2. Molecular Physics and Thermodynamics

2.1. Two balloons of the same volume are filled with gases at the same pressure, one with hydrogen and the other with helium. Which of the two has the greater buoyancy (including the weight of the bag) and what is the ratio of buoyancies?

2.2. Which of the lines in the figure reflects correctly on the log-log scale the temperature dependence of the root-mean-square velocity of molecules?

2.3. Why is the trace of the silver molecules in the Stern experiment for measuring the velocities of molecules sharp in the case of fixed cylinders (Figure (a)) and blurred in the case of rotating cylinders (Figure (b))?

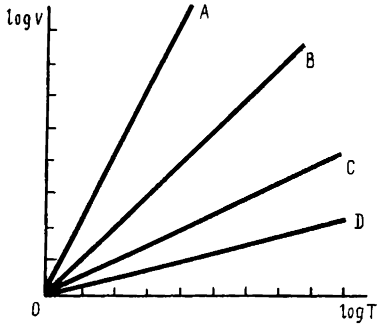


Fig. 2.2

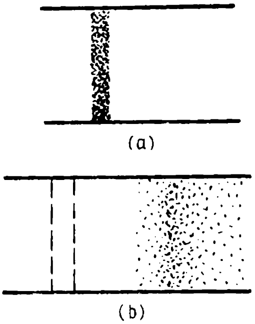

(a)
(b)

Fig. 2.3

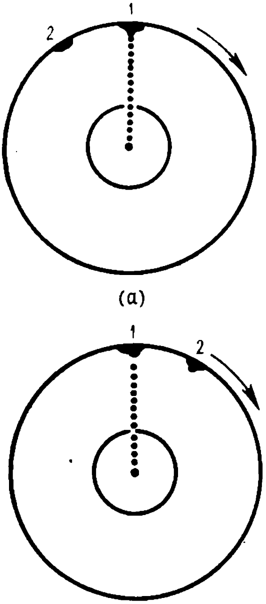
2.4. Usually, in depicting the results of the Stern experiment, one registers the positions *1* and *2* of the traces of silver for, respectively, fixed and rotating cylinders (Figure (a)). However, a student depicted the traces in a manner shown in Figure (b). The instructor remarked that such a position of traces contradicts the experimental results, and yet the student was able to defend his position. Under what condition can such an experimental situation occur? What are the chances of encountering it in actual experiments?

2.5. The functions $F(v) = \mathrm{d}N/\mathrm{d}v$ and $f(v) = (1/N_0)\,\mathrm{d}N/\mathrm{d}v$, with N the number of molecules having velocity v and N_0 the total number of molecules in a given volume, are laid off on the vertical axes in Figures (a) and (b), respectively. What is the physical meaning of each hatched segment in these figures?

2.6. All the ordinates of curve *2* are twice the corresponding ordinates of curve *1*. What is the difference between the velocity distribution functions represented by these curves?

2.7. A segment from velocity v_2 to velocity v_3 on the graph representing the velocity distribution function is isolated (see Figure (b) accompanying Problem 2.5). How can we on the basis of this graph determine the energy of all the molecules whose velocities lie within the specified range and the average energy of these molecules?

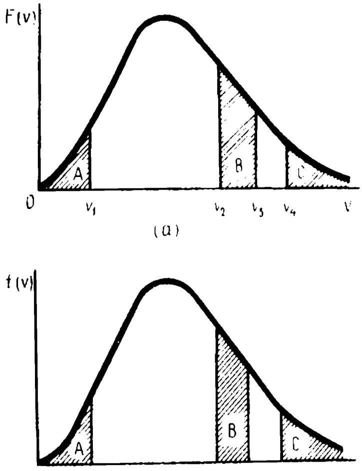
2.8. The velocity distribution for molecules can be represented as a function of the ratio of the given velocity to the most probable one. It is then expedient to lay off on the vertical axis the ratio of the value of the function for the given velocity to the value of the function for the most probable velocity. Will the distribution curve constructed in this manner be valid for different gases, different number of molecules, and different temperatures or



(a)

(b)

Fig. 2.4



(a)

(b)

Fig. 2.5

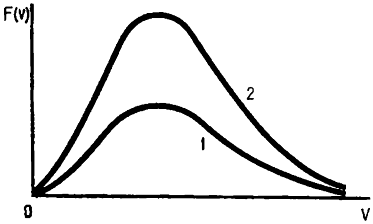


Fig. 2.6

will it be necessary to reconstruct the curve anew for each case?

2.9. The Maxwellian distribution can be represented not only by a function of molecule velocities but also by a function of the energies of the molecules. This latter function gives the number of molecules whose energies lie within the interval from w to $w + \mathrm{d}w$, or

$$\mathrm{d}N = N_0 f(w)\, \mathrm{d}w. \tag{2.9.1}$$

Find the expression for this function and see whether it refers only to one gas or is valid for any gas.

2.10. Let us assume that, contrary to the real (Maxwellian) distribution of molecule velocities, all the molecules at a certain level, say at sea level, have the same velocity equal to the root-mean-square velocity at a given temperature. Let us also assume that, in accordance with the ideal gas model, there are no collisions between the molecules. How would the kinetic energy of molecules vary with altitude under such conditions? Up to what altitude would an atmosphere consisting of nitrogen and oxygen extend?

2.11. Here are two explanations of the buoyancy of a balloon filled with a light gas. According to the first, the buoyancy is simply the Archimedes' force equal to the weight of the air that would occupy the volume of the balloon (filled with the gas), while according to the second, the buoyancy is the difference between the barometric pressures acting on the upper and lower sections of the balloon. Do these explanations contradict each other?

2.12. The average displacement of a Brownian particle in time t is $\langle l \rangle$. What is the average displacement $\langle l \rangle$ of the same particle in time $2t$?

2.13. If the mean free path of a molecule in a gas is $\langle l \rangle$, what is the mean free path of the molecule along an arbitrary coordinate axis?

2.14. Because of the chaotic motion of molecules in a gas the free paths of molecules have different values. If on the vertical axis we lay off the logarithm of the number of molecules whose free paths exceed a certain value x and on the horizontal axis the value of x, the graph representing the dependence of these two quantities is a straight line with a negative slope,

$$\log N = \log N_0 - ax.$$

How can one find the free path of molecules using such a graph?

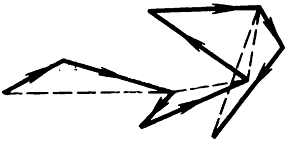


Fig. 2.12

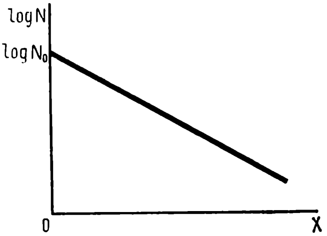


Fig. 2.14

2.15. A vessel is divided by a porous partition into two parts, *1* and *2*, of equal volume. After the air was pumped out of the vessel, part *1* was filled with hydrogen and part *2* with nitrogen. The initial pressures of the gases are the same. Draw a rough sketch of the graph of how the pressures of the gases in the vessel change with the passage of time.

2.16. The temperature of a gas in a vessel changes depending on whether the vessel is open or closed, and so does the diffusion coefficient. The temperature dependence of the diffusion coefficient *D* for both cases is shown in the figure on the log-log scale. Which line corresponds to the case of an open vessel and which to the case of a closed vessel? The effective cross sections of the molecules are assumed to be constant.

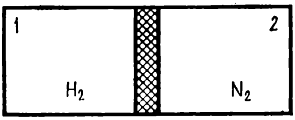


Fig. 2.15

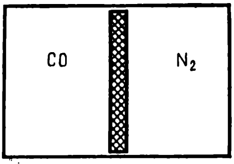


Fig. 2.17

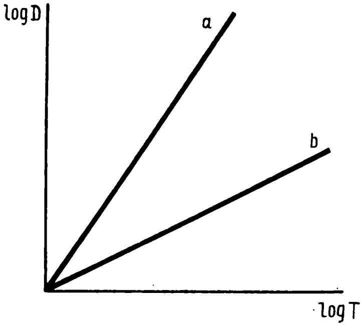


Fig. 2.16

2.17. A vessel is divided by a solid partition into two parts of equal volume. One part is filled with nitrogen and the other with carbon monoxide. It may be assumed that the cross-sectional areas of the molecules of the two gases are the same. The relative molecular masses of both gases are also the same (equal to 28). Finally, the pressures in both parts are the same. After the partition is lifted, the gases begin to diffuse into each other. How does the amount of each gas that has transferred to the part occupied by the other gas depend on the initial pressures of the gases?

2.18. A gas is inclosed in a vessel and has a pressure at which the mean free path of the molecules exceeds considerably the size of the vessel. The collisions that the molecules have with the walls of the vessel may be considered elastic. The vessel is placed in a vacuum and has a small orifice through which the gas molecules escape into the vacuum. Is the average energy of the molecules leaving the vessel the same as that of the molecules remaining in the vessel? Is the velocity distribution for the molecules in both groups the same? The gas is assumed to be ideal, so that no Joule-Thomson effect is present.

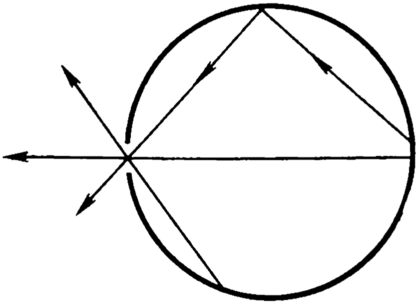


Fig. 2.18

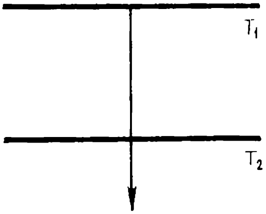


Fig. 2.19

2.19. A heat flux passes through a gas from a heated plate with a temperature T_1 to a cold plate with a temperature T_2. The linear dimensions of the plates are large compared to the distance between them. Is the temperature gradient the same along the entire heat flux? Why when measuring the thermal conductivity coefficient must we place the plates horizontally, with the plate with the higher temperature placed above the one with the lower temperature?

2.20. Liquid nitrogen ($t = -196$ °C) is inside a Dewar vessel. The air surrounding the vessel has a temperature $t = 20$ °C. The pressure of the residual gas between the walls of the vessel is about 10^{-4} Pa (roughly 10^{-6} mm Hg). The mean free path of the "molecules" of air at atmospheric pressure is about 10^{-7} m. What is the temperature of the air between the walls of the vessel?

2.21. Steady-state heat transfer through a gas occurs between two parallel walls. The experiment is conducted in such conditions that the only process by which the heat is transferred is pure thermal conduction. The dependence of the thermal conductivity coefficient λ is measured as a function of the gas pressure p, with the experiment conducted twice, for two different distances between the walls. The results are shown in the figure. What curve corresponds to the greater distance between the walls?

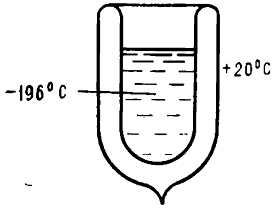


Fig. 2.20

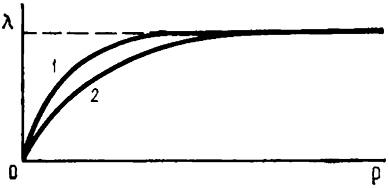


Fig. 2.21

2.22. Figures (a), (b) and (c) depict three cyclic processes in the pV-, VT-, and pT-coordinates. The curvilinear sections in Figure (a) are isotherms. Depict the same processes in the pT- and VT-coordinates (for process (a)), the pV- and pT-coordinates (for process (b)), and the pV- and VT-coordinates (for process (c)).

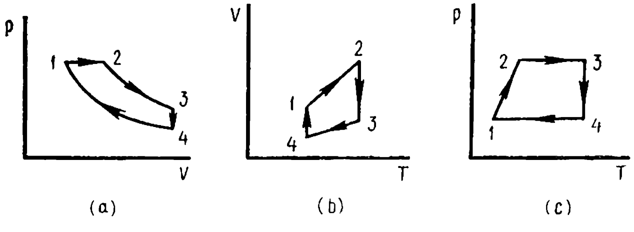


Fig. 2.22

2.23. A gas is inside a cylinder closed by a piston. The piston is held from above by a spring whose elastic properties obey Hooke's law. Produce a rough sketch, in the pV-coordinates, of the curve that represents the change in state of the gas upon heating and determine the work that is done in the process if the volume of the gas varies from V_1 to V_2 and the pressure varies from p_1 to p_2.

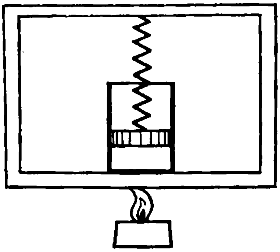


Fig. 2.23

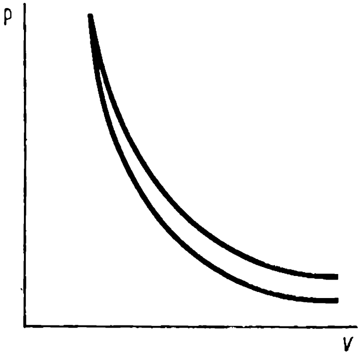


Fig. 2.24

2.24. The figure demonstrates the adiabatic curves for two gases, helium and carbon dioxide. Which curve corresponds to which gas?

2.25. A gas expands from an initial state characterized by a pressure p_1 and a volume V_1 in two ways, isothermically and adiabatically, to the same volume V_2. In which of the two processes is the final pressure higher and in which is the work greater?

2.26. The amount of heat supplied to an ideal gas is laid off on the horizontal axis and the amount of work performed by the gas is laid off on the vertical axis. One of the straight lines in the figure is an isotherm and the other two are isobars of two gases. The initial states of both gases (pressure, temperature, volume) are the same, and the scales on the two axes coincide. Which straight line corresponds to which process? How many degrees of freedom does each gas have? (Vibrational degrees of freedom are not to be taken into account.) The graphs of what processes coincide with the coordinate axes?

2.27. The straight lines in the figure depict the variations in temperature as a function of the amount of heat supplied in different processes involving the change of state of a monatomic and a diatomic gas. Which processes correspond to these straight lines? The graphs of what processes coincide with the coordinate axes? The initial

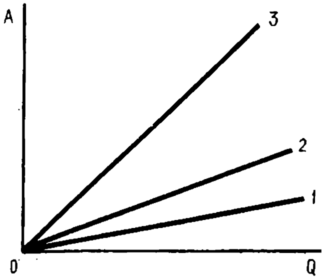


Fig. 2.26

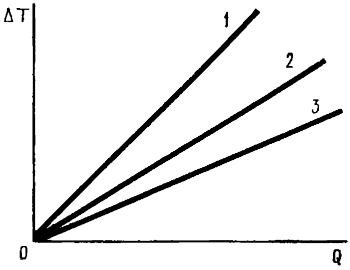


Fig. 2.27

states (temperature, volume, pressure) of the two gases are the same.

2.28. One of the straight lines in the figure depicts the dependence of the work done on the temperature variations for an isobaric process. The other two are the adiabatic curves for argon and nitrogen. Which straight line

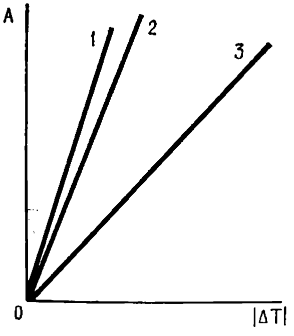


Fig. 2.28

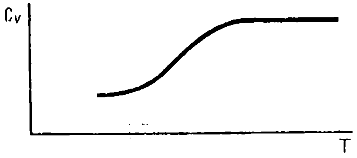


Fig. 2.29

corresponds to which process? How should one depict an isotherm and an isochor in these coordinates? Bear in mind that on the horizontal axis we lay off the difference between the higher and the lower temperature.

2.29. For temperatures close to room temperature and somewhat higher, the molar heat capacity of hydrogen agrees, with good accuracy, with the results predicted by the classical theory of heat capacity for ideal gases, a theory that allows for three translational and two rotational degrees of freedom for diatomic gases. However, at low temperatures the heat capacity of hydrogen drops and at about 40 K becomes the same as that of a monatomic gas. What is the explanation for this? Why such behavior is not observed in other diatomic gases?

2.30. When diatomic gases are heated, their heat capacity exhibits a peak in the high-temperature region. Similar behavior is observed in multiatomic gases. What is the explanation for this?

2.31. Draw a rough sketch for the compressibility of an ideal gas as a function of pressure for two cases, one when

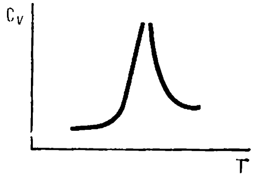


Fig. 2.30

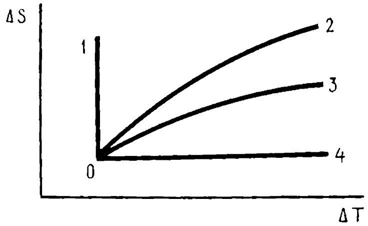


Fig. 2.34

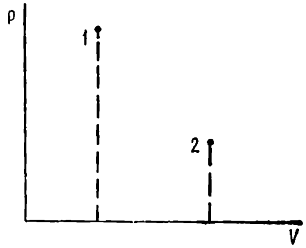


Fig. 2.32

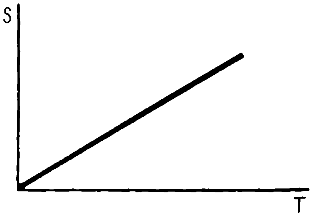


Fig. 2.37

the gas is compressed isothermically and the other when the gas is compressed adiabatically.

2.32. A gas is transferred from a state *1* to a state *2* by two processes: (a) first by an isochor and then by an isobar, and (b) first by an isobar and then by an isochor. Will the work done in both cases be the same, will the amount of heat required in the processes be the same, and will the increment of entropy in the processes be the same?

2.33. Draw the Carnot cycle for a monatomic gas on the log-log scale using the pT- and VT-coordinates.

2.34. A gas is transferred from an initial state *0* to other states *1*, *2*, *3*, and *4* via different isoprocesses. Which curve representing the dependence of entropy on temperature corresponds to which process?

2.35. Draw the Carnot cycle in the ST-coordinates.

2.36. Two objects with initial temperatures T_1 and T_2 (with $T_1 > T_2$) are brought into contact. The objects are isolated from their surroundings, and the masses and heat capacities of the two objects coincide. How does the total entropy of these objects change as the temperatures become equal?

2.37. Suppose that the entropy grows linearly with temperature in a process. How does the heat capacity vary with temperature?

2.38. A gas is transferred from a state *1* to a state *2* in two ways: (a) directly by an isobar, and (2) first by the isochor *1-3*, then by the isobar *3-4*, and, finally, by the isochor *4-2*. Show, by direct calculation, that the entropy increment in both cases is the same.

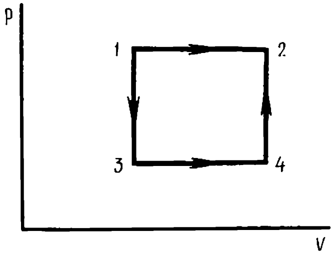


Fig. 2.38

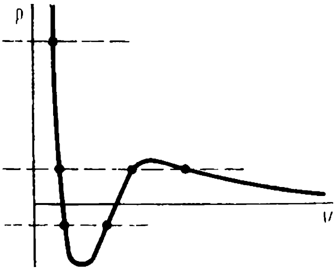


Fig. 2.40

2.39. A heat engine operates according to a cycle that consists of two isochors and two isobars. Prove that the entropy of the heater-gas-cooler system increases as the engine operates. How does the entropy of the gas change in the process? The heat capacities of the heater and cooler are assumed to be infinite.

2.40. According to the van der Waals equation, which is a third-degree equation in the volume, the theoretical isotherm of a real gas may have either one or three intersections with a horizontal line, the intersections corresponding to either one or three real roots of the equation. With three roots it may so happen that two are equal (maxima and minima on the isotherm) or even all three are equal (the critical point). However, on an isotherm built for a sufficiently low temperature there is a section lying below the horizontal axis, and a horizontal line in this case intersects the section only at two points (two roots in V). Where in this case is the compulsory third root?

2.41. The section *1-3* on the theoretical isotherm of a real gas (the van der Waals isotherm) is assumed to be unrealistic because of its absolute instability. What is the reason for this instability?

2.42. Changes in the state of a real gas or liquid that are realized under ordinary conditions at a constant temperature are represented by the so-called Andrews isotherm, which consists of a section (*1-2*) representing the unsaturated vapor, a section (*2-4-6*) representing the two-phase state (saturated vapor and liquid), and a section (*6-7*) representing the liquid. This isotherm differs from the theoretical van der Waals isotherm (*1-2-3-4-5-6-7*), which corresponds to a one-phase transition of the entire mass of vapor into liquid. On the van der Waals isotherm there are sections corresponding to metastable states (*2-3* and *5-6*), which can be realized in certain conditions. What are these states and what are the conditions for their realization?

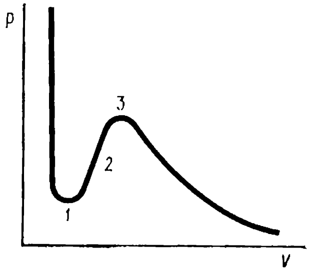


Fig. 2.41

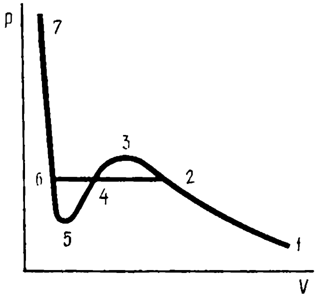


Fig. 2.42

2.43. Using the second law of thermodynamics, prove that the areas of the hatched sections between the theoretical and experimental isotherms of a real gas must be equal.

2.44. When a liquid evaporates, the heat supplied to it is used partially to do work in overcoming the forces of cohesion between the molecules (the internal heat of vaporization) and partially to do work against the forces caused by external pressure (the external heat of vaporization). How to determine the external heat of vaporization from the graph representing the experimental isotherm of a real gas?

2.45. Gas cylinders and pipes intended for operation under high pressures are usually tested not by pumping air or a gas into them but by filling them with a liquid, water or oil, and raising the pressure up to the test value. This is done in accordance with safety regulations. What is the explanation for this?

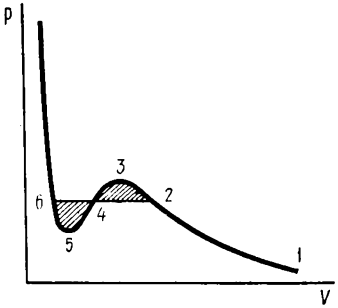


Fig. 2.43

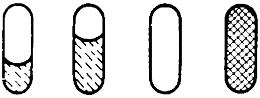

(a) (b) (c) (d)

Fig. 2.46

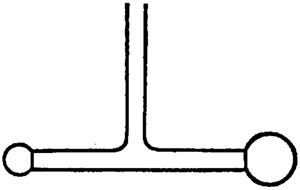


Fig. 2.49

2.46. To demonstrate the transition to the critical state, a liquid (usually ethyl ether) is placed inside a small sealed thick-walled glass tube. The tube is then sealed off (Figure (a)) and slowly heated. It is found that in the process of heating the boundary between the liquid and the vapor above the liquid rises and the meniscus becomes flatter (Figure (b)). It is extremely difficult to observe the transition through the critical temperature because of intense convective fluxes, but the result is seen because at this temperature the meniscus disappears completely (Figure (c)). Upon slowly cooling the tube it is found that at the same temperature the entire volume becomes cloudy, so that light cannot pass through the tube (Figure (d)). If the temperature is lowered still further, the volume becomes transparent and there appears a meniscus, which separates the two phases. Explain the reasons for the observed phenomena.

2.47. How does the temperature of a liquid change under adiabatic evaporation?

2.48. The bending of the surface of a liquid creates excess pressure (known as the Laplace pressure). Because of this the pressure inside a soap bubble is somewhat higher than the atmospheric pressure. In a drop, too, there is excess pressure. Suppose we have a drop of liquid and a soap bubble of the same liquid and the same diameter. Where is the pressure greater: inside the drop or inside the bubble?

2.49. Two soap bubbles of different diameters are blown out using a T-shaped pipe (see the figure). Will the diameters of the bubbles remain unchanged?

2.50. Three drops of different diameters are in the atmosphere of the vapor of the liquid from which the drops are formed. The pressure of the vapor is such that the drop with the medium diameter (Figure (b)) is in equilibrium with the vapor. Is this equilibrium stable? How will the drops of the smaller (Figure (c)) and the larger (Figure (a)) diameters behave?

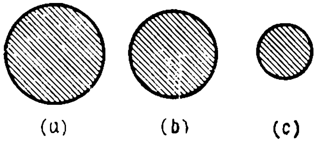


Fig. 2.50

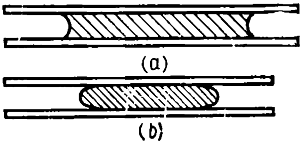


Fig. 2.51

2.51. Two drops are placed between two parallel glass plates, a drop of water (Figure (a)) and a drop of mercury (Figure (b)). What forces act on the plates in each case?

2.52. Inside two conical pipes there is a drop of water (Figure (a)) and a drop of mercury (Figure (b)). Where does each drop tend to move?

2.53. Which of the curves shown in the figure depicts correctly the temperature dependence of surface tension?

Curve *1* falls off to zero at the boiling point of the liquid, curve *2* falls off to zero at the critical temperature, curve *3* tends to zero asymptotically, and curve *4* shows that surface tension is temperature independent.

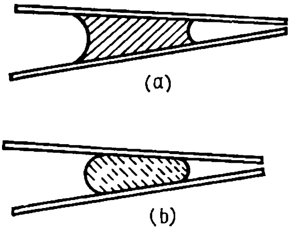


Fig. 2.52

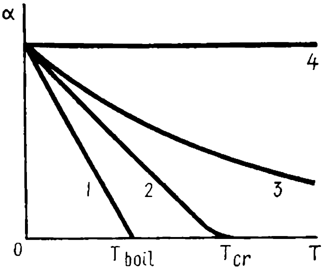


Fig. 2.53

2.54. A capillary tube is placed vertically in water. The diameter of the tube is such that surface tension "lifts" the liquid to an altitude h_0. But the height of the tube above the liquid, h, is less than h_0. How in this case will the column of liquid in the tube behave?

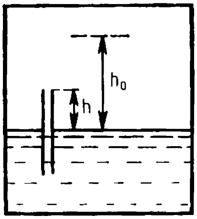


Fig. 2.54

2.55. A viscous liquid is flowing due to a pressure head Δp along a pipe of length l and diameter D. Will the volume flow remain the same if instead of this pipe we use four parallel pipes of the same length but with the diameter of each pipe being equal to $D/2$?

2.56. A viscous liquid is flowing along a horizontal pipe of diameter $D = 2R$. At some point in time a particle of rust or boiler scale gets detached from the upper part of the pipe and falls downward. Assuming that this particle acquires a constant fall velocity v_y practically at once (at this velocity the force of gravity, Archimedes' force, and the drag of the liquid balance each other), find the trajectory of the particle and the distance the particle travels in the horizontal direction due to the flow of the liquid. The maximal velocity of the liquid (along the pipe's axis) is v_{xm}.

2.57. When ice with a temperature below 0 °C is mixed with water with a temperature above 0 °C, there are four possibilities: the ice melts and the final temperature is above 0 °C, the water freezes and the final temperature is below 0 °C, part of the ice melts and the temperature of the mixture becomes 0 °C, and part of the water freezes

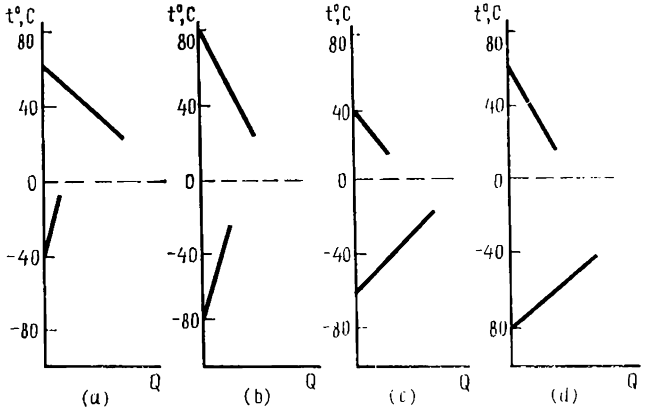


Fig. 2.57

and the temperature of the mixture becomes 0 °C. On the horizontal axis we lay off the amount of heat that the water gives off in cooling and freezing (the upper straight

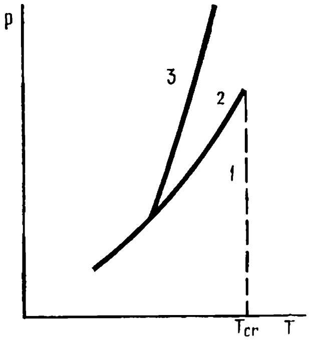


Fig. 2.58

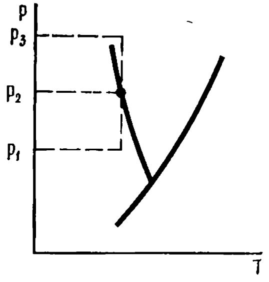


Fig. 2.59

lines) and the amount of heat that the ice absorbs in heating and melting (the lower straight lines). The scale along the horizontal axis is arbitrary, that is, the scale value is not specified. The temperature (in degrees Celsius) is laid off on the vertical axis. Find the final result of mixing whose beginning is shown in each figure. When either all the water freezes or all the ice melts, determine the final temperature.

2.58. A phase diagram represents the relationship between the temperature and pressure at the boundary that separates two phases. To which phases do the regions *1*, *2*, and *3* correspond?

2.59. The phase diagram of water is shown schematically in the figure. Using this diagram, explain this particular dependence of the melting point of ice on the external pressure.

2.60. The compressibility of a liquid does not remain constant under pressure variations. How, knowing the dependence of compressibility on pressure within a certain pressure interval from p_1 to p_2, can we find the ratio of volumes at these values of pressure?

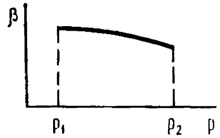


Fig. 2.60

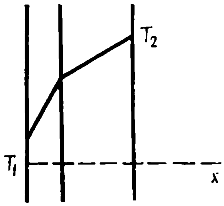


Fig. 2.62

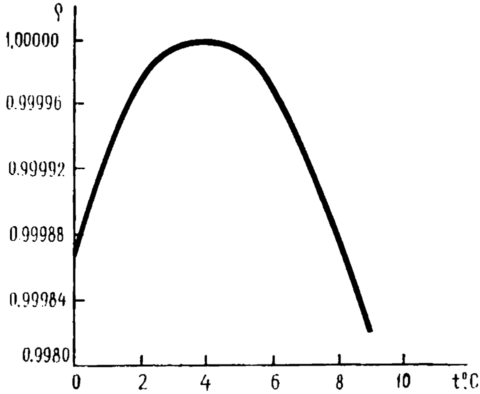


Fig. 2.61

2.61. As is known, the density of water at first grows when water is heated from 0 °C but then, at 4 °C, begins to drop, as shown in the figure. Does the explanation of this lie in the fact that in introducing the metric system of units the weight of a definite volume of water at 4° C was taken as the unit of weight (subsequently this was taken as a unit of mass)?

2.62. The wall of a house consists of two layers with different thermal conductivity coefficients. The temperature of the outer wall is T_1 and that of the inner wall is T_2. Temperature variations inside the wall are shown in the figure. What layer, the inner or the outer, has a higher thermal conductivity coefficient?

2.63. A rod with a cross-sectional area S and initial length l is elongated by Δl due to a tensile stress. The modulus of longitudinal elasticity of the material of the rod, or Young's modulus, is E. Find the bulk energy density for the deformation of the rod.

2.64. Two bars *1* and *2* of the same cross-sectional area and the same length but made of different materials are clamped between two undeformable walls. The materials of the bars differ in mechanical and thermal properties. What must be the relationship between Young's moduli and the linear coefficients of thermal expansion so that heating the bars does not change the position of the boundary between them? Under what conditions does the deformability of the walls have no effect on the result?

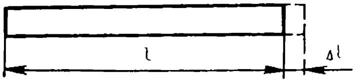


Fig. 2.63

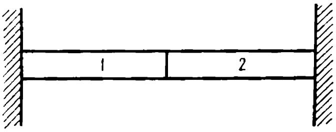


Fig. 2.64

2. Molecular Physics and Thermodynamics

2.1. The buoyancy, or lifting power, is the difference between the weight of the air in the volume occupied by the balloon and the weight of the gas filling the balloon. According to the ideal-gas law, the latter weight is

$$P = \frac{pVM}{RT} g,$$

where V is the volume of the balloon, p the pressure of the gas, and M the molecular mass of the gas. Accordingly, the lifting power is given by the formula

$$F = \frac{pVg}{RT} (M_{\text{air}} - M_{\text{gas}}),$$

and the buoyancy ratio is

$$\frac{F_{H_2}}{F_{He}} = \frac{M_{\text{air}} - M_{H_2}}{M_{\text{air}} - M_{He}}. \qquad (2.1.1)$$

Into Eq. (2.1.1) we can substitute the relative molecular masses. The relative molecular mass of hydrogen is 2, that of helium is 4, and that of air we assume to be equal to 29. Thus,

$$\frac{F_{H_2}}{F_{He}} = \frac{29-2}{29-4} = 1.08.$$

2.2. The root-mean-square velocity of molecules is

$$v = \sqrt{3RT/M}.$$

Taking logs, we get

$$\log v = \frac{1}{2} \log (3R/M) + \frac{1}{2} \log T.$$

The slope of the straight line log v vs. log T must be 0.5, and the dependence of the logarithm of velocity on the logarithm of temperature is given by straight line C in the figure accompanying the problem.

2.3. Since the velocities of the molecules are different, it takes the molecules different times to fly from the slit to the outer cylinder. Because of this the cylinders rotate through angles that are different for different molecules. The greater the velocity of a molecule, the closer will its track be to the track for fixed cylinders.

2.4. The position of the tracks shown in Figure (b) accompanying the problem is possible if during the time of flight of the molecules from the slit in the inner cylinder to the wall of the outer cylinder the cylinders perform more than one-half of a full revolution (in Figure (b) this is almost one full revolution). Of course, for this to happen, the linear velocity of the outer cylinder must exceed many times the velocity of the molecules, which is practically impossible.

2.5. The number of molecules in the velocity interval from v to $v + \mathrm{d}v$ is

$$\mathrm{d}N = F(v)\,\mathrm{d}v.$$

Accordingly, in Figure (a) accompanying the problem, the hatched segments represent the following quantities: segment A represents the number of molecules whose velocities do not exceed v_1, or

$$N_A = \int_0^{v_1} F(v)\,\mathrm{d}v,$$

segment B represents the number of molecules whose velocities are not lower than v_2 and do not exceed v_3, or

$$N_B = \int_{v_2}^{v_3} F(v)\,\mathrm{d}v,$$

and segment C represents the number of molecules whose velocities are not lower than v_4, or

$$N_C = \int_{v_4}^{\infty} F(v)\,\mathrm{d}v.$$

In Figure (b) accompanying the problem, each hatched segment represents the ratio of the corresponding number of molecules to the total number of molecules, that is, the probability of molecules having velocities that lie within the specified velocity interval.

2.6. Since for each velocity interval from v to $v + \mathrm{d}v$ the number of molecules is

$$\mathrm{d}N = F(v)\,\mathrm{d}v$$

and since $F_2(v) = 2F_1(v)$, the total number of molecules corresponding to distribution *2* is twice the number of molecules corresponding to distribution *1*.

2.7. The number of molecules in the velocity interval from v to $v + \mathrm{d}v$ is

$$\mathrm{d}N = F(v)\,\mathrm{d}v.$$

Each of these molecules has an energy $mv^2/2$. All molecules in the velocity interval from v_1 to v_2 have the energy

$$W = \int\limits_{v_1}^{v_2} \frac{mv^2}{2} F(v)\,\mathrm{d}v.$$

To find the average energy w of such molecules, we must divide W by the number of molecules:

$$w = \frac{m}{2}\,\frac{\int\limits_{v_1}^{v_2} v^2 F(v)\,\mathrm{d}v}{\int\limits_{v_1}^{v_2} F(v)\mathrm{d}v}.$$

2.8. According to Maxwell's law, the number of molecules of a gas whose velocities lie within the interval from v to $v + \mathrm{d}v$ is given by the formula

$$\mathrm{d}N = N_0 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right). \qquad (2.8.1)$$

Since the most probable velocity is

$$v_\mathrm{p} = \sqrt{2kT/m},$$

we can represent (2.8.1) in the form

$$\mathrm{d}N = N_0 4\pi^{-1/2} \left(\frac{v}{v_\mathrm{p}}\right)^2 \exp\left[-\left(\frac{v}{v_\mathrm{p}}\right)^2\right] \mathrm{d}\left(\frac{v}{v_\mathrm{p}}\right).$$

The distribution function $F(v/v_\mathrm{p})$ then assumes the form

$$F\left(\frac{v}{v_\mathrm{p}}\right) = N_0 4\pi^{-1/2} \left(\frac{v}{v_\mathrm{p}}\right)^2 \exp\left[\left(-\frac{v}{v_\mathrm{p}}\right)^2\right].$$

For $v/v_\mathrm{p} = 1$ we have

$$F(1) = N_0 4\pi^{-1/2} \mathrm{e}^{-1} \approx 0.83 N_0.$$

The $F(v/v_\mathrm{p})$-to-$F(1)$ ratio (see the figure),

$$F\left(\frac{v}{v_\mathrm{p}}\right) \Big/ F(1) = \left(\frac{v}{v_\mathrm{p}}\right)^2 \exp\left[1 - \left(\frac{v}{v_\mathrm{p}}\right)^2\right],$$

is the same for any number of molecules of any gas at any temperature and, therefore, is a universal function.

2.9. From formula (2.9.1) it follows that

$$f(w) = \frac{1}{N_0}\frac{dN}{dw},$$

or

$$f(w) = \frac{1}{N_0}\frac{dN}{dv}\frac{dv}{dw}.$$

Since $v = (2w/m)^{1/2}$, elementary transformations yield

$$dN = N_0 \frac{2}{\sqrt{\pi}}\left(\frac{w}{kT}\right)^{1/2} \exp\left(-\frac{w}{kT}\right) d\left(\frac{w}{kT}\right).$$

This representation is convenient since the dimensionless ratio w/kT is taken as the independent variable and the distribution function proves to be valid not only for all gases but also for any temperature. The function $f(w)$ is shown in the figure.

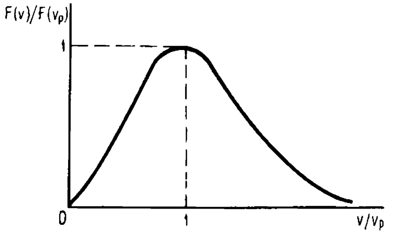


Fig. 2.8

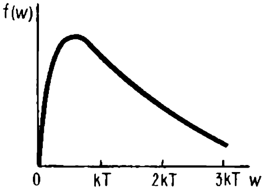


Fig. 2.9

2.10. The total energy of the molecules of a gas is the sum of their kinetic and potential energies. Assuming that the potential energy is zero at the initial level, for any other level we have $w_{\text{pot}} = mgh$. Since the total energy remains constant, or $w_{\text{kin}} + w_{\text{pot}} = \text{const}$, we have

$$w_{\text{kin}} + w_{\text{pot}} = w_{\text{kin}0}.$$

Hence, at a given level the kinetic energy is

$$w_{\text{kin}} = w_{\text{kin}0} - mgh.$$

The maximal altitude to which the molecules can rise is determined by the condition $w_{\text{kin}} = 0$, whence

$$h = w_{\text{kin}0}/mg.$$

By hypothesis, $w_{\text{kin}0} = (3/2)\,kT$. Substituting $k = R/N_A$ and $m = M/N_A$, we get

$$h = 3RT/2Mg.$$

Substituting the values of the molecular masses, we find that at $T = 300$ K the maximum altitude for nitrogen is 13.6 km, for oxygen 11.9 km, and for hydrogen 191 km. Since the kinetic energy of the molecules decreases as the altitude grows, the "temperature" of a gas decreases, too, but differently for different gases. Different gases have different "temperatures" at the same altitude above sea level. At the highest level where the molecules of a given gas can still be found, the "temperature" of the gas is 0 K.

Note, in conclusion, that by its very meaning the barometric formula, which is derived on the assumption that the temperature of the gas is constant, is equivalent to the statement that the Maxwellian velocity distribution is valid. Indeed, the barometric formula leads to Boltzmann's formula for the distribution of molecules in potential energy. The same formula can be obtained using the Maxwell formula.

2.11. To answer this question, we assume, for the sake of simplicity, that the balloon is a cylinder with its axis vertical and having a length h. If we denote by p_0 the pressure on the lower base of the balloon, then the pressure on the upper base is

$$p = p_0 \exp(-Mgh/RT).$$

Since $Mgh/RT \ll 1$, we can expand the exponential and retain only the first two terms:

$$p = p_0 (1 - Mgh/RT). \qquad (2.11.1)$$

The buoyancy is given by the formula

$$F = S(p_0 - p),$$

where S is the base area of the cylinder. Substituting the difference $p_0 - p$ from (2.11.1), we get

$$F = MghS/RT,$$

or

$$F = p_0MgV/RT.$$

The fraction p_0M/RT constitutes the density of air, p_0MV/RT the mass of the air that would occupy the volume of the balloon, and p_0MgV/RT the weight of this mass of air. Thus, the two explanations are equivalent.

2.12. If we take two subsequent displacements, l_1 and l_2, during time t in which these displacements took place the particle is displaced by l^*, with

$$l^{*2} = l_1^2 + l_2^2 + 2l_1l_2 \cos\alpha$$

(see the figure accompanying the answer). Since the displacements are completely random both in length and direction, while the angle between two successive displacements is independent of the displacements, we conclude, first, that

$$\langle l_1^2\rangle = \langle l_2^2\rangle$$

and, second, that the third term is zero because all directions are equally probable. Thus,

$$\langle l^{*2}\rangle = 2\langle l_1^2\rangle = 2\langle l_2^2\rangle.$$

One must bear in mind that we have averaged the squares of the displacements and not the displacements proper.

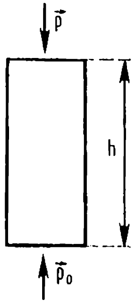


Fig. 2.11

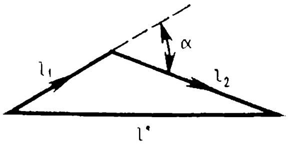


Fig. 2.12

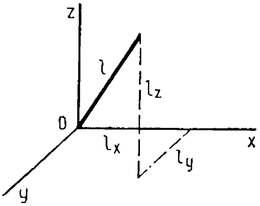


Fig. 2.13

However, since there is a constant relationship between the mean square and the square of the arithmetic mean for a definite distribution function, we can always replace the ratio of mean squares with the ratio of the squares of the mean,

$$\frac{(\langle l^*\rangle)^2}{2T} = \frac{(\langle l\rangle)^2}{T}$$

and, hence,

$$\langle l^*\rangle = \sqrt{2}\,\langle l\rangle.$$

This result can be applied to any interval of time, which makes it possible to establish the following relationship between the displacements of a Brownian particle and the time it takes the particle to perform these displacements:

$$\frac{(\langle l\rangle)^2}{t} = \text{const}.$$

This is the main law of Brownian motion. It is also valid for the motion of molecules in a gas.

2.13. Any concrete path of a molecule can be decomposed along three arbitrary coordinate axes of a Cartesian system, with

$$l^2 = l_x^2 + l_y^2 + l_z^2.$$

For each separate path these projections are, generally speaking, different, but since the motion is chaotic and, hence, the probabilities are the same for all three directions, these projections are equal, on the average, so that

$$\langle l_x^2\rangle = \langle l_y^2\rangle = \langle l_z^2\rangle.$$

If we are interested in a projection along a definite direction, which, like all others, is arbitrary, then we can write

$$\langle l^2\rangle = 3\langle l_x^2\rangle.$$

The relationship between the mean of a square and the square of a mean is the same for all directions, so that we can write

$$\langle l\rangle = \pm\sqrt{3}\,\langle l_x\rangle.$$

The two signs correspond to two opposite directions of motion.

2.14. If the mean free path of the molecules is λ, then the probability that on a segment $\mathrm{d}x$ a molecule experiences a collision will be $\mathrm{d}x/\lambda$. Out of the N molecules that have covered the distance x without colliding, $N\,(\mathrm{d}x/\lambda)$ molecules experience collisions over segment x. Hence, the number of molecules that have traveled without colliding will change by

$$\mathrm{d}N = -N\frac{\mathrm{d}x}{\lambda}.$$

If N is the total number of molecules, then the number of molecules that have traveled a distance no less than x without colliding is determined through integration:

$$\int_0^N \frac{\mathrm{d}N}{N} = -\int_0^x \frac{\mathrm{d}x}{\lambda},$$

or

$$\ln N = \ln N_0 - x/\lambda.$$

Since on the vertical axis we lay off base-10 logarithms, a and λ are linked in the following manner:

$$\lambda = 2.3/a.$$

Modern electronics possesses a number of methods for determining the number of particles (molecules, atoms, ions, electrons) whose path exceeds a definite distance, which makes it possible to find the mean free path.

2.15. Since the diffusion coefficient of hydrogen is higher than that of nitrogen, hydrogen will flow from part *1* to part *2* faster than nitrogen will flow from part *2* to part *1*. For this reason, at first the pressure in part *1* drops and in part *2* it rises. But then the rate of hydrogen diffusion lowers (since the amount of hydrogen in part *2* grows and the nitrogen continues to diffuse into part *1*). As a result, the pressure in part *2* begins to drop and the pressure in part *1* begins to grow. The process continues until the pressure in both parts becomes equal and the partial pressures of the two gases in each part become equal.

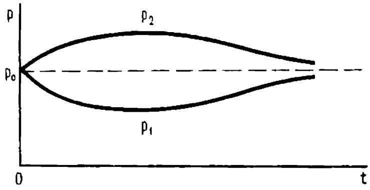


Fig. 2.15

2.16. The diffusion coefficient of the gas is

$$D = \frac{1}{3}\lambda v.$$

In the closed vessel, the mean free path remains constant* and the temperature dependence of the diffusion coefficient is determined only by the average velocity of the molecules, which is proportional to the square root of the temperature. The same relationship exists between the temperature and the diffusion coefficient:

$$D \propto T^{1/2}.$$

In the open vessel, that is, at constant pressure, the concentration of molecules is inversely proportional to the temperature and, hence, the mean free path is proportional to the temperature. Therefore, for this case we have

$$D \propto T^{3/2}.$$

On the logarithmic scale the slope of a straight line is equal to the exponent in the power function. Hence, curve (a) (with the slope equal to 3/2) corresponds to the open vessel and curve (b) (with the slope equal to 1/2) corresponds to the closed vessel.

---

* Here we have ignored the temperature dependence of the effective cross section (the Sutherland correction term).

2.17. The diffusion rate, which characterizes the variation of the number dN of molecules passing through the cross-sectional area S of the vessel per unit time dt in the direction of the concentration gradient dn/dx, is

$$\frac{dN}{dt} = -D\frac{dn}{dx}S.$$

Here $D = (1/3)\lambda v$ is the diffusion coefficient. Since the diffusion coefficient is inversely proportional to the pressure (because the mean free path is inversely proportional to the pressure) and the concentration gradient at each moment is proportional to the pressure, the number of molecules diffusing in this or that direction is pressure independent. This conclusion holds, of course, only if the mean free path of the molecules is many times smaller than the linear dimensions of the vessel. Note that since the initial number of molecules of each gas is proportional to the pressure, the evening out of the concentrations occurs the faster the lower the pressure of the gas.

2.18. The average kinetic energy of translational motion of molecules is (3/2) kT. The average energy of the molecules moving toward a wall of the vessel is $2kT$. This is explained by the fact that the flux of molecules with a certain velocity is proportional to $n_v v$, where n_v is the concentration of the molecules having this velocity. Therefore, the higher the velocity, the greater the number of molecules moving in a given direction. Hence, in the velocity distribution of the molecules remaining in the vessel there appears a deficit of fast molecules, which leads to a decrease in the average energy of the molecules and a distortion in the distribution function. On the other hand, the average energy of the molecules leaving the vessel for the vacuum becomes higher than it was in the vessel. If the pressure of the gas is not low but the orifice is so small that no collisions occur in it, the average energy inside the vessel still decreases, if only this decrease is not compensated for by heat supplied to the walls of the vessel. Under these conditions, the Maxwellian velocity distribution is restored via the collisions of molecules in the vessel, but now this distribution corresponds to a lower temperature. The restoration of the distribution function occurs partially because molecules collide with the walls of the vessel.

2.19. The heat flux is determined by the relationship

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -\lambda \frac{\mathrm{d}T}{\mathrm{d}x}.$$

For the thermal conductivity of an ideal gas we have the following formula:

$$\lambda \propto v, \quad \text{or} \quad \lambda \propto T^{1/2}.$$

For the flux to be steady-state (time independent), the following formula must hold true:

$$\lambda \frac{\mathrm{d}T}{\mathrm{d}x} = \text{const}.$$

Hence,

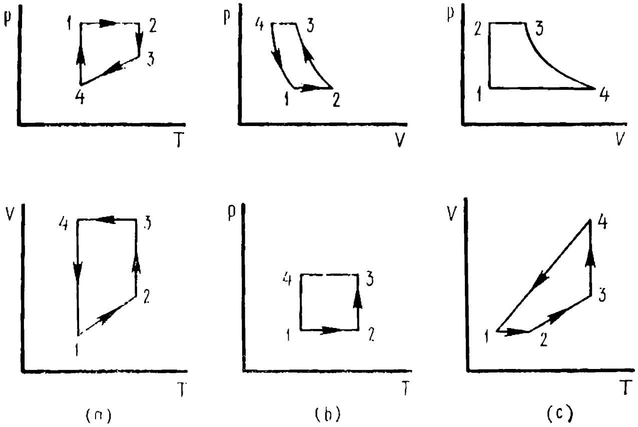
$$T^{1/2} \frac{\mathrm{d}T}{dx} = \text{const}.$$

We see that the higher the temperature the lower is the gradient. The gradient must increase from the hot plate to the cold plate. The position of the plates can be explained by the necessity of reducing convection to a minimum.

2.20. Under the specified conditions, we cannot apply the concept of temperature to the residual gas between the walls of the Dewar vessel. The mean free path of the molecules of the gas is about 100 m, so that while moving between the walls the molecules practically never collide with each other and no thermodynamic equilibrium, which could be characterized by a temperature, can establish itself between the walls.

2.21. Within a broad pressure range the thermal conductivity coefficient is independent of the gas pressure. A dependence (i.e. a drop in thermal conductivity as the pressure lowers) becomes noticeable if the mean free path of molecules becomes comparable to the distance between the walls between which the heat transfer occurs. The greater this distance, the greater the mean free path (and the lower the pressure) at which the thermal conductivity coefficient begins to change. Therefore, curve *1* corresponds to the greater distance (see the figure accompanying the problem).

2.22. Section *1-2* in Figure (a) accompanying the problem corresponds to isobaric heating, section *2-3* to



(a) (b) (c)

Fig. 2.22

isothermal expansion, section *3-4* to isochoric cooling, and section *4-1* to isothermal compression. In the pT- and VT-coordinates this process is depicted in Figure (a) accompanying the answer. The processes depicted in Figure (b) accompanying the problem proceed in the following order: *1-2* is isobaric heating, *2-3* isothermal compression, *3-4* isobaric cooling, and *4-1* isothermal expansion. In the pV- and pT-coordinates this cycle is depicted in Figure (b) accompanying the answer. The cycle depicted in Figure (c) accompanying the problem consists of isochoric heating *1-2*, isobaric heating *2-3*, isothermal expansion *3-4*, and isobaric cooling *4-1*. In the pV- and VT-coordinates this cycle is depicted in Figure (c) accompanying the answer.

2.23. When the piston moves upward by Δx, the spring is compressed by Δh. Suppose $F = -k\Delta h$ is the elastic force produced in the spring by this compression. This force contributes to the force acting on the piston and, hence, increases the pressure of the gas in the cylinder by

$$\Delta p = \frac{|F|}{S} = \frac{k\,\Delta h}{S} = \frac{k\,\Delta V}{S^2},$$

where S is the surface area of the piston. Thus, the increase of the gas volume caused by heating is accompanied by a proportional increase in the pressure. On the diagram this is depicted by a straight line with a positive slope whose value depends on the surface area of the piston and the elastic properties of the spring. The work is measured by the hatched area in the figure accompanying the answer and is

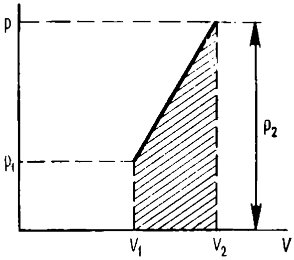


Fig. 2.23

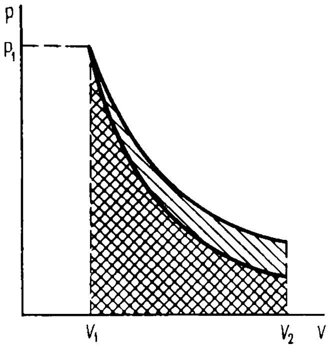


Fig. 2.25

$$A = (p_1 + p_2)(V_2 - V_1)/2.$$

2.24. The adiabatic p-V relation is of the form

$$pV^{\gamma} = \text{const},$$

where the exponent γ is the ratio of the specific heat capacity of the gas at constant pressure to the specific heat capacity of the gas at constant volume:

$$\gamma = c_p/c_V.$$

This ratio can be expressed in terms of the number of degrees of freedom, i. A helium molecule has three degrees of freedom and that of carbon dioxide has six. Therefore, for helium we have $\gamma = 5/3 = 1.67$ and for carbon dioxide we have $\gamma = 8/6 = 1.33$. The greater the exponent, the steeper is the curve. The upper curve (see the figure accompanying the problem) corresponds to carbon dioxide and the lower curve corresponds to helium.

2.25. An adiabatic curve is steeper than an isotherm (see the figure accompanying the answer), with the final pressure being lower in the adiabatic process than that in the isothermal process. This means that the area lying below the appropriate curve (this area characterizes the work) is smaller for the adiabatic process than for the isothermal.

2.26. The first law of thermodynamics for an isothermal process can be written in the form $Q = A$. Hence, the straight line corresponding to this process must be inclined at an angle of 45° to the horizontal axis (curve *3* in the figure accompanying the problem). For an isobaric process we have

$$Q = \Delta U + A.$$

Since the work for one mole of the gas done in an isobaric process is

$$A = R\Delta T$$

and the amount of the absorbed heat is

$$Q = C_p \Delta t = \frac{i+2}{2} R\Delta T,$$

with i the number of degrees of freedom, we have

$$\frac{A}{Q} = \frac{2}{i+2}.$$

The slope of the straight line representing the A vs. Q dependence must equal 2/5 for a monatomic gas, 2/7 for a diatomic gas, and 2/8 for a multiatomic gas. Straight line *1* corresponds to a multiatomic gas and straight line *2* to a monatomic gas. Work is not performed in an isochoric process, and this coincides with the horizontal axis, while heat is not absorbed in an adiabatic process, and this coincides with the vertical axis.

2.27. Processes depicted by straight lines coinciding with the coordinate axes are quite obvious. The horizontal axis ($\Delta T = 0$) represents an isothermal process and the vertical axis ($Q = 0$) represents an adiabatic process. The molar heat capacity of a monatomic gas involved in an isochoric process is

$$C_V = (3/2)\,R,$$

and that of a diatomic gas is

$$C_V = (5/2)\,R.$$

The molar heat capacity of a monatomic gas involved in an isobaric process is

$$C_p = (5/2)\,R,$$

and that of a diatomic gas is

$$C_p = (7/2)\,R.$$

The heat capacity C_V of a diatomic gas coincides with the heat capacity C_p of a monatomic gas. For this reason there are three straight lines in the figure accompanying the problem instead of four, with straight line *2* corresponding to C_p of a monatomic gas and C_V of a diatomic gas. Straight line *3* corresponds to an isobaric process involving a diatomic gas and straight line *1* corresponds to an isochoric process involving a monatomic gas.

2.28. For the sake of brevity we denote $(m/M)\,R$ by a. Then

$$pV = aT.$$

For both gases the work performed in an isobaric process is

$$A = p\,(V_2 - V_1) = a\Delta T,$$

while that performed in an adiabatic process is

$$A = \frac{p_1A_1 - p_2V_2}{\gamma - 1} = a\,\frac{T_1 - T_2}{\gamma - 1} = a\,\frac{|\Delta T|}{\gamma - 1}.$$

Substituting the values of γ for nitrogen (7/5) and argon (5/3), we get

$$A = 2.5 \mid \Delta T \mid \quad \text{(for nitrogen)},$$

$$A = 1.5 \mid \Delta T \mid \quad \text{(for argon)}.$$

Selecting the scales on the coordinate axes of the figure accompanying the problem in such a manner that $a = 1$, we find the slopes of the straight lines to be 2.5 and 1.5 for the adiabatic processes and 1 for the isobaric process. The straight line *1* depicts the adiabatic process involving nitrogen, the straight line *2* depicts the adiabatic process involving argon, and the straight line *3* depicts the isobaric process for both gases. The vertical axis ($\mid \Delta T \mid = 0$) depicts an isotherm and the horizontal axis ($A = 0$) an isochor.

2.29. The classical theory of heat capacity does not allow for the quantum nature of periodic motion (vibrational and rotational). According to quantum theory, the angular momentum of a rotating object may assume only values specified by the condition

$$J\omega = \hbar\sqrt{j(j+1)}, \qquad (2.29.1)$$

where $\hbar$ is the Dirac-Planck constant (the Planck constant h divided by 2π), J is the moment of inertia of the object, and j is the so-called rotational quantum number, which can take on any integral values starting from zero. Equation (2.29.1) enables finding the possible values of the rotational kinetic energy:

$$W = \frac{J\omega^2}{2} = \frac{\hbar^2}{2J} j(j+1).$$

The minimal nonzero value is

$$W_m = \hbar^2/J.$$

A molecule acquires and exchanges rotational energy through collisions with other molecules. Thus, the question of whether a molecule can have rotational energy in addition to translational is solved by comparing the value W_m of the minimal nonzero rotational energy with a quantity of the order of kT at room temperature. The separation of atoms in a hydrogen molecule is 0.74 nm and the mass of each atom is 1.67×10^{-27} kg, so that the moment of inertia of a hydrogen molecule is 4.6 ×

10^{-48} kg·m^2. Bearing in mind that $\hbar = 1.05 \times 10^{-34}$ J·s, we get

$$W_m = 2.4 \times 10^{-21} \text{ J}.$$

At room temperature ($T \approx 300$ K),

$$kT = 4.1 \times 10^{-21} \text{ J}.$$

The fact that kT somewhat exceeds W_m makes the occurrence of rotational motion in a molecule quite probable. Hence, the rotational degrees of freedom will contribute to the heat capacity of hydrogen. At temperatures of the order of 40 K the probability of rotational motion is practically nil; it is said that the rotational degrees of freedom "freeze out" and only the translational degrees of freedom remain, which is reflected in the value of the heat capacity. The diatomic gas that is closest to hydrogen in the Periodic Table is nitrogen, and the mass of a nitrogen atom is fourteen times the mass of a hydrogen atom. The separation of the atoms in a nitrogen atom is 0.11 nm. Accordingly, the moment of inertia of a nitrogen molecule is thirty one times that of a hydrogen molecule, so that down to very low temperatures the value of kT is considerably higher than W_m and there is practically no "freezing out" of rotational degrees of freedom. At the same time, for monatomic gases, whose moment of inertia is several orders of magnitude lower than that of hydrogen, the minimal energy of rotational motion is so high that even at very high temperatures only the translational degrees of freedom manifest themselves and the heat capacity follows the predictions of classical theory quite accurately.

2.30. According to classical theory of heat capacity of ideal gases, the value of heat capacity for each given process (say, an isochoric process) must not depend on the temperature of the gas. This theory does not allow for the quantum nature of periodic processes, namely, rotational and vibrational motion. In classical theory, the probability of rotational motion of diatomic and multiatomic molecules is assumed to be independent of the temperature of the gas and the same (per each degree of freedom) as that of translational motion. Quantum theory requires allowing for the different probabilities of periodic processes, with the probability growing with temperature. Calculations have shown that for many diatomic gases at low temperatures the vibrational degrees of freedom can be ignored, but the role of these degrees of freedom grows with temperature. For sufficiently high temperature the bonds between the atoms may break and dissociation occurs. This requires large energy expenditure. In some respects this process resembles phase transitions (melting and boiling, for instance), when supplying heat does not lead to a rise in temperature.

2.31. The compressibility is defined by the following formula:

$$\beta = -\frac{1}{V}\frac{dV}{dp}.$$

In an isothermal process,

$$d(pV) = p dV + V dp$$

and, hence, $\beta = 1/p$. In an adiabatic process,

$$\gamma p V^{\gamma-1} dV + V^{\gamma} dp = 0$$

and, hence, $\beta = 1/\gamma p$.

In all cases the dependence of the compressibility on pressure is depicted by hyperbolas that differ only in a numerical factor. On the log-log scale the pressure dependence of the compressibility is depicted by straight lines (in the figure accompanying the answer the straight lines correspond to adiabatic processes involving argon and carbon dioxide and to the isothermal process).

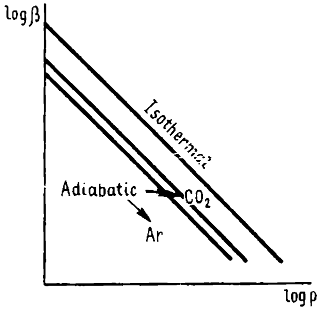


Fig. 2.31

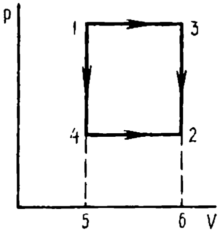


Fig. 2.32

2.32. In the figure accompanying the answer the processes are depicted by broken lines *1-3-2* and *1-4-2*. In the first case, the work is measured by the area bounded by the broken line *5-4-2-6*, while in the second it is measured by the area bounded by the broken line *5-1-3-6* and exceeds the first area by the area of *4-1-3-2-4*. Since in both cases the initial states (1) and the final states (2) are the same, the increment of internal energy is the same, too, but the process *1-3-2* requires additional heat for the system to perform greater work. Since entropy is a function of state, the change of entropy in both cases is the same.

2.33. The three quantities characterizing the state of an ideal gas, p, V, and T, are linked through power relationships for all processes involving an ideal gas:

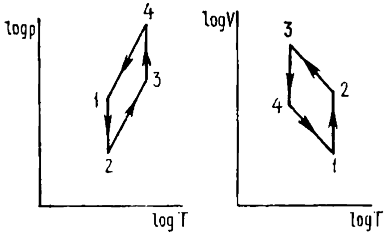
$$V/T = \text{const} \quad \text{(isobaric process)},$$

$$p/T = \text{const} \quad \text{(isochoric process)},$$

$$pV = \text{const} \quad \text{(isothermal process)},$$

$$\left.\begin{aligned} pV^{\gamma} &= \text{const} \\ VT^{1/(\gamma-1)} &= \text{const} \\ p/T^{\gamma/(\gamma-1)} &= \text{const} \end{aligned}\right\} \quad \text{(adiabatic process)}.$$

On the log-log scale all these processes are depicted by straight lines that differ in their slopes. Isothermal expansion is depicted by a vertical straight line in the downward direction in the pT-coordinates and in the upward direction in the VT-coordinates. An adiabatic process is depicted by a straight line with a slope $\gamma/(\gamma - 1)$ in the pV-coordinates and by a straight line with a negative slope $-(\gamma - 1)^{-1}$ in the VT-coordinates. A collection of such straight segments can be used to depict the Carnot cycle in the pT-coordinates (Figure (a)) and in the VT-coordinates (Figure (b)).



(a) (b)

Fig. 2.33

2.34. The increment of the entropy in a process is given by the formula

$$\Delta S = \Delta Q/T.$$

The straight line *0-1* in the figure accompanying the problem corresponds to an isothermal process, since it is parallel to the vertical axis (T = const). The straight line *0-4* depicts a process in which the entropy does not change, that is, a process in which no heat is supplied to or removed from the system, or an adiabatic process. Out of curves *0-2* and *0-3* the former corresponds to a higher entropy increment. The process represented by this curve will require a larger amount of heat for bringing the system to a given temperature than the process represented by curve *0-3* will require for bringing the system to the same temperature. Of two processes, the isochoric and the isobaric, the latter requires more heat to perform work on the system. Thus, curve *0-2* corresponds to an isobaric process and curve *0-3*, to an isochoric.

2.35. The first process in the Carnot cycle is isothermal expansion. In the process the gas absorbs heat and its entropy increases. On the diagram this process is shown by the straight line *1-2*. This is followed by adiabatic expansion, which is accompanied by a drop in temperature. Since in an adiabatic process the gas is thermally isolated, the entropy cannot change, which is represented by the straight line *2-3*. At the temperature achieved at the end of this process the third process begins, namely, isothermal compression, in which the gas gives off heat and its energy decreases (the straight line *3-4*). The final process is adiabatic compression, which returns the gas to the initial state. The entropy does not change in this last process, just as in adiabatic expansion. The process is depicted by the straight line *4-1*.

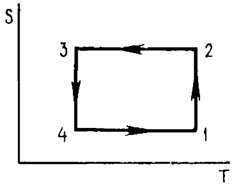


Fig. 2.35

2.36. If m is the mass of each object and c is the specific heat capacity, then the total entropy increment is

$$\Delta S = \int_{T_1}^{T_2} \frac{dQ}{T} + \int_{T_2}^{T_1} \frac{dQ}{T} = cm\left(\ln\frac{T}{T_1} + \ln\frac{T}{T_2}\right).$$

Replacing T with $(T_1 + T_2)/2$, we can write

$$\Delta S = cm \ln\frac{(T_1+T_2)^2}{4T_1T_2},$$

or

$$\Delta S = \Delta S_1 + \Delta S_2 = cm \ln \left[\frac{(T_1 - T_2)^2}{4T_1T_2} + 1 \right].$$

The expression in square brackets is greater than unity, with the result that

$$\Delta S > 0.$$

2.37. The entropy increment in the process is

$$\Delta S = \Delta Q/T = c\Delta T/T. \qquad (2.37.1)$$

According to the figure accompanying the problem,

$$\mathrm{d}S = a\,\mathrm{d}T. \qquad (2.37.2)$$

The straight line in the figure passes through the origin since by the Nernst heat theorem the entropy at $T = 0$ is zero. Combining these two equations, we get

$$a\,\mathrm{d}T = c\,\mathrm{d}T/T \quad \text{and} \quad c = aT.$$

The heat capacity changes in proportion to the temperature, just as entropy does.

This result can be obtained without carrying out calculations, solely on dimensional grounds. Entropy (irrespective of whether we are speaking of the entropy of the system or the molar entropy or the specific entropy) has the same dimensionality as heat capacity (irrespective of whether we are speaking of the heat capacity of the system or the molar heat capacity or the specific heat capacity). For this reason the dependence of heat capacity on temperature must be the same, to within a constant factor, as the dependence of entropy on temperature. In the case at hand the constant factors coincide, too.

2.38. The entropy increments on different segments are

$$\Delta S_{1\text{-}2} = c_p \int_{T_1}^{T_2} \frac{\mathrm{d}T}{T} = c_p \ln \frac{T_2}{T_1} = c_p \ln \frac{V_2}{V_1},$$

$$\Delta S_{1\text{-}3} = c_V \int_{T_1}^{T_3} \frac{\mathrm{d}T}{T} = c_V \ln \frac{T_3}{T_1} = -c_V \ln \frac{p_1}{p_3} = -\ln \frac{p_2}{p_4},$$

$$\Delta S_{3\text{-}4} = c_p \int_{T_3}^{T_4} \frac{\mathrm{d}T}{T} = c_p \ln \frac{T_4}{T_3} = c_p \ln \frac{V_4}{V_3} = c_p \ln \frac{V_2}{V_1},$$

$$\Delta S_{4\text{-}2} = c_V \int_{T_4}^{T_2} \frac{\mathrm{d}T}{T} = c_V \ln \frac{T_2}{T_4} = c_V \ln \frac{p_2}{p_4}.$$

If we add all four quantities, we get

$$\Delta S_{1\text{-}3\text{-}4\text{-}2} = \Delta S_{1\text{-}3} + \Delta S_{3\text{-}4} + \Delta S_{4\text{-}2} = c_p \ln \frac{V_2}{V_1} = \Delta S_{1\text{-}2},$$

which is what we set out to prove.

2.39. For the sake of making the calculations shorter, let us select the mass in such a manner that in the appropriate system of units $(m/M)\ R = 1$. In this case the temperature of the heater, which is the highest temperature in the cycle (point c) is

$$T_{\text{h}} = p_2 V_2.$$

The temperature of the cooler (the coldest point in the cycle is point a) is

$$T_{\text{c}} = p_1 V_1.$$

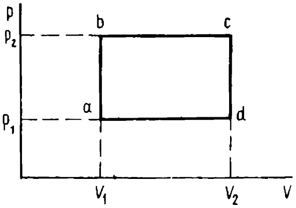


Fig. 2.39

The temperatures at points b and d are p_2V_1 and p_1V_2, respectively. The entropy increment for the heater in the a-b process is

$$\Delta S_{a\text{-}b} = -\frac{c_V V_1 (p_2 - p_1)}{p_2 V_2},$$

and in the b-c process it is

$$\Delta S_{b\text{-}c} = -\frac{c_p p_2 (V_2 - V_1)}{p_2 V_2}.$$

The entropy increment for the cooler in the c-d process is

$$\Delta S_{c\text{-}d} = +\frac{c_V V_2 (p_2 - p_1)}{p_1 V_1},$$

and in the d-a process it is

$$\Delta S_{d\text{-}a} = +\frac{c_p p_1 (V_2 - V_1)}{p_1 V_1}.$$

Adding all these entropy increments and carrying out the necessary transformations, we get

$$\Delta S = c_V (p_2 - p_1) \left[\frac{V_2}{p_1 V_1} - \frac{V_1}{p_2 V_2} \right] + c_p (V_2 - V_1) \left(\frac{1}{V_1} - \frac{1}{V_2} \right).$$

All the differences in the brackets are positive, and hence

$$\Delta S > 0.$$

The entropy increment for a gas performing a cycle and returning as a result to the initial state is equal to zero.

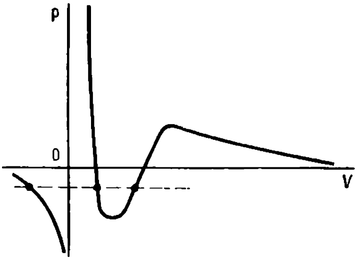


Fig. 2.40

2.40. If we solve the van der Waals equation for p, we get

$$p = \frac{m}{M}\,\frac{RT}{(V-b)} - \frac{a}{V^2}.$$

This equation is of a hyperbolic nature, and because of this it must have a branch in the third quadrant, which contains, at a sufficiently low temperature and a negative pressure, the third root. Since this root corresponds to a negative volume, it has no physical meaning and is usually not depicted on diagrams. Note that Boyle's law also contains an "extra" root. It also lies in the third quadrant and for this reason has no physical meaning and is usually not depicted on diagrams.

2.41. The van der Waals equation presupposes complete homogeneity of the substance (vapor or liquid), that is, the same density in all (however small) volumes. In real media, however, there are fluctuations. Suppose we are considering state *2* on the curve (see the figure accompanying the problem). The parameters of this state (or point) determine the average values of the concentration and energy of the molecules. In small volumes the values of the concentration are somewhat larger or smaller than the average value because of the randomness of molecular motion. The same is true of the energy of molecules in small volumes. In accordance with the isotherm, in volumes of higher density the pressure is somewhat lower than the average, while in volumes of lower density the pressure is somewhat higher. Therefore, in the former the density continues to rise and in the latter, to drop. As a result the entire substance separates into two phases with a higher and a lower density, and the pressure in both is the same. The greater density is that of the liquid and the lower is that of the saturated vapor of this liquid.

2.42. Section *2-3* corresponds to supersaturated vapor. For this state to realize itself, there must be no dust, ions, or aerosols in the space where this state occurs for the vapor to condense on and form drops of liquid. Section *6-5* corresponds to the so-called superheated liquid. This state can be arrived at if we boil and degasify the liquid prior to heating it, then heat it in such a way so that it fills the entire volume of the vessel, and finally cool it again. The liquid will find itself under a pressure that is lower than that of the saturated vapor. Especially interesting is the state of a liquid corresponding to the section of the isotherm lying below the horizontal axis (see the figure accompanying Problem 2.40). This state corresponds to uniform stretching of the liquid. The state can be achieved by repeating, say, Torricelli's experiment in modern vacuum conditions. Before filling the tube with mercury, all gases must be evacuated from the tube via prolonged heating and the mercury must be pumped into the tube under a vacuum. In this case there is no Torricellian vacuum above the mercury when we turn the tube over, the mercury sticks to the inner surface of the tube thanks to molecular adhesion, and the part of it lying above the level corresponding to atmospheric pressure will be under negative pressure (see the figure accompanying the answer). Thus, it is possible to obtain negative pressure (uniform stretching) of the order of three atmospheres.

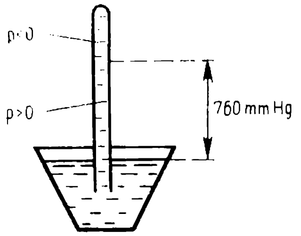


Fig. 2.42

2.43. We use the reductio ad absurdum proof. In Figures (a) and (b) accompanying the answer we have two variants that differ from the variant shown in the figure accompanying the problem. In each of these variants the arrows show a cyclic isothermal process. As a result of each of these processes, useful work is done (the amount of this work is equal to the hatched area) with an efficiency of 100% thanks to complete utilization of the heat received from the heater, which of course contradicts the second law of thermodynamics and, hence, is impossible. If we assume that the hatched areas in the figure accompanying the problem are the same, the works done along the paths *2-4-6* and *2-3-4-5-6* are equal. But doesn't this contradict the second law of thermodynamics, that is, can a cyclic process along the path *2-4-3-2* be performed? One must bear in mind that while points *2* and *6* correspond to a single (i.e. the same for both curves) one-phase state, point *4* corresponds to two different states, a one-phase state on the theoretical curve and a two-phase state on the experimental curve. The entropies of these two states are different, and so are the internal energies of these states, energies related to the interaction between the molecules.

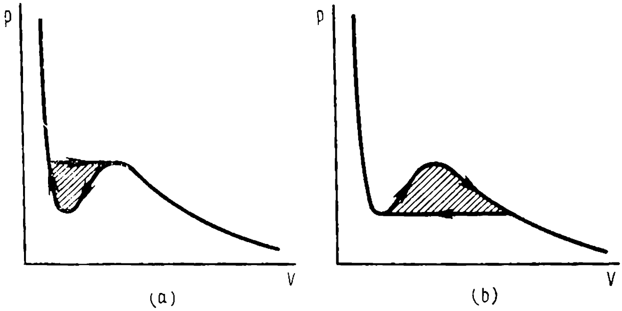


Fig. 2.43

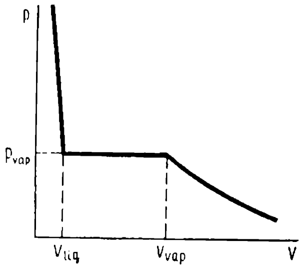


Fig. 2.44

2.44. Suppose that under the piston there is a liquid and its saturated vapor, whose pressure is counterbalanced by the external pressure. If heat is supplied to the liquid isothermally, the liquid evaporates and the piston rises. The work done by the vapor when the vapor increases its volume by ΔV is given by the formula

$$A = p_{\text{vap}} \Delta V,$$

where p_{vap} is the pressure of the saturated vapor. If at the beginning there is only liquid whose volume is V_{liq}

and at the end only vapor whose volume is V_{vap}, the entire work done during evaporation is

$$A = p_{\text{vap}}(V_{\text{vap}} - V_{\text{liq}}).$$

This work is measured by the area bounded by the horizontal section of the isotherm, the horizontal axis, and the segments from 0 to p_{vap} at V_{liq} and V_{vap}.

2.45. As the pressure is raised from the atmospheric to the test pressure, a liquid or gas accumulates energy, which is equal to the hatched area under the curve. If the cylinder or pipe fails, only a small fraction of the energy is liberated by the liquid (Figure (a)) because of the small compressibilities of liquids, and the pressure falls to the atmospheric practically immediately. In the case of a gas the accumulated energy may be extremely high (Figure (b)) and the consequences of its liberation may be catastrophic.

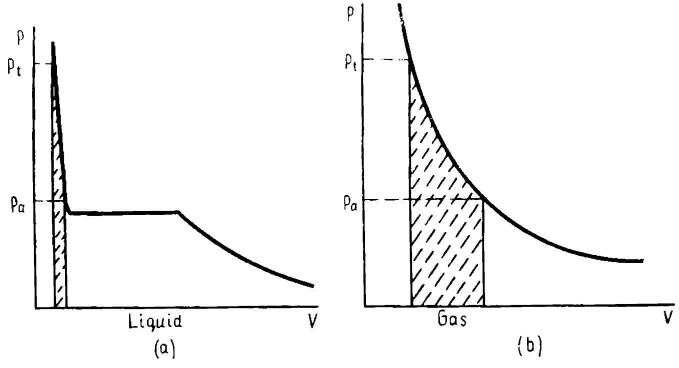


Fig. 2.45

2.46. When a liquid is heated, its density drops, so that the volume it occupies may increase notwithstanding evaporation. The decrease in the density of the liquid and the simultaneous increase in the density of the vapor lead to a drop in surface tension. As a result the meniscus becomes flatter and at the critical point disappears completely. Of special interest is the phenomenon of critical opalescence, discovered by T. Andrews in 1869, which consists in the medium becoming suddenly "cloudy" at the critical state. This phenomenon serves as a vivid illustration of fluctuation effects. Extremely small fluctuations in the density of the medium, fluctuations that are due to the random movements of molecules, lead to a situation in which the density in some microscopic volumes becomes, at certain moments, somewhat higher than the one corresponding to the critical point, and these volumes transform into the liquid, while the neighboring volumes remain being a gas (the ones with the lower density). In subsequent moments this situation may change. In this sense the entire volume filled with the fluid consists of constantly changing liquid-gas interfaces on which the light is scattered.

2.47. When a liquid is evaporating, energy is constantly required for performing work against external forces (the external heat of evaporation) and against the forces of cohesion between the molecules (the internal heat of evaporation). When a liquid is evaporating adiabatically, the energy necessary for evaporation is taken away from the internal energy, whence the liquid cools off. This decrease in internal energy may be so great that the remaining liquid may transform into the solid state. Even if the heat insulation is not perfect, cooling may still be considerable. This property, for one thing, is employed in some types of commercial and house refrigerators.

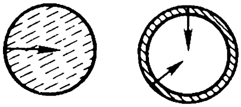


Fig. 2.48

2.48. A drop has only one spherical surface while a bubble has two, the inner and the outer, whose curvatures are almost the same in magnitude but opposite in sign. For this reason the two surfaces of a bubble create excess pressure directed toward the center of the bubble. Thus, the excess inner pressure in a bubble is approximately twice as large as in a drop (of the same radius).

2.49. The excess pressure inside a bubble is determined by the formula

$$\Delta p = 4\sigma/r,$$

where r is the radius of the bubble, and σ is the surface tension. Because of this the pressure inside the smaller bubble is greater and the bubble contracts, while the larger bubble grows. Equilibrium is attained when the film of the smaller bubble forms a surface near the outlet of the pipe with a curvature radius that coincides with the one of the larger bubble.

2.50. The vapor pressure above the convex surface of a liquid is higher than that above the flat surface, with the corresponding difference being the greater the smaller the curvature radius of the surface.* Hence, for the smaller drop (Figure (c)) the vapor is unsaturated, while for the greater drop (Figure (a)) the vapor is supersaturated. Drop (a) evaporates, while drop (c) grows. The equilibrium of drop (b) is unstable, since if the size somewhat decreases, the drop begins to evaporate, while if the size increases, the drop grows.

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* The excess pressure is determined via the Thomson formula

$$\Delta p = \frac{p_{\text{vap}} M \sigma}{RT\rho r},$$

where p_{vap} is the vapor pressure above the surface, M the molecular mass (weight), R the universal gas constant, T the temperature, σ the surface tension of the liquid, ρ the density of the liquid, and r the curvature radius of the surface.

2.51. The curvature of the surface of a liquid creates an excess pressure (known as Laplace pressure) directed toward the center of curvature. This pressure is the higher the smaller the radius of curvature of the surface. In the case of water, the excess pressure (negative) tends to stretch the drop, while in the case of mercury it tends to compress the drop. For this reason, the plates with the drop of water between them are under forces that bring them together ("attractive forces"), while the plates with mercury between them tend to move apart ("repulsive forces").

2.52. The excess Laplace pressure, caused by the curvature of the liquid surface, is directed toward the center of curvature of the surface and is inversely proportional to the radius of curvature. For this reason, the drop of water is under a negative pressure (that in absolute value is greater than the pressure acting on the mercury drop) in the narrow part of the pipe and this pressure is directed toward the tapered end, with the result that the drop tends to move toward the tapered end. In the case of mercury, the pressure is directed in opposition, that is, toward the wide end of the pipe, and it is in this direction that the drop tends to move.

2.53. Surface tension (the surface tension coefficient) is defined as the ratio of the free energy of the surface layer of the liquid to the area of this surface. The free energy here is understood to be the energy that can be converted into work. This energy is determined by the interaction of the molecules of the surface layer with the other molecules, where the interaction with the molecules of the vapor above the surface is usually ignored. As the temperature is increased, the interaction of the molecules of the surface layer with the molecules in the bulk of the liquid weakens and that of the surface layer molecules with the vapor molecules grows. At the critical temperature both interactions become equal, the interface between liquid and vapor disappears, and so does surface tension. Thus, it is curve *2* that reflects the correct temperature dependence of the surface tension coefficient.

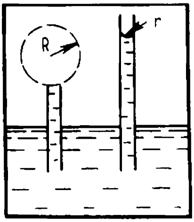

Fig. 2.54

2.54. If we assume that the water wets the wall of the tube in an ideal manner, then, if the tube is sufficiently high ($h > h_0$), and the diameter of the tube is small, the radius of the meniscus is equal to that of the tube. If $h < h_0$, the water will rise in the tube and reach the upper end. After this the curvature of the meniscus will decrease until it reaches a value that satisfies the equation

$$h = \frac{2\sigma}{\rho g R},$$

where R is now not the radius of the tube but the radius of curvature of the meniscus, $r < R$.

2.55. Although the cross-sectional area of all four pipes of diameter $D/2$ each is equal to that of one pipe of radius D, the volume flow through these pipes is lower. This follows from Poiseuille's law

$$Q = \frac{\pi \Delta p D^4}{128 \eta l}.$$

Thus, the volume flow through each of the four pipes of $D/2$ diameter is lower than that through the big pipe not by a factor of four but by a factor of 16 (at the same pressure head), with the result that the total volume flow through the four pipes will be one-fourth of the flow through the big pipe.

2.56. The transverse distribution of velocities in the flow of a viscous liquid in a horizontal pipe is determined

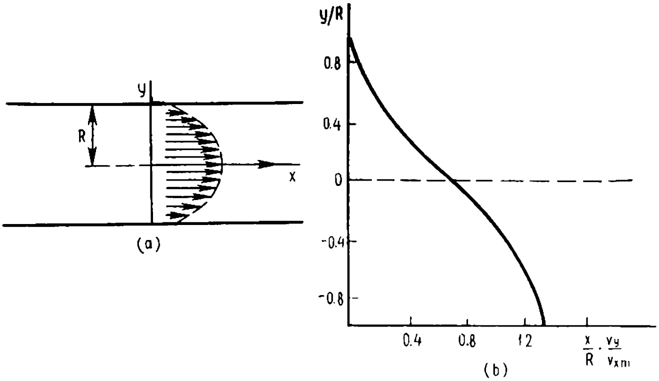

Fig. 2.56

via the formula (Figure (a))

$$v_x = v_{xm}\left[1-\left(\frac{y}{R}\right)^2\right].$$

The radial coordinate y is reckoned from the pipe's axis. The time it takes the particle to fall from the wall to a point whose ordinate is y is

$$t = (R - y)/v_y.$$

In the course of this fall the particle will be shifted in the horizontal direction over a distance

$$x = \int_R^y v_x\,\mathrm{d}t = -\frac{v_{xm}}{v_y}\int_R^y\left[1-\left(\frac{y}{R}\right)^2\right]\mathrm{d}y$$

$$= \frac{v_{xm}}{v_y}\left[\frac{2}{3}-\frac{y}{R}+\frac{1}{3}\left(\frac{y}{R}\right)^3\right]R.$$

At the lowest possible point ($y = -R$) we have

$$x = \frac{4}{3}\,\frac{v_{xm}}{v_y}\,R = \frac{2}{3}\,\frac{v_{xm}}{v_y}\,D.$$

The shape of the particle's trajectory in Figure (b) is represented in dimensionless coordinates, y/R and $(x/R) \times (v_y/v_{xm})$.

2.57. Each figure accompanying the problem contains the initial segments of the graphs representing the cooling of water or the heating of ice. Continuing these graphs, we arrive at the intersection point in each figure. If the point of intersection lies above the horizontal line corresponding to a temperature of 0 °C, the final temperature is positive, when the point lies below this line, the final temperature is negative. If the graphs meet on the line $t = 0$ °C, the final temperature is 0 °C and the amount of the phase that has a horizontal section on the graph prior to intersection will decrease. The ratio of the length of this section to the total length of the horizontal section corresponding to this phase determines the fraction of the initial mass of this phase that has transformed into the other phase. When analyzing the graphs, we must bear in mind that the slopes of the straight lines are determined by the mass of water or ice and their specific heat capacity by the formula

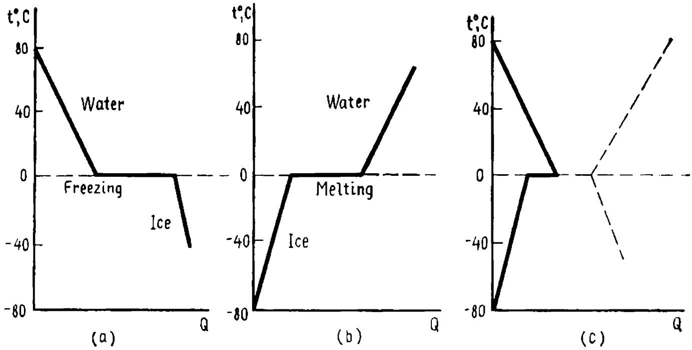

Fig. 2.57

$$\frac{\Delta t}{\Delta Q} = \frac{1}{cm}.$$

Here one must bear in mind that the specific heat capacity of water is twice as high as that of ice. The length of the horizontal sections corresponding to the water freezing or the ice melting is determined by the fact that the amount of heat required for melting a certain amount of ice is equal to the amount of heat required for heating the same mass of water to 80 °C. For the sake of illustration, Figure (a) accompanying the answer shows the diagram for the cooling off of a mass of water from 80 to 0 °C, then the freezing of this water, and finally the cooling off of the ice down to $t = -40$ °C. Figure (b) accompanying the answer shows the reverse process in which the same amount of ice is heated from —80 to 0 °C, then melted, and finally heated in the form of water to 60 °C. The scales along the horizontal axes are arbitrary but equal, with the amount of heat expressed in arbitrary units. (It is easy to see that all this has no effect on the answer.) The two diagrams are combined in Figure (c) accompanying the answer. In the present case we see that the final temperature is 0 °C and half of the ice has melted. Applying this procedure to the case illustrated by Figure (a) accompanying the problem, we see that the ice has completely melted and the final temperature is 10 °C; for Figure (b) accompanying the problem, half of the ice has melted and the final temperature is 0 °C; for Figure (c) accompanying the problem, the case is similar to (b) but half of the water has frozen; finally, for Figure (d), all the water has frozen and the final temperature is —20 °C.

2.58. At the lowest possible pressures and the highest possible temperatures a substance may exist only in the vapor state (region *1*). Compressing the vapor at relatively high temperatures, we can transform it into the liquid state provided that the temperature is below the critical. The curve separating region *1* from region *2* corresponds to pressures and temperatures at which the liquid is in equilibrium with the saturated vapor of this liquid, with the region *2* corresponding to the liquid. T_{cr} on the temperature axis stands for the critical temperature. By cooling the liquid, we arrive at temperatures at which there is equilibrium between the liquid and the solid phase—this corresponds to region *3*. At low pressures there can be equilibrium between the vapor and the solid, but there is only one value of temperature and pressure at which equilibrium can exist between all three phases. This is the so-called triple point, and it is at this point that all three curves meet.

2.59. As distinct from the majority of substances, the ice-water system has an equilibrium curve with a negative slope. In view of this, higher pressures correspond to a lower temperature at which ice and water are in equilibrium. If ice was under an external pressure p_1 at a certain temperature and then this pressure was increased to p_3, then at a certain pressure p_2, whose value lies on the phase equilibrium curve, the ice will melt. The anomalous dependence of the melting point of ice on pressure is linked with the anomalous relation between the densities of water and ice. As a rule, the density of the solid phase is higher than that of the liquid, but for water the situation is the opposite: the density of ice is lower than that of water. This property is extremely important for the preservation of life in ponds, lakes, and rivers. If the density of water were lower than that of ice, all ponds, lakes and rivers would freeze solid.

2.60. Compressibility is defined thus:

$$\beta = -\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}p},$$

whence $\mathrm{d}V/V = -\beta\,\mathrm{d}p$. Hence,

$$\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = -\int_{p_1}^{p_2} \beta\,\mathrm{d}p.$$

Integration yields

$$\ln (V_1/V_2) = \int_{p_1}^{p_2} \beta\,\mathrm{d}p.$$

The integral on the right-hand side gives the area bounded by the curve, the horizontal axis, and the vertical straight lines at p_1 and p_2. After evaluating this integral, we turn to the volume ratio. If the compressibility were pressure independent, the volume ratio would be

$$V_1/V_2 = \exp\,[\beta\,(p_2 - p_1)].$$

2.61. At a maximum point the derivative $\mathrm{d}\rho/\mathrm{d}t$ is zero. For this reason near a maximum the deviations in the density from the maximum value for small deviations in the precision with which the temperature is measured are at a minimum, with the result that in the neighborhood of the maximum the precision with which density is determined is the highest.

2.62. As is known, the heat flux is determined by the equation

$$\frac{dQ}{dt} = -\lambda \frac{dT}{dx} S.$$

Assuming that the heat flux is steady-state and, hence, dQ/dt is the same at all points of the wall, we find that where the absolute value of the gradient dT/dx is greater, the respective thermal conductivity coefficient is smaller. Hence, the inner layer of the wall has a higher thermal conductivity.

2.63. To elongate the rod by Δl, we must apply, according to Hooke's law, the force

$$F = \frac{ES}{l} \Delta l. \qquad (2.63.1)$$

The work of elongation performed from x to $x + \Delta x$ is

$$dA = F\,dx = \frac{ES}{l} x\,dx,$$

and the work performed from 0 to Δl is

$$A = \frac{ES}{2l} (\Delta l)^2.$$

Multiplying the numerator and denominator by l and introducing the notation

$$\Delta l/l = \varepsilon$$

(the strain, or extension per unit length), we get

$$A = \frac{ESl}{2} \varepsilon^2.$$

The performed work goes to increasing the internal energy of the rod, that is, the energy of elastic deformation. Dividing this energy by the volume of the rod, we get the bulk energy density

$$w = E\varepsilon^2/2.$$

From (2.63.1) it follows that

$$E\varepsilon = F/S = \sigma,$$

where σ is the internal mechanical stress. For this reason, the bulk energy density can be represented as

$$w = \sigma\varepsilon/2.$$

2.64. For each bar the thermal linear strain is

$$\Delta l/l = \alpha \Delta T,$$

while the mechanical linear strain is

$$\Delta l/l = -\sigma/E,$$

where σ is the internal mechanical normal stress (Young's modulus), which is the same for both bars. The sum of the two strains is zero:

$$\alpha \Delta T - \sigma/E = 0.$$

Hence, $\alpha E = \sigma/\Delta T$. Since the right-hand side is the same for both bars, we can write $\alpha_1 E_1 = \alpha_2 E_2$, or

$$\alpha_1/\alpha_2 = E_2/E_1.$$

If the walls possess the same mechanical properties, the deformability of the walls has no effect on the result.