the fact that the physical properties of the bodies are not the same in different directions, but coincide in parallel directions. Crystalline bodies are divided into single *crystals and polycrystals*. Single crystals are characterized by a periodically repeating structure throughout the volume. Polycrystalline bodies consist of a large number of

randomly placed small crystals that have grown together. Metals most often have a polycrystalline structure.

**Liquid crystals** (*anisotropic liquid*) are substances in a state intermediate between solid crystalline and isotropic liquid. Liquid crystals, while preserving the main features of a liquid, for example, fluidity, have a characteristic feature of solid crystals - anisotropy of properties. In the absence of external influences in liquid crystals, the dielectric constant, magnetic susceptibility, electrical conductivity, and thermal conductivity are anisotropic.

Liquid crystals consist of elongated or disc-shaped molecules, the interaction between which tends to line them up in a certain order. At high temperatures (above the critical temperature), thermal motion prevents this, and the substance is an ordinary liquid. At temperatures below the critical temperature, a distinct direction appears in the liquid, along which the molecular axes are mainly oriented.

Liquid crystals are widely used in small-sized electronic watches, calculators, measuring devices as indicators for displaying information. A liquid crystal requires voltages of the order of 1 V and powers of the order of 1  $\mu$ W. The use of liquid crystalline states plays a significant role in the technology of ultra-strong polymer and carbon fibers. The role of liquid crystals in a number of vital mechanisms of the human body has been established. Complex biologically active molecules (for example, DNA) and even microscopic bodies (for example, viruses) can be in the liquid crystalline state.

In 1912, the German physicist M. Laue (1879-1960) discovered the diffraction of X-rays in crystals. Since X-ray radiation has an electromagnetic nature, their diffraction can only occur on chains of atoms or ions, the distances between which are comparable to the wavelength of X-ray radiation. The reality of the spatial structure was proved. A structure characterized by the periodic arrangement of particles (or atoms, or molecules, or ions) in space is called a **crystal lattice**. The points where the particles are located are called **nodes of the crystal lattice**.

Crystals can be classified according to two principles:

1) **Physical sign** - depending on the physical nature of the forces acting between the crystal particles. In this case, we will get four types of crystals: ionic, atomic, metallic and molecular.

Ions of opposite signs (*NaCl, KBr, CaO*, etc.) are located alternately in the nodes of the crystal lattice of ionic crystals.

In atomic crystals, atoms of one or another substance are located at the nodes of the crystal lattice.

There are positive ions in the nodes of the metal crystal lattice. When lattices are created, valence electrons become "common" for the entire volume of the metal. Therefore, valence electrons in metals are called collectivized. In this case, we can say that there is a free electron gas inside the

metal crystal.

Molecules of matter are located in the nodes of the crystal lattice of molecular crystals.

## 2) *Crystallographic feature*

The most important geometric property of crystals, crystal lattices and their elementary cells is symmetry relative to certain directions (axes) and planes. The number of possible types of symmetry is limited. The French crystallographer O. Bravais (1811-1863) started the geometric theory of the structure of crystals and showed that depending on the ratio of values and mutual orientation of the edges of elementary crystal cells, there can be 14 types of crystal lattices, which were called Bravais lattices.

There are primitive (simple), base-centered, volume-centered, and face-centered Bravais lattices. If the nodes of the crystal lattice are located only at the vertices of the parallelepiped, which is a unit cell, then such a lattice is called primitive or simple. If, in addition, there are nodes in the center of the base of the parallelepiped, then the lattice is called base-centered, if there is a node at the intersection of the spatial diagonals, the lattice is called volume-centered, and if there are nodes in the center of all side faces, it is face-centered.

Almost half of all elements form crystals of cubic or hexagonal symmetry, which we will consider in detail. In crystals of the cubic system, three are possible lattices: simple, volume-centered and face-centered. In the cubic system, all angles of the unit cell are straight and all its edges are equal to each other. The elementary cell of the hexagonal system is a straight prism based on a rhombus with angles of 60 and 120°. Two angles between cell axes are straight, and one is equal to 120°.

In real crystals, the particles are not always arranged as they should be. The incorrect arrangement of an atom or group of atoms – that is, defects in the crystal lattice – increases the energy of the crystal.

The simplest are atomic defects. These can be vacant nodes (vacancies), that is, empty places in the crystal lattice, or impurity atoms located not in lattice nodes, but in internodes - in the spaces between crystal atoms.

Defects in the crystal structure can be not only point, but also long, and in such cases it is said that dislocations have formed in the crystal. The simplest types of dislocations are edge and screw dislocations.

Educational edition

**PHYSICS**

**EDUCATIONAL AND METHODOLOGICAL LITERATURE  
SUMMARY OF LECTURES  
FROM EDUCATIONAL DISCIPLINE  
PHYSICS  
PART II**

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