

1 INTRODUCTION

This booklet follows the structure of the study guide “Mechanics”. Some thermodynamical concepts are inherently rather complex; meanwhile, understanding all the details of that complexity are not necessary for a successful solving of Olympiad problems. Because of that, the material is divided into two categories: (a) basic topics, learning of which is sufficient for solving a majority of the Olympiad problems, and (b) an advanced material, which is primarily aimed for deepening the understanding of the origins of thermodynamics and is given in a small shrift or moved into Appendices.

Thermodynamics differs from the other branches of physics in that its laws are statistical and hence, are not absolutely strict: they are valid only with a certain accuracy and certain probability. For macroscopic systems, these statistical laws are based on averaging over many atoms and molecules; owing to that, the relative statistical fluctuations of average quantities are very small, so that the accuracy of the statistical laws is very high.

This claim can be also stated mathematically. Mathematical statistics teaches us that if the value of a certain random quantity is obtained independently N times, the standard deviation of the respective average value (averaged over these N realizations) is \sqrt{N} times smaller than the standard deviation of a single measurement. For instance, the root-mean-square (rms) of the speeds of N molecules (\bar{v}) has a standard deviation $\delta\bar{v}$ which is \sqrt{N} times smaller than that of a single molecule, δv . The latter has the same order of magnitude as the rms speed itself, $\delta v \sim \bar{v}$. Hence, the relative magnitude of fluctuations of the rms speed of N molecules can be estimated as $\delta\bar{v}/\bar{v} \sim 1/\sqrt{N}$. To get an idea about typical numerical values, let us consider a gas inside a volume of one cubic centimetres. Under normal conditions, one mole occupies a volume of 22.4 litres, and one cubic centimetre contains $N \approx 6 \times 10^{23} \frac{1}{22400} \approx 3 \cdot 10^{19}$ molecules, hence the relative statistical fluctuations of the thermodynamical quantities are of the order of $1/\sqrt{N} \approx 5 \cdot 10^{-9}$, i.e. really negligible.

Within the framework of school physics and for a majority of the Olympiad problems, the statistical nature of the thermodynamics remains unnoticed, because the formulae of thermodynamics and molecular kinetics can be applied exactly in the same way as all the other physical formulae.

2 Heat and temperature

def. 1: Heat is the energy of the thermal motion of a system.

Note that the term “thermal motion” stands for a random motion of the microscopic particles making up the bodies (most typically atoms and molecules). These particles are so small and move so fast that typically, the thermal motion cannot be directly seen.

Since the overall energy of any closed system is conserved, the following very useful conclusion can be drawn directly from this definition (formulated as a “fact”).

fact 1: the full energy (thermal+mechanical etc.) of a closed system is conserved:

$$\Delta U = \Delta Q - \Delta W,$$

1. INTRODUCTION

where ΔU is the change of the internal (thermal) energy, ΔQ — the amount of heat given to the system, and

$$\Delta W = p\Delta V$$

is the mechanical work done by the system while expanding; p stands for the pressure at the system’s external boundary, and ΔV denotes the change of the system’s volume.

This formula (the thermodynamical energy conservation law) is referred to as the **1st law of thermodynamics** (1LTD). All the three terms of this law are signed quantities: if the system gives away some heat then $\Delta Q < 0$; if the volume contracts then the work done by the system is negative, $\Delta W < 0$ (instead of W , one can also use the work done by external forces ΔW_e in which case $\Delta W_e = -\Delta W$).

The expression for the work here assumes that the relative changes of the system properties are small, so that the pressure p can be considered constant; thus, it would be more correct to substitute the Δ -symbols (which are typically used to designate a finite change) with differentials, or to write

$$W = \int p dV.$$

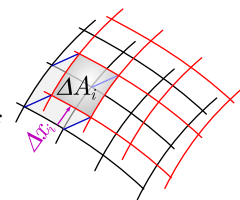
This formula implies that the work can be found as the surface area under $p(V)$ -graph and can be derived as follows. Let us consider a small surface area ΔA_i of the interface separating the system under study from the rest of the space, and let us denote with Δx_i that component of its displacement which is perpendicular to the surface element ΔA_i ; we can consider so short time interval that the displacement Δx_i remains as small as needed. The pressure force acting on the surface element $\Delta F_i = p\Delta A_i$, and its work $\Delta W_i = \Delta F_i \Delta x_i = p\Delta V_i$, where $\Delta V_i = \Delta A_i \Delta x_i$ is the increase of the system’s volume under the surface element ΔA_i . In order to find the total work, we need to sum over the entire interface,

$$\Delta W = \sum_i p\Delta V_i = p \sum_i \Delta V_i = p\Delta V.$$

For an infinitesimal volume increment dV , it is rewritten as $dW = p dV$ and can be integrated over the whole process to yield $W = \int p dV$.

In order to be able to solve problems, we also need the concept of temperature, which is intuitively clear for everyone, but a correct definition of which is quite complicated. Classical (non-digital) thermometers measure the temperature using the thermal expansion of liquids: warmer liquid takes more space than a colder one. However, this cannot be used as a good definition of temperature: different liquids expand at a different rate, and most importantly, this approach would be applicable only to moderate temperatures (at high temperatures, all the matter is in the plasma state, and at temperatures close to the absolute zero, the few substances which remain in the liquid state undergo phase transitions).

We know that if the temperature outside is low, we feel cold: our body gives away some heat, and according to the definition 1, the kinetic energy of our body molecules becomes lower. Inversely, if the temperature is high, it’s hot: our body cannot give away as much heat as is produced via physiological processes, and the kinetic energy of our body molecules starts rising. Therefore we can start with a qualitative definition of the temperature:



def. 2: Temperature is a quantity which characterizes the direction of heat exchange between two bodies, both of which have reached a thermal equilibrium: when brought into contact, the heat flows from a body of a higher temperature to the body of a lower temperature (equal temperatures correspond to a zero heat flux).

This definition is usable (not self-contradictory) only if we have the following property. Consider an arbitrary set of three bodies A , B , and C ; suppose that when A and B are brought into contact, heat flows from A to B , and when B and C are brought into contact, heat flows from B to C . Then we can be sure that when A and C will be brought into contact, heat will flow from A to C . Experimental observations confirm this property (so we can use def. 2), and actually even a more generic property which is known as the *second law of thermodynamics* (2LTD):

fact 2: Whichever tricks are used (heat engines, Maxwell's demons¹, etc), if no external work is done, heat can flow only from a body of a higher temperature to a body of a lower temperature (i.e. the direction of heat flow cannot be reversed as compared to what is observed in the case of a direct contact of two bodies).

Within the theory of *classical thermodynamics*, 2LTD is a postulate following from experimental data; within the *statistical thermodynamics*, the methods of mathematical statistics are used to show that for processes involving macroscopic bodies (i.e. made of a large number of molecules), outcomes violating 2LTD will have negligible probabilities (the proof is mathematically complicated and will not be provided here).

Note that the thermal energies of two bodies of equal temperature are not necessarily equal; however, for a fixed body, thermal energy is a monotonously increasing function of its temperature².

Now we have a qualitative definition of temperature, but we still lack a quantitative one. For many problems it is enough to know and understand the simplified and classical one:

def. 3: Temperature is a measure of a body at thermal (quasi)equilibrium: if two bodies of different temperatures are brought into contact, heat flows from the higher temperature body to the lower temperature one. For a given body, temperature is a monotonously increasing function of its internal heat energy. Kelvin's temperature scale is defined so that zero heat energy corresponds to $T = 0$ K, ice melts by atmospheric pressure at 273.15 K, and water boils at 373.15 K.

This definition is clearly insufficient for designing thermometers suitable for very low temperatures. Apart from this definition, there is also the Kelvin's one which will be discussed in section 4. The best and most generic definition is based on the statistical approach to thermodynamics (in which case the 2LTD is derived from the laws of statistics); let us consider this in more details. Quantum mechanics tells us that a body (a set of particles which are bound by forces into a finite region of space) is characterized by a countable set of its stationary states — the states where the total energy has a well-defined value. For *statistical thermodynamics* we need to consider two

bodies: one small (or moderately-sized) and one huge, which is assumed to be in a thermal contact with the small one, i.e. the two bodies can exchange energy. For instance, the small body can be a single atom of a monomolecular gas, and the heat reservoir can be the rest of the gas. The large one is referred to as the *heat bath* and is needed to ensure that when the small body obtains or gives away due to random fluctuations some of its thermal energy, the temperature would remain constant. Therefore, it needs to be much large (have much larger heat capacitance) than the body which we analyse.

Let the energy levels of the body states be denoted by E_i (e.g. for a single, almost free atom, $E_i = p_i^2/2m$, where p_i is the momentum of the atom in its i -th state).

fact 3: It can be shown using mathematical statistics (see Appendix 1) that the probabilities of the body for being in the i -th or j -th state satisfy the Boltzmann's law:

$$\frac{p_i}{p_j} = e^{-\beta(E_i - E_j)}.$$

The constant β depends on (and describes) the state of the heat reservoir, i.e. on the temperature; it is easy to see that smaller values of β correspond to higher mean energies of the body. Therefore, the temperature of the reservoir can be defined as

$$\tilde{T} = 1/k\beta = \frac{E_i - E_j}{k \ln(p_j/p_i)},$$

where k is a constant which could be freely chosen, but is taken equal to be $k_B \approx 1.38 \times 10^{-23}$ J/K to ensure agreement with def. 3.

To sum up, the Boltzmann's law

$$p \propto e^{-E/k_B T}$$

serves as the definition of temperature which coincides with the Kelvin's temperature scale; here \propto denotes proportionality and E is the system's energy. The only difference with the Kelvin's scale is that with the statistical temperature definition, one can also have negative temperatures — assuming that the body and heat reservoir have finite number of quantum-mechanical states, and the net energy of the reservoir is so high that higher energy states are more probable than the lower ones.

def. 4: Each body is characterized by its thermal capacitance C which shows how much heat needs to be given to raise the temperature by one degree: $C = dQ/dT$.

Note that this definition, when written for finite increments as $C = \Delta Q/\Delta T$, assumes that there are no phase transitions (such as melting or boiling) within the considered temperature range, because phase transitions incur additional heat absorption or heat release.

def. 5: In order to bring a substance from one phase to another (typically from solid phase to liquid or from liquid phase to gaseous phase), certain amount of heat needs to be given to the substance, which is proportional to the mass m of the substance: $Q = \lambda m$. The factor λ is referred to as the *latent heat* (e.g. latent heat of evaporation or latent heat of melting).

Typically, for moderate temperature increments near room temperature, the heat capacitance can be assumed to be constant; in that case, we can write $\Delta Q = C\Delta T$. In the case

¹See http://en.wikipedia.org/wiki/Maxwell%27s_demon

²This can be shown using 2LTD and a construction involving Carnot cycles (ideal heat engines).

of larger temperature increments, this is no longer valid and integration is needed: $\Delta Q = \int C dT$.

fact 4: At low temperatures, the heat capacitance of crystal materials is proportional to the third power of temperature, $C \propto T^3$.

If the body which is being heated expands, the supplied heat is partially converted into mechanical work. Therefore, the heat capacitance depends on the conditions under which the body is held; most often, heat capacitance at constant volume C_V and the heat capacitance at constant pressure C_p are used.

fact 5: If a body is heated at a constant volume, no expansion work is done, so that according to the 1LTD, C_V can be used to find the change of the internal energy of the thermal motion of molecules: $dU = C_V dT$ and

$$U = \int_0^T C_V(T') dT'.$$

This integration makes use of the fact that at $T = 0$, there is no thermal motion of molecules, and hence, internal energy is zero. In particular, for crystal materials at low temperatures when $C = AT^3$ integration yields $U = \frac{1}{4}T^4$.

In the case of liquids and crystals, the volume change is typically small so that the expansion work is negligibly small and $C_p \approx C_V$; however, this not valid for gases, in which case $c_p = C_V + R$ (this will be discussed later in more details).

pr 1. [IPhO-1996] A thermally insulated piece of metal is heated under atmospheric pressure by an electric current so that it receives electric energy at a constant power P . This leads to an increase of the absolute temperature T of the metal with time t as follows:

$$T(t) = T_0[1 + a(t - t_0)]^{1/4}$$

Here a , t_0 and T_0 are constants. Determine the heat capacity $C_p(T)$ of the metal (temperature dependent in the temperature range of the experiment).

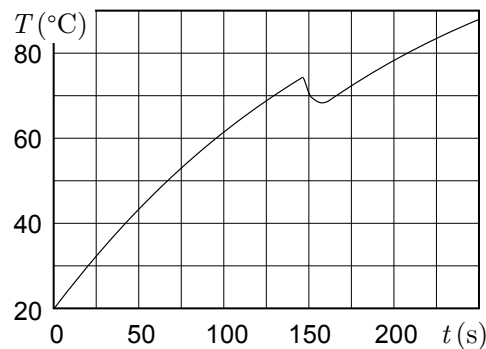
The solution of this problem is rather straightforward: it is enough to apply the definition 4 and make some mathematical manipulations to eliminate time t . We can still try to formulate an appropriate “idea” as follows.

idea 1: The body temperature T and the net heating power P are related via equality $P \equiv \frac{dQ}{dt} = C \frac{dT}{dt}$. Therefore, the tangent to the $T(t)$ curve is proportional to the net power and inversely proportional to the heat capacitance; many problems can be solved by using this observation.

In the case of the problem 1, this idea is to be used algebraically. In those cases when a $T(t)$ -dependence is provided in a graph, it tells us that as long as the heat capacitance of a body remains approximately constant, we can find how many times the net heating power is changed by determining the slopes of the tangent at two different points of the $T(t)$ -graph. Let this be illustrated with the following problem.

pr 2. [EstPhO-2004] Water is being heated in an electric kettle. At a certain moment of time, a piece of ice at temperature $T_0 = 0^\circ\text{C}$ was put into the kettle. Figure depicts the dependence of the water temperature as a function of time.

What was the mass of the ice if the heating power of the kettle $P = 1\text{ kW}$. The latent heat of melting for ice $L = 335\text{ kJ/kg}$, the heat capacitance of water $c = 4.2\text{ kJ/kg}\cdot\text{K}$. The room temperature $T_1 = 20^\circ\text{C}$.



In the case of this problem, we can also formulate a fact, and a rather simple idea.

fact 6: The heat exchange rate (i.e. the *heat flux*, measured in Watts) between a body and the environment is a function of the temperatures of the body and of the environment, T_1 and T_2 , respectively; for a small tempera difference $\Delta T \equiv T_1 - T_2$, the heat flux is proportional to ΔT ; this is referred to as the Fourier's law. For larger temperature differences, the dependence becomes nonlinear, because (a) heat conductivity of the materials may depend on the temperature, (b) the heat flux due to heat radiation is a non-linear function of T_1 and T_2 (however, it can be still linearized for small values of ΔT); (c) large temperature differences may cause convection of air and fluids which will enhance heat flux in a nonlinear way. Pay attention that the heat flux goes to zero for $T_1 = T_2$!

[pr 4.]

idea 2: Heat exchange rate of a body with the environment is a function of the temperatures; hence, for processes during which the temperature change remains small, the heat exchange rate can be assumed to be constant. In particular, if a body has reached a thermal equilibrium while being heated with a power P_0 , it has reached a temperature T_0 by which the heat loss power equals exactly to P_0 : $P_{HL}(T_0) = P_0$; hence, if the heater is suddenly switched off, the initial cooling power of the body (due to the heat loss to the environment) is P_0 .

it's very important to keep in mind the equality between heat gained and heat lost

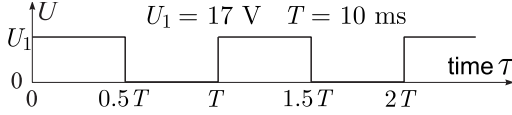
Returning to the problem 2, the graph allows us to determine, how long time-delay τ in the heating process has been caused by the piece of ice: this is the time needed to melt and heat the meltwater up to the current water temperature. The value of the ice-heating-time τ would allow us to determine the mass of ice from the 1LTD if the net heating power (P minus the energy loss to the environment) were known. The average net power received by the kettle during that period when the ice is being melted and the meltwater being heated can be determined from the graph using the ideas 2 and 1.

The particular case mentioned at the end of the idea 2 is illustrated with the following problem.

pr 3. [EstPhO-2001] The filament of a halogen lamp has length $l = 5.0\text{ cm}$ and is made of tungsten. At the working temperature of the lamp $T_0 = 3200^\circ\text{C}$, the density of the tungsten $\rho = 18\,200\text{ kg/m}^3$, the specific heat $c = 235\text{ J/(K}\cdot\text{kg)}$, and the

2. HEAT AND TEMPERATURE

resistivity $\rho_{el} = 9.95 \times 10^{-7} \Omega \cdot m$. When a voltage of rectangular waveform as shown in graph is applied to the leads of the lamp, the temperature of the filament will reach the nominal value T_0 (strictly speaking, this is the average temperature; the interior regions of the filament are slightly hotter). However, due to voltage oscillations, there are small oscillations of the filament's temperature; find the amplitude of these oscillations ΔT .



The usage of the linear dependence mentioned in the fact 6 is illustrated by the following problem.

pr 4. A small house is being heated by an electric heater of power $P = 1 \text{ kW}$ which maintains the interior temperature $t_1 = 19^\circ\text{C}$; the outside temperature $t_0 = 0^\circ\text{C}$. A man enters the house, upon which the room temperature starts rising and achieves a new value $t_2 = 20^\circ\text{C}$. Find the “heating power” of the man.

Here the task of figuring out that the Fourier's law can be used (because the temperature difference is much smaller than the temperatures in Kelvins) is left to those who solve the problem. Be aware that for some loosely formulated problems, the Fourier's law is assumed to be used even when its applicability is actually questionable (for instance for temperatures $T_1 = 273 \text{ K}$ and $T_2 = 373 \text{ K}$).

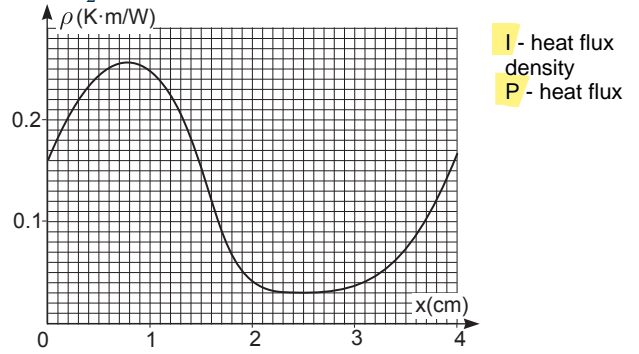
idea 3: The problems on heat exchange rate are analogous to the problems on electrical circuits. There are following matching pairs: temperatures correspond to voltages, heat energy - to a charge, heat fluxes — to currents, a thermal resistance (proportionality coefficient between the heat flux and ΔT , c.f. idea 6) — to an electrical resistance, heat capacitance — to electrical capacitance. The both Kirchoff's law remain valid for heat exchange processes: while the counterpart of the voltage law is quite useless due to triviality (along a closed circuit, the sum of temperature increments is zero), the counterpart of the current law is useful and can be referred to as the continuity of thermal fluxes: if the bodies of a system have reached stationary temperatures, for each body, the sum of heat fluxes entering it equals to zero.

pr 5. [EstFin-2003] Thermal resistivity is a characteristic of a material and is defined as the coefficient of proportionality between the temperature gradient $\frac{dT}{dx}$ and the heat flux density (here we assume that the heat flux is parallel to the x -axis). Note that the unit of the heat flux density is W/m^2 , hence the unit of the thermal resistivity is $\text{K} \cdot \text{m}/\text{W}$.

(i) A microprocessor of power dissipation $P = 90 \text{ W}$ is cooled using a flowing water; the thermal contact between the processor and the water is established via a copper plate of thickness $d = 5 \text{ mm}$ and surface area $s = 100 \text{ mm}^2$. Determine the temperature difference between the microprocessor and the flowing water. Thermal resistivity of copper $\rho = 2.6 \text{ mm} \cdot \text{K}/\text{W}$.

(ii) A wire is made of different alloys so that its thermal resistivity depends on the coordinate along the wire as shown in

the figure. The cross-sectional area of the wire $S = 1 \text{ mm}^2$ and length $l = 4 \text{ cm}$. Find the heat flux through the wire if one end of the wire is kept at the temperature $T_1 = 100^\circ\text{C}$ and the other — at $T_2 = 0^\circ\text{C}$.



Second half of this problem makes use of a rather generic method.

idea 4: Calculation of many physical quantities can be reduced (sometimes not in an obvious way) to the calculation of surface areas under a graph (i.e. to an integral).

More specifically, if a system is described by a parameter x (which can be time, coordinate, velocity, etc.) and a quantity A can be expressed as $A = \sum_i F_i \Delta x$, where Δx is a small interval of the parameter x , the sum is taken over all the small intervals, and F_i is a function of x (but not a function of A) then at the limit $\Delta x \rightarrow 0$ we can write $A = \int F(x) dx$, i.e. A is the surface area under the graph $F(x)$.

In order to illustrate this method, let us consider the following mechanical problem. For a boat in water, the friction force is given as a function of speed $F(v)$, depicted in a graph (it has a crossover from a linear function at small speeds to a parabola for large speeds). You are asked to find, how far will travel a boat of a given mass m and initial speed v asymptotically (i.e. upon waiting for a very long time). Let us divide the displacement into small pieces, $s = \sum \Delta s$, where $\Delta s = v \Delta t$. If the function $v(t)$ were known, the last formula would have been completed our task. However, the force is given to us as a function of v , hence we need to substitute Δt with Δv . Force is directly related to the acceleration, $a(v) = \frac{dv}{dt} = F(v)/m$, which gives us a hint that we should try substituting Δt via Δv while introducing the acceleration:

$$\Delta t = \Delta v \cdot \frac{\Delta t}{\Delta v} = \frac{\Delta v}{\Delta v / \Delta t} = \frac{\Delta v}{a}.$$

This result serves us perfectly well:

$$s = \sum v \Delta t = \sum \frac{v}{a} \Delta v = \sum \frac{vm}{F(v)} \Delta v \rightarrow \int \frac{vm}{F(v)} dv,$$

i.e. the displacement equals to the surface area under a graph which depicts $\frac{vm}{F(v)}$ as a function of v .

The next problem makes also use of the continuity of heat flux; however, it also requires the knowledge of the Stefan-Boltzmann law for heat radiation.

fact 7: For “grey” bodies (which absorb a constant fraction of the incident electromagnetic radiation, independently of its wavelength), the heat radiation flux density (i.e. radiated energy per unit area) $w = \varepsilon \sigma T^4$, where T is the temperature of the body, $\varepsilon \in [0, 1]$ — the absorption factor, and $\sigma = 5.67 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$ — the Stefan-Boltzmann constant.

The factor ε shows, which fraction of the incident light is absorbed; for a perfectly black surface $\varepsilon = 1$; for a perfectly white surface $\varepsilon = 0$. This formula is derived using the assumption that the radiating body is in a thermal equilibrium with the electromagnetic waves in the adjacent vacuum; a knowledge of quantum mechanics and application of the Boltzmann's distribution are required, as well as certain mathematical skills.

pr 6. [IPhO-1992] A satellite represents a homogeneous sphere of diameter $D = 1$ m; you may assume that all the parts of the satellite have the same temperature. The satellite orbits around Earth (but is not in its shade). The Sun can be considered to be an absolutely black body with the surface temperature $T_{\odot} = 6000$ K, the radius of the Sun $R_{\odot} = 6.96 \times 10^8$ m, the orbital radius of the Earth around the Sun $L = 1.5 \times 10^{11}$ m. Find the temperature of the satellite assuming that it is coated with a perfectly grey paint (the absorption factor is independent of the wavelength of the electromagnetic radiation). You may neglect the heat radiation of the Earth.

For this problem, the following fact is to be used (those who are “afraid” of the surface integral can skip to the paragraph next to the fact).

fact 8: In a stationary state, the Gauss theorem is valid for heat fluxes (this is completely analogous to the Gauss theorem for the electric and magnetic fields): $\oint \vec{w} \cdot d\vec{S} = P$, where the integral is taken over a closed surface, P is the heat power released inside the surface, the heat flux density vector \vec{w} is parallel to the propagation direction of the heat energy, the vector $d\vec{S}$ is parallel to the surface normal, and is equal by modulus to the surface area of a small (infinitesimal) surface element.

This is essentially a mathematical formulation of the continuity law for the heat flux. In the case of a spherically symmetric geometry (with an isotropic spherical heat source), the surface integral simplifies to the product of the heat flux density with the surface area of a sphere:

$$4\pi R^2 w = P,$$

where $w = w(R)$ is the heat flux density at the distance R from the centre of the heat source.

The next problem completes the topic of heat flux continuity.

pr 7. [IPhO-1996] Perfectly black hot surface is kept at a constant temperature T_h . There is another perfectly black cold surface which is parallel to the first one, and is kept at a constant temperature T_l ; there is a vacuum in the space between the plates. In order to reduce the heat flux between the plates, a screen is used, which is made of N parallel thermally insulated perfectly black plates (in the figure, $N = 2$). Such a screen is placed between the hot and cold plates, parallel to them. By which factor x will the heat flux be reduced once a thermal equilibrium is reached? The edge effects caused by the finite size of the plates can be neglected.

3. GASES



This problem leads us to a system of N linear equations. In general, solving such a system of equations is not an easy task; this particular system, however, can be easily solved. It should not be surprising, because long mathematical calculations are not compatible with the format of physics Olympiads; we can formulate an appropriate recommendation — as a “non-physical” idea.

idea 5: As a rule, the problems of physics Olympiads do not require long mathematical calculations. If you obtain a long or difficult system of equations then most likely one of the following is valid: (a) you have followed a non-optimal (i.e. more complicated than necessary) solving method; (b) the method is good, and the system of equations is only seemingly complex, e.g. almost all the unknowns can be eliminated simultaneously using the symmetries of the equations.

pr 8. [EstOpen-2014] Consider a black cube which is made from a perfectly heat-conducting material. A parallel beam of light with intensity I (W/m²) falls onto this cube. The equilibrium temperature T of the cube depends on its orientation; find the minimal and maximal values of T (T_{\min} and T_{\max} , respectively).

This problem is physically quite straightforward, but full (rigorous) solution requires mathematical skills in the field of vector calculus.

idea 6: In the case of a homogeneous vector field $\vec{F}(x, y, z) \equiv \vec{F}_0$, its flux $\Phi = \int_S \vec{F} \cdot d\vec{S}$ through a (possibly curved) surface S can be found as the dot product of a certain effective flat surface element $\vec{S}_{\text{eff}} = \int_S d\vec{S}$, $\Phi = \vec{S}_{\text{eff}} \cdot \vec{F}_0$.

3 Gases

In statistical physics (thermodynamics), it is relatively easy (i.e. difficult, but in many cases still possible) to make calculations if everything is very regular, for instance in the case of crystalline solids. It is even easier to make calculations when everything is chaotic, for instance in the case of gases and plasmas, because then the physical quantities can be averaged. The most difficult to analyse are media where order and disorder exist together - such as fluids, granular media, solids near phase transition, etc. Because of that, high school physics deals only with the chaotic case — with gases.

A good model which describes the reality quite well is the model of *ideal gases*.

def. 6: An ideal gas is made up of molecules of negligible size (as compared with the average intermolecular distances) which behave as elastic balls (monoatomic gas) or spring-ball-systems (polyatomic gas), and move randomly colliding with each other and with the walls of the container. It is assumed that there are no other forces between the molecules than the contact forces (for instance, electrostatic interactions need to be negligible as electrostatic forces act over a distance).

This equation is essentially just e to the negative power of the kinetic energy in the x direction divided by kT (which can be associated with the Boltzmann's law) 3. GASES

Let n be the number density of the molecules (number per unit volume), and $f(v_x)$ — their distribution function over v_x (the x -component of the velocity), defined so that $\Delta n = n f(v_x) \Delta v_x$ gives us the number density of such molecules for which the x -component of the velocity lies within the interval $[v_x; v_x + \Delta v_x]$ (here, Δv_x denotes a small velocity increment). According to the Boltzmann's distribution, $f(v_x) = A e^{-mv_x^2/2kT}$ (which in this form is referred to as the *Maxwell's distribution*)³, where the factor A is such that the area under the $f(v_x)$ -graph is unity, i.e. $A = 1 / \int_{-\infty}^{\infty} e^{-mv_x^2/2kT} dv_x$.

The integral in the last expression can be taken using two techniques. The first (and the simpler) technique is to change integration variable by substituting $x = v_x/v_T$, where $v_T = \sqrt{2kT/m}$, this allows us to get rid of the parameter v_0 in the integrand. Indeed, since v_0 constant (independent of the integration variable), $dv_x = v_T dx$ and

$$\int_{-\infty}^{\infty} e^{-mv_x^2/2kT} dv_x = v_T \int_{-\infty}^{\infty} e^{-x^2} dx.$$

A second trick (which we don't discuss here) needs to be applied to show that $\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$, resulting in

$$f(v_x) = e^{-mv_x^2/2kT} / v_T \sqrt{\pi}.$$

fact 9: Velocity distribution of molecules in a gas is given by the Maxwell's distribution,

$$dN = \frac{N}{v_T \sqrt{\pi}} e^{-v_x^2/v_T^2} dv_x \quad v_T = \sqrt{2kT/m},$$

where N is the total number of molecules, and v_x is the x -component of the molecules. In the isotropic 3-dimensional case, it can be also written for the speed,

$$dN = \frac{4N}{v_T^3 \sqrt{\pi}} v^2 e^{-v^2/v_T^2} dv.$$

In order to derive the last equation, we assumed uncorrelated motion in x , y , and z -directions so that the individual distributions can be multiplied: $dN = \left(\frac{N}{v_T \sqrt{\pi}} \right)^3 e^{-(v_x^2+v_y^2+v_z^2)/v_T^2} dv_x dv_y dv_z$, and integrated over a spherical layer in $v_x - v_y - v_z$ -space, $\int dv_x dv_y dv_z = 4\pi v^2 dv$.

Let us find an expression for the pressure. We do this in two parts: first we make calculations assuming that all the molecules approach the wall with the same speed u (let the x -axis be perpendicular to the wall; then u is the x -component of the molecule's velocity), and then we generalize the result to the realistic case of different speeds. Pressure is defined as force per unit area, $p = F/A$; the force is found as the momentum given to the wall per unit time, $F = 2Nmu/t$, where N is the number of molecules colliding with the wall during a time period t . The coefficient two reflects the fact that the average speed with which the molecules depart from the wall after collision equals to the approaching speed⁴, hence each molecule receives momentum $2mu$ from the wall. During the time period t , only those molecules will reach the wall which are within the near-wall-layer of thickness ut and move towards the wall. Thus, the total number of collisions is found as the number of molecules within the layer of volume $V = Av_T t$, reduced by a factor of two (only half of the molecules move in the direction of the wall): $N = \frac{1}{2} nV \approx Aut$. Thus, the force exerted to the wall

is found as $F = 2muN/t = nm u^2 A$. Now, let us recall that in reality, molecules can have different speeds, so that we need to average the result, $F = nm \langle u^2 \rangle A$, where angular braces denote averaging. Finally, the pressure $p = F/A$ is found as

$$p = nm \langle u^2 \rangle.$$

So, the pressure is expressed in terms of the mean square of the x -component of the velocity. This expression can be also rewritten in terms of the average net speed $\langle v^2 \rangle$ as $p = \frac{1}{3} nm \langle v^2 \rangle$. Indeed, $v^2 = v_x^2 + v_y^2 + v_z^2$ (where $v_x \equiv u$) and therefore, $\langle v^2 \rangle = 3 \langle u^2 \rangle$ (we have taken into account that due to statistical isotropy, in average all the propagation directions of the molecules are equivalent, hence $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$).

Using the Maxwell's distribution one can express the average values in terms of integrals: $\langle v_x^2 \rangle = \int v_x^2 f(v_x) dv_x$. This integral can be taken (see appendix 2), resulting in $\langle v_x^2 \rangle = kT/m$, i.e. the average kinetic energy related to the motion along the x -axis

$$\left\langle \frac{m}{2} v_x^2 \right\rangle = \frac{1}{2} kT.$$

Using this expression we obtain

$$p = nm \langle u^2 \rangle = nkT.$$

Once we substitute $n = N/V = \frac{m}{\mu} N_A/V$ (N_A is the Avogadro number, μ is the molar mass of the gas, m is the total mass of the gas, and V is its volume), we obtain $pV = \frac{m}{\mu} N_A kT = \frac{m}{\mu} RT$, where $R = kN_A$ is called the *gas constant*. This law is known as the *ideal gas law*; sometimes it is convenient to express it in terms of the gas density ρ as $p\mu = \rho RT$. Let us sum up our results.

fact 10: Ideal gas state is described by the law

$$pV = \nu RT,$$

which can be also expressed as

$$p = nkT \quad \text{or} \quad p\mu = \rho RT.$$

method 1: Various estimation problems related to gases can be done in the same way as we derived the ideal gas law, i.e. using the *molecular kinetic approach*.

Exact calculations require often integration (averaging using the Maxwell's distribution). However, in the case of Olympiad problems, it is typically enough to make only estimates, and there is no need to use the Maxwell's distribution. This is due to two reasons: (a) taking complex integrals does not test the knowledge of physics, (b) in many cases even seemingly exact calculations are exact only for the so-called *vacuum approximation* when the mean free path (the distance travelled by a molecule between two subsequent collisions with other molecules is much larger than the characteristic dimensions of the system), and only approximate otherwise.

pr 9. In vacuum and weightlessness, at the bottom of a cylindrical vessel (a cup), there is a layer of solid substance of molar mass μ . This substance sublimates slowly (evaporates from the solid phase into gaseous phase) and pushes thereby the vessel to the opposite direction. Estimate the terminal

³Strictly speaking, the Boltzmann's distribution is valid for the average occupancy of a quantum-mechanical state; here we make use of the fact that for an elastic ball in a box, the quantum-mechanical levels are evenly distributed over the values of v_x .

⁴Strictly speaking, for a single collision, the departure speed is random and depends on the momentary speed of that wall's molecule with which it collides. However, when averaged over many collisions and assuming that the gas and the wall have equal temperatures, the average departure velocity is such as if there were an elastic collision with a flat wall

speed of the vessel. The mass of the vessel M , and the initial mass of the substance $m \ll M$; the temperature of the vessel is T ; the process can be assumed to be isothermal (cooling due to evaporation and heat radiation remains negligible). The cross-sectional area of the vessel is A .

pr 10. Natural uranium consists of mainly two isotopes, U^{238} and U^{235} , whereas the relative concentration of the latter is 0,7%. Uranium is “enriched” (i.e. the concentration of U^{235} is increased) by implementing a multi-stage process, where at each stage, evaporated chemical compound UF_6 is led through a porous wall. The porous wall can be considered to be a thin film having microscopic holes in it (the size of the holes is smaller than the mean free path of the molecules, but larger than the dimension of the molecules). How many stages is needed to increase the U^{235} content to 1,4%? The molar mass of fluoride (F) is 19 g/mol.
 Very often difficult problems can be solved not by using exact calculations but by using proportionality and ratios

pr 11. [PhysCup-2012] Determine or estimate the net heat flux density P between two parallel plates at distance L from each other, which are at temperatures T_1 and T_2 , respectively. The space between the plates is filled with a monoatomic gas of molar density n and of molar mass M . You may use the following approximations:

- (i) the gas density is so low that the mean free path $\lambda \gg L$;
- (ii) $T_1 \gg T_2$;
- (iii) when gas molecules bounce from the plates, they obtain the temperature of the respective plates (for instance, this will happen if they are absorbed/bound for a short time by the molecules of the plate, and then released back into the space between the plates);
- (iv) you may neglect the black body radiation.

Note that “Estimate” means that the numeric prefactor of your expression does not need to be accurate.

The internal energy U of a monomolecular gas (i.e. the net kinetic energy of the molecules) can be expressed in terms of the temperature using the above obtained result $m\bar{v}_x^2 = kT$. Indeed, a single atom essentially cannot rotate due to its small dimensions⁵. Therefore, U is found as the product of the energy of a single molecule with the number of molecules N ,

$$U = N \frac{m}{2} (\bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2).$$

Due to statistical isotropy $\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2 = kT$; substituting $N = \nu N_A$ (where ν stands for the number of moles) and $N_A k = R$ we obtain

$$U = \frac{3}{2} \nu RT.$$

In the case of diatomic and polyatomic molecules, the molecules obey also rotational energy $U_r = \frac{1}{2} N (I_x \bar{\omega}_x^2 + I_y \bar{\omega}_y^2 + I_z \bar{\omega}_z^2)$, where I_x , I_y and I_z denote momenta of inertia with respect to different axes, and ω_x , ω_y and ω_z — the respective angular velocities. Using the Boltzmann’s distribution for the rotational motion around the x -axis, $p \propto e^{-I_x \omega_x^2 / 2kT}$, we obtain an expression which is very similar to the one which we had for translational motion (just v_x is substituted by ω_x and m — with I_x). Because of that, the result is also the same, $U_r = \frac{3}{2} \nu RT$. However, one should keep in mind that if we have a diatomic

3. GASES

molecule (or polyatomic linear molecule, such as CO_2), it cannot rotate around the axis passing through its atoms (let it be the z -axis). Therefore, rotation will take place only around the x - and y -axis; the rotational energy is reduced respectively: $U_r = \nu RT$.

Let us notice that each of the so-called *degrees of freedom* (translational motion along the x -axis, rotation around the x -axis, translational motion along the y -axis, etc) contribute to the overall internal energy always the same amount $\frac{1}{2} \nu RT$ ($\frac{1}{2} kT$ if we speak about the average energy of a single molecule). Because of that, the internal energy of a gas is conveniently expressed in terms of the number of degrees of freedom i as

$$U = \frac{i}{2} \nu RT.$$

For a monoatomic gas $i = 3$, for a diatomic gas (and a linear polyatomic gas) $i = 5$; for all other cases $i = 6$. In the case of a mixture of gases (such as air), the effective number of degrees of freedom may turn out to be fractional.

Using the last expression we can easily derive an expression for the internal energy of a gas by constant volume. If the volume remains constant, there is no mechanical work done ($A = \int p dV = 0$), hence all the heat given to the gas goes to the increase of the internal energy, $C_V = dU/dT = \frac{i}{2} \nu R$. Particularly simple expression is obtained for the molar heat capacitance, $c_V = C_V/\nu$:

$$c_V = \frac{i}{2} R.$$

If we are dealing with an isobaric process (at a constant pressure) then the internal energy change can be, of course, calculated using the previous result, but according to the 1LTD, part of the heat goes to the work performed by the gas, $\Delta A = p \Delta V = \nu R \Delta T$. Hence, the heat given to the gas $\Delta Q = \Delta U + \Delta A = \frac{i+2}{2} \nu R \Delta T$, i.e. the molar heat capacitance for isobaric processes

$$c_p = \frac{i+2}{2} R.$$

Rule “ $\frac{1}{2} kT$ per each degree of freedom” is valid, however, only for moderate temperatures. When temperature is large enough then molecules will start oscillating similarly to balls which are connected with springs, and oscillation energy needs to be included, as well. In that case one can say that the oscillatory degrees of freedom are excited. For relative light gas molecules, such as the components of air, the critical temperature at which the oscillations are excited is well above the room temperature. Meanwhile, heavy gas molecules (e.g. Br_2) oscillate already at the room temperatures. It should be emphasized that the $\frac{1}{2} kT$ -rule is not valid for the oscillatory degrees of freedom. It appears that each excited oscillatory degree of freedom contributes full kT to the heat energy of a molecule. Thus, each oscillatory degree of freedom increases the effective number of degrees of freedom by 2, e.g. for $i = 5 + 2 = 7$ for Br_2 at room temperature.

The reason why oscillatory degrees of freedom contribute twice as much as the translational and rotational degrees of freedom lies in the structure of quantum mechanical energy levels. For translational and rotational energy, the energy level is a quadratic function of the level order number n , $E_n = h^2 n^2 / 8L^2 m$; here, L stands for the length of the box where our particle is placed. Meanwhile, for oscillatory motion, energy is a linear function of the order number, $E_n = \hbar \omega (n + \frac{1}{2})$, where ω is

⁵The reasons are quantum-mechanical, and to a certain will be discussed later.

the natural frequency. Therefore, the average oscillation energy can be calculated using the Boltzmann's distribution as

$$\bar{E} = \sum_0^{\infty} \hbar\omega n e^{-\hbar\omega n/kT} / \sum_0^{\infty} e^{-\hbar\omega n/kT}.$$

The sums can be taken to find $\bar{E} = kT$.

On the other hand, **at very low temperatures, even the rotational degrees of freedom of polyatomic molecules may not be excited**; this means that their effective number of degrees of freedom is 3. In order to determine if one or another degree of freedom is excited, it is necessary to compare the energy level difference ΔE between the ground level and the first excited level with the average energy of a degree of freedom kT : the respective degree of freedom starts to become excited at $T \sim E/k$.

Indeed, let us consider two energy levels E_0 and E_1 . According to the Boltzmann's distribution, $p_1/p_0 = e^{-(E_1-E_0)/kT}$. If $E_1 - E_0 \gg kT$ then the probability of being at the excited state is exponentially small and hence, the related average energy increase is exponentially small, as well.

Now it becomes also clear why the molecules of heavy gases start oscillating at lower temperatures than light gases. The natural frequencies $\omega \approx \sqrt{k/m}$ of heavy molecules are lower than that of light molecules (the stiffness of a chemical bond as a "spring" has always the same order of magnitude, the main difference comes from the effective mass m). This means that the energy level difference $\Delta E = \hbar\omega$ is correspondingly smaller, leading to a lower excitation temperature.

Thus, the effective number of degrees of freedom depends on temperature; furthermore, for such a temperature range where the effective number is changing from one value to another, the system behaviour is not well described by an integer value of i . Because of that, instead of i , often molar heat capacities c_V and c_p are used. If the behaviour of a gas is well described by the model of ideal gas, it is enough to give just the value of c_V as c_p can then be found from the equality $c_p = c_V + R$. Conversely, if for a certain gas $c_p - c_V \neq R$ then it does not behave as an ideal gas, and relationship $pV = \nu RT$ does not hold well. Meanwhile, it is well possible that for an ideal gas, $2c_V/R$ is not an integer: fractional values just show that the current temperature is close to the excitation temperature of a certain degree of freedom. Let us make an intermediate summary.

fact 11: For an ideal gas,

$$c_V = \frac{i}{2}R; \quad c_p = c_V + R; \quad \Delta U = \nu c_V \Delta T,$$

where i is the number of excited degrees of freedom (oscillatory degrees of freedom are to be added with double weight). A certain degree of freedom is excited when kT is larger than the energy level difference of the quantum mechanical states corresponding to the given degree of freedom. As a rule of thumb, near room temperature for a monoatomic gas $i = 3$, for diatomic gas $i = 5$, and for polyatomic gases $i = 6$.

Thus far we used the concept of the degrees of freedom without proper definition; let us discuss this notion in more details.

def. 7: The number of degrees of freedom shows, how many parameters (generalized coordinates) is needed to describe completely the state of a system.

For instance, in order to describe a point mass in three-dimensional space, $j = 3$ coordinates are needed; for N point

3. GASES

masses we need already $j = 3N$ coordinates. In order to describe the spatial placement of a solid body, 6 coordinates are needed: apart from the coordinates of a certain point of the body (e.g. the centre of mass), orientation needs to be described by additional 3 coordinates (two angles describing the direction of an axis of the body, and one angle describing rotation around that axis). In the case of a linear molecule, last coordinate, the rotation angle, is not needed, therefore $j = 5$.

If a system consists of N point masses, the motion of which is limited by certain restrictions (e.g. the distance between two point masses is fixed with a rod, or the angle between the lines connecting a certain point A with two neighbouring points has a fixed value), the number of degrees of freedom can be found using the formula $j = 3N - r$, where r on is the number of restrictions. In the case of molecules, the bonds are the chemical bonds which also serve as the springs and can give rise to oscillations; in that case, r is the number of oscillatory degrees of freedom. Knowing that for a linear molecule, the total number of degrees of freedom $j = 5$, and for planar or three-dimensional molecules $j = 6$, we can use this formula to find the number of oscillatory degrees of freedom as $r = 3N - j$. For instance, CO_2 molecule is linear: $N = 3$ and $j = 5$, hence $r = 4$. Note that in the theory of coupled oscillators, it is shown that the number of oscillatory degrees of freedom equals to the number of natural modes and natural frequencies.

Let us consider one problem on the topic of degrees of freedom.

pr 12. [EstAcadPhO-2006] Toy "Supermag" makes it possible to construct, among others, polyhedrons — e.g. tetrahedrons, cubes, and many irregular polyhedrons, where the edges of the polyhedron are made of magnetic bars, which are connected at the vertices with the help of steel balls. The steel balls fix the endpoint of a steel bar to itself firmly, but the angle between magnetic bars meeting at a steel ball can be changed with a little effort. It appears that a tetrahedron is a rigid construction, but a cube can be easily deformed. Prove the following theorem: a convex polyhedron is rigid then and only then if all the faces of the polyhedron are triangles.

In order to solve this problem, the formula $j = 3N - s$ is used, but one more formula is needed — the Euler's formula for graphs (including polyhedrons) relating the number of vertices N , faces f , and edges e via equality $N + f = e + 2$. Euler's theorem is provided here without proof (which is actually not difficult and is based on mathematical induction). In order to solve problem 12, it is necessary to prove that if all the faces are triangular, the number of degrees of remaining freedom $j = 3N - s$ equals to that of a rigid body. If the number of degrees of freedom were larger, it would be needed to use more parameters than in the case of a rigid body to describe its state, i.e. it cannot be rigid.

As we have learned, atoms and ions connected in molecules with chemical bounds can oscillate as spring-block systems. This applies not only to molecules, but also to crystal materials. **Similarly to heavy gases, in the case of many crystal materials, all the oscillatory degrees of freedom are excited. In the case of N -ion(atom)-crystal substance, there are $3N$ degrees of freedom; almost all these degrees of freedom (except for 6 degrees of freedom of a solid body) are oscillatory.** Since

N is very large, we can forget about that 6, so that the internal energy can be expressed as $U = 3\nu RT$. Therefore, molar heat capacitance $c_V = 3R$. In the case of light ions, it may still happen that the highest-frequency natural modes have $\omega > kT/\hbar$ and therefore are not excited yet. In that case, the internal energy is smaller than $3\nu RT$, and the effective number of degrees of freedom per single ion (atom) is an increasing function of temperature, approaching asymptotically the limit value $i=6$ (as all degrees of freedom are oscillatory, the number of spatial coordinates is multiplied by two). Let us also recall that at low temperatures it starts as a cubic function of T . Let us derive the $c_V \propto T^3$ law for low temperatures via rough estimates (for a diamond, this is valid even for room temperatures). Each excited oscillatory degree of freedom carries energy kT ; thus we need to estimate the number of excited oscillations, i.e. number of natural modes with $\omega < kT/\hbar$. Natural oscillation modes of a crystal can be considered as standing sound waves. Sound wave frequency is expressed as $\omega = c_s \kappa$, where c_s is sound speed, and $\kappa = 2\pi/\lambda$ — a wave vector. Thus, all standing waves with wave vector $\lambda kT/\hbar c_s$ and wavelength $\lambda > \hbar c_s/kT$ will be excited. Let the crystal have a cubic shape of side length L . At the free boundary of the crystal, there can be no strain, hence for the displacement vectors of the molecules, there must be antinodes at the boundary. Therefore, L must be a multiple of the half-wavelength: $L\kappa_x = m_x\pi$, where κ_x is the projection of the wave vector to the x -axis, and m_x is the number of nodes along x . For the smallest excited wavelength, $\lambda_s = \hbar c_s/kT$ and $m_x = 2L/\lambda_s$. Note that all those standing waves which have smaller number of nodes are also excited. Similarly, along y - and z -axes, for excited oscillations the number of nodes varies between 1 and $2L/\lambda_s$. The number of different standing waves is found as the number of different triplets (m_x, m_y, m_z) , which is equal to $(2L/\lambda_s)^3$. Then, the internal energy is found as

$$U \approx MkT \approx kT(2LkT/\hbar c_s)^3 \propto T^4.$$

Therefore, the internal energy is proportional to T^4 , and the heat capacitance $C_V = \frac{dU}{dT} \propto T^3$.

Now, let us turn to the problems which are not related to the molecular kinematic approach, and instead, require the knowledge of the ideal gas law and its internal energy. Many Olympiad problems are based merely on those two equations; in the case of the next problem, the only “trick” is that unlike for ordinary isohoric, isobaric, etc. processes, it is not the amount of gas which is conserved, but the pressure, hence the number of moles will change according to $\nu T = \text{Const}$.

pr 13. [EstPhO-2003] An aerostat (an air balloon made of unstretchable skin) has volume V_0 , is filled with hydrogen, and hovers stably at a certain height where the external pressure is p , and the air temperature is T_{air} . Due to sunlight, the aerostat is heated up to a temperature T_1 . As a result, part of the air exits the balloon via a valve. The valve is made so that the if the interior pressure exceeds the exterior one, the excess gas is released; the valve never lets gas enter the balloon from outside. Now, the sunlight is shaded by a cloud: the balloon’s temperature drops, and volume becomes smaller. How much ballast (which mass m) needs to be thrown out to keep the aerostat at the same height (where the pressure is still equal to p)? Both air and hydrogen can be treated as ideal gases, the molar masses are μ_{H_2} and μ_{air} , respectively.

The next problem deals with a more complicated energy transfer process; the following idea will be useful.

3. GASES

idea 7: If two reservoirs are connected via a narrow pipe, narrow valve, etc, then a quasi-equilibrium is possible: while the temperatures of the two reservoirs to the other sides of the pipe are different, the pressures are equal. Thus, there is a mechanical equilibrium, but no thermal equilibrium (it takes much longer time to reach the latter).

pr 14. Consider a balloon which has thick rigid walls and from which all the air has been pumped out. Now, the valve of the balloon is slightly opened, and the balloon is slowly filled with the air from outside. Find the temperature of the air inside the balloon once the air flow has stopped (since a mechanical equilibrium has been reached). The room temperature is T , the balloon walls have low heat conductance and heat capacitance so that heat flux through the walls can be neglected.

The first step towards the solution of this problem is understanding to what is spent the work done by external air $p\Delta V$: how is it converted to heat and how is the external volume change ΔV related to the volume of the cavity V . Let us also notice that presumably the size of the valve opening is larger than the mean free path length, so that a molecular kinetic approach is not needed, and instead, macroscopic approach is to be applied: a narrow (but still macroscopic) stream of air enters the cavity thorough the valve.

Adiabatic processes

Typical reply to the question of what are adiabatic processes tends to be that these are so fast processes with a gas that there is essentially no heat exchange with the gas (during the given time period, the heat transferred conductively and radiatively to the gas remains much smaller than the internal energy of the gas).

However, this is only half of the truth, and actually the less important half. In order to understand this, let us consider the following simple problem. Thermally isolated vessel is divided into two halves via a wall. Let one of the halves contain a gas at a pressure p , and let the other one be empty (i.e. contain vacuum at a negligibly small pressure). The wall separating the two halves is removed instantaneously; what is the pressure of the gas inside the vessel upon achieving mechanical and thermal equilibrium?

Since the wall is removed instantaneously, the gas cannot perform any mechanical work (the wall does not move in the direction of the force). There is no thermal exchange to the environment and so according to the 1LTD the internal energy remains constant, hence the temperature does not change. Meanwhile, the volume is increased twice and due to the ideal gas law, this means that the pressure is decreased twice. So, we dealing with an isothermal process, and not with an adiabatic one!

As a matter of fact, the main requirement for having an adiabatic process is that the process needs to be sufficiently slow — the characteristic time of the process needs to be much longer than the period of natural oscillation of the system. In the case of gases, the natural oscillation modes are standing waves; the period of the slowest mode is $c_s/2L$, where L is the vessel length and the factor two accounts for the fact that the

wavelength of the longest standing wave has wavelength equal to $2L$; c_s denotes the speed of sound. Thus, $v/L \ll c_s/2L$, hence $v \ll c_s$, where v is the speed of the container walls (or of a piston).

def. 8: Adiabatic process is a process by which the system parameters change so slowly that the characteristic time of changing is much longer than the period of the slowest mode of natural oscillations; also, there should be no dissipative processes (where mechanical energy is converted to heat), e.g. friction. In the case of gases, this means that the speed of the container walls needs to be much smaller than the speed of sound, and also there should be no external heat supply.

Adiabatic processes in such a wider-than-thermodynamical sense play important role also in quantum mechanics, electrodynamics, etc.

In the course of analytical mechanics it is shown that for adiabatic processes on periodically oscillating systems, the so-called adiabatic invariant is conserved; this is the surface area of the loop drawn by the oscillator in the phase plane (the curve in $x - p_x$ -plane $\oint p_x dx$, where x is the coordinate and p_x — the corresponding momentum), c.f. the booklet of mechanics. While a general proof is complicated, a problem of the mechanics booklet dealt with a particle bouncing back and forth between two slowly moving plates; it was shown that $Lv = \text{Const}$, v being the particle's speed and L — the distance between the walls.

Now, let us consider one-dimensional gas: there are many particles bouncing along the x -axis between the plates. From the molecular kinetic theory, the pressure of such a gas $p = nm\bar{v}^2$. The number density of the particles is, of course, inversely proportional to the “volume”, which is in the one-dimensional case just the distance between the plates L , i.e. $n \propto 1/L$. Due to the adiabatic invariant, the speed of each of the molecules is inversely proportional to L and hence, the average speed follows the same law, $\bar{v} \propto 1/L$. Thus, $p \propto 1/L^3$, or alternatively, $pL^3 = \text{Const}$. This is our adiabatic law for the one-dimensional gas: $pV^\gamma = \text{Const}$, with $V = L$ and $\gamma = 3$.

What is even more important, is that in quantum mechanics, the surface area in phase space is related to the quasi-classical quantization rule, for n -th quantum-mechanical energy level, $\oint p_x dx = n\hbar$. Now, if the potential changes slowly in time, the adiabatic invariant is conserved, hence the system will remain at the same quantum-mechanical energy level (with the same order number) as it was at the beginning (exceptions are possible only in the case of a “separatrix-crossing”, e.g. if the “potential well” becomes so narrow that the given bound state disappears, and the particle formerly bound to the well becomes free).

idea 8: During adiabatic processes, particles remain at their initial quantum-mechanical levels. When combining this observation with the Boltzmann's law, it is often possible to find the new temperature.

pr 15. Expansion of our Universe can be considered as an adiabatic processes for the photons of the microwave background radiation: the wavelength of the photons grows proportionally to the linear size of the Universe. How many times

3. GASES

will change the temperature of the radiation, if the linear size of the universe grows two times? What is the adiabatic exponent for a photon gas?

For the adiabatic processes with gases, it is also required that the heat exchange rate of the given gas is negligibly small (as compared with the internal energy change): $\Delta Q = 0$. If we recall the adiabatic motion of a particle between two walls, we see that the no-heat-exchange requirement is very much consistent with that adiabatic process: the particle did not receive any external energy apart from the energy received from the moving wall (heat flux corresponds to an external energy source for the kinetic energy of the molecules), and there were no energy losses due to friction or other processes. So, the adiabatic process with a gas can be arbitrarily slow, in principle, but in practice, for too slow processes the heat exchange can no longer be ignored.

Before we derive the adiabatic law for gases, let us note that at Olympiads, this derivation is typically not needed, it suffices just to use the law.

To begin with, we apply the 1LTD to an adiabatic process on one mole of gas, $dU = pdV$, where $dU = c_V dT$, i.e.

$$c_V dT = -pdV.$$

Note that even though the volume is not constant, the internal energy change is expressed in terms of c_V . This is a standard method: with constant volume, there is no mechanical work done and hence, all the provided heat $c_V dT$ goes to the change of the internal energy dU .

idea 9: Internal energy change can be calculated as

$$dU = c_V dT.$$

We want to derive relationship between the pressure and volume, so we need to eliminate here the temperature; to that end, we use the ideal gas law, $RT = pV$, hence

$$RdT = pdV + Vdp.$$

Here we applied the differentiation rule $d(pV) = pdV + Vdp$. Now we can easily eliminate dT from these two equations to obtain

$$pdV(c_V + R) + c_V Vdp = 0.$$

Let us notice that $c_V + R = c_p$, and introduce the adiabatic index defined as

$$\gamma = c_p / c_V.$$

This allows us to rewrite the last equation as

$$\gamma \frac{dV}{V} + \frac{dp}{p} = 0.$$

If we integrate this equality, the first term yields $\int \gamma \frac{dV}{V} = \gamma \ln V = \ln V^\gamma$, and the second one — $\int \frac{dp}{p} = \ln p$, so that $\ln V^\gamma + \ln p = \ln pV^\gamma = \text{Const}$, hence

$$pV^\gamma = \text{Const}.$$

Now, let us return to the one-dimensional gas discussed before; it has one degree of freedom, thus $c_V = \frac{1}{2}R$ and $c_p = \frac{3}{2}R$ so that $\gamma = 3$, which is in a complete agreement with our result for the adiabatic invariant. Let us make an intermediate summary.

fact 12: Adiabatic law, which is valid simultaneously with the ideal gas law $pV/T = \text{Const}$, states that

$$pV^\gamma = \text{Const}; \text{ kus; } \gamma = c_p / c_V.$$

Combining this with the gas law we have also equalities

$$TV^{\gamma-1} = \text{Const}; \text{ and; } T^\gamma \propto p^{\gamma-1}.$$

idea 10: For adiabatic processes, the work done can be calculated as the change of internal energy (since there is no heat exchange):

$$\Delta A = \nu \frac{i}{2} R \Delta T = \int p dV.$$

For real-life problems when the applicable assumptions are not explicitly stated, it is important to understand, when the heat exchange rate can be neglected (then the process is adiabatic), and when the heat exchange is so fast that the process is essentially isothermal. Here it is useful to compare characteristic time scales of thermal relaxation time τ_{th} (the time during which the temperature differences decrease by a factor of e), and the characteristic time of the process itself (e.g. the time during which the system is brought from its initial state to the final state). It is useful to know that the thermal relaxation time depends on the system size (linear dimension) L , being proportional to L^2 ; in the case of air under normal conditions, for $L \approx 1$ cm, $\tau_{th} \approx 1$ s.

Next we proceed to the discussion of atmospheric processes.

idea 11: When air masses are in vertical motion, typically during day time, but also during cyclonal activity and strong winds, the vertical motion of air incurs adiabatic expansion. This results in the so-called adiabatic atmosphere, where the temperature falls with the height h ,

$$T^\gamma \propto p^{\gamma-1}, \quad p = p_0 - \rho gh;$$

here the expression for p is valid for moderate height differences when the variation of the air density ρ can be neglected.

Indeed, air masses are very large and hence, even though the air may rise slowly, the thermal relaxation time is even slower, so that the process is adiabatic. During daytime, the vertical motion of air is caused by sunlight heating the ground, which in its turn, heats the air via thermal conductivity (note that as air is transparent, it doesn't absorb light, and hence, direct heating by sunlight is negligible). The heated air has smaller density than the colder air at higher altitudes, and starts rising. At the ground level, void cannot be created, so there must be also descending air masses. So, air moves up and down, resulting in a fairly good vertical mixing, and adiabatic atmosphere. What does it mean in terms of temperature drop at high altitudes, we'll learn through the following problem.

pr 16. What is the temperature at the top of a hill of height $H = 200$ m if at the bottom of the valley $t_0 = 20^\circ\text{C}$? You can assume that when air masses move along the slope of the hill, air expansion and/or contraction can be considered to be adiabatic. The air pressure at the valley level $p_0 = 10^5$ Pa, air density $\rho = 1,29$ kg/m³ and adiabatic index $\gamma = 1,4$.

This problem can be solved very fast if we make use of the fact that here, the relative pressure change is very small.

idea 12: In the case of equalities involving products, e.g. $a^\alpha b^\beta = \text{Const}$, if the relative changes of variables are small ($\Delta a \ll a$, $\Delta b \ll b$) then it is convenient to use approximate calculation based on logarithmic differentiation,

$$0 = d \ln(a^\alpha b^\beta) = \alpha \frac{da}{a} + \beta \frac{db}{b} \Rightarrow \alpha \frac{\Delta a}{a} = -\beta \frac{\Delta b}{b}.$$

If the hill height would be very large, so that air density difference between the top and bottom of the mountain would be

3. GASES

significant, it would be necessary to use here the Boltzmann's distribution $\rho \propto e^{-\mu gh/RT}$. While for $\mu gh \ll RT$, this is expression can be simplified using linear term of the Taylor's expansion $e^x \approx 1 + x$, the same approximate result can be obtained (arguably) more easily using the following idea.

idea 13: If the height differences are small and there is no need to apply the Boltzmann's distribution, the air pressure change can be found as the air column pressure $\Delta p = \rho gh$, where ρ can be considered in the first approximation to be independent of height.

Using the result of this problem, it becomes also clear, why mountain peaks are snowy — for instance 3 km would correspond to the temperature difference of 30 degrees. In reality, the temperature difference remains somewhat lower since the air which ascends along the mountain slopes is being heated due to heat conductance from the mountain surface (see above).

During calm night weather, the adiabatic atmosphere may not be observed. This is because the Earth's surface gives away heat via radiation and cools down; lower air masses are also cooled via heat conduction. Let us note that heat radiation of the air itself is negligible: being transparent, it doesn't absorb radiation; due to the 2LTD, absorption and radiation are symmetric phenomena and therefore clean air cannot radiate. Lower cold air layers have higher density and therefore, a very stable air stratification is formed: there is almost no vertical air motion. Such a phenomenon is called "inversion". In the case of inversion, all the waste gases remain near the surface, giving rise to high air pollution.

Bernoulli equation, $\frac{1}{2}\rho v^2 + \rho gh + p = \text{Const}$ (where ρ is the density, v — speed, p — pressure, g — free fall acceleration, and h — height) is a well-known equality expressing the fact that in the case of a stationary flow, the energy flux entering any volume must be equal to the energy flux exiting that volume; otherwise, the total amount of energy inside that volume would start growing, contradicting the assumption of stationarity. Bernoulli equation, however, is valid only in the case of incompressible flows. As we have seen above, atmospheric air flows are typically adiabatic, in which case the energy balance equation needs to take into account the change of internal energy of the gas, and the work done by expansion.

idea 14: For problems set on stationary gas flow, two conservation laws are to be used. **First**, along streamlines

$$\frac{v^2}{2} + gh + c_p T = \text{const},$$

where $c_p = C_p/M$ is the specific heat of the gas per unit mass by constant pressure (C_p denotes the molar specific heat, and M — the molar mass). This equality reflects energy conservation. Alternatively, if the flow speed is much smaller than the sonic speed and density variations along streamlines remain small, $\frac{\Delta \rho}{\rho} \ll 1$, the original Bernoulli law

$$\frac{1}{2}\rho v^2 + \rho gh + p = \text{const}$$

can be also used.

Second,

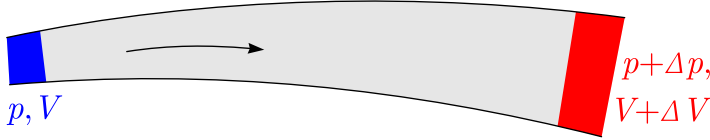
$$\rho v A = \text{const},$$

where A is the cross-sectional surface area of a fictitious tube formed by streamlines; this reflects mass conservation as ρv

is equal to the mass flux density (mass passing a unit cross-sectional area per unit time).

It should be emphasized that in the case of gas flows when ρ is not constant, $\frac{v^2}{2} + gh + c_p T = \text{const}$ holds exactly; meanwhile, the Bernoulli law is valid only at the limit $\frac{\Delta \rho}{\rho} \ll 1$.

The fact that the Bernoulli law can be used at the limit $\frac{\Delta \rho}{\rho} \ll 1$ is actually non-trivial. Indeed, the Bernoulli law is derived from energy balance: work done by pressure is converted into kinetic and/or potential energy. However, when gas is compressible, there is also a conversion into internal energy due to compression.



Consider a displacement of a certain amount of gas inside a fictitious tube made from streamlines as shown in figure: let us assume that before displacement, this volume of gas occupied the region shaded into blue and grey. As the result of displacement, now it occupies the region shaded into grey and red. There is no change in the state of the grey region, but gas from blue region has been moved into the red region. The change in kinetic energy is $\frac{m}{2}(v_r^2 - v_b^2)$, where v_b and v_r stand for the gas speeds at the blue and red positions, respectively. Energy balance is written as

$$W = \frac{m}{2}(v_r^2 - v_b^2) + \Delta U,$$

where ΔU is the change of the internal energy, and the work done by external pressure

$$W = pV - (p + \Delta p)(V + \Delta V).$$

Now, consider a longer displacement of gas — such that the gas of the blue region has covered the whole distance from blue to red, and occupies now the volume shaded into red. During that displacement, the process on the parcel was adiabatic, so $\Delta U = -\int p dV$; assuming $\frac{\Delta p}{p} \ll 1$ (which is equivalent to requiring $\frac{\Delta \rho}{\rho} \ll 1$), the integral can be approximated as $\Delta U = -p\Delta V$. Returning to the energy balance equation, we can write

$$\frac{m}{2}(v_r^2 - v_b^2) = V\Delta p + \Delta V\Delta p,$$

which gives us the Bernoulli law if we neglect the quadratically small term $\Delta V\Delta p$ and assume that the densities at the blue and red positions are approximately equal, $\frac{m}{V} \approx \frac{m}{V+\Delta V}$. This is valid if the relative change in the flow speed is much larger than the relative change in density, which is true if the flow speed is much smaller than the sonic speed.

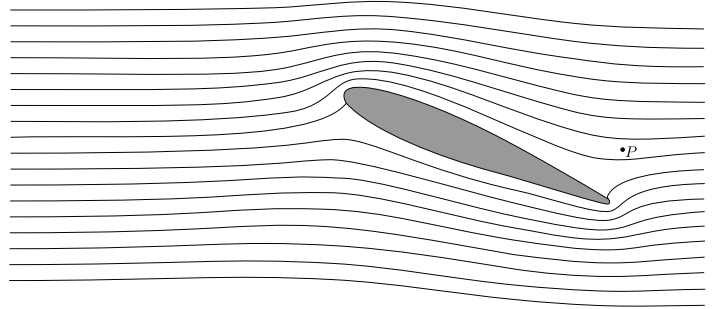
When we derived here the Bernoulli law, we used a trick which can be also formulated as an idea.

idea 15: If a column of liquid or gas, a rod or a rope (and so on) moves parallel to itself so that the new state and old state mostly overlap, and there are only small regions where the state has been changed (e.g. the red and blue regions in the figure above), the change of the total energy (momentum, angular momentum, etc.) can be calculated by considering only those regions where the state has been changed.

pr 17. Prove that for a stationary gas flow, along streamlines $\frac{v^2}{2} + gh + c_p T = \text{const}$.

3. GASES

pr 18. [IPhO-2012] In the fig. below, a cross-section of an aircraft wing is depicted together with streamlines of the air flow around the wing, as seen in the wing's reference frame. Assume that (a) the air flow is purely two-dimensional (i.e. that the velocity vectors of air lie in the figure plane); (b) the streamline pattern is independent of the aircraft speed; (c) there is no wind; (d) the dynamic pressure is much smaller than the atmospheric pressure $p_0 = 1.0 \times 10^5 \text{ Pa}$. You can use a ruler to take measurements from the fig. on the answer sheet.



- If the aircraft's ground speed is $v_0 = 100 \text{ m/s}$, what is the speed of the air v_P at the point P (marked in fig.) with respect to the ground?
- In the case of high relative humidity, as the ground speed of the aircraft increases over a critical value v_{crit} , a stream of water droplets is created behind the wing. The droplets emerge at a certain point Q . Mark the point Q in fig. on the answer sheet. Explain qualitatively (using formulae and as few text as possible) how you determined its position.
- Estimate the critical speed v_{crit} using the following data: relative humidity of the air is $r = 90\%$, specific heat of air at constant pressure $c_p = 1.00 \times 10^3 \text{ J/kg} \cdot \text{K}$, pressure of saturated water vapour: $p_{sa} = 2.31 \text{ kPa}$ at the temperature of the unperturbed air $T_a = 293 \text{ K}$ and $p_{sb} = 2.46 \text{ kPa}$ at $T_b = 294 \text{ K}$.

Idea 14 is also useful when deriving sound speed c_s in a gas. Then, however, we need one more idea.

idea 16: In order to find the propagation speed of a pulse in homogeneous medium, for instance gas or stretched rope, it is convenient to use a moving reference frame where the pulse is at rest.

Let us consider a sound wave which propagates in the direction of x -axis; then, the air density $\rho = \rho(x - c_s t)$. Following the idea 16, we consider a frame which moves with speed c_s , with coordinate axis $x' = x - c_s t$. In that frame, the density perturbation remains constant in time, $\rho = \rho(x')$. This means that we can use idea 14, so that we obtain two equations:

$$\begin{aligned} (\rho_0 + \Delta \rho)(v + c_s) &= \rho_0 c_s, \\ \frac{1}{2}(v + c_s)^2 + c_p T &= \frac{1}{2}c_s^2 + c_p T_0, \end{aligned}$$

where $v \ll c_s$ is the speed of gas in laboratory frame. In sound wave, the density perturbations are typically small so that we can assume $\Delta \rho \ll \rho$. Upon opening the braces and neglecting quadratically small terms (e.g. $v\Delta \rho$ and v^2), we obtain

$$\rho_0 v + c_s \Delta \rho = 0, \quad c_s v + c_p \Delta T = 0.$$

If the wavelength is long enough (much longer than the mean free path length of the gas molecules), the gas flow is adiabatic, so that we can relate ΔT to $\Delta \rho$ via adiabatic law $T\rho^{1-\gamma} =$

const. Using the idea 12, we obtain $\frac{\Delta T}{T_0} + (1 - \gamma) \frac{\Delta \rho}{\rho_0} = 0$, hence $\Delta T = (\gamma - 1) \frac{T_0}{\rho_0} \Delta \rho$. With this, our equations can be rewritten as

$$\rho_0 v + c_s \Delta \rho = 0, \quad \rho_0 c_s v + c_p (\gamma - 1) \frac{T_0}{\rho_0} \Delta \rho = 0,$$

where $c_p (\gamma - 1) = M^{-1} C_p \frac{C_p - C_v}{C_v} = M^{-1} C_p \frac{R}{C_v} = \gamma \frac{R}{M}$. This is a set of two linear equations with two unknowns, v and $\Delta \rho$ which can have non-zero solutions only if the determinant is zero (the equations are linearly dependent), i.e.

$$c_s^2 = \gamma \frac{RT_0}{M}.$$

When calculating c_s , we have ignored one important fact: in the case of straight streamlines (what we have in the case of planar wavefronts/one-dimensional wave propagation), apart from energy and mass conservation, we have also the conservation of linear momentum of the gas.

pr 19. Show that in the case of gas flow along straight streamlines, due to Newton's II law for the gas parcels,

$$\rho v^2 + p = \text{const.}$$

It should be emphasized that this last law is valid only in the case of straight streamlines: otherwise, the pressure force by which the walls of the fictitious tube (made from streamlines) act on the gas parcels would also contribute to the acceleration along streamlines.

When we calculated c_s , we used three equations: energy conservation law, $\frac{1}{2}v^2 + c_p T = \text{const}$, mass conservation $\rho v = \text{const}$, and adiabatic law $\rho^{1-\gamma} T = \text{const}$. We could have substituted the adiabatic law with the momentum conservation law $\rho v^2 + p = \text{const}$, and still we would have obtained the same result. This means that if the amplitude of the density perturbations is small, the four equations are linearly dependent, and the adiabatic law can be derived from the remaining three: Thus, as long as the amplitude of the wave is small, the sound propagation is adiabatic. On the other hand, for large amplitudes this is no longer the case: the three conservation laws (known as the *Rankine-Hugoniot conditions*) may (and will) be in contradiction with the adiabatic law. Therefore, in the case of large-amplitude shock waves, the process on gas is not adiabatic, and part of mechanical energy is converted into heat.

pr 20. In the case of a shock wave, a high-pressure region propagates in gas with a speed which is somewhat larger than the sound speed. Consider a shock wave in which air density grows exactly two times; how many times is such a shock wave faster than the sound speed?

Interface between liquid and vapours

The liquid (and crystal) particles (atoms, molecules, ions) are bound to each other via chemical bonds — forces which depend on the distance between particles in a complicated way. By origin, these forces have electrostatic nature: the interplay of quantum-mechanical laws and electrostatic interactions between orbital electrons and atomic nuclei results in the force between particles being a complex function of the positions of interacting particles. At small distances between the atomic nuclei, the force becomes repulsive (positive charges of nuclei

3. GASES

repel), at moderate distances the force is attractive (this keeps the particles together in the liquid or crystal phase), and at large distances the force decays faster than the electrostatic law of r^{-2} . Attraction at moderate distances means that the potential energy (with respect to an infinite distance) for a typical near-neighbour-pair is negative; let the average potential energy per particle be $-U_0$. For particles inside the liquid (or crystal) phase, the number of near neighbours is larger than for the particles at the surface. Respectively, the average potential energy of the inter-particle forces per particle at the surface is also smaller by modulus than U_0 ; let us denote the energy difference by ΔU_0 . Now we can draw two conclusions.

First, increasing the surface area of a liquid will increase the number of particles at the surface, and hence, the overall energy of molecular forces. Naturally, the number of particles adjacent to the surface is proportional to the surface area A , and so is the overall energy W associated with the particles being at the surface instead of being inside the bulk of the liquid: $W = \sigma A$, where the coefficient σ characterizes the molecular forces of the liquid, and is called **the surface tension**. This phenomenon will be discussed in the next section.

Second, in order to pull out a particle from the liquid phase, it needs to obtain energy U_0 (this energy is analogous to the work function in the Einstein's equation of photoelectric effect). Thus far we have learned that in thermodynamical systems, particles can be in higher- and lower-energy-states, which means that the liquid molecules can obtain also, due to random interactions with other molecules, energy exceeding U_0 , and as a result, "jump out" of the liquid phase. This process (molecules jumping out of the liquid) gives rise to *evaporation*: the number of molecules in liquid phase will decrease. However, there is also the reverse process, *condensation* at the liquid surface. Indeed, if the gaseous phase above the liquid surface contains the molecules of the liquid, the vapour molecules (which are in a random motion) can hit the liquid surface and get "stuck" to it.

For a molecule, the probability of having an additional energy exceeding U_0 is proportional to $e^{-U_0/kT}$; the **evaporation rate** is proportional to that probability and hence, increases very rapidly with the temperature. **Condensation rate**, on the other hand, is less sensitive to the temperature (is proportional to the speed of the molecules, i.e. \sqrt{T}), and depends mostly on the concentration of the vapour molecules in the gaseous phase. Obviously, if the evaporation rate exceeds the condensation rate, the amount of liquid is decreasing, and *vice versa*. If we take a certain amount of liquid and seal it tightly into a bottle, the two processes reach an equilibrium: the concentration of the vapour molecules in the gaseous phase will reach such a value that the evaporation rate equals to the condensation rate.

def. 9: Vapour with such a concentration which leads to the condensation rate being equal to the evaporation rate at the given temperature is called the *saturation vapour*.

Most often, the amount of vapours is measured as the partial pressure caused by the given type of molecules in the gaseous phase. This method is valid owing to the Dalton's law.

fact 13: Dalton's law states that pressure is an additive

quantity: the total pressure exerted by a gas equals to the sum of *partial pressures*: $p = P_A + P_B + \dots$, where p_A is the pressure due to the molecules of type A , p_A — that of molecules of type B , etc.

This law follows directly from the principles of molecular kinetic theory: pressure is the momentum of molecules transferred to the container walls per unit time and unit surface area, and according to the laws of mechanics, momentum is an additive quantity (the momentum of an entire system is the sum of the momenta of all its parts).

Returning to the vapours, the saturation vapour is typically characterised via its pressure, the *saturation vapour pressure*.

def. 10: The *relative humidity* is defined as the ratio of the vapour pressure to the saturation vapour pressure at the given temperature of the gas.

There is another process which is very similar to evaporation: **sublimation**. In the case of sublimation, the only difference is that the molecules go straight from solid phase to gaseous phase; examples for sublimation include water at temperatures below 0°C , and iodine at room temperatures. In the case of sublimation, the notions of saturation pressure, vapour pressure, and relative humidity remain intact.

The following problem tests understanding of the concept of saturation pressure.

pr 21. In vacuum and weightlessness, at the bottom of a cylindrical vessel (a cup), there is a layer of solid substance. This substance sublimates slowly (evaporates from the solid phase into gaseous phase) and pushes thereby the vessel to the opposite direction. The mass of the vessel is M , and the initial mass of the substance $m \ll M$. The cross-sectional area of the vessel is A , and the pressure of saturated vapours of the substance at the temperature T is p_0 . What is the acceleration of the vessel? Provide answer for two cases: (a) the mean free path length λ of the molecules at the saturation pressure is much smaller than the length of the vessel, and (b) much larger than that.

If the current vapour pressure is smaller than the saturation vapour pressure (i.e. relative humidity is smaller than 100%), evaporation at a liquid surface dominates over condensation, and the mass of liquid is slowly decreasing. On the other hand, if the relative humidity is larger than $r = 100\%$, condensation dominates over evaporation. However, unlike evaporation, condensation can take place not only at the free liquid surface, but also start forming droplets. Still, the vapour molecules cannot start forming a droplet at an empty space as in the case of a very small droplet (of the size of few molecules), the liquid phase is not yet formed, and molecular attraction forces are not strong enough to keep molecules together (the binding energy is smaller than that of a liquid phase, U_0). Therefore, in order to start forming a droplet, a condensation centre is needed: it may be dust particle or tiny salt crystal hovering in air. So, around each such condensation centre, a tiny droplet is formed; this is a mist. If there is a sufficiently large number of condensation centres, the tiny droplets “suck away” all the excess vapour, leading to $r = 100\%$. If the number of con-

3. GASES

densation centres is smaller, each of the droplets will need to absorb the vapours from a larger volume, so the process will take longer time. In the case of extremely clean air, when there are only very few condensation centres, for a certain period of time $r > 100\%$ is possible, such a gas is called an *oversaturated vapour*.

Now, let us discuss in more details evaporation at $r < 100\%$. In the case of water vapours in air, air is most often relatively dry, with r ranging typically from 40% to 80%. This is the case because free water surface forms only a small fraction of all the surfaces: solar heating reduces r by increasing the saturation pressure, but the vapour pressure remains almost constant since there no vapour sources (in the form of liquid water) are available. Even relatively close to water surfaces, r will remain moderate: there is not enough time for establishing a thermal equilibrium, evaporation is relatively slow and moving air brings new dry air masses into contact with the water surface.

However, at a narrow layer near water surface, the air moves slowly due to friction against the water surface; let the thickness of this (almost) stagnant layer of air be δ (note that δ depends on the wind speed: strong wind makes the stagnant layer narrower). The air molecules in the stagnant layer prevent the water vapour molecules leaving into the bulk of the air: water molecules hit often the air molecules and move randomly back and forth; as a result, their departure speed from the water surface is slow as compared with the thermal speed. If the mean free path λ of the vapour molecules is much smaller than the thickness of that surface layer (which is normally the case) then we can consider separately a thin layer of air which is directly above the water surface, with the thickness of few λ (this layer is the lowest part of the stagnant layer). Within that layer, let us consider two processes: **first**, molecules jumping from the water into the thin layer and then returning to the liquid phase after performing few collisions with air molecules; **second**, vapour molecules leaving the stagnant layer of thickness δ . Since $\lambda \ll \delta$, the characteristic time scale of the first process is much smaller than that of the second process. If one process is much faster than the other, a quasi-equilibrium is reached for the faster process. Therefore, inside the thin layer of thickness λ , thermal quasi-equilibrium is reached between the water molecules in the liquid phase and vapour phase: the water molecules jump out from the liquid phase almost as often as the vapour molecules hit the surface and get stuck into the liquid. By the definition of the saturation pressure, this means that inside the thin layer, the vapour pressure equals to the saturation pressure (at the water surface temperature).

If there were no collisions with the air molecules, i.e. if the mean free path of the molecules were very large and those molecules which jump out of the surface would never return, the evaporation rate could be derived from the saturation vapour pressure. Indeed the full saturation pressure can be divided into two components: the momentum per unit time and unit area, (a) exchanged by those molecules which jump out of the water, with those molecules which remain in the liquid-phase, and (b) transferred by those vapour molecules which hit the water surface and get “stuck” into it, to the liquid water. At equilibrium, both processes have equal intensities, hence both

[pr 21.]

contribute half of the saturation pressure. If the second component were missing, the vapour pressure would be reduced to the half of the full saturation pressure, and the evaporation intensity (number of molecules leaving per unit time and unit area) could be expressed in terms of the saturation pressure, temperature, and molar mass using the kinetic theory of gases.

In reality, however, as long as we are not dealing with sublimation in vacuum, the vapour molecules cannot leave freely the boundary layer, and many molecules end up colliding again with the water surface, and condensing at it. Then, the effective evaporation rate is defined by the interplay of two processes: molecules (a) jumping out of the water surface, and (b) diffusing through the boundary layer. As discussed earlier, directly above the water surface, the water and vapours are at equilibrium, i.e. $r = 100\%$. At the top of the stagnant layer, air motion brings fresh air with relative humidity r equal to that of the bulk of the air masses. The thickness of the stagnant layer depends mainly on the wind speed; narrower layer means higher vapour concentration gradient, and hence, larger flux of vapour molecules, i.e. larger evaporation speed. Therefore, moist things dry faster if the relative humidity of air is low, and if there is a strong wind.

idea 17: If the dependence between two physical quantities y and x is given as a graph where y is plotted versus x [$y = f(x)$], and you are asked to find, which value of x (or f) is taken, and from theoretical considerations one can derive another functional dependence between f and x , for instance $y = ax + b$, then the solution can be found as the intersection point of two graphs, $y = f(x)$ and $y = ax + b$.

Thus, it suffices to draw a line $y = ax + b$ onto the (provided to you) graph $y = f(x)$, and read out the intersection point coordinates. If the theoretical dependence is not linear, plotting efforts are increased: either you redraw the graph $y = f(x)$ using other coordinates — such that the theoretical dependence would be given by a straight line — or plot onto the given graph $y = f(x)$ the curve corresponding to the theoretical dependence. In generic case, there is no need for the theoretical dependence to be a linear function; however, linear dependences are not too rare. For instance, in the case of electrical circuits, Kirchoff's laws ensure linearity, c.f. idea ?? from the booklet of electrical circuits.

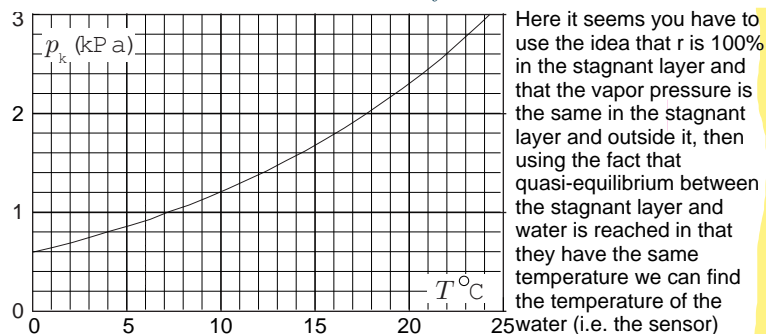
pr 22. [EstPhO-1997] One method for finding relative humidity is based on taking the readings of a dry and a wet thermometer. The wet thermometer has a wet piece of cloth wrapped around its sensor. For the method to yield an accurate result, a wind must blow onto the wet sensor (you can create it using a fan). Throughout this problem, you can use the graph of the pressure of saturated water vapours as a function of temperature.

When wind blows onto the wet sensor, there will be two processes influencing the sensor temperature: first, wind removes the high-humidity air from the neighbourhood of the wet cloth surface so that the water can evaporate; second, it increases the heat flux from the warm air towards the colder sensor by reducing the thickness of the stagnant air layer where the temperature drop is localized. For question a) you may neglect

3. GASES

the effect of the heat flux (i.e. assume that the heat conductivity of air is very small). In what follows, assume that the air temperature $T_0 = 20^\circ\text{C}$.

a) Find the temperature difference between the wet and dry thermometers if the relative humidity $r = 90\%$.



b) If we assume that the wind blows with a fixed speed, then the conductive heat flux Q_c (measured in watts) is proportional to the difference between the temperature of the air T_0 and that of the wet cloth T , $Q_c = a(T_0 - T)$. The coefficient of proportionality a depends on the shape and size of the wet cloth, as well as on the wind speed. Apart from the heat flux due to conductivity, there is also heat flux due to evaporation: evaporating molecules take away heat according to the latent heat of evaporation. This evaporation heat flux Q_e is proportional to the evaporation rate, which in its turn is proportional to the difference of the saturation pressure (at the temperature of the wet cloth), $p_s(T)$, and the pressure of vapours in the surrounding air, p_a . Thus, $Q_e = b[p_s(T) - p_a]$, where the coefficient b depends on the same things as the coefficient a .

However, it appears that the ratio a/b is a quantity which can be assumed to be constant for a wide range of conditions, assuming that the saturation pressure is much smaller than the atmospheric pressure. It does depend slowly on the air pressure and temperature, but for any reasonable temperatures and air pressures at the sea level it can be taken to be equal to $a/b = 65 \text{ Pa/K}$. Taken into account what has been mentioned above, what would be the reading of the wet thermometer if the air is absolutely dry (i.e. $r = 0$)?

c) Derive as simple as possible expression for finding the difference between the readings of the wet and dry thermometers within the relative accuracy of 10% which could be applied for $T_0 = 20^\circ\text{C}$ and for the humidity range $80\% < r < 100\%$.

d) A laundry is drying so that there is no direct sunlight falling onto it. In one case, the humidity is 95%, in the other case — 80%; all the other conditions are exactly the same. How many times faster will dry the laundry in the second case?

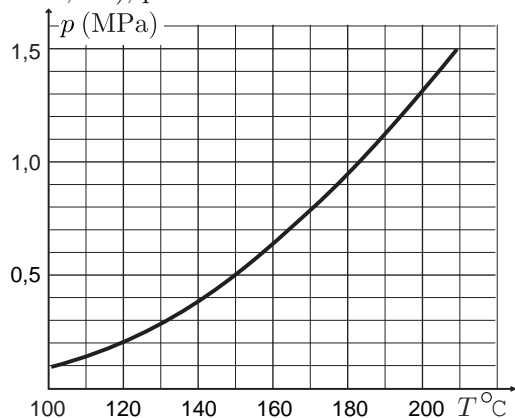
fact 14: Liquid will start boiling if the condition $p_s(T) > p_{\text{atm}}$ is satisfied.

Conversely, if $p_s(T) < p_{\text{atm}}$, the external pressure will not allow expansion of a bubble: larger external pressure would always compress the bubble back to its initial tiny size (defined by the impurity size, or the number of non-soluble molecules of some other gas inside it).

Only extremely clean liquids can be almost free of evaporation centres, in which case it is possible to have what is called **overheated liquids**: while $p_s(T)$ is slightly larger than p_{atm} , due

to the absence of evaporation centres inside the liquid, evaporation can take place only at the surface. Even though this process is now relatively fast (no wind is needed to accelerate evaporation as the vapours can now freely push away the air), there is no evaporation from the bulk in the form of bubbles, i.e. there is no boiling. This is very similar to the oversaturated vapours discussed earlier. Furthermore, under similar conditions (of very clean liquids) it is possible to have overcooled liquids which stay in the liquid phase below the melting point. For instance, a very clean water can stay liquid at few degrees below 0°C . **Both for overheated and overcooled liquids, shaking can initiate a very fast phase transition:** for overheated liquid, the excess heat is released via latent heat during partial evaporation, and in the case of overcooled liquid, part of the liquid solidifies releasing latent heat and raising the temperature to the melting point value.

It should be noted that overcooling can happen also with rain droplets, which leads to the phenomenon known as glaze frost: as soon as a droplet hits a solid surface (road, electrical wires, etc), part of the water solidifies at that solid surface.



pr 23. Geysers can be considered as large underground reservoirs which are filled with ground water and are being heated by hot walls. Such a reservoir is connected with the earth surface via a narrow and deep channel, which in the geyser's rest state (inactivity period) is filled with relatively cold water (the channel's walls are cold and do not heat the water inside the channel). The geyser becomes active when the water in the reservoir starts boiling; during the activity period, the channel connecting the reservoir with the ground surface is filled with water vapours. The fresh water supply rate of the reservoir is so slow that the inflow can be neglected during the (relatively very short) activity period; meanwhile, it is so fast that the entire reservoir and the entire channel (up to the ground surface) becomes filled with the water during the (relatively very long) inactivity period.

Let the height difference between the endpoints of the channel be $h = 90\text{ m}$. The latent heat of evaporation for water $\lambda = 2.26 \times 10^6\text{ J/kg}$; its specific heat $c = 4.2 \times 10^3\text{ J/kg} \cdot \text{K}$. The dependence of the saturated water vapour pressure on temperature is depicted in the graph. Find how large fraction of the water in the reservoir is lost during a single activity period.

If we have an interface between two liquids, the facts 13 and 14 need to be combined: into the bubbles at the interface of

3. GASES

two liquids, the molecules of both liquids can enter in the vapour phase. According to the Dalton's law, the pressure inside the bubble will be equal to $p_{1s} + p_{2s}$, where p_{1s} and p_{2s} are the saturation pressures of the first and second liquid at the given temperature, respectively.

fact 15: At the interface of two liquids, boiling can start at considerably lower temperatures than in both liquids, separately: boiling will start when the condition $p_{1s} + p_{2s} > p_{\text{atm}}$ is satisfied.

pr 24. [IPhO-1989] Consider two liquids A and B insoluble in each other. The pressures p_i ($i = A, B$) of their saturated vapours obey, to a good approximation, the formula $\ln(p_i/p_0) = a_i/T + b_i$, where p_0 denotes the normal atmospheric pressure, T — the absolute temperature of the vapour, and a_i and b_i ($i = A, B$) — certain constants depending on the liquid. The values of the ratio p_i/p_0 , $i = A, B$, for the liquids A and B at the temperature 40°C and 90°C are given in the table below.

T (°C)	p_A/p_0	p_B/p_0
40	0,248	0,07278
90	1,476	0,6918

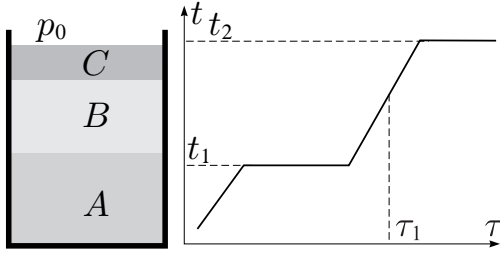
a) Determine the boiling temperatures of the liquids A and B under the pressure p_0 .

The liquids A and B were poured into a vessel in which the layers shown in figure were formed. The surface of the liquid B has been covered with a thin layer of a non-volatile liquid C , which is insoluble in the liquids A and B and vice versa, thereby preventing any free evaporation from the upper surface of the liquid B . The ratio of molecular masses of the liquids A and B (in the gaseous phase) is $g = M_A/M_B = 8$

The masses of the liquids A and B were initially the same, each equal to $m = 100\text{ g}$. The heights of the layers of the liquids in the vessel and the densities of the liquids are small enough to make the assumption that the pressure in any point in the vessel is practically equal to the normal atmospheric pressure p_0 . The system of liquids in the vessel is slowly, but continuously and uniformly, heated. It was established that the temperature t of the liquids changed with time τ as shown schematically in the figure. Determine the temperatures t_1 and t_2 corresponding to the horizontal parts of the diagram and the masses of the liquids A and B at the time τ_1 . The temperatures should be rounded to the nearest degree (in $^\circ\text{C}$) and the masses of the liquids should be determined to one-tenth of gram.

REMARK: Assume that the vapours of the liquids, to a good approximation,

- (1) obey the Dalton law stating that the pressure of a mixture of gases is equal to the sum of the partial pressures of the gases forming the mixture and
- (2) can be treated as perfect gases up to the pressures corresponding to the saturated vapours.



Surface tension

As we saw in the previous chapter, the molecules of a substance in the liquid phase are being attracted by the other liquid molecules and therefore have a certain negative potential energy with respect to infinity. Notice that those liquid molecules which are directly at the liquid-gas interface are being attracted by other molecules only from the side of the liquid phase. Therefore, for the molecules directly at the surface, as compared with the molecules in the bulk of the liquid, the number of attracting neighbours is smaller and respectively, the negative potential energy is also smaller by modulus. This missing negative energy can be interpreted as a positive energy of the surface, which is proportional to the number of molecules at the surface, which is in its turn proportional to the surface area of the liquid,

$$U = S\sigma,$$

where the coefficient of proportionality σ is called the surface tension. At room temperature, it takes typically values from 17 mN/m (diethyl ether) to 73 mN/m (water); and 480 mN/m for mercury. In the case of water, very small concentrations of substances known as surfactants can lower the surface tension two- or three-fold.

Now, let us consider a rectangular shape $a \times b$ of a liquid surface, and a process where we increase the side length a by Δa . By doing so we increase the surface area by $b\Delta a$, and hence, the surface energy by $\sigma b\Delta a$. As the energy was increased, some work must have been done. In order to increase the side length a , we needed to pull one edge of length b by Δa . Let us assume that in order to do so, a force F was needed. Then, from the energy balance we can equate the work done $F\Delta a$ with the energy increase $\sigma b\Delta a$; hence,

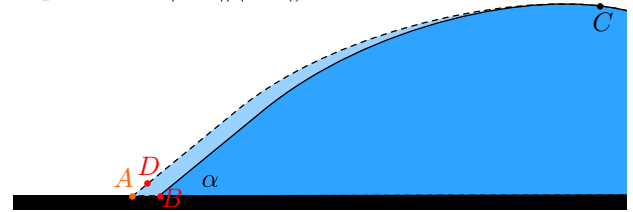
$$F = \sigma a,$$

i.e. σ is the force per unit length. **To sum up, similarly to the tension in rope, we can say that if we make an imaginary cut line of length L on the surface, the two halves of the surface pull each with force $F = \sigma L$.**

Note that **surface tension exists** not only at a free liquid surface, i.e. liquid-air interface, but **also at liquid-liquid interfaces between two insoluble liquids**, liquid-solid interfaces, solid-gas interfaces, and solid-solid interfaces. However, unless we have nano-scale (or smaller) objects in which case the surface-area-to-bulk-volume ratio (and along with it, the relative importance of the surface energy) is anomalously large, surface tension doesn't have noticeable effects at solid-solid and solid-air interfaces due to the fact that the size and shape of these surfaces is fixed by the shape of the solid bodies. As an exception, the energy of a solid-air interfaces becomes important if it is adjacent to a solid-liquid and solid-air interface. Let us consider this case in more details.

3. GASES

Let us consider the contact line of three substances, a gas (e.g. air), a liquid (e.g. water), and a solid (e.g. a glass where the water is kept). Thus we have liquid-gas, solid-gas, and solid-liquid interfaces; let the respective surface tensions be σ_{l-g} , σ_{s-g} and σ_{s-l} . We study the equilibrium for the position of the contact line of the three substances. Solid surface cannot be deformed, so this contact line can move only along the solid surface. Now, suppose that the length of the contact line is L and it moved towards the liquid phase from its initial position by a small distance $|AB| = a$, see figure depicting a cross-section of the system. Then the solid-gas surface energy was increased by $\sigma_{s-g}aL$, and the solid-liquid surface energy was decreased by $\sigma_{s-l}aL$. Suppose that the liquid-air and solid-liquid surfaces form angle α , see figure. Note that the figure is drawn assuming that the overall volume of the liquid is so large that the displaced liquid volume ABC flowing rightwards of the point P does not incur any significant changes in the liquid surface shape in that region. Then, the displacement of contact line will reduce the liquid-air surface energy by $\sigma_{l-g}aL \cos \alpha$. Indeed, from the right triangle ABC , the liquid-gas surface length is decreased by $|AD| = |AB| \cos \alpha$ (we ignore the length difference $|CD| - |CB|$ which has second-order smallness in the small parameter $|AB|/|AC|$).



Now we can conclude using the energy balance that it is energetically favourable for the contact line to move rightwards if $\sigma_{l-g} \cos \alpha + \sigma_{s-l} > \sigma_{s-g}$, and leftwards, if the opposite inequality holds; the equilibrium is possible only if

$$\sigma_{l-g} \cos \alpha + \sigma_{s-l} = \sigma_{s-g}.$$

Now we can express for the so-called contact angle α

$$\cos \alpha = \frac{\sigma_{s-g} - \sigma_{s-l}}{\sigma_{l-g}}.$$

In the case of normal liquids and surfaces, the contact angle is larger than 0 and smaller than π ; cases with $\alpha < \pi/2$ are referred to as *hydrophilic* or *wetting*, and cases with $\alpha > \pi/2$ — *hydrophobic* or *non-wetting*. In the case of *perfect wetting*, $\cos \alpha = 1$. In the case of even smaller values of σ_{l-g} we would obtain $\cos \alpha > 1$, which is clearly impossible; instead, inequality $\sigma_{l-g} + \sigma_{s-l} < \sigma_{s-g}$ means that the gas-solid surface tension σ_{s-g} is so large and the surface tensions of the liquid is so small that it is energetically useful for a drop of liquid to disperse over the whole solid surface so that it will be covered completely with a thin layer of liquid. If such a liquid is kept in a vessel with vertical walls, it would be even energetically favourable for the liquid to “climb” up along the walls: in the case of extremely thin liquid layer, gravitational potential energy would be negligible. However, the flow rate of the liquid in an extremely thin layer will be extremely slow due to viscous drag. Because of that, such behaviour can be observed only if there is no viscous drag, in the case of *superfluidity* (helium at very low temperatures).

If there were interfaces with $\sigma_{l-g} + \sigma_{s-g} \leq \sigma_{s-l}$, it would be energetically favourable to keep a narrow air gap between the

liquid and solid: liquid would not be sticking to the surface, and liquid droplets would be able to move essentially without a drag along the surface. While there are no such surfaces, there are interfaces for which $\cos \alpha$ is fairly close to -1 . For instance, the contact angle of mercury on most surfaces is around 140° .

pr 25. For some natural materials (e.g. lotus leaves), and for materials with modern nano-technological coatings, the contact angle of liquids is increased due to the micro-structure of the surface: there are microscopical “whiskers” which keep the droplets on the tips of the whiskers and reduce thereby the contact area between the liquid and the solid material. If the apparent contact area of a droplet with such a surface is A , and the real contact area due to the microscopic whiskers is rA with $r = 0.006$, what is the contact angle? Assume that without “whiskers”, the contact angle would be $\alpha_0 = 110^\circ$.

Note that the energy minimum condition can be also interpreted as the force balance condition for the line where the three phases meet (point A in figure): forces σ_{l-g} , σ_{s-l} , and σ_{s-g} (per unit length) pull the liquid molecules at the three-phase-contact-line along the liquid-gas, solid-liquid, and solid-gas interfaces, respectively. Hence, then the equality $\sigma_{l-g} \cos \alpha + \sigma_{s-l} = \sigma_{s-g}$ represents the equilibrium condition for the horizontal direction (along which the line could move if the area covered by the liquid were to contract or expand).

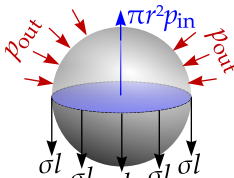
Let us sum up what we have learned.

fact 16: Interfaces between phases carry energy; each interface is characterized by the surface tension coefficient σ which gives the energy per unit area. As a direct consequence, σ gives also the force per unit length of a fictitious cut of the interface (known as the *surface tension* or *capillary force*).

Now, let us study the *capillary pressure* which is the gauge pressure due to spherical liquid-air interface of radius r , such as one would have in the case of a bubble inside a liquid, or a small droplet hovering in the air. Let us divide the bubble into two halves by a plane passing through its centre, and consider the force balance for one of the halves. To begin with, we need a new idea. *capillary pressure* is essentially pressure resulting from the surface tension forces

idea 18: It is often useful to consider a force balance condition for fictitiously separated part of a liquid involving gravity force, surface tension force, and force due to hydrostatic pressure.

Let us consider, for instance, an air bubble inside a liquid, and let us cut it fictitiously into two equal halves by a flat surface. The body for which we write the force balance consists of the air inside the half-bubble, and the hemispherical liquid-air interface around it. The forces acting on this body are: the capillary force across the cut line pulling towards the other half, $F_1 = 2\pi\sigma r$; the force due to the hydrostatic pressure p_{in} inside the bubble, $F_2 = \pi r^2 p_{in}$, exerted by the other half of the bubble and pushing the two halves apart from each other; the force F_3 due to the hydrostatic pressure p_{out} outside the sphere acting in the same direction as the capillary force. Note that p_{out} acts onto a curved surface so that the calculation of the resultant force would require integration $p_{out} \hat{x} \cdot d\vec{S}$, where \hat{x} is



3. GASES

a unit vector along the axis of the hemisphere, and $d\vec{S}$ is an infinitesimal surface element (its modulus being equal to the corresponding surface area, and pointing parallel to the surface normal). However, if such an hemisphere were surrounded both from the curved and flat sides by the same hydrostatic pressure (cf. a half of a watermelon subject to the air pressure in atmosphere), the body would obviously remain still at rest, i.e. the pressure forces to both sides would be equal. Therefore $F_3 = \pi r^2 p_{out}$. And so, the equilibrium condition for the hemisphere is written as $\pi r^2 p_{out} + 2\pi\sigma r = \pi r^2 p_{in}$, hence

$$p_{in} - p_{out} = 2\sigma/r.$$

In the case of a cylindrical surface, we can use a completely similar approach to obtain $p_{in} - p_{out} = \sigma/r$.

However, cylindrical geometry can be analysed also using a different approach: consider the force balance for a very small surface element (in figure, $\alpha \ll 1$) in the perpendicular direction to the surface (the x -axis in figure). The surface tension force F , tangent to the surface, is applied to the edges of the surface element, yielding $F_x = -\frac{1}{2}\sigma l \sin \alpha \approx -\frac{1}{2}\sigma l \alpha$ (l is the length of the surface element perpendicularly to the figure plane). The area of the surface element $\Delta A = l r \alpha$, and hence, the force balance is written as $(p_{in} - p_{out}) l r \alpha = 2F_x = \sigma l \alpha$, yielding immediately $p_{in} - p_{out} = \sigma/r$. Notice also that in the figure above, the liquid-gas interface can be thought to be a rope of tension T , in which case we obtain the normal force per unit length of the rope $n = T/R$.

Finally, the last paragraph illustrates a very important and universal method in physics, *differential calculus* approach. Differential calculus has many flavours: for instance, in mathematics, we speak most often about taking derivatives and integrals, and solving differential equations. In physics, it is a very useful skill to know how to show that one or another physical quantity is a certain integral (cf. idea ?? from the electrical circuits booklet). Let us try to give a specific recipe — summary about what was done in the previous paragraph.

idea 19: Consider (infinitesimally) small volumes (line segments, etc.) and write down applicable force balances and/or conservation laws for these volumes to derive either a relationship between physical quantities, or differential equations describing a physical quantity as a function of other quantities. Make use of the smallness of these quantities: drop anything which has higher order of smallness (e.g. squared small quantities).

Let us also sum up the capillary pressure results.

fact 17: The gauge pressure due to capillary forces across a curved interface is $\Delta p = 2\sigma/r$ in spherical geometry, and $\Delta p = \sigma/r$ in cylindrical geometry. this can be derived from virtual work

It appears that these expressions can be generalized to arbitrary shapes of the interface; here we just provide the result,

$$p_{in} - p_{out} = \sigma(r_1^{-1} + r_2^{-1}),$$

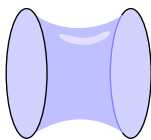
where r_1 and r_2 are the curvature radii of two curves at their crossing point P ; the two curves are formed as the intersection lines of the air-liquid interface with two planes, assuming that

all the three surfaces are mutually perpendicular at the point P . It can be shown that while the individual curvatures r_1 and r_2 depend on the orientation of the two plains, the sum $\sigma(r_1^{-1} + r_2^{-1})$ remains invariant when the planes are rotated around the normal drawn through the point P to the air-liquid interface.

In particular, the volume of a meniscus, the mass of a droplet falling from a water tube, etc. can be found using the idea 18, i.e. from the force balance condition for the surface tension force and the gravity force. The following problem serves as an illustration here.

pr 26. [EstPhO-1995] Measuring cylinder has volume $V = 100$ ml and height $h = 20$ cm. There are marker lines drawn on the cylinder after each 1ml. Suppose the cylinder is used for measuring water volume, and the reading is taken according to the lowest point of the curved water surface. How large mistake is made due to the fact that the water surface is curved, and not flat? Surface tension coefficient for water $\sigma = 0.073$ N/m; Assume that water wets perfectly the walls of the cylinder.

pr 27. [EstAcadPhO-2003] Two coaxial rings of radius $R = 10$ cm are placed to a distance L from each other. There is a soap film connecting the two rings as shown in figure. Derive a differential equation describing the shape $r(z)$ of the film, where r is the radial distance of the film from the symmetry axis, as the function of the distance z along the axis. Show that $\cosh x$ is one of its solutions. When the distance between rings is slowly increased, at a certain critical distance L_0 , the soap film breaks. Find L_0 .

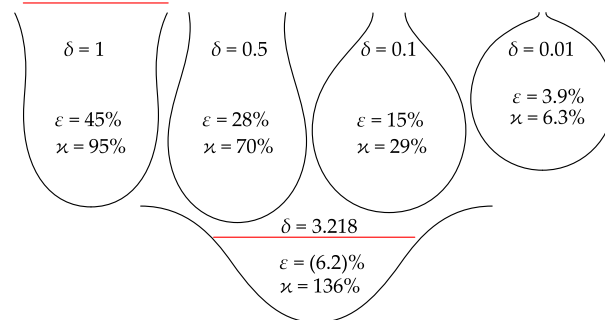


It is tempting to apply the idea 18 to the droplets falling from a tap, straw, or syringe, to relate the mass of a droplet to the internal diameter of the tap.

pr 28. Consider droplets falling from a syringe as the A a syringe is kept vertically an pointing downwards; it is pressed slowly so that liquid drops are falling from the tip of its needle (the needle's tip is flat, i.e. is cut perpendicularly to its axis). The surface tension of the liquid is σ , its density is ρ , free fall acceleration is g , and internal diameter of the needle d ($d \ll \sqrt{\sigma/\rho g}$) Find the mass m of a falling droplet (provide a correction to your answer by taking into account the small pressure force due to the gauge pressure inside the droplet).

This approach is, indeed, valid if the internal diameter d of the tap/syringe is small. However, if that is not the case, the problem becomes much more complicated. Based on the static force balance for horizontal layers of a growing droplet, a differential equation can be composed to determine the shape of the droplet. When liquid is being injected into the droplet, it is growing, and its shape is changing; at a certain moment, maximal size is achieved: with larger droplet volumes, for the given diameter of the tap, there are no solutions of the differential equation. This is the moment when the droplet falls. In the figure below, the shapes of falling droplets are depicted for different syringe (tap) radii r (indicated in dimensionless units, $\delta = r/\lambda$, where $\lambda = \sqrt{\sigma/\rho g}$ is the characteristic length scale at which capillary and hydrostatic pressures have the same order of magnitude, $\sigma/\lambda = \rho g \lambda$).

3. GASES



One can spot two issues which can invalidate the solution of the problem 28 for $\delta \gtrsim 0.5$: (a) **at the droplet's upper rim** (where it is connected to the tap), **the droplet walls are no longer vertical** (hence, the force balance needs to include the cosine of the angle between a vertical line and the surface tangent); (b) the pressure force due to the gauge pressure inside the droplet needs to be calculated more precisely (**curvature radii and hence, the gauge pressure change along the height of the droplet**). Furthermore, it is not clear, which part of the droplet separates from the tap when the droplet starts falling: it is apparently somewhat less than the whole volume depicted in the figure. The figure above indicates the relative correction to the droplet's mass ϵ due the above mentioned effects (for $\delta = 0.5$ and $\delta = 1$, it is assumed that what separates as a falling droplet is the part beneath the narrowest part of the droplet). Parameter κ shows the relative difference of the gauge pressures at the bottom and at the top of the droplet; **red line shows the level of zero gauge pressure**.

The case $\delta = 3.218$ (also shown in figure) yields the largest droplet (with all the volume beneath the rim of the tap being taken into account); it is also the droplet which is hanging from a horizontal ceiling when water vapours condense on it. When the tap radius is further increased, the droplets become even flatter, and at $\delta \approx 3.83$, the droplet's height becomes zero. When the tap radius is larger than 3.83λ , the tap can no longer contain water: due to what is known as the *Rayleigh-Taylor instability*, water flows out.

idea 20: Equilibrium states of a system can be found as its minimal total energy state; this is valid not only for mechanical systems, but also for systems involving thermodynamic (electromagnetic etc.) phenomena.

pr 29. [EstPhO-1995] Liquid is poured onto a horizontal totally non-wetting surface where it forms a pool (a layer of liquid). Find the thickness of the layer if the density of the liquid is ρ and the surface tension coefficient is σ . What would be the thickness if it were a partially wetting liquid, with the angle between the air-liquid and liquid-solid interfaces being equal to α ($0 < \alpha < \pi$)?

pr 30. Find the height of the meniscus in the case of problem 26, i.e. the height difference between the highest and lowest points of the air-liquid interface. Use the data of problem 26; the liquid density is ρ .

Finally, regarding instabilities due to surface tension: **any liquid tries to take the shape of minimal energy, which in the case of weightlessness is a sphere. Because of that, any other shapes, such as cylindrical or flat (soap films) are unstable.**

Three remembering devices for the Carnot' cycle:

1) tata (therm-adiab-therm-adiab) 2) (ta) < - expands (ta) < - contracts 3) all heat exchanges with reservoirs are isothermally

4. ENTROPY AND CARNOT CYCLE

In the case of a cylindrical shape, the instability evolves fairly fast; consider the following problem.

pr 31. [Seagull-2014] Due to instability (known as the Plateau-Rayleigh instability), a tap water stream breaks into droplets at a certain height. This process can be modelled by the instability of a long water cylinder in weightlessness. Let the diameter of the cylinder be $d = 1\text{ mm}$; estimate the time period T during which the amplitude of the most unstable perturbations will increase by a factor of $e \approx 2.718$. The surface-tension of water $\gamma = 72\text{ g/s}^2$, and the density $\rho = 1\text{ g/cm}^3$.



Due to the same reason, falling droplets don't have the shape of a droplet, because a sharp tip would imply a huge capillary pressure beneath the tip, and would push the fluid immediately towards the regions of smaller pressure (larger curvature radius). Instead, the falling droplets take a shape which (due to air drag) is similar to the shape of small droplets lying on a hydrophobic surface: slightly ellipsoidal. Similarly, thin films are unstable, but in the case of very thin films (soap films), the characteristic time for the growth of instabilities is very large. Soap films are therefore fairly stable, and can be met often in problems; in that case, **don't forget the factor "2" for pressures, forces and energies reflecting the fact that a film has two interfaces: inner and outer ones!**

4 Entropy and Carnot cycle

The classical theory of thermodynamics is built around the concept of *reversible processes*.

def. 11: Reversible processes are processes for which the system under consideration is always at a thermodynamical quasi-equilibrium (those parts of the system which are in a thermal contact must have almost the same temperature), and there should be no dissipation (i.e. conversion of mechanical energy into heat) inside the system.

So, the system can have two or more thermally isolated parts of different temperatures, but each of such parts should be thermally isolated (there should be no heat flux between them). As soon as heat is allowed to flow from one part to another, the temperatures of these parts must be almost equal: in that case, the direction of the heat flow can be *reversed* by changing the temperatures only by a very small amount. For a perfectly reversible process, the temperature difference should be infinitely small, so that the temperature change required for a process reversal would be infinitely small. However, such a process would be also infinitely slow, because the heat flow rate between the bodies would be also infinitely small. Thus, **real processes can be reasonably close to being reversible, but never perfectly reversible**. Notice that for a reversed process, all the quantities (exchanged heat, work) obtain opposite signs.

As mentioned before, the best definition of temperature is based on statistical thermodynamics; this, however, is based on quantum mechanics, and in pre-quantum-mechanical era, a different definition, the Kelvin's one was used. Since we are already equipped with the statistical definition of temperature,

there is strictly speaking no need to discuss the Kelvin's one: in the case of positive temperatures, these two are identical. However, discussion of the Kelvin's temperature scale serves us as a useful exercise, and it provides additional insight to thermodynamics.

The Kelvin's definition of temperature is based on the *Carnot' cycle* which will be discussed later in more details; here it is enough to know its definition.

def. 12: Carnot' cycle is a reversible process with a gas which has four stages:

- (i) the gas expands isothermally (i.e. at a constant temperature) while receiving slowly heat Q_1 from a heat reservoir⁶ at a temperature T_1 ,
- (ii) it expands adiabatically (i.e. slowly without receiving or giving away any heat) and is thereby cooled (cf. fact 12) down to a temperature T_2 ;
- (iii) the gas is brought to a thermal contact with another heat reservoir of temperature T_2 ; the gas gives away heat Q_2 to the reservoir and contracts therefore isothermally;
- (iv) the gas is compressed adiabatically until it reaches the temperature T_1 .

Note that thus far we don't have quantitative definitions of temperature, but we know that the temperatures T_1 and T_2 are different, $T_1 > T_2$: based on the fact 2 we know that if the reservoirs were brought into contact, there would be a heat flow from the first one to the second one.

Since the pressure of the gas falls when cooling down (see Section 3), the net mechanical work performed by the gas during the whole cycle is positive (contribution of the expansion stage $A_1 = \int_{\text{exp}} p dV > 0$ dominates over that of the contraction stage, $A_2 = \int_{\text{contr}} p dV < 0$). Hence, due to the 1LTD, $Q_1 = Q_2 + A_1 + A_2 > Q_2$. So, the system works as a *heat engine*: the heat difference goes to mechanical work $W = Q_1 - Q_2$; the ratio $\eta \equiv \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$ is called the *efficiency of the heat engine*.

def. 13: Heat engine is a device which converts heat energy into a mechanical work using a temperature difference between the heating and cooling bodies; heat pump makes use of mechanical work to "pump" heat energy from a body with lower temperature to a body with higher temperature. Ideal heat engine is based on Carnot' cycle; ideal heat pump makes use of the reversed Carnot cycle (all the stages are reversed: contraction is substituted with expansion, cooling is substituted with heating, etc).

pr 32. Show that for a Carnot' cycle, the efficiency can depend only on the temperatures of the heating and cooling bodies and does not depend on which gas is used as the working gas.

The solution here is based on the 2LTD, which we formulate as an idea.

idea 21: The 2LTD can be used to prove by contradiction impossibility or nonexistence of various things. To that end, it is necessary to show that when assuming that the opposite is true, one can construct a scheme by which energy is trans-

⁶heat reservoir — so large thermally isolated body that receiving or giving away some heat will not cause any noticeable changes in its temperature.

ferred from a body of lower temperature to a body with a higher temperature while no net work is done. These constructions usually make use of ideal heat engines and/or heat pumps.

The solution of problem 32 can be directly used to show more generic (and very useful) statement, which we formulate as a fact.

fact 18: Any reversible heat engine (not necessarily based on Carnot' cycle) which takes heat from a heat bath at a single fixed temperature T_1 , and gives away heat to another heat bath at another fixed temperature T_2 , must have (and does have) exactly the same efficiency as a Carnot' cycle, $\eta_C = 1 - \frac{T_2}{T_1}$. For non-ideal (non-reversible) heat engines, the efficiency can be only smaller than η_C and never larger than that.

This efficiency expression follows directly from the following temperature definition. According to the Problem 32, the ratio Q_2/Q_1 is a quantity which depends only on the temperatures of the heat reservoirs. This fact can be used to quantify the temperatures by defining the ratio of the temperatures of two bodies as

$$T_1/T_2 = Q_1/Q_2,$$

where Q_1 and Q_2 are the heat amounts received and given away, respectively, by a fictitious Carnot' cycle using these two bodies as the heating and cooling heat reservoirs. This is the Kelvin's temperature definition; the temperature unit 1 K is defined by postulating that the water's triple point⁷ temperature is $T_0 = 273.16$ K. This value for T_0 is chosen so that at the atmospheric pressure, the difference of the boiling and melting temperatures of water would be equal to 100 K. Note that using this definition, the Carnot' cycle efficiency can be rewritten as $\eta_C = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$.

pr 33. Show that fact 18 is a consequence of the fact 2.

As mentioned, in statistical thermodynamics it is shown that with the statistical definition of temperature (from the Boltzmann's law) \tilde{T} , in the case of a Carnot cycle $Q_1/Q_2 = \tilde{T}_1/\tilde{T}_2$. This means that the Kelvin's definition and the definition from statistical mechanics are identical; equality of units is achieved if the constant k in the Boltzmann's law is taken equal to $k_B \approx 1.38 \times 10^{-23}$ J/K.

pr 34. [IPhO-1992] A manufacturer advertises a special paint in the following way: "This paint will reflect more than 90% of all incoming radiation (both visible light and infrared) but it will radiate at all frequencies (visible light and infrared) as a black body, thus removing lots of heat from the satellite. Thus the paint will help keep the satellite as cool as possible." Can such paint exist? Why or why not?

A consequence of this problem is that radiation and absorption properties of a material must be identical throughout the entire spectrum. It can be similarly shown that a partially reflecting material must have equal transmittance from both sides. It may seem that dark window glasses are more transparent when looking from inside of a darkly lit room, but this is a mere illusion: when looking from outside, a small fraction of reflected abundant outside light can easily dominate over

the transmitted part of the light coming from inside, but the opposite is not true. The effect can be enhanced by overlaying an absorbing and reflecting layers and turning the reflecting layer outside. Then, while total transmittance is equal from both sides, the reflectance from outside is larger because from outside, reflected light does not pass through the absorbing layer.

idea 22: The fact (No. 18) that all reversible heat engines have the same efficiency $\eta_C = 1 - \frac{T_2}{T_1}$ can be used to solve a series of problems.

First of all, this idea applies to all the problems which deal with heat engines if these engines involve heat baths with exactly two different temperatures. In particular, one should keep in mind that devices based on the thermoelectric effect (see fact 20) can theoretically be reversible (of course, ohmic dissipation in such devices is irreversible and needs thus to be excluded from energy balance). In some cases, it is possible to solve a problem (derive an equation) by making a *thought experiment* with a suitably designed hypothetical heat engine, see the next problem.

pr 35. Derive the so-called Clausius-Clapeyron equality relating the temperature derivative of the saturation pressures of a substance, $\frac{dp_s}{dT}$, to the latent heat of evaporation λ , temperature T , saturation pressure p_s , and molar mass μ .

By how much will change the pressure of saturated vapours of water if the temperature is decreased from $T_0 = 100.0^\circ\text{C}$ down to $T_1 = 99.9^\circ\text{C}$? Atmospheric pressure $P_0 = 1.0 \times 10^5$ Pa, latent heat of evaporation for water $L = 2260$ kJ/kg. Hint: consider Carnot cycle where work is being done by water vapours, and both cooling and heating reservoirs are made of water, at temperatures T_0 and T_1 , respectively.

pr 36. Note that the Clausius-Clapeyron equality can be written as a Boltzmann's law, $p_S = p_0 e^{-U/k_B T}$; express U in terms of the parameters listed in problem 35, and interpret it physically.

def. 14: Classical (unrelated to quantum mechanics) entropy S is defined only via increments (similarly to potential energy):

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

where ΔQ is the heat given to the system, and T — the temperature of the system.

Conclusion: adiabatic process is an isoentropic process.

While in classical thermodynamics, only entropy increments are defined, in statistical thermodynamics which is based on quantum mechanics, absolute values of entropy are well-defined; roughly speaking, it is $S = k_B \ln N$, where N is the number of thermally excited quantum-mechanical states; more precisely $S = -k_B \langle \ln p_i \rangle_i$, where p_i is the probability of the i -th quantum-mechanical state, and angular braces denote averaging over all the possible states. Using mathematical statistics, one can show that this definition yields $\Delta S = \Delta Q/T$, in agreement with the classical definition.

It is quite easy to see that for a closed system undergoing reversible processes, the entropy is conserved. Indeed, since heat

⁷Triple point of a substance — such a combination of temperature and pressure that the solid, liquid and gaseous states are all in thermal equilibrium with each other.

exchange between its different parts takes place at the same temperature then by exchanging a certain amount of heat, the two parts obtain equal by modulus and opposite entropy increments. However, in the case of irreversible processes, according to the 2LTD (idea 2) that part of the system which gives away heat ($-\Delta Q < 0$) has larger temperature than that part which receives the heat, $T_1 > T_2$. Hence, the total entropy change for the entire system $\Delta S = -\frac{\Delta Q}{T_1} + \frac{\Delta Q}{T_2} > 0$ is positive.

fact 19: The entropy of a closed system remains constant in reversible processes and grows in irreversible ones.

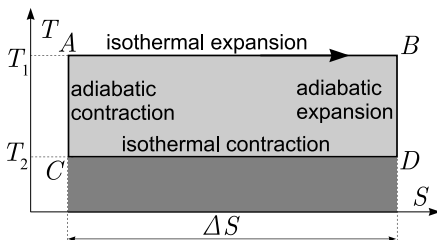
Being equipped with the statistical definition of entropy, we can say that if a system evolves by itself, the total number of excited quantum-mechanical states can only grow. This can be formally shown using mathematical statistics. The number of excited states can be also considered as a parameter describing the degree of order: more occupied states implies less order. So, the degree of order of a closed system is can only increase. Yo can use this as an excuse if your room becomes messy.

Finally, notice that the facts 19 and 18 are also often referred to as the 2LTD, which is OK since these are equivalent to fact 2: an entropy reduction would directly mean that heat has been transferred from a lower temperature body to a higher temperature one.

We have shown already equivalence between the fact 2 and 19. A hypothetical heat engine with $\eta > \eta_C$ is referred to as *perpetuum mobile of second kind*, and it is as impossible as the perpetuum mobile of the first kind (the one which violates energy conservation law). However, people tend to trust the laws of statistics less than the other laws of nature (else, who would buy lottery tickets!). This has resulted in a large number of failed attempts at creating perpetuum mobile of second kind, but also in really interesting paradoxes. Perhaps the most famous one is the Maxwell's demon: a nano-scaled guy who sits at a gate between two parts of a vessel and who opens the gate when a fast molecule is approaching, and keeps the gate closed otherwise. Apparently, the temperature at the other side of the vessel would start rising, violating 2LTD. The resolution of the paradox is that the guy needs to obtain information about approaching molecules and needs to probe these by sending, for instance, photons. However, photons scattered from molecules would contribute to an increase of entropy.

Now, let us consider the forward and reversed Carnot' cycles in more details.

idea 23: The processes involving Carnot' cycle are typically most conveniently studied using a $S-T$ -diagram, because then, the process has a rectangular shape.



While we have already derived the efficiency of a Carnot' cycle starting from the Kelvin's definition of temperature, let us do it, once again, starting from the definition of entropy and using the $S-T$ -diagram. Let the S -axis be horizontal,

and length of the rectangle — ΔS . According to the definition of entropy, the heat received from the heating reservoir $\Delta Q_1 = \int_A^B T dS = T_1 \Delta S$ is the surface area of the large rectangle; similarly, the heat given to the cooling reservoir $\Delta Q_2 = \int_C^D T dS = T_2 \Delta S$ is the surface area of the dark-grey rectangle. According to the energy conservation law, the work done $\Delta W = \oint_{ABCD} T dS = \Delta Q_1 - \Delta Q_2 = \Delta S(T_1 - T_2)$ is the surface area of the light grey rectangle. According to the definition of efficiency,

$$\eta_C = \frac{\Delta W}{\Delta Q_1} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}.$$

Reversed Carnot' cycle has a counter-clock-wise motion in the $S-T$ -diagram: all contractions become expansions (and vice versa), heat flow direction is reversed, and mechanical work becomes negative, i.e. a work needs to be done to keep the process going on. Such a reversed heat engine can be used for two purposes: for heat pumps and fridges. In a fridge, a working gas takes heat from the interior of the fridge at the inside-temperature T_2 , flows through the ribs at the back of the fridge and gives there more heat away at the ribs' temperature $T_1 > T_2$; the electrical engine of the fridge keeps the process going on. The fridge efficiency (often called the *coefficient of performance*, or *COP*) is characterized by the ratio of the heat Q_2 which is taken away from the inside, and work W done by the engine (consumed electrical power),

$$\eta_{\text{fridge}} = \frac{Q_2}{W} = \frac{T_2}{T_1 - T_2}.$$

From this expression we can deduce that the efficiency of a fridge can be both larger and smaller than one, but it is very difficult to achieve extremely low temperatures, because the efficiency goes down together with the temperature inside the fridge.

Heat pump can be considered as a fridge, which has its hot ribs inside our living rooms, and which takes heat from the colder heat reservoirs outside the house (air or ground). Now, what is useful to us is the heat Q_1 received by our living room, so that the efficiency of a heat pump

$$\eta_{\text{HP}} = \frac{Q_1}{W} = \frac{T_1}{T_1 - T_2},$$

which is always larger than one: it works always more efficiently than an electrical radiator. cool

Finally, let us discuss the *thermoelectric effect*. To begin with, let us recall problem 36: for a molecule to be able to leave the liquid phase, a certain energy U needs to be supplied. This means that effectively, the liquid phase molecules obey potential energy $-U$ with respect to vapour phase molecules; this potential energy is referred to as the *chemical potential*, and is equal to the change of total energy when one particle is added to a system (final energy minus the particle's and system's initial energies). Similarly to molecules in liquid phase, **electrons in metals** (semiconductors, dielectrics) are also described by chemical potential, often referred to as the *Fermi level* E_F . The Fermi level of a material depends on temperature; if the temperature of a wire changes along its length, the Fermi level will also change along its length. As a result, electrons move towards lower Fermi levels (smaller potential energy), creating a surplus of charges and an electric field. Finally, an equilibrium is reached: electrostatic potential compensates Fermi level difference. So, at equilibrium, there is a changing potential along the wire. Let us summarize.

4. ENTROPY AND CARNOT CYCLE

fact 20: If a wire is being heated from its one end, and cooled at the other end so that the temperatures of its endpoints are T_h and T_c , respectively, then there will be a voltage

$$V = S(T_h - T_c)$$

between the endpoints, where the *Seebeck coefficient* S takes different for different materials. This is known as the *Seebeck effect*.

A *thermocouple* is a device made of wires of two different materials which are selected so that the difference of Seebeck coefficients would be as large as possible. A wire of material A is connected at its two endpoints, the *junctions*, to the wires of material B ; if the junctions are kept at different temperature, an electromotive force is created at the output terminals of the thermocouple. Thermocouples which are used for generation of electrical energy are called *thermoelectric generators*. Thermocouples take and release heat at the junctions, and perform electrical work, so they operate as heat engines. If we were to reverse such a heat engine, we would need to supply a current into it from an external source. Then we would expect that one of the junctions would release heat, and the other would absorb heat; this is, indeed, what will happen, and is referred to as the *Peltier effect*. The direction of current defines, which of the junctions will absorb heat.

For majority of metals, S takes values remaining less than $10 \mu\text{V/K}$, and for certain metal alloys up to $30 \mu\text{V/K}$ ($70 \mu\text{V/K}$ for bismuth). What matters in the case of a thermocouple, is the difference of Seebeck coefficients of the two wire materials, and in the case of *chromel* and *constantan* pair, the difference at the room temperature is $62 \mu\text{V/K}$. For semiconductor materials, S can reach much higher values.

Now we can ask, how close to being reversible is the thermoelectric effect. For a system to be reversible, all its parts need to have reached a state very close to a thermal equilibrium. In the case of a thermocouple, however, we have a wire which connects cold and warm junctions: the temperature difference creates a heat flux through the wire, which is very irreversible. For the process to be reversible, the irreversible heat flux

$$\Phi_{ir} = \frac{\kappa A}{l}(T_h - T_c)$$

(where κ is the heat conductivity, A — cross-sectional area, and l — length) needs to be small as compared with the reversible heat flux which is spent on producing the electrical power,

$$\Phi_r = \frac{P}{\eta_C} = \frac{V^2}{R} \frac{T_h}{T_h - T_c} = \frac{S^2(T_h - T_c)T_h}{\rho l/A}.$$

So, the process can be considered to be reversible if

$$\frac{\Phi_r}{\Phi_{ir}} = \frac{S^2 T_h}{\kappa \rho} \gg 1.$$

This dimensionless parameter is called the *merit factor* and denoted by

$$ZT \equiv \frac{S^2 T}{\kappa \rho};$$

currently the materials with highest merit factor reach values $ZT \approx 2.5$, but theoretically there is no upper limit for ZT . It appears that in the case of $ZT \approx 2.5$, the maximal efficiency of a thermocouple is 30% of the Carnot' cycle efficiency. It is a challenge for material sciences to create materials with higher merit factors which could be used for making compact thermoelectric generators.

pr 37.

A thermocouple is being used as a battery: one of its solder joints is at the room temperature $T_1 = 20^\circ\text{C}$, the other is kept inside a glass of water with ice, at temperature $T_2 = 0^\circ\text{C}$. The output leads are connected to a resistor $R = 10\Omega$, connected in series with an ammeter which shows that current $I = 10\text{mA}$. How much ice is melted during $t = 10\text{h}$ if the glass with ice has very good thermal insulation and room temperature remains constant? Latent heat of melting for ice $\lambda = 330\text{kJ/kg}$. Assume the energy transfer processes in the thermocouple to be reversible.

appendix 1: Motivation of the Boltzmann's law

The reason why an energy level occupation probability vanishes exponentially with energy lies in the fact that in the case of a heat reservoir which is supposed to consist of a large number of subsystems, the number of quantum-mechanical states grows exponentially with the total energy E_{tot} . Let us consider simplifyingly a body which has several equispaced energy levels, $E_0, E_1 = E_0 + \mathcal{E}, \dots, E_n = E_0 + n\mathcal{E}$. Further, let the heat reservoir be made of a large number $N \gg n$ identical particles, each of which has two energy levels, 0 (ground level) and \mathcal{E} (the excited state), and let the total number of particles at the excited state be M (with $M, N - M \gg n$). Now, the body is brought to a contact with the reservoir; let us assume that its energy becomes equal to $n\mathcal{E}$. Due to the energy conservation law, this will decrease the number of excited particles inside the heat reservoir by n . Thus, the number of excited particles is $M - n$; the number of different states of heat reservoir satisfying this condition equals to the number of different ways of selecting $M - n$ particles from the set of N particles, given by

$$\binom{N}{M-n} = \frac{N!}{(M-n)!(N-M+n)!}.$$

For the ground level of the body, the number of the heat reservoir states is similarly given by

$$\binom{N}{M} = \frac{N!}{M!(N-M)!}.$$

Since all these states are equally probable, the ratio of probabilities for the n -th excited state and the ground state of the body is given by the ratio of the number of states,

$$\frac{p_n}{p_0} = \frac{N!}{(M-n)!(N-M+n)!} \frac{M!(N-M)!}{N!} = \frac{(M-n+1)(M-n+2)\dots M}{(N-M+1)(N-M+2)\dots (N-M+n)} \approx \left(\frac{M}{N-M}\right)^n.$$

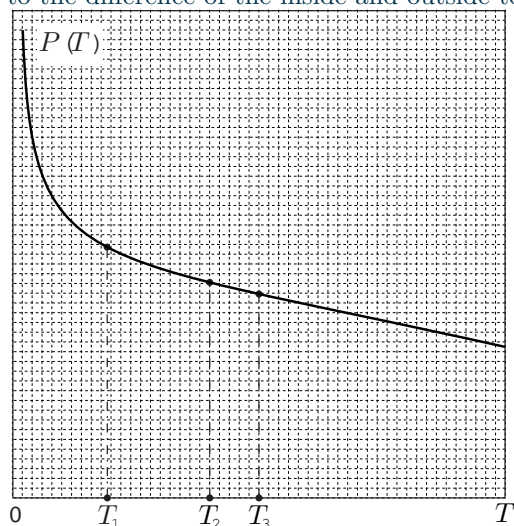
Here, $\frac{M}{N-M}$ is a number which characterizes the state of the heat reservoir; we can introduce the parameter $\beta = -\frac{1}{\mathcal{E}} \ln\left(\frac{N}{M} - 1\right)$, which leads us to the Boltzmann's law

$$\frac{p_n}{p_0} = e^{-\beta E_n}.$$

This “proof” is probably not too satisfying for a mathematically oriented reader, because we made very limiting assumptions for the particles of the heat reservoir. For a more generic proof, one can introduce the energy level density $g(E)$ of the “particles” making up the heat reservoir, express the energy level density of the entire reservoir as the N -th convolution of $g(E)$ with itself, calculate it in the *Fourier space* (because the Fourier transform of a convolution is just the product of the Fourier transforms), take the inverse Fourier transform and estimate it asymptotically (for $N \rightarrow \infty$) using the *saddle point method* — these techniques are well beyond the scope of this booklet.

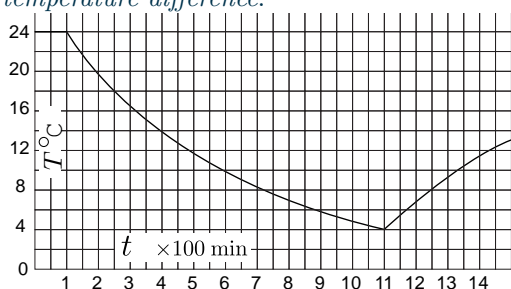
Revision problems

pr 38. [EstPhO-2007] Certain room is being heated using a heating device the output power $P(T)$ of which depends on the room temperature T as shown in figure. If the outside temperature is T_1 then the room temperature will reach value T_2 (see figure). Which room temperature will be reached if the outside temperature is T_3 ? (find the solution graphically using the figure). The heat exchange loss rate of the room is proportional to the difference of the inside and outside temperatures.

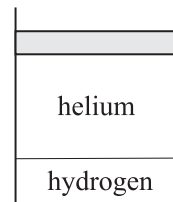


pr 39. [EstPhO-2000] The nominal voltage of a light bulb is $V_0 = 26\text{ V}$ and nominal current $I_0 = 0.12\text{ A}$. Cold tungsten filament of this light bulb has resistance $R_0 = 24\ \Omega$. Estimate the length l and the diameter d of this filament. Also, at which temperature T is this filament supposed to emit light (when working in nominal regime)? The resistivity of tungsten at room temperature $\rho_0 = 5.3 \times 10^{-8}\ \Omega \cdot \text{m}$. For metals, the resistivity can be taken to be proportional to the temperature in Kelvins. Treat tungsten as a perfectly grey body which absorbs $k = 0.3$ of the incident radiation at any wavelength. Stefan-Boltzmann constant $\sigma = 5.67 \times 10^{-8}\text{ W}/(\text{m}^2 \cdot \text{K}^4)$. Neglect thermal expansion of the filament.

pr 40. [EstPhO-2006] Due to cold weather, heating system was broken and temperature in a room started decreasing. A fan heater was quickly bought and switched on. During all that period, the room temperature changed in time as shown in graph. Which room temperature will be reached in long term? Outside temperature remained constant. Note that due to certain construction elements, the heat exchange rate between the room and outside environment was a *nonlinear function of the temperature difference*.



pr 41. In a thermally isolated cylinder, a piston can move without friction up and down. The cylinder is divided into two compartments by a freely moving weightless wall which conducts slowly heat, see figure. Initially the gas temperatures are equal, and the volume of hydrogen is 3 times smaller than that of helium. Helium receives a certain amount of heat, because of which the piston moves up by $d_1 = 5\text{ cm}$. After waiting for some longer period of time, an additional displacement of the piston was observed. By how much and in what direction the piston moved additionally? Gases can be considered to be ideal. Molar heat capacitance at constant pressure is $C_{PH_2} = 7/2R$ for hydrogen, and $C_{PHe} = 5/2R$ for helium.

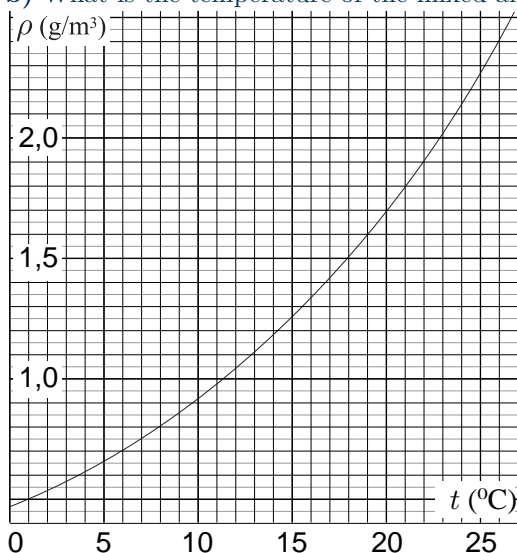


pr 42. [EstFin-2006] According to the wide-spread belief, it is useful to keep window open when drying laundry even if the relative humidity outside is 100%, because the temperature of the incoming air rises and thereby the relative humidity drops. Let us analyse, do these arguments hold, when heating is switched off.

Suppose that inside a room, the volume of air $V_1 = 20\text{ m}^3$ from inside at the temperature $t_1 = 25^\circ\text{C}$ is mixed with the volume of air $V_2 = 10\text{ m}^3$ from outside at the temperature $t_2 = 1^\circ\text{C}$. The specific heat of the air (by fixed pressure) $c_p = 1005\text{ J}/(\text{kg} \cdot \text{K})$ can be assumed to be constant for the given temperature range; the heat exchange with the medium can be neglected. For the time being, you may neglect the possibility of (partial) condensation of the vapour.

a) Prove that the total volume of the air will not change i.e. that the volume of the mixed air $V = V_1 + V_2$.

b) What is the temperature of the mixed air T ?



c) The graph below shows the dependence of the saturated vapour density for water as a function of temperature. Before mixing, both the interior and exterior air had relative humidity of $r_0 = 100\%$. What is the relative humidity r of the mixed air (if it happens to increase then assume that an oversaturated vapour with $r > 100\%$ is formed)?

d) If you happened to obtain $r > 100\%$ then the oversaturated vapour breaks down into a fog which contains tiny water

4. ENTROPY AND CARNOT CYCLE

droplets. In that case, what is the mass m of the condensed water (i.e. the total mass of the water droplets)? Air density $\rho_0 = 1.189 \text{ kg/m}^3$; latent heat of vaporization for water $q = 2500 \text{ kJ/kg}$.

pr 43. [IPhO-1999] A cylindrical vessel, with its axis vertical, contains a molecular gas at thermodynamic equilibrium. The upper base of the cylinder can be displaced freely and is made out of a glass plate; let's assume that there is no gas leakage and that the friction between glass plate and cylinder walls is just sufficient to damp oscillations but doesn't involve any significant loss of energy with respect to the other energies involved. Initially the gas temperature is equal to that of the surrounding environment. The gas can be considered as perfect within a good approximation. Let's assume that the cylinder walls (including the bases) have a very low thermal conductivity and capacity, and therefore the heat transfer between gas and environment is very slow, and can be neglected in the solution of this problem. Through the glass plate we send into the cylinder the light emitted by a constant power laser; this radiation is easily transmitted by air and glass but is completely absorbed by the gas inside the vessel. By absorbing this radiation the molecules reach excited states, where they quickly emit infrared radiation returning in steps to the molecular ground state; this infrared radiation, however, is further absorbed by other molecules and is reflected by the vessel walls, including the glass plate. The energy absorbed from the laser is therefore transferred in a very short time into thermal movement (molecular chaos) and thereafter stays in the gas for a sufficiently long time. We observe that the glass plate moves upwards; after a certain irradiation time we switch the laser off and we measure this displacement.

- Using the data below and - if necessary - those on the sheet with physical constants, compute the temperature and the pressure of the gas after the irradiation.
- Compute the mechanical work carried out by the gas as a consequence of the radiation absorption.
- Compute the radiant energy absorbed during the irradiation.
- Compute the power emitted by the laser that is absorbed by the gas, and the corresponding number of photons (and thus of elementary absorption processes) per unit time.
- Compute the efficiency of the conversion process of optical energy into a change of mechanical potential energy of the glass plate.

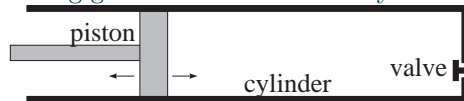
Thereafter the cylinder axis is slowly rotated by 90° , bringing it into a horizontal direction. The heat exchanges between gas and vessel can still be neglected.

- State whether the pressure and/or the temperature of the gas change as a consequence of such a rotation, and - if that is the case - what is its/their new value.

Data: Room pressure: $p_0 = 101.3 \text{ kPa}$; Room temperature: $T_0 = 20.0^\circ\text{C}$; Inner diameter of the cylinder: $2r = 100 \text{ mm}$; Mass of the glass plate: $m = 800 \text{ g}$; Quantity of gas within the vessel: $n = 0.100 \text{ mol}$; Molar specific heat at constant volume of the gas: $c_V = 20.8 \text{ J/(mol} \cdot \text{K)}$; Emission wavelength of the laser: $\lambda = 514 \text{ nm}$; Irradiation time: $\Delta t = 10.0 \text{ s}$; Displacement of the movable plate after irradiation: $\Delta s = 30.0 \text{ mm}$.

pr 44. [EstPhO-1998] A tire is being pumped using a hand pump. A manometer shows that the excess pressure (the difference between the pressures inside and outside) is $p_1 = 2 \times 10^5 \text{ Pa}$, the air pressure $p_0 = 1 \times 10^5 \text{ Pa}$. Find the temperature of the air which enters the tire through the valve. The pump has two valves. One of them lets gas into the pump from the atmosphere; it opens as soon as the pressure inside the pump becomes lower than p_0 , and closes as soon as it becomes larger than p_0 . The other lets gas from the pump into the tire; it opens as soon as the pressure inside the pump becomes larger than the pressure inside the tire, and closes as soon as this inequality no longer holds. Room temperature $T_0 = 20^\circ\text{C}$

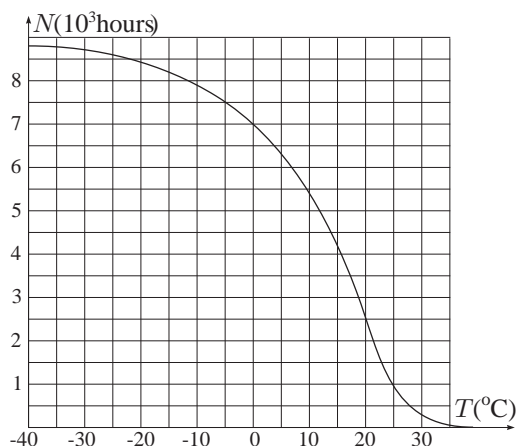
pr 45. [EstPhO-2002] The main components of a car engine are: a cylinder, a piston which moves inside it, and a valve for letting gases in and out of the cylinder.



The working cycle of the engine consists of the following stages:
 I. *Gas entry:* the piston moves from the rightmost position to left; fresh air comes in through the valve and fills the cylinder.
 II. *Pressure increase:* the valve closes, and the piston moves back to the rightmost position; the air is compressed adiabatically.
 III. *Work:* Fuel is injected into the cylinder, and is ignited. You may assume that the fuel burns instantaneously. Gas starts expanding and pushes the piston to the leftmost position.
 IV. *Gas disposal:* valve is opened, piston moves to right and the gas is pushed out from the cylinder. The process starts periodically repeating.

- Depict the entire cycle in $p - V$ -diagram.
- Find the efficiency η .

Data. Adiabatic index for air $\gamma = 1.4$. The compression factor is defined as the ratio of the largest and smallest volumes of the cylinder, $k = V_l/V_s$; here $k = 10$. Neglect friction when the piston moves. The number of fuel molecules is much smaller than the number of air molecules inside the cylinder. The air is to be considered as an ideal gas, one mole of which has internal energy equal to $U = c_V T$, where c_V is its molar heat capacitance by constant volume.



pr 46. [EstPhO-2002] Archive storage rooms need to maintain constant temperature $T_0 = 15^\circ\text{C}$ throughout the year. Find the annual electricity expenses needed to maintain that

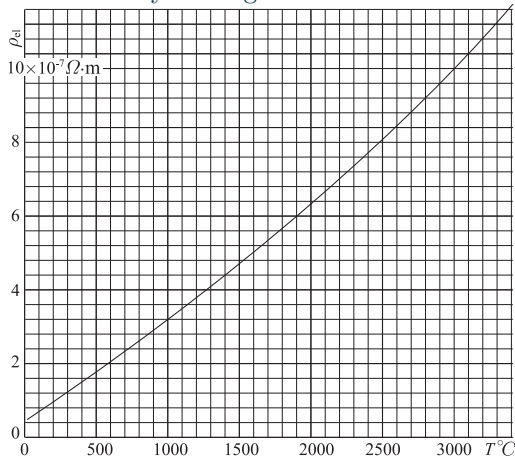
4. ENTROPY AND CARNOT CYCLE

temperature if the heat exchange rate throughout the walls of the building $P = C\Delta T$, where $C = 200 \text{ W/K}$ and ΔT is the temperature difference inside the storage room and outside the building. In order to regulate the temperature inside the room, heat pump is used; the heat pump can also operate as an air conditioner. If the device is used as an air conditioner (for cooling the room), the efficiency $\eta_c = 10$ (usually referred to as coefficient of performance, COP; this is the ratio of the cooling power to the consumed electrical power); if used as an heat pump (for heating), the efficiency $\eta_h = 6$ (COP; the heating power and electrical energy consumption rate ratio). The attached $N - T$ -graph depicts how many hours in year (N) the outside air temperature was higher than T . The electrical energy cost is $c = 0.1 \text{ EUR/kWh}$.

pr 47. [EstPhO-2001] Using the assumptions and numerical data of problem 3, and the density of tungsten at room temperature $\rho = 19\,250 \text{ kg/m}^3$, answer the following questions.

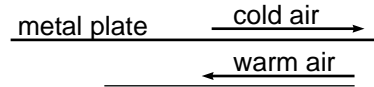
a) A smaller-than-nominal direct voltage $U_0 = 3 \text{ V}$ is applied to the leads of the halogen bulb. How long does it take for the tungsten filament to reach temperature $T_1 = 40^\circ\text{C}$ starting from the room temperature $T_r = 20^\circ\text{C}$?

b) Accidentally, a too large DC voltage $U_1 = 120 \text{ V}$ is applied to the leads of the lamp. How long does it take to reach the melting temperature $T_2 = 3410^\circ\text{C}$ of the tungsten? Heat losses can be neglected, as well as the temperature dependence of the tungsten's density and specific heat; use the graph depicting the resistivity of tungsten as a function of temperature.

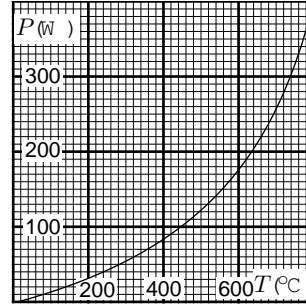


pr 48. [EstFin-2005] a) Consider a simplified model of the air ventilation system of a house using a passive heat exchanger. The exchanger consists of a metal plate of length x and width y and thickness d dividing the air channel into two halves, one for incoming cold air, and another for outgoing warm air. Both channels have constant thickness h , air flow velocity is v see Figure. Thermal conductance of the metal is σ (the heat flux through a unit area of the plate per unit time, assuming that the temperature drops by one degree per unit thickness of the plate). Specific heat capacity of the air by constant pressure is c_p , air density is ρ (neglect its temperature dependence). You may assume that the air is turbulently mixed in the channel, so that the incoming and outgoing air temperatures T_{in} and T_{out} depend only on the coordinate x (the x -axis is taken parallel to the flow velocity), i.e. $T_{\text{in}} \equiv T_{\text{in}}(x)$ and $T_{\text{out}} \equiv T_{\text{out}}(x)$. Assuming that the inside and outside temperatures are T_0 and

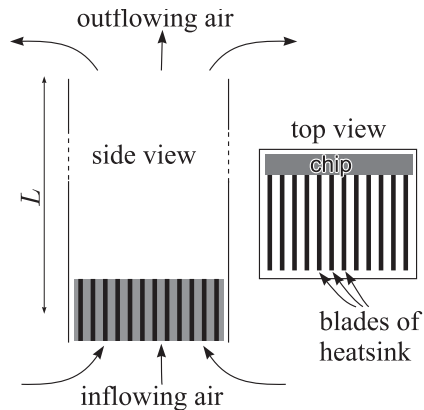
T_1 , respectively, what is the temperature T_2 of the incoming air at the entrance to the room?



b) Attached is a plot of the heat exchange rate P of the wire of an electric heater as a function of temperature (assuming the room temperature is $T_0 = 20^\circ\text{C}$). The operating temperature of the wire is $T_1 = 800^\circ\text{C}$. The heater is switched off; find the time after which the temperature of the wire will drop down to $T_2 = 100^\circ\text{C}$. The heat capacitance of the wire is $C = 10 \text{ J/K}$.



pr 49. [EstFin-2004] Consider a passive cooling system depicted in figure. Cold air (at normal conditions: $p_0 = 10^5 \text{ Pa}$, $T_0 = 293 \text{ K}$) flows over the heat sink of a chip of power dissipation $P = 100 \text{ W}$, into a vertical pipe of length $L = 1 \text{ m}$ and cross-sectional area $S = 25 \text{ cm}^2$. After passing the pipe, air enters the ambient room. Assume that the air inside the pipe becomes well mixed; neglect the viscous and turbulent friction of air inside the pipe and heat sink. Air can be considered as an ideal gas with adiabatic exponent $\gamma = 1.4$ and molar mass $\mu = 29 \text{ g/mol}$; gas constant $R = 8.31 \text{ J/(K} \cdot \text{mol)}$

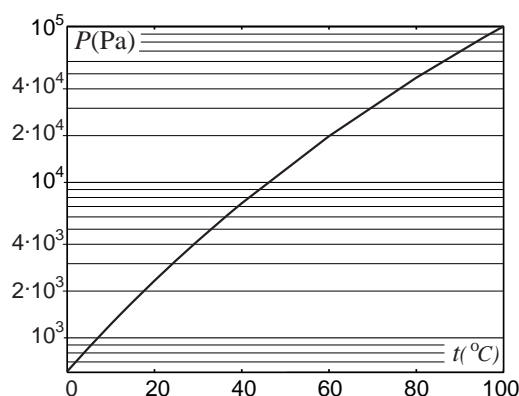


- Express heat capacitance at constant pressure c_p via quantities γ and R .
- Find a relationship between the outflowing air density ρ and temperature T (the relationship may contain also the parameters defined above).
- Find a relationship between the air flow velocity in the pipe v and outflowing air density ρ (the relationship may contain also the parameters defined above).
- Express the power dissipation P in terms of the air flow velocity v , the outflowing air temperature T , and density ρ (the relationship may contain also the parameters defined above).
- What is the temperature T of the outflowing air? In your calculations, you may use approximation $T - T_0 \ll T_0$.

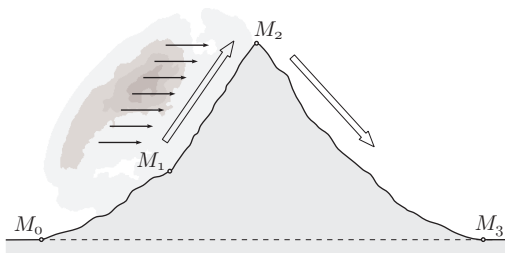
pr 50. [EstPhO-2000] Glycerol is stored in a tightly closed vessel of volume $V = 1$ l; inside glycerol, there is an air bubble of volume $w = 1$ ml. At temperature $T_0 = 20^\circ\text{C}$, the pressure inside the vessel is $p_0 = 1$ atm. The linear expansion coefficient of the vessel material is very small and the vessel walls are thick. The volumetric expansion coefficient of the glycerol $\alpha = 5.1 \times 10^{-4} \text{ K}^{-1}$. Air can be treated as an ideal gas.

- a) Find the dependence of the pressure inside the bottle as a function of temperature.
b) At which temperature and for which physical reason the obtained equality will no longer be valid?

pr 51. [EstPhO-2003] Juice bottle is being pasteurised at temperature $t_1 = 80^\circ\text{C}$ so that a light cap lies freely on the bottle rim (excess gas can exit freely from the bottle, but outside air cannot come in). Then the cap is tightly fixed so that air can no longer enter and exit from the bottle; the cap is so rigid that its deformation due to excess pressure can be neglected. The bottle is cooled down to the room temperature $t_2 = 20^\circ\text{C}$. What is the pressure under the bottle cap? Assume that the physical properties of the juice are identical to that of water; the pressure of saturated water vapours is depicted as a function of temperature in a graph. Atmospheric pressure $P_0 = 1.01 \times 10^5$ Pa.



pr 52. [IPhO-1987] Moist air is streaming adiabatically across a mountain range as indicated in the figure. Equal atmospheric pressures of $p_0 = 100$ kPa are measured at meteorological stations M_0 and M_3 and a pressure of $p_2 = 70$ kPa at station M_2 . The temperature of the air at M_0 is $t_0 = +20^\circ\text{C}$. As the air is ascending, cloud formation sets in at $p_1 = 84.5$ kPa. Consider a quantity of moist air ascending the mountain with a mass of 2000 kg over each square meter. This moist air reaches the mountain ridge (station M_2) after 1500 seconds. During that rise an amount of $m = 2.45$ g of water per kilogram of air is precipitated as rain.



- a) Determine temperature T_1 at M_1 where the cloud ceiling forms

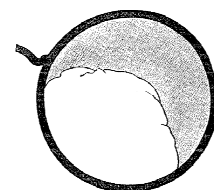
- b) What is the height h_1 (at M_1) above station M_0 of the cloud ceiling assuming a linear decrease of atmospheric density?
c) What temperature T_2 is measured at the ridge of the mountain range?
d) Determine the height of the water column (precipitation level) precipitated by the air stream in 3 hours, assuming a homogeneous rainfall between points M_1 and M_2 .
e) What temperature T_3 is measured in the back of the mountain range at station M_3 ? Discuss the state of the atmosphere at station M_3 in comparison with that at station M_0 .

Hints and Data. The atmosphere is to be dealt with as an ideal gas. Influences of the water vapour on the specific heat capacity and the atmospheric density are to be neglected; the same applies to the temperature dependence of the specific latent heat of vaporisation. The temperatures are to be determined to an accuracy of 1 K, the height of the cloud ceiling to an accuracy of 10 m, and the precipitation level to an accuracy of 1 mm. Specific heat capacity of the atmosphere in the pertaining temperature range: $c_p = 1005 \text{ J/(kg} \cdot \text{K)}$. Air density for at the station M_0 (i.e. for p_0 and T_0) is $\rho_0 = 1.189 \text{ Kg/m}^3$. Specific latent heat of vaporisation of the water within the volume of the cloud: $q_V = 2500 \text{ kJ/kg}$; free fall acceleration $g = 9.81 \text{ m/s}^2$. Adiabatic index for both wet and dry air $\gamma = c_p/c_V = 1.4$.

pr 53. In a science fiction novel, the following situation is described. There is an emergency on a spaceship, and an astronaut got by an accident to a distance of $L = 100$ m from the spaceship. He has a cup with solidified water (ice) and uses the sublimation (evaporation) of ice to return to the spaceship. Estimate, how realistic is this method. You may assume that the sublimation takes place at a constant temperature $T = 272$ K, by which the pressure of saturated vapours is $P = 550$ Pa. Estimate the dimensions of the cup and the mass of the water by yourself.

pr 54. [EstFin-2009] Lord Rayleigh had in 1891 a lecture about taking photos of physical processes. Among others, he showed a photo of a soap film, which is falling apart (see figure). Instead of a flash, he used an electric spark (well, nowadays the flashes are also based on electric sparks). Estimate, how precise must have been the timing, i.e. estimate the time for a soap film to fall apart. Let the thickness of the soap film be $h = 1 \mu\text{m}$, the ring diameter $D = 10$ cm and the surface tension $\sigma = 0.025 \text{ N/m}$.

Hint: you may use a model, according to which the already broken part of the soap film gathers into a single front and moves all together towards the still preserved part of the film.



pr 55. Consider two soap bubbles which have “stuck” together. Now three soap film parts can be distinguished: one separates the interior of the first bubble from the outside air — this has curvature radius R ; second separates the interior of the second bubble from the outside air — this has curvature radius $2R$; third separates the interiors of the two bubbles. Find the surface area of the third soap film part.

pr 56. [EstFin-2013] Sun-rays are focused with a lens of diameter $d = 10\text{ cm}$ and focal length of $f = 7\text{ cm}$ to the black side of a thin plate. One side of the plate is perfectly black, and the other side is perfectly white. Angular diameter of the Sun is $\alpha = 32'$ and its intensity on the surface of the Earth is $I = 1000\text{ W/m}^2$, Stefan-Boltzmann constant $\sigma = 5.670 \times 10^{-8}\text{ W/(m}^2\text{K}^4)$. (i) Find the temperature of the heated point of the plate. (ii) Using thermodynamic arguments, estimate the maximal diameter-to-focal-length ratio of a lens.

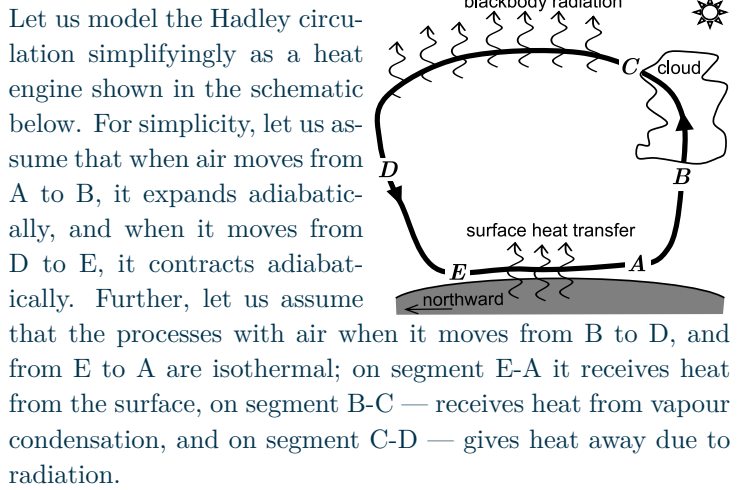
pr 57. [EstFin-2008] There is wet wood burning in a fireplace on the ground. Seven meters above ground, the smoke is at a temperature of $t_7 = 40^\circ\text{C}$. Disregard the exchange of heat with the surrounding air and assume that the atmospheric pressure at the ground is constant in time and equal to $p_0 = 1000\text{ hPa}$; the air temperature $t_0 = 20^\circ\text{C}$ is independent of height⁸. Assume that the smoke represents an ideal gas of a molar mass $\mu = 29\text{ g/mol}$ (i.e. equal to the molar mass of the air), and of a molar specific heat at constant volume $C_V = 2.5R$; universal gas constant $R = 8.31\text{ J/kg} \cdot \text{K}$. How high will the smoke column rise?

pr 58. [IPhO-2014] A bubble of radius $r = 5.00\text{ cm}$ is a soap film of thickness $h = 10.0\text{ }\mu\text{m}$ containing a diatomic ideal gas. It is placed in vacuum. The soap film has surface tension $\sigma = 4.00 \times 10^{-2}\text{ N/m}$ and density $\rho = 1.10\text{ g/cm}^3$.

- Find a formula for the molar heat capacity of the gas in the bubble, for a process in which the gas is heated so slowly that the bubble remains in mechanical equilibrium. Evaluate your answer.
- Find a formula for the frequency ω of small radial oscillations of the bubble and evaluate it under the assumption that the heat capacity of the soap film is much greater than the heat capacity of the gas in the bubble. Assume that the interior of the bubble reaches thermal equilibrium much faster than the period of oscillations; also, the total mass of the gas is much smaller than the mass of the soap film. Neglect the possibility of soap film's evaporation.

pr 59. [APhO-2014] Let us consider the so-called *Hadley circulation*: this is a large-scale circulation of air masses, which rise at a certain geographical latitude (close to the equator) from lower atmospheric layers (from near-surface regions) to higher altitudes. During this rising phase the air cools adiabatically which leads to a condensation of air vapours, cloud formation and rain. The cool air moves at higher atmospheric layers in north-south direction (while radiating heat slowly away into space) until it reaches higher geographical latitudes, where it descends to Earth's surface while heating adiabatically. Finally, the warm air moves along Earth's surface to its starting point while being heated by surface (which is hot due to sunlight).

⁸Actually, during day time, this is not the case: air temperature decreases with height. However, during evening and night, due to heat radiation, the lower layers of air cool more rapidly than upper layers, and it may easily happen that the temperature is roughly independent of height.

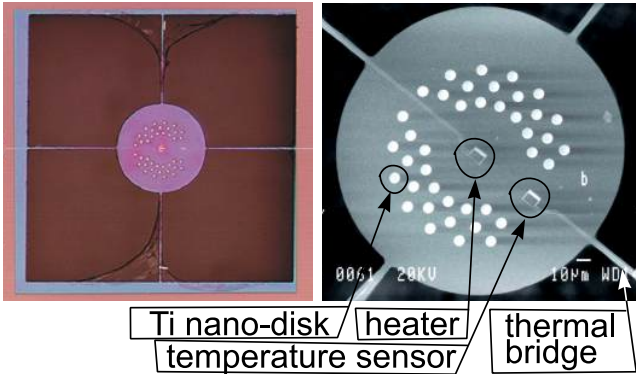


Let us model the Hadley circulation simplifyingly as a heat engine shown in the schematic below. For simplicity, let us assume that when air moves from A to B, it expands adiabatically, and when it moves from D to E, it contracts adiabatically. Further, let us assume that the processes with air when it moves from B to D, and from E to A are isothermal; on segment E-A it receives heat from the surface, on segment B-C — receives heat from vapour condensation, and on segment C-D — gives heat away due to radiation.

- Given that atmospheric pressure at a vertical level owes its origin to the weight of the air above that level, and knowing that $p_A = 1000\text{ hPa}$ and $p_D = 225\text{ hPa}$, order the pressures p_A , p_B , p_C , p_D , p_E , respectively at the points A, B, C, D, E by a series of inequalities.
- Let the temperature next to the surface and at the top of the atmosphere be T_H and T_C respectively. Given that the pressure difference between points A and E is 20 hPa , calculate T_C for $T_H = 300\text{ K}$. Note that the ratio of molar gas constant (R) to molar heat capacity at constant pressure (c_p) for air is $\kappa = 2/7$.
- Calculate the pressure p_B .
- For an air mass moving once around the winter Hadley circulation, using the molar gas constant, R , and the quantities defined above, obtain expressions for the net work done per unit mole W_{net} ignoring surface friction and for the heat loss per unit mole Q_{loss} at the top of the atmosphere.
- What is the value of the ideal thermodynamic efficiency ε_i for the winter Hadley circulation?
- Prove that the actual thermodynamic efficiency ε for the winter Hadley circulation is always smaller than ε_i .
- Which of the following statements best explains why ε is less than the ideal value? Tick the correct answer(s). There can be more than one correct answer.
 - We have ignored work done against surface friction.
 - Condensation occurs at a temperature lower than the temperature of the heat source.
 - There is irreversible evaporation of water at the surface.
 - The ideal efficiency is applicable only when there is no phase change of water

pr 60. [EstFin-2008] A microcalorimeter is a thin circular silicon nitride membrane, thermally isolated from the surroundings, except that it is thermally connected to the wafer by four thin and narrow thermal bridges (see Figure). The microcalorimeter is equipped with a small heater in the middle of the membrane and a similar structure on the edge of the membrane working as a thermometer. This micro calorimeter is used to study the thermal properties of nanoscale Ti disks (light tiny dots in Fig). The thermal power of the heater depends sinusoidally on time, $P = P_0 \cos(\omega t)$ (negative power

implies a withdrawal of heat). The circular frequency ω is sufficiently low, so that for any moment of time t , the temperature of the microcalorimeter $T(t)$ can be considered constant across its entire surface, and the temperature profile along the thermal bridges can be considered linear. The wafer, to which the bridges are connected, is large and thick enough, so that its temperature T_0 can be considered to be constant all the time. Each of the four bridges have length L and cross sectional area of S ; the thermal conductance of them is κ . Thermal conductance is defined as the heat flux (measured in Watts) per surface area, assuming that the temperature drop is 1°C per 1 m. The heat capacity of the microcalorimeter (with Ti-disks) is C .



a) Find the thermal resistance R between the microcalorimeter and the wafer (i.e. the ratio of the temperature difference and heat flux).

For questions (ii) and (iii), use quantity R , without substituting it via the answer of question (a).

b) Write down the heat balance equation for the microcalorimeter and find the temperature of the microcalorimeter as a function of time $T(t)$ [you may seek it in the form $T = T_0 + \Delta T \sin(\omega t + \phi)$].

c) In order to study the thermal properties of the Ti-nanodisks, the amplitude of the sinusoidal oscillations of $T(t)$ should change by as large as possible value, as a response to a small change of C (which is caused by the Ti-disks). Find the optimal circular frequency ω_0 .

d) We have assumed that the temperature profile along the bridges is linear, i.e. their heat capacity can be neglected. For high frequencies $\omega \gtrsim \omega_c$, this is not the case. Estimate the critical frequency ω_c in terms of κ , l , specific heat c and density ρ of the bridge material.

pr 61. [EstFin-2010] In order to study the thermal properties of a thermos bottle, let us model it as two concentric spherical vessels, with radii $R_1 = 7\text{ cm}$ and $R_2 = 10\text{ cm}$. The gap between the walls of the vessels contains vacuum (hence, the heat conductivity can be neglected).

a) Find the radiative heat flux (i.e. transmitted heat per unit time) between the walls of the bottle, assuming that the ambient temperature is $T_2 = 293\text{ K}$ and the inner sphere is filled with liquid nitrogen at the boiling temperature $T_1 = 77\text{ K}$. The emissivities of all the surfaces are equal to that of stainless steel: $\varepsilon = 0.1$. *Remark:* The emitted heat flux per unit area is given Stefan-Boltzmann's law $P = \varepsilon \sigma T^4$, where $\sigma = 5.67 \times 10^{-8}\text{ W/m}^2\text{K}^4$ (assuming that ε is independent of the wavelength).

b) Estimate, how long time does it take for a full evaporation of the liquid nitrogen (the vapour escapes through an over pressure valve). For the liquid nitrogen, density $\rho = 810\text{ g/l}$ and latent heat of vaporization $\lambda = 199\text{ kJ/kg}$. *NB! If you were unable to find P (for question a), express the evaporation time symbolically (i.e. using the symbol P).*

pr 62. [EstFin-2011] Let us study how a vacuum can be created inside a bulb by pumping. Let the volume of the bulb be V , and the pump consist in a piston moving inside a cylinder of volume αV , where $\alpha \ll 1$. The pumping cycles starts with piston being pulled up; when the pressure inside the cylinder becomes smaller than inside the bulb, a valve V_A (connecting the cylinder and the bulb) opens and remains open as long as the piston moves up. When piston is released, it starts moving down, at that moment, the valve V_A closes. As long as the valve V_A is open, the pressures of the bulb and the cylinder can be considered as equal to each other. When the piston moves down, the pressure in the cylinder increases adiabatically until becoming equal to the outside pressure $p_0 = 10^5\text{ Pa}$; at that moment, another valve V_B opens letting the gas out of the cylinder. When the piston reaches the bottommost position, there is no residual air left inside the cylinder. Now, the piston is ready for being lift up: the valve V_B closes and V_A opens, marking the beginning of the next pumping cycle. The air inside the bulb can be considered isothermal, with the temperature being equal to the surrounding temperature T_0 . The adiabatic exponent of air $\gamma = c_p/c_v = 1.4$.

a) How many pumping cycles N needs to be done to reduce the pressure inside bulb from $p = p_0$ down to $p = \beta p_0$, where $\beta \ll 1$?

b) What is the net mechanical work done during such a pumping (covering all the N cycles)?

c) What is the temperature of the air released from the cylinder to the surroundings at the end of the pumping process (when the pressure inside the bulb has become equal to βp_0)?

d) According to the above described pumping scheme, there is a considerable loss of mechanical work during the period when the piston is released and moves down. Such a loss can be avoided if there is another pump, which moves in an opposite phase: the force due to outside air pressure pushing the piston down can be transmitted to the other pump for lifting the piston up. What is the net mechanical work done when such a pumping scheme is used?

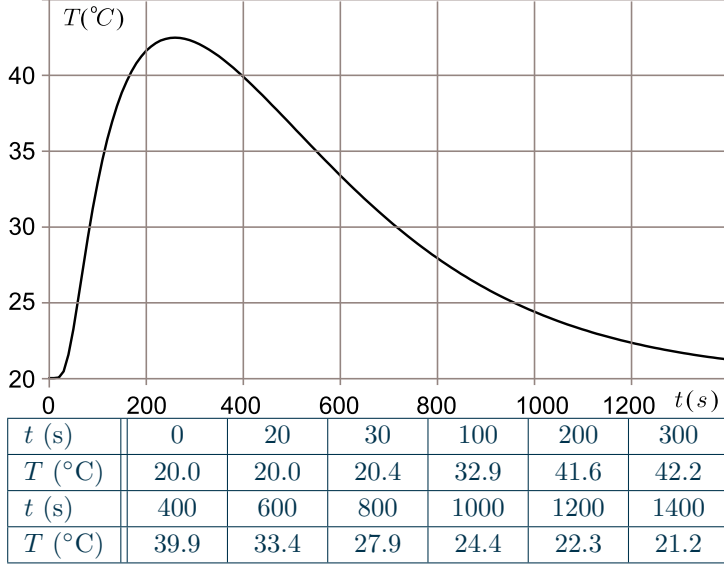
pr 63. [EstFin-2011] Consider a heat sink in the form of a copper plate of a constant thickness (much smaller than the diameter d of the plate). An electronic component is fixed to the plate, and a temperature sensor is fixed to the plate at some distance from that component. You may assume that the heat flux (i.e. power per unit area) from the plate to the surrounding air is proportional to the difference of the plate temperature at the given point (the coefficient of proportionality is constant over the entire plate, including the site of the electronic component).

a) The electronic component has been dissipating energy with a constant power of $P = 35\text{ W}$ for a long time, and the average plate temperature has stabilized at the value $T_0 = 49^\circ\text{C}$.

4. ENTROPY AND CARNOT CYCLE

Now, the component is switched off, and the average plate temperature starts dropping; it takes $\tau = 10$ s to reach the value $T_1 = 48^\circ\text{C}$. Determine the heat capacity C (units $\text{J}/^\circ\text{C}$) of the plate. The capacities of the electronic component and the temperature sensor are negligible.

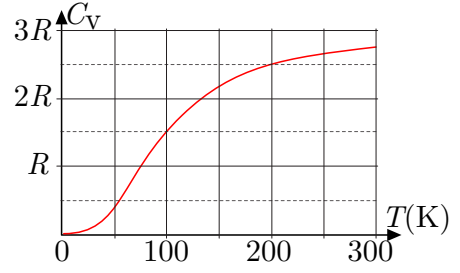
b) Now, the electronic component has been switched off for a long time; at the moment $t = 0$, a certain amount of heat Q is dissipated at it during a very short time. In the Figure and Table, the temperature is given as a function of time, as recorded by the sensor. Determine the dissipated heat amount Q .



pr 64. [Seagull-2016] What would be the temperature in the middle of a celestial body of the size of our Moon in Kelvins if the following assumptions can be made. The celestial body consists of an homogeneous solid material of average density $\rho = 3 \frac{\text{g}}{\text{cm}^3}$ and heat conductivity $k = 3 \text{ W/m} \cdot \text{K}$, and has the shape of a sphere of radius $R = 2000 \text{ km}$. It radiates heat as a perfectly black body, i.e. the heat flux density at its surface $w = \sigma T^4$, where $\sigma = 5.67 \times 10^{-8} \text{ J/s} \cdot \text{m}^2 \cdot \text{K}^4$ and T is its surface temperature. There is no external heat flux falling onto the surface of this celestial body. Due to nuclear decay of various isotopes (mostly uranium-238 and its decay products), the power density released in the crust material $P = 7 \times 10^{-12} \text{ W/kg}$.

pr 65. [EstFin-2011] Calculate the thermal efficiency of an ideal-gas cycle consisting of two isotherms at temperatures T_1 and T_2 , and two isochores joining them. (An isochore is a constant-volume process.) The engine is constructed so that the heat released during the cooling isochore is used for feeding the heating isochore

pr 66. [EstFin-2014] Consider a cube of side length $a = 1 \text{ cm}$, made of aluminium (density $\rho = 2.7 \text{ g/cm}^3$, molar mass $M_A = 23 \text{ g/mol}$). The heat capacitance of one mole of aluminium is given as a function of temperature in the graph below. The speed of light $c = 3 \times 10^8 \text{ m/s}$, universal gas constant $R = 8.31 \text{ J/(kg} \cdot \text{K)}$. The initial temperature of the cube is $T_0 = 300 \text{ K}$.



a) What is the total heat energy of such a cube at the initial temperature T_0 ?

b) Now, the cube has 5 faces painted in white (reflects all relevant wavelengths) and one face painted in black (absorbs all these waves). The cube is surrounded by vacuum at a very low temperature (near absolute zero); there is no gravity field. Initially, the cube is at rest; as it cools down due to heat radiation, it starts slowly moving. Estimate its terminal speed v_1 .

c) At very low temperatures, the heat capacitance of aluminium is proportional to T^3 , where T is its temperature. Which functional dependence $f(t)$ describes the temperature as a function of time [$T = A \cdot f(Bt)$, where A and B are constants] for such very low temperatures under the assumptions of the previous question?

d) Now, the cube has 5 faces covered with a thermal insulation layer (you may neglect heat transfer through these faces). One face is left uncovered. The cube is surrounded by hydrogen atmosphere at a very low temperature (molar mass of hydrogen molecules $M_H = 2 \text{ g/mol}$). The cube starts cooling down due to heat transfer to the surrounding gas; you may neglect the heat radiation. Initially, the cube is at rest; as it cools down, it starts slowly moving. Estimate the order of magnitude of its terminal speed v_2 . Assume that the surrounding gas is sparse, so that the mean free path of the molecules is much larger than a . Assume that $v_2 \ll c_s$ where c_s is the speed sound in the atmosphere surrounding the cube.

pr 67. [PhysCup] As compared to ordinary light bulbs, light emitting diodes (LED) provide very high lighting efficiency. The reason is that the spectral energy distribution of ordinary lamps is close to black body radiation, in which case one can say that the photons are in thermal equilibrium with the black body. Then, the total energy radiated by a black body per unit area, unit time, and unit frequency interval is given by Planck's law

$$I = \frac{2\pi h}{c^2} \frac{\nu^3}{e^{h\nu/kT} - 1},$$

where ν is the frequency, $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ — the Planck constant, $c = 2.997 \times 10^8 \text{ m/s}$ — the speed of light, $k = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$ — the Boltzmann constant, and T — the temperature; note that

$$\int_0^\infty I d\nu = \sigma T^4,$$

where $\sigma = 5.678 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$ is the Stefan-Boltzmann constant. With a black body radiation, a lot of energy is wasted by radiating non-visible light. Meanwhile, LED-s can be constructed so that they radiate almost only visible light.

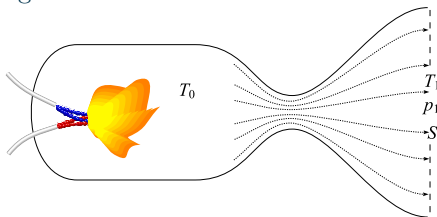
⁹P. Santhanam et al, *Thermoelectrically Pumped Light-Emitting Diodes Operating above Unity Efficiency*, Phys. Rev. Lett. **108**, 097403 (2012)

In recent experiments⁹, it has been reported that such LED-s have been constructed which have efficiency higher than 100%. Here the efficiency is defined as the ratio of the radiated light energy to the consumed electrical energy.

Based on reasonable approximations, find what is the theoretically highest possible efficiency of a LED assuming that:

- (a) the LED has a heat sink which is kept at the room temperature $T_0 = 293\text{ K}$ (via a fast enough heat exchange with the surrounding medium);
- (b) the LED emits light at wavelengths smaller than $\lambda_0 = 700\text{ nm}$
- (b) the surface area of the light-emitting part of the LED is $S = 1\text{ mm}^2$;
- (c) the light emission power of the LED is $P = 1\text{ }\mu\text{W}$.

pr 68. [EstOpen-2010] A liquid rocket engine is schematically shown in the figure below. Burning products are formed inside the combustion chamber at a high pressure and temperature, and expand adiabatically while leaving the chamber through the nozzle. If the nozzle is correctly constructed (the neck diameter needs to correspond to the burning rate), exhaust gases continue adiabatic expansion after passing through the throat, up to the exit from the nozzle. As a result, a major part of the heat energy is converted into kinetic energy of the exhaust gases at the exit of the nozzle. The temperature of the exhaust gases inside the combustion chamber is T_0 ; at the exit, the cross-sectional area of the nozzle is S , temperature of the exhaust gases is T_1 , and pressure is p_1 . Find the thrust force F assuming that $T_0 \gg T_1$, the effect of atmospheric pressure on the thrust can be neglected, and the kinetic energy of the gases inside the combustion chamber is negligible (as compared to the thermal energy). The heat capacitance of one mole of the exhaust gases by constant volume is $c_V = \frac{5}{2}R$, where R is the universal gas constant.



pr 69. During a day time, air masses in atmosphere are usually in a turbulent (random) motion, up and down, which leads to what is referred to as *adiabatic atmosphere*: when a parcel of air (a fictitious volume) is raising up, it is expanding and cooling adiabatically; in adiabatic atmosphere, the surrounding air is in mechanical and thermodynamical equilibrium with the raising air parcel (has exactly the same pressure and temperature). Find, how depends air temperature T on height h in adiabatic atmosphere. At the ground level ($h = 0$), $T = T_0$; express your answer in terms of the adiabatic index of air γ , molar mass μ , universal gas constant R , and free fall acceleration g .

pr 70. [IPhO-2006] At the bottom of a 1000 m high skyscraper, the outside temperature is $T_{\text{bot}} = 30^\circ\text{C}$. The ob-

jective is to estimate the outside temperature T_{top} at the top. Consider a thin slab of air (ideal nitrogen gas with adiabatic coefficient $\gamma = 7/5$) rising slowly to height z where the pressure is lower, and assume that this slab expands adiabatically so that its temperature drops to the temperature of the surrounding air.

- a) How is the fractional change in temperature dT/T related to dp/p , the fractional change in pressure?
 - b) Express the pressure difference dp in terms of dz , the change in height.
 - c) What is the resulting temperature at the top of the building?
- Data:* Boltzmann constant: $k_B = 1.38 \times 10^{-23}\text{ J}\cdot\text{K}^{-1}$, Mass of a nitrogen molecule: $m = 4.65 \times 10^{-26}\text{ kg}$, Gravitational acceleration: $g = 9.80\text{ m}\cdot\text{s}^{-2}$.

pr 71. [IPhO-2006] An egg, taken directly from the fridge at temperature $T_0 = 4^\circ\text{C}$, is dropped into a pot with water that is kept boiling at temperature T_1 .

- a) How large is the amount of energy U that is needed to get the egg coagulated?
- b) How large is the heat flow J that is flowing into the egg?
- c) How large is the heat power P transferred to the egg?
- d) For how long do you need to cook the egg so that it is hard-boiled?

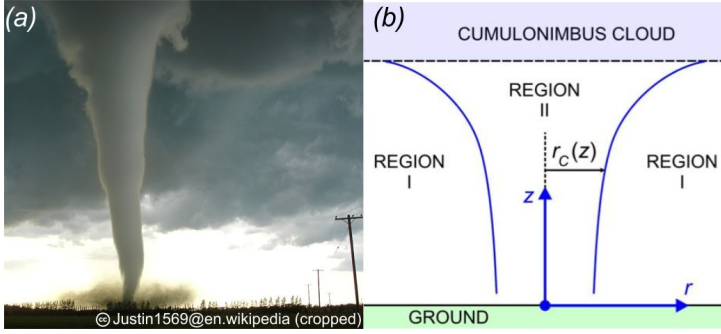
Hint: You may use the simplified form of Fourier's Law $J = \kappa \Delta T / \Delta r$, where ΔT is the temperature difference associated with Δr , the typical length scale of the problem. The heat flow J is in units of $\text{W}\cdot\text{m}^{-2}$.

Data: Mass density of the egg: $\mu = 10 \times 10^3\text{ kg}\cdot\text{m}^{-3}$, specific heat capacity of the egg: $C = 4.2\text{ J}\cdot\text{K}^{-1}\text{g}^{-1}$, radius of the egg: $R = 2.5\text{ cm}$, coagulation temperature of albumen (egg protein): $T_c = 65^\circ\text{C}$, heat transport coefficient: $\kappa = 0.64\text{ W}\cdot\text{K}^{-1}\text{m}^{-1}$ (assumed to be the same for liquid and solid albumen)

pr 72. [EstPhO-2000] A tightly closed vessel with thick and solid walls is filled with glycerin. Inside the glycerin, there is a bubble of air of volume $w = 1\text{ ml}$. At temperature $T_0 = 20^\circ\text{C}$, the pressure in the vessel is $p_0 = 1\text{ atm}$. The total volume of the vessel $V = 11$ linear thermal expansion coefficient of the vessel is negligibly small. The volumetric thermal expansion coefficient of glycerin $\alpha = 5.1 \times 10^{-4}\text{ K}^{-1}$. Express the pressure inside the vessel as a function of temperature; at which temperatures and why your expression becomes invalid?

pr 73. [WoPhO-2012] Tornado is a violent vortex (rotating column) of air connecting the base of cumulonimbus¹⁰ cloud and the ground. A distinct feature of the tornado is its funnel-like core or condensation funnel (Region II) which is made of small water droplets that condense as they are sucked into the core as shown in Fig. 1(b). This region is defined by the core radius $r_C(z)$ which generally increases with altitude forming the signature funnel-shape of the tornado. Region I is the region outside tornado core. In our simplified model, region I and II have different velocity distribution profile as we will explore later.

¹⁰Cumulonimbus cloud is a towering vertical cloud that is very tall, dense, and involved in thunderstorms and other rainy weather.



In what follows, you may use the following data:

gravitational acceleration $g = 9.8 \text{ m/s}^2$,

air density $\rho_{\text{air}} = 1.2 \text{ kg/m}^3$,

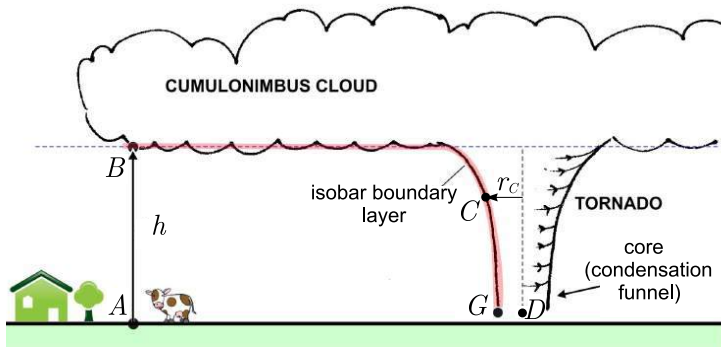
molar mass of dry air $M_{\text{air}} = 0.029 \text{ kg/mol}$,

universal gas constant $R = 8.314 \text{ J/(mol} \cdot \text{K)}$,

pressure at point A (see figure) $P_0 = 1.0 \times 10^5 \text{ Pa}$,

temperature at point A (see figure) $T_0 = 15^\circ\text{C}$,

heat capacity ratio of air $C_p/C_v = 1.4$.



A) The calm weather. We will investigate the atmospheric pressure of the troposphere (the lowest part of the atmosphere) where most of the weather phenomena including tornado occurs. Let us start from a calm weather location at point A far away from the tornado.

i) Assuming ideal gas law, constant gravity acceleration and a constant temperature T_0 . Show that the atmospheric pressure as a function of altitude z is $P(z) = P_0 e^{-\alpha z}$; express α in terms of the constants listed above.

ii) For simplicity we neglect the dependence of air density, ρ_{air} on z . Derive the pressure as a function of altitude, $P(z)$.

iii) Using your result in (ii) calculate the pressure at point B on the base of the cumulonimbus! (use $h = 1 \text{ km}$)

B) The shape. Inside the tornado's core the water vapour condenses into liquid droplets as the air spirals into the core forming condensation funnel. The water vapour condenses when the temperature drops below dew point. The temperature drop is caused by a pressure drop so the points where the water vapour starts to condense lay on a surface of equal pressure, called *isobar boundary layer* shown as red boundary in figure. This is the boundary between region I and II. For now we only consider region I. Consider a point G (see figure) very close to the ground ($z \approx 0$) located at radial distance $r = r_G$ from the axis (point C). At that point, the wind speed v_G can be treated as the ground rotation speed of the tornado. We further make the following assumptions: the tornado is stationary (only has rotation and no translation); the radial velocity of the wind is much smaller than the tangential speed $v = v(r)$ which will be assumed to be independent of altitude z (depends only on r); turbulence very close to the ground can be ignored; air mass

density (ρ_{air}) can be assumed to be constant.

i) Show that in both region I and II,

$$\frac{dP}{dr} = \rho_{\text{air}} \frac{v^2}{r}.$$

ii) In region I, calculate the wind velocity v as a function of r , in terms of v_G and r_G .

iii) Estimate the air speed v_G .

iv) Derive the shape of the condensation funnel, i.e. find the function $r_C(z)$, where r_C denotes the radial distance of a point C at the boundary layer (see figure). Sketch this tornado shape in dimensionless quantities z/h vs. r/r_G , where h is the height defined in figure.

v) Most tornadoes look like funnel (the radius is larger at higher altitude) while some are more uniform in diameter, like a pipe. Which type has the higher ground rotation speed v_G ?

C) The core. Now we will consider both region I and II.

i) In region II ($r < r_C$) the tornado core behaves as rigid body, derive expression for the (tangential) speed $v(r)$ in this region.

ii) Calculate the pressure at the center of the tornado (point D, at the same altitude as point G).

iii) Estimate the temperature T_D at the center of the tornado.

iv) Based on your finding in (iii) suggest, what could be a possible source of tornado's tremendous energy.

D) Windows. The differential pressure near a tornado is thought to cause poorly ventilated houses to "explode" even though the tornado is only passing at a distance. Therefore some people suggest that the windows have to be opened to let the pressure in the house equilibrates with outside. Then, however, wind and debris can freely enter the house. Consider a house with all windows and openings closed with a roof of dimension (width \times length \times thickness) $15 \text{ m} \times 15 \text{ m} \times 0.1 \text{ m}$ and mass density $\rho_{\text{roof}} = 800 \text{ kg/m}^3$. The tornado is coming fast and passing at a distance $d = 2r_G$ away from the house.

i) What is the lift-force-to-weight ratio for the roof?

ii) Shall you open or close the windows?

pr 74.

[IPhO-2004] A rubber balloon filled with helium gas goes up high into the sky where the pressure and temperature decrease with height. In the following questions, assume that the shape of the balloon remains spherical regardless of the payload, and neglect the payload volume. Also assume that the temperature of the helium gas inside of the balloon is always the same as that of the ambient air, and treat all gases as ideal gases. The universal gas constant is $R = 8.31 \text{ J/(mol} \cdot \text{K)}$ and the molar masses of helium and air are $M_H = 4.00 \times 10^{-3} \text{ kg/mol}$ and $M_A = 28.9 \times 10^{-3} \text{ kg/mol}$, respectively. The gravitational acceleration is $g = 9.8 \text{ m/s}^2$.

A-i) Let the pressure of the ambient air be P and the temperature be T . The pressure inside of the balloon is higher than that of outside due to the surface tension of the balloon. The balloon contains n moles of helium gas and the pressure inside is $P + \Delta P$. Find the buoyant force F_B acting on the balloon as a function of P and ΔP .

ii) On a particular summer day in Korea, the air temperature T at the height z from the sea level was found to be $T(z) = T_0(1 - z/z_0)$ in the range of $0 < z < 15 \text{ km}$ with $z_0 = 49 \text{ km}$ and $T_0 = 303 \text{ K}$. The pressure and density at the sea level

4. ENTROPY AND CARNOT CYCLE

were $P_0 = 1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$ and $\rho_0 = 1.16 \text{ kg/m}^3$, respectively. For this height range, the pressure takes the form $P(z) = P_0(1 - z/z_0)^\eta$. Express η in terms of z_0 , ρ_0 , P_0 , and g , and find its numerical value to the two significant digits. Treat the gravitational acceleration as a constant, independent of height.

B) When a rubber balloon of spherical shape with un-stretched radius $0r$ is inflated to a sphere of radius r_0 ($r \geq r_0$), the balloon surface contains extra elastic energy due to the stretching. In a simplistic theory, the elastic energy at constant temperature T can be expressed by

$$U = 4\pi r_0^2 \kappa RT (2\lambda^2 + \lambda^{-4} - 3),$$

where $\lambda \equiv r/r_0$ (≥ 1) is the size-inflation ratio and κ is a constant in units of mol/m^2 .

i) Express ΔP in terms of parameters given in Eq. above, and sketch ΔP as a function of $\lambda = r/r_0$.

ii) The constant κ can be determined from the amount of the gas needed to inflate the balloon. At $T_0 = 303 \text{ K}$ and $P_0 = 1 \text{ atm}$, an un-stretched balloon ($\lambda = 1$) contains $n_0 = 12.5$ moles. It takes $n = 3.6n_0 = 45$ moles in total to inflate the balloon to $\lambda = 1.5$ at the same T_0 and P_0 . Express the balloon parameter a , defined as $a = \kappa/\kappa_0$, in terms of n , n_0 , and λ , where $\kappa_0 = r_0 P_0 / 4RT_0$. Evaluate a to the two significant digits.

C) A balloon is prepared as in (C-ii) at the sea level (inflated to $\lambda = 1.5$ with $n = 3.6 = 45$ moles of helium gas at $T_0 = 303 \text{ K}$ and $P_0 = 1 \text{ atm}$). The total mass including gas, balloon itself, and other payloads is $M_T = 1.12 \text{ kg}$. Now let the balloon rise from the sea level.

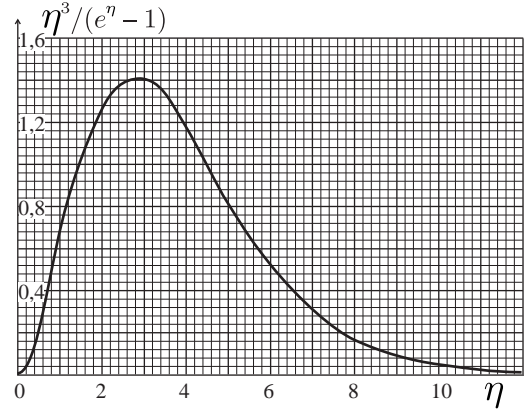
i) Suppose that the balloon eventually stops at the height z_f where the buoyant force balances the total weight. Find z_f and the inflation ratio λ_f at that height. Give the answers in two significant digits. Assume there are no drift effect and no gas leakage during the upward flight.

pr 75. [IPhO-1992] This is a continuation of the problem 6; here we repeat the numerical data: the satellite is a sphere of radius 1 m all points of which have the same temperature. The satellite is near Earth, but is not shaded by it; The surface temperature of the Sun $T_\odot = 6000 \text{ K}$, and its radius $R_\odot = 6.96 \times 10^8 \text{ m}$, The distance between the Earth and the Sun $L = 1.5 \times 10^{11} \text{ m}$ Stefan-Boltzmann constant $\sigma = 5.67 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$.

The blackbody radiation spectrum $u(T, f)$ of a body at temperature T obeys Planck's radiation law

$$u(T, f)df = A \frac{\eta^3 d\eta}{e^\eta - 1}$$

where $u(T, f)$ is the energy density of the electromagnetic radiation in a frequency interval $(f, f + df)$, and $\eta = hf/kT$; constant A can be expressed in terms of fundamental constants c (the speed of light), k (Boltzmann's constant), and h (Planck's constant): $A = \frac{8\pi^5 k^4}{15c^3 h^3}$. The blackbody spectrum, integrated over all frequencies f and directions of emission, gives the total radiated power per unit area $P = \int u(T, f)df = \sigma T^4$ as expressed in the Stefan-Boltzmann law given above. The figure shows the normalized spectrum $u(T, f)/AT^4$ as a function of η .



In many applications it is necessary to keep the satellite as cool as possible. To cool the satellite, engineers use a reflective coating that reflects light above a cut-off frequency but does not prevent heat radiation at lower frequency from escaping. Assume that this (sharp) cut-off frequency corresponds to $hf/k = 1200 \text{ K}$.

Estimate now, what is the temperature of the satellite.

Hint: exact calculation is not required; because of that, instead of precise and complicated integrations use approximate calculations where possible. The value of the following integral is known:

$$\int_0^\infty \frac{\eta^3 d\eta}{e^\eta - 1} = \frac{\pi^4}{15}.$$

Function $\eta^3/(e^\eta - 1)$ maximum is near $\eta \approx 2.82$. For small values of η , approximation $e^\eta \approx 1 + \eta$ can be used.

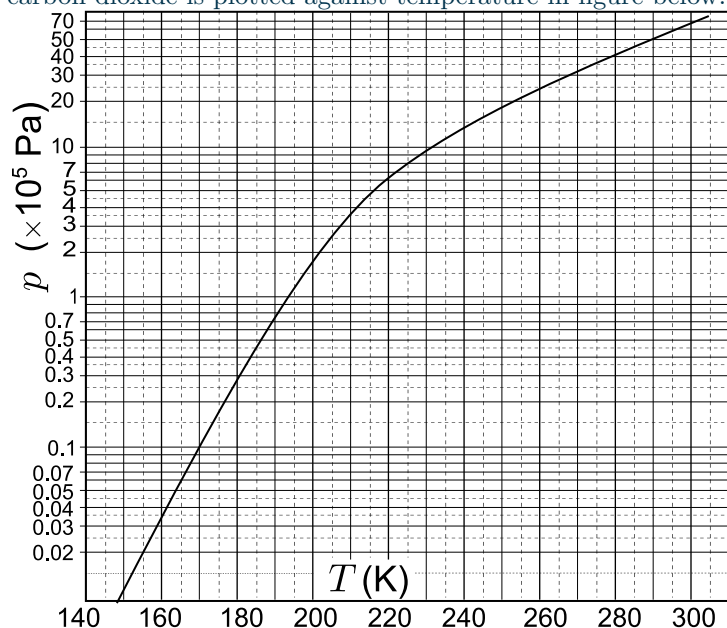
pr 76. [IPhO-2000¹¹] Ideal heat engine receives heat from body A and gives it away to body B ; both bodies have equal heat capacitance C . Initial temperature of body A was T_1 and that of body B — T_2 . What is the maximal amount of work which can be done by such a heat engine?

pr 77. Both solder joints of a thermocouple exchange heat with the surrounding air at the rate $P_e = \kappa \Delta T$, where ΔT is the difference between the temperature of a solder joint and that of the air; the constant $\kappa = 30 \mu\text{W/K}$. The thermocouple sensitivity α is defined as the proportionality coefficient between the thermocouple voltage and the temperature difference between the solder joints; in this case, $\alpha = 50 \mu\text{V/K}$. The thermocouple is fed with electric current $I = 10 \text{ mA}$; find the temperature of the colder solder joint if the air temperature $t_a = 20^\circ\text{C}$. Assume the energy transfer processes in the thermocouple to be reversible.

pr 78. [EstPhO-2010] A disc of radius $r = 1 \text{ cm}$ is made from dry ice (carbon dioxide in solid phase), and is pressed against a plate which is made from a material of high heat conductivity. The disc is pressed against the plate with force $F = 100 \text{ N}$, which is applied to the centre of the disc and is almost (but not exactly) perpendicular to the plate. When the plate temperature is low, the friction force between the disk and plate keeps the disk at rest. However, when the plate temperature rises above a critical value T_0 , the friction force disappears almost completely, and the disc starts sliding along the plate. Find T_0 . Air pressure is 101 kPa , triple point pressure

¹¹Voted out by the International Board from the final text

of carbon dioxide is $p_t = 5.1 \times 10^5$ kPa, saturation pressure of carbon dioxide is plotted against temperature in figure below.

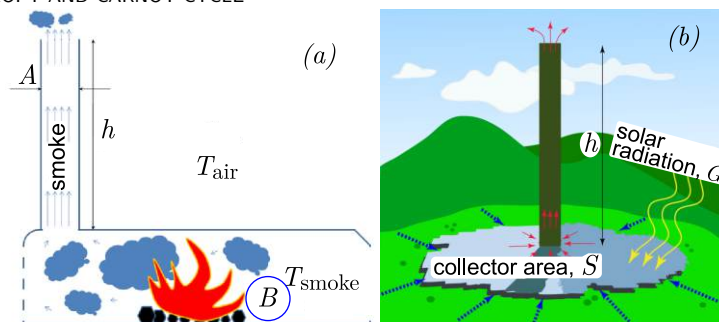


pr 79. [EstPhO-2009] Room is being heated by an electrical radiator of power $P = 1$ kW. Outside temperature is $t_0 = 0^\circ\text{C}$, the room temperature has been stabilized at $t_1 = 20^\circ\text{C}$. A ventilation window is opened, supplying now a fresh air at the volume rate $v = 201/\text{s}$. What will be the new room temperature? Air can be considered to be an ideal bimolecular gas.

pr 80. [IPhO-1997] On a given day, the air is dry and has a density $\rho = 1.250$ kg/m³. The next day the humidity has increased and the air is 2% by mass water vapour. The pressure and temperature are the same as the day before. What is the air density ρ' now? Mean molar mass of dry air: $M_a = 28.8$ g/mol; molar mass of water: $M_w = 18$ g/mol. Assume ideal-gas behaviour.

pr 81. [IPhO-2010] **Chimney.** Gaseous products of burning are released into the atmosphere of temperature T_{air} through a high chimney of cross-section A and height h (see figure a). The solid matter is burned in the furnace which is at temperature T_{smoke} . The volume of gases produced per unit time in the furnace is B . Assume that:

- ◇ the velocity of the gases in the furnace is negligibly small;
- ◇ the average molar mass of the gases produced in the furnace (smoke) equals to that of the air, and these gases can be treated as ideal;
- ◇ chimney is not very high (not higher than a hundred meters);
- ◇ smoke temperature can be assumed to be constant throughout the entire length of the chimney.



- a) What is the minimal height of the chimney needed for an efficient withdrawal of the gases? Express answer in terms of B , A , T_{air} , $g = 9.81$ m/s², and $\Delta T \equiv T_{\text{smoke}} - T_{\text{air}}$. In all subsequent tasks assume that this minimal height is the height of the chimney.
- b) Assume that two chimneys are built to serve exactly the same purpose. Their cross sections are identical, but are designed to work in different parts of the world: one in cold regions, designed to work at an average atmospheric temperature of -30°C and the other in warm regions, designed to work at an average atmospheric temperature of 30°C . The temperature of the furnace is 400°C . It was calculated that the height of the chimney designed to work in cold regions is 100 m. How high is the other chimney?
- c) How does the velocity of the gases vary along the height of the chimney? Make a sketch/graph assuming that the chimney cross-section does not change along the height.
- d) How does the pressure of the gases vary along the height of the chimney?

Solar power plant. The chimney operation principle can be used to construct a particular kind of solar power plant, *solar chimney*. The idea is illustrated in figure b. The Sun heats the air underneath the collector of area S with an open periphery to allow the undisturbed inflow of air. As the heated air rises through the chimney (red arrows), new cold air enters the collector from its surrounding (blue arrows) enabling a continuous flow of air through the power plant. The flow of air through the chimney powers a turbine, resulting in the production of electrical energy. The energy of solar radiation per unit time per unit of horizontal area of the collector is G . Assume that all that energy can be used to heat the air in the collector (the mass heat capacity of the air is c , and one can neglect its dependence on the air temperature). We define the efficiency of the solar chimney as the ratio of the kinetic energy of the gas flow and the solar energy absorbed in heating of the air prior to its entry into the chimney.

- e) What is the efficiency of the solar chimney power plant?
- f) Make a graph showing how the efficiency of the chimney changes with its height.

The prototype chimney built in Manzanares, Spain, had a height of 195 m, and a radius 5 m. The collector is circular with diameter of 244 m. The specific heat of the air under typical operational conditions of the prototype solar chimney is 1012 J/kg · K, the density of the hot air is about 0.9 kg/m³, and the typical temperature of the atmosphere $T_{\text{air}} = 295$ K. In Manzanares, the solar power per unit of horizontal surface is typically 150 W/m² during a sunny day.

- g) What is the efficiency of the prototype power plant? Write

down the numerical estimate.

- h) How much power could be produced in the prototype power plant?
- i) How much energy could the power plant produce during a typical sunny day?
- j) How large is the rise in the air temperature as it enters the chimney (warm air) from the surrounding (cold air)? Write the general formula and evaluate it for the prototype chimney.
- k) What is the mass flow rate of air through the system?

pr 82. Air (a mixture of oxygen and nitrogen) is stored in a closed container equipped with a piston on one end at a temperature of $T = 77.4\text{ K}$. The total amount of the gas mixture occupies volume $V_0 = 1.00\text{ l}$ and its initial pressure is $p_0 = 0.500\text{ atm}$. With the help of the piston the gas mixture is slowly compressed at constant temperature. Using plausible assumptions, plot the pressure of the system as a function of its volume until one tenth of the initial volume, if the ratio of the number of moles of oxygen to the number of moles of nitrogen is $n_{\text{O}_2} : n_{\text{N}_2} = 21 : 79$. Find the pressure and volume at distinctive points of these isothermal curves.

You can use the following data: boiling point of liquid nitrogen at $p_1 = 1.00\text{ atm}$: $T_{\text{N}_2} = 77.4\text{ K}$; boiling point of liquid oxygen at $p_1 = 1.00\text{ atm}$: $T_{\text{O}_2} = 90.2\text{ K}$; heat of vaporization of oxygen: $\lambda_{\text{O}_2} = 213\text{ J/g}$ (can be assumed to be constant for $T_{\text{N}_2} \leq T \leq T_{\text{O}_2}$). Neglect solubility of gaseous nitrogen in liquid oxygen and vice versa.

pr 83. [WoPhOSR-2013] Thermal atmospheric escape is a process in which small gas molecules reach speeds high enough to escape the gravitational field of the Earth and reach outer space. This process, known as Jeans escape, is believed to have been responsible for the loss of water from Venus and Mars atmospheres, due to their lower escape velocity.

In what follows we assume that the distribution of the molecules of the atmosphere is given by the Maxwellian distribution. Thus at any temperature there can always be some molecules whose velocity is greater than the escape velocity. A molecule located in the lower part of the atmosphere would not be able to escape to outer space even though its velocity is greater than the limit velocity because it would soon collide with other molecules, losing a big part of its energy. In order to escape, these molecules need to be at a certain height: such that density is so low that their probability of colliding is negligible. The region in the atmosphere where this condition is satisfied is called exosphere and its lower boundary, which separates the dense zone from the exosphere, is called exobase. You may assume that the temperature near the exobase is roughly $T = 1000\text{ K}$; universal gas constant $R = 8.31\text{ J/K} \cdot \text{mol}$, free fall acceleration $g \approx 9.5\text{ m/s}^2$, Avogadro number $N_A = 6.02 \times 10^{23}\text{ 1/mol}$.

a) *Exobase height.* Exobase is defined as the height above which a radially outward moving particle will suffer less than one backscattering collision on average. This means that the mean free path has to be equal to the *scale height* H , which is defined as such an height increment which leads to the atmosphere's density dropping e times. What is the average molar mass of the Earth's atmosphere at the exobase if $H = 60\text{ km}$?

b) The mean free path λ is the average distance covered by a moving particle in a gas between two consecutive collisions and this can be expressed by the following equality:

$$\lambda = (\sigma n)^{-1},$$

where σ is the effective cross sectional area; $\sigma = 0.2\text{ nm}^2$ for the collisions of an hydrogen atom with the air molecules (with molecular composition corresponding to exobase), and n is the number of molecules per unit volume. We know that at an altitude of $h_0 = 250\text{ km}$, the pressure is $p_0 = 21\text{ }\mu\text{Pa}$, and temperature can be assumed to be constant between the exobase and the reference height h_0 . Determine the mean free path for the hydrogen atoms at the altitude h_0 .

c) Determine the exobase height h_{EB} .

d) *Atmospheric escape.* Particles in the exobase with enough outwards velocity will escape gravitational attraction. Assuming a Maxwellian distribution, determine the probability that a hydrogen atom has a velocity greater than the escape velocity in the exobase.

e) Determine the hydrogen atoms flux (number of particle per unit area and per unit time) that will escape the atmosphere, knowing that the concentration of hydrogen atoms in the exobase is $n_H = 1 \times 10^{11}\text{ m}^{-3}$. You may assume that the hydrogen is in a monoatomic state: when atmospheric molecules reach a certain height lower than h_{EB} , they split into atoms due to solar radiation.

The following calculations will show that thermal atmospheric escape cannot be the single processes that explains why some gases are present in the atmosphere and some others are not.

f) Knowing that the current average molar mass of the atmosphere is $M_{\text{Atm}} = 29\text{ gr/mol}$, atmospheric pressure $P_0 = 1 \times 10^5\text{ Pa}$, and a fraction of $\chi_H = 5.5e-7$ of the atmospheric molecules are hydrogen molecules, estimate the number N_H of hydrogen atoms in the Earth's atmosphere. Neglect the presence of other hydrogen-containing molecules.

g) Let us make a robust model and assume that the concentration of hydrogen atoms in the exobase remains constant over time. Find out how much time would it take for half of the hydrogen atoms to escape the Earth's atmosphere.

h) Now let us consider helium atoms; currently, their concentration in the exobase is $n_{\text{He}} = 2.5 \times 10^{12}\text{ m}^{-3}$, and they make $\chi_{\text{He}} = 5 \times 10^{-6}$ of the atmospheric molecules. Let us use now a more realistic model and assume that their concentration in exobase is proportional to their concentration in the lower atmosphere.

i) Suggest a reason, why there is currently still some hydrogen in the Earth's atmosphere.

pr 84. [IPhO-2012] Let us model the formation of a star as follows. A spherical cloud of sparse interstellar gas, initially at rest, starts to collapse due to its own gravity. The initial radius of the ball is r_0 and the mass — m . The temperature of the surroundings (much sparser than the gas) and the initial temperature of the gas is uniformly T_0 . The gas may be assumed to be ideal. The average molar mass of the gas is μ and its adiabatic index is $\gamma > \frac{4}{3}$. Assume that $G \frac{m\mu}{r_0} \gg RT_0$, where R is the gas constant and G — the gravity constant.

4. ENTROPY AND CARNOT CYCLE

a) During much of the collapse, the gas is so transparent that any heat generated is immediately radiated away, i.e. the ball stays in a thermodynamic equilibrium with its surroundings. How many times (n) does the pressure increase while the radius is halved ($r_1 = 0.5r_0$)? Assume that the gas density stays uniform.

b) At some radius $r_3 \ll r_0$, the gas becomes dense enough to be opaque to the heat radiation. Calculate the amount of heat Q radiated away during the collapse from the radius r_0 down to r_3 . Assume that the gas density stays uniform¹²

c) For radii smaller than r_3 you may neglect heat radiation. Determine how the temperature T of the ball depends on its radius $r < r_3$.

d) Eventually we cannot neglect the effect of the pressure on the dynamics of the gas and the collapse stops at $r = r_4$ (with $r_4 \ll r_3$). However, the radiation can still be neglected and the temperature is not yet high enough to ignite nuclear fusion. The pressure of such a protostar is not uniform anymore, but rough estimates with inaccurate numerical prefactors can still be done. *Estimate* the final radius r_4 and the respective temperature T_4 .

pr 85. [APhO-2010]¹³ Sonoluminescence is a phenomenon when strong sound waves put small bubbles inside a liquid (e.g. water) into oscillatory motion; collapsing bubbles may heat the entrapped gas so much that it will emit black body radiation in visible range of wavelengths.

Throughout the problem, you may use the following model. All times t , the bubble of radius $R = R(t)$ is spherical and its centre remains stationary in the water of density $\rho_0 = 1.0 \times 10^3 \text{ kg/m}^3$. The entrapped gas density ρ pressure P , and temperature T are always uniform inside the bubble as its size diminishes. The liquid containing the bubble is assumed to be isotropic, nonviscous, incompressible, and very much larger in extent than the bubble. This means that we can consider a fictitious water sphere of radius $r \gg R$ centred around the bubble, and it will contract isotropically during the contraction of the bubble. Heat exchange between the gas and the surrounding water can be neglected. All effects due to gravity and surface tension are neglected so that for any t , the pressure inside the liquid is a function of r only: $P = P(r)$ for $r > R$. You may assume that the ambient pressure $P_0 = P(r \rightarrow \infty) = 1.01 \times 10^5 \text{ Pa}$ and the water temperature $T_0 = 300 \text{ K}$ remain constant in time. Initially, the bubble has radius $R_i = 7R_0$, entrapped gas temperature $T = T_0$, and the surrounding water is motionless (i.e. $\frac{dR}{dt} = 0$); here $R_0 = 5.00 \mu\text{m}$ denotes the equilibrium radius of the bubble at which the entrapped gas would have pressure P_0 with $T = T_0$. The ratio of specific heat at constant pressure to that at constant volume for the gas is $\gamma = 5/3$.

You may find it useful to know that the kinetic energy of the surrounding water can be expressed in terms of the bubble's

shrinking speed \dot{R} as

$$E_k = 2\pi\rho_0 R^3 \dot{R}^2.$$

a) Find the minimal radius R_m and maximal temperature T_m of the bubble during the shrinking process.

b) Find the radius R_f of the bubble at the moment t_f when the bubble's shrinking speed is maximal.

c) Most of the heat radiation is emitted between $t = t_f$ and the moment t_m when the minimal radius is reached. Estimate the total duration of the radiation period.

d) For our model to remain valid, the heat loss Q due to radiation must be much smaller than the internal energy of the gas U ; let us require that $Q \leq \frac{1}{5}U$. This means that if we consider the entrapped gas as a sphere of radius R emitting thermal radiation at emissivity a , the emissivity should be not too large, $a \leq a_0$. Estimate the value of a_0 . Stefan-Boltzmann constant $\sigma = 5.678 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$.

pr 86. [APhO-2007] a) For a metal at thermal equilibrium, the average energy of the conduction electrons makes a certain contribution to the specific heat. According to the classical physics the conduction electrons in metals constitute free electron gas trapped into the volume of the metal, and this gas can be considered to be ideal. Find the average contribution of each electron to the specific heat at constant volume (c_V) using the classical model.

b) Experimentally it has been shown that the specific heat of the conduction electrons at constant volume in metals depends on temperature, and the experimental value at room temperature is about two orders of magnitude lower than its classical counterpart. This is because the electrons obey the quantum statistics rather than classical statistics. According to the quantum theory, for a metallic material the density of states of conduction electrons (the number of electronic states per unit volume and per unit energy) is proportional to the square root of electron energy E , then the number of states dE within energy range for a metal of volume V can be written as

$$dS = CV\sqrt{E}dE,$$

where C is the normalization constant, determined by the total number of electrons of the system. The probability that the state of energy E is occupied by electron is called the *Fermi distribution*,

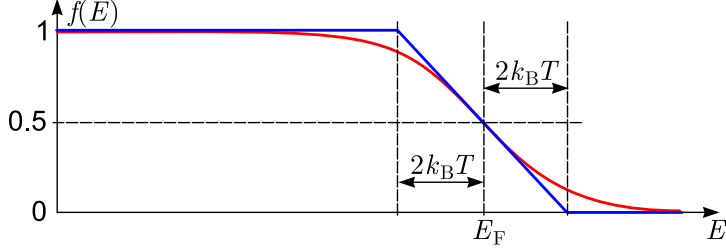
$$f(E) = \left[1 + \exp\left(\frac{E - E_F}{k_B T}\right) \right]^{-1},$$

where $k_B = 1.381 \times 10^{-23} \text{ J/K}$ is the Boltzmann constant and T is the absolute temperature, while E_F is called Fermi level. Usually at room temperature E_F is about several eVs for metallic materials ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$) and therefore $k_B T \ll E_F$, in which case the Fermi distribution behaves as shown in figure by red curve; you are allowed to approximate it by a piece-wise linear function as depicted by blue line. Additionally, you may neglect the dependence of Fermi level on

¹²This is valid as long as the gravitational energy dominates over the heat energy; in the original IPhO problem, the students needed to conclude this by themselves, based on the dynamics of the gas cloud. It should be emphasized that such a model with a ballistic contraction stage deviates from the standard model of protostar collapse in which case a gas cloud contracts due to radiative cooling while maintaining a quasi-equilibrium between gravitational and pressure forces.

¹³Subtasks are cut from this version: you have a freedom of bypassing unnecessarily long mathematical calculations, but you need to demonstrate more independence.

temperature so that its value can be expressed in terms of the total number of electrons by putting $T = 0$.



Express the average contribution of each electron to the specific heat at constant volume in terms of k_B , E_F , and T using the quantum mechanical model. Give a qualitative explanation for the deviation of the classical result from that of quantum theory.

pr 87. [EstFin-2014]¹⁴ Let us consider a system of N independent magnetic dipoles (spins) in a magnetic field B and temperature T . Each spin has two states: spin up, and spin down; the x -component of its dipole moment takes values $+\mu_B \equiv \frac{e\hbar}{2m}$ and $-\mu_B$, respectively (x is a fixed axis).

a) What is the average value of the total energy E_s of the spin system as a function of B and T ?

b) At the high temperature limit $T \gg \frac{\alpha B m}{k}$, what is the heat capacity C of such a spin system?

pr 88. [EstOpen-2001] In order to store $\nu = 1$ mol of ideal gas at temperature T_0 , a vessel made of steel (density ρ) is used. Assume that the vessel's walls are much thinner than the vessel's linear dimensions. According to the specification, the mechanical stress in the walls (force per cross-sectional area) must be everywhere (and for any direction) not larger than σ_0 . What is the minimal mass of the vessel?

appendix 2: Finding mean kinetic energy from Maxwell's law

Using substitution rule,

$$\int_{-\infty}^{\infty} e^{-v_x^2/v_0^2} dv_x = v_0 \int_{-\infty}^{\infty} e^{-x^2} dx.$$

Integration is essentially taking a sum, and we know that a derivative of a sum is the sum of the derivatives. Hence, we can take derivative from the both sides of this equality by v_0 ; left-hand-side yields

$$\begin{aligned} \frac{d}{dv_0} \int_{-\infty}^{\infty} e^{-v_x^2/v_0^2} dv_x &= \int_{-\infty}^{\infty} \frac{d}{dv_0} e^{-v_x^2/v_0^2} dv_x = \\ &= 2v_0^{-3} \int_{-\infty}^{\infty} v_x^2 e^{-v_x^2/v_0^2} dv_x, \end{aligned}$$

and the right-hand-side yields

$$\frac{d}{dv_0} v_0 \int_{-\infty}^{\infty} e^{-x^2} dx = \int_{-\infty}^{\infty} e^{-x^2} dx.$$

This means that

$$\int_{-\infty}^{\infty} v_x^2 e^{-v_x^2/v_0^2} dv_x = \frac{1}{2} v_0^3 \int_{-\infty}^{\infty} e^{-x^2} dx.$$

Let us recall that $f(v_x) = e^{-v_x^2/v_0^2} / \int_{-\infty}^{\infty} e^{-v_x^2/v_0^2} dv_x$. So we can rewrite the expression for the root-mean-square velocity as

$$\bar{v}_x^2 = \int_{-\infty}^{\infty} v_x^2 e^{-v_x^2/v_0^2} dv_x / \int_{-\infty}^{\infty} e^{-v_x^2/v_0^2} dv_x = \frac{1}{2} v_0^2.$$

Now, if we substitute back $v_0 = \sqrt{2k_B T/m}$ (which corresponds to the Maxwell's distribution), we obtain finally

$$\bar{v}_x^2 = k_B T.$$

Hints

- Express the constant heating power as $P = \frac{dQ}{dt}$ and substitute $dQ = C_p dT$; this allows you to find C_p as a function of time t ; eliminate t using the provided dependence $T = T(t)$.
 - Some hints are already given after the problem; determine the net heating power at the average ice-heating-temperature $T_2 \approx 72^\circ\text{C}$ by comparing the tangents of the $T(t)$ -curve at $T = T_1$ (c.f. the fact 6) and $T = T_2$.
 - In average, electrical heating power equals to the cooling power due to heat loss. The temperature oscillations are small, hence (according to the idea 2) the cooling power is almost constant; meanwhile, heating power oscillates between a maximal value U_1^2/R and zero according to a rectangular waveform. Here, the filament's resistance R can be expressed in terms of the filament's length l and cross-sectional area S (the value of the latter is not given but we may hope that it will cancel out from the final answer). Now we can express the thermal power drawn to (from) the filament for both of the half-periods, and find the temperature oscillations amplitude from the 1LTD.
 - Based on the fact 6, determine how many percents has increased the thermal flux to the environment, and use this to conclude, how many percents has increased the heat production rate inside the house.
 - Follow the idea 3; the thermal resistance of the copper plate is calculated in the same way as an electrical resistance, $R_T = \rho d/s$.
 - Recall the idea 7: for dynamical processes, at first, a mechanical equilibrium is reached, which means the equality of pressures; the other equilibria (e.g. thermal) will be reached later (if ever within a reasonable time frame). In particular, this means that if there is evaporation from a water surface, and because of that, close to the water surface, there is an higher concentration of water vapours, then there must be a lower concentration of air molecules. Indeed, while due to mechanical equilibrium, the total pressure must remain equal to the atmospheric one, it also equals to the sum of the vapour pressure and air pressure 13. Equivalently can be said that the air pressure equals to the atmospheric pressure minus the vapour pressure.
- If the saturation pressure $p_s(T)$ becomes larger than the atmospheric pressure p_{atm} then mechanical equilibrium is no longer possible: as we learned earlier, very close to the water surface, there is thermal quasi-equilibrium and $r = 100\%$ and hence, in that layer, the vapour pressure $p_v = p_s(T)$. The total pressure p in that layer is sum of the vapour pressure and air pressure, hence $p \geq p_v > p_{\text{atm}}$. Therefore, the vapours at the liquid surface will have larger pressure than the atmospheric one, and the surrounding air will be pushed away. Furthermore, if there were a small bubble inside the liquid, it would also have higher pressure of vapours inside than the pressure of the surroundings, hence the bubble would start growing. It should be noted that there are always either microscopic bubbles or other

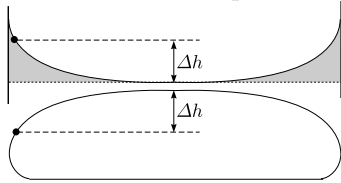
¹⁴Text here is somewhat modified

impurities inside the liquid which can serve as evaporation centres.

25. Apply the same approach what was used to derive expression for the contact angle in terms of surface tensions, but keep in mind that solid-liquid contact area is now smaller.
26. We have a meniscus as shown in figure, and separate a fraction of water (depicted in grey) by a fictitious horizontal plane passing the flat bottom of the meniscus, and consider the force balance for the grey volume. At the separation plane inside the liquid, the hydrostatic pressure equals to the atmospheric one. Indeed, at the bottom of the meniscus, through the flat water-air interface, there is no capillary pressure, hence the hydrostatic gauge pressure must be zero; inside the liquid, the hydrostatic pressure is a function of height only, so the pressure remains equal to the atmospheric one through the horizontal plane. So, the volume depicted by grey in the figure is surrounded by atmospheric pressure, i.e. there is no extra net force acting on it due to pressure.



29. Notice that the volume of the water is fixed: if the layer thickness were small, the gravitational energy would be small, but the surface energy would be large (the opposite also holds). Express the total energy for a fixed amount of liquid.
30. Use the fact 17 and idea 19 to conclude that the shape of the cross-section of the meniscus is identical to the cross-section of the pool of liquid laying on the desk (cf. problem 29). Indeed, the surface curvature depends only on the surface tension and gauge pressure, which can be matched in the case of the meniscus and a pool as shown in figure.



32. Assuming the opposite, consider two heat engines with different efficiencies. The Carnot' cycle is reversible, so we'll use the engine of higher efficiency as a heat pump (with reversed Carnot' cycle): it takes heat from a body of lower temperature and gives it to a body of higher temperature; a net mechanical work needs to be done to operate the heat pump. Show that if the work done by the heat engine of lower efficiency is used to propel the heat pump of higher efficiency, the net effect of the entire system would be in violation to 2LTD.
46. For the cooling period, during the number of days ΔN for which the temperature stayed in the (small) range between T and $T + \Delta T$, the heat loss is $P_c = (T - T_0)C\Delta N \cdot 3600s/h$. $(T - T_0)\Delta N$ is a horizontal narrow rectangular region between the graph and the vertical line $T = T_0$, hence the total heat loss is related to the area between the graph and the line $T = T_0$.

Answers

1. $4PT^3/aT_0^4$
2. $m = Q/(L + c\Delta T) \approx 28 \text{ g}$ ($Q = 500 \text{ W} \cdot 37 \text{ s}$)
3. $\Delta T = \frac{U_1^2 T}{8\rho_e \rho c l^2} \approx 34 \text{ K}$
4. $P' = P \frac{t_2 - t_1}{t_1 - t_0} \approx 53^\circ \text{C}$
5. $\Delta T = P\rho d/s \approx 11.7 \text{ K}$; $Q = (T_1 - T_2)S/\int \rho dx \approx 18 \text{ mW}$
6. $T = T_\odot \sqrt{R_\odot/2L} \approx 290 \text{ K}$
7. $N + 1$
8. $T_{\min} = (I/\sigma)^{1/4}$, $T_{\max} = (\sqrt{3}I/\sigma)^{1/4}$
9. $v \approx \frac{m}{M} \sqrt{\frac{RT}{\mu}}$
10. $N \approx 162$
11. $\Phi \approx \frac{3}{2}nRT_1 \sqrt{\frac{RT_2}{M}}$
13. $\Delta m = (\frac{1}{T_{\text{air}}} - \frac{1}{T_1}) \frac{p_0 V_0}{R} (\mu_{\text{air}} - \mu_{\text{H}})$
14. $T = 1.4T_0$.
15. is reduced by 2 times; $\gamma = \frac{4}{3}$
16. $\Delta T = \frac{\rho_0 T_0 g \Delta h}{p_0} \frac{\gamma - 1}{\gamma} = 2.1 \text{ celsius}$
18. a) $v_P \approx 23 \text{ m/s}$; b) where the distance between the lines is the smallest; c) $v_{\text{crit}} \approx 23 \text{ m/s}$,
20. $\sqrt{2.5}$
21. (a) $a = \frac{p_0 S}{M}$; (b) $a = \frac{p_0 S}{2M}$
22. a) $\Delta T \approx 1.5^\circ \text{C}$
b) $\Delta T \approx 6.5^\circ \text{C}$
c) $\Delta T = 12.1(1 - r)$
d) ≈ 4
23. $\kappa = \frac{T - T_{100^\circ \text{C}}}{\lambda} c = 0.154$
24. a) $T_A = 350 \text{ K}$ $T_B = 100 \text{ K}$
b) $t_1 \approx 67^\circ \text{C}$ $t_2 = 100^\circ \text{C}$ $\frac{m_A}{m_B} \approx 22$
25. 175°
26. $\Delta V = \frac{2\pi}{\rho} \sqrt{\frac{V\pi}{h}} = 0.58 \text{ ml}$
27. 13.3 cm
29. $h = \sqrt{\frac{2\sigma}{\rho g} (1 + \cos \alpha)}$
30. $h = \sqrt{\frac{\sigma}{\rho g}}$
35. $\frac{dp_s}{dT} = p_s \frac{\lambda \mu}{RT^2}$; $\Delta P = \frac{T_0 - T_1}{T_0^2} \frac{p_0 \mu L}{R} \approx 350 \text{ Pa}$
36. $U = L/\mu N_A$ — exit work, negative potential energy of a molecule in the liquid phase.
37. $m = \frac{I^2 R t T_2}{(T_1 - T_2) \lambda} \approx 1.5 \text{ g}$
38. $T_3 \approx 1.4T_2 \approx 3.5T_1$
39. $T = \frac{V_0}{I_0 R_0} T_0 = 2650 \text{ K}$
 $d = \sqrt[3]{\frac{4V_0 I_0 \rho_0}{\pi^2 R_0 k \sigma T^4}} = 1.5 \times 10^{-5} \text{ m}$
 $l = \frac{R_0 d^2 \pi}{4\rho_0} = 0.0566 \text{ m}$
41. $d_2 = \frac{1}{11} d_1$
42. b) $T = \frac{V_1 + V_2}{\frac{V_1}{T_1} + \frac{V_2}{T_2}} \approx 16.5^\circ \text{C}$; c) $r \approx 1.22$; d) $m \approx 7.5 \text{ g}$.

4. ENTROPY AND CARNOT CYCLE

43. a) $T_2 = T_0 + \frac{\Delta s(p_0 \pi r^2 + mg)}{nR} = 322 \text{ K}$
 $p = p_0 + \frac{mg}{\pi r^2} = 102.32 \text{ kPa}$
b) $W = (mg + p_0 \pi r^2) \Delta s = 24.1 \text{ J}$
c) $Q = \Delta(p_0 \pi r^2 + mg) \left(\frac{c_V}{R} + 1 \right) = 84 \text{ J}$
d) $P = \left(\frac{c_V}{R} + 1 \right) \frac{\Delta s}{\Delta t} (p_0 \pi r^2 + mg) = 8.4 \text{ W}$
 $\dot{n} = P \frac{\lambda}{hc} = 2.2 \times 10^{19} \text{ s}^{-1}$
e) $\eta = \frac{1}{\left(1 + \frac{p_0 \pi r^2}{mg}\right) \left(1 + \frac{c_V}{R}\right)} = 2.8 \times 10^{-3}$
f) $T_3 = T_2 \left(\frac{p_0}{p} \right)^{\frac{\gamma-1}{\gamma}} = 321 \text{ K}$
44. $T_1 = 3^{\frac{\gamma-1}{\gamma}} T_0 \approx 400 \text{ K}$
45. $\eta = 1 - k^{1-\gamma} = 0.602$
46. $a = 290 \text{ EUR}$
47. a) $\rho_{20} \rho_{\text{el}} c l^2 (T_1 - T_r) / U_0^2 = 25 \text{ ms}$
b) $\rho_{20} c l^2 U_0^{-2} \int \rho_{\text{el}} dT = 1.5 \text{ ms}$
48. a) $T_2 = \frac{x \sigma T_0 + \rho h c_p v d T_1}{x \sigma + \rho h c_p v d}$.
b) $t = -C \int_{T_1}^{T_2} \frac{dT}{P(T)} \approx 120 \text{ s}$
49. a) $c_p = \frac{\gamma}{\gamma-1} R$
b) $\rho = \frac{p_0 M}{RT}$
c) $\Delta \rho g L = \rho_0 v^2$ ($2 \Delta \rho g L = \rho_0 v^2$ is also OK, cf. Mechanics Pr. 29.)
d) $T = T_0 \left[1 + \frac{1}{g L} \left(\frac{P g L}{S p_0} \frac{\gamma-1}{\gamma} \right)^{\frac{2}{3}} \right] \approx 322 \text{ K}$
50. a) $p = p_0 \frac{w}{w - V \alpha (T - T_0)} \frac{T}{T_0}$
b) $T_{\text{max}} = T_0 + \frac{w}{V \alpha} = 22.0^\circ \text{C}$
51. $p \approx 45 \text{ kPa}$
52. a) $T_1 = T_0 \left(\frac{p_1}{p_0} \right)^{1-\frac{1}{\gamma}} = 279 \text{ K}$
b) $h_1 = \frac{2}{g \rho_0} \frac{p_0 - p_1}{1 + \frac{p_1}{p_0} \frac{T_0}{T_1}} = 1410 \text{ m}$
c) $T_2 = T_1 \left(\frac{p_2}{p_1} \right)^{1-\frac{1}{\gamma}} + \frac{q_V m}{c_p} = 271 \text{ K}$
d) $h = 35 \text{ mm}$
e) $T_3 = T_2 \left(\frac{p_3}{p_2} \right)^{1-\frac{1}{\gamma}} = 300 \text{ K}$
53. $L = \frac{1}{2} \frac{m^2}{M p S} \frac{RT}{\mu} + \left(t - \frac{1}{p S} \sqrt{\frac{2RT}{\mu}} \right) \frac{m}{M} \sqrt{\frac{RT}{2\mu}}$
 $t \approx 160 \text{ s}$
54. $t \sim \frac{1}{100} \text{ s}$
56. $T = \sqrt{\frac{d}{\alpha f} \sqrt{\frac{I}{\sigma}}}$; $D/F > 2$
57. 1900 m.
58. a) $C = 4R$; b) $\omega = r^{-1} \sqrt{8\sigma/\rho h}$
59. a) $p_E > p_A > p_D > p_B > p_C$; b) 195 K; c) 220 hPa; d) $W_{\text{net}} = R(T_H - T_C) \ln(p_E/p_A)$, $Q_{\text{loss}} = RT_C \ln(p_D/p_C)$; e) $\varepsilon_i = 0.35$; g) II & III.
60. a) $R = L/4\kappa S$;
b) $T = T_0 + \frac{P_0 \cos(\omega t + \arcsin(C\omega/\sqrt{C^2\omega^2 + R^{-2}}))}{\sqrt{C^2\omega^2 + R^{-2}}}$;
c) $\omega = 1/\sqrt{2}CR$;
d) $\omega_c \approx \kappa/c\rho L^2$.
61. a) $P = Q_{di} - Q_{do} = \frac{\varepsilon \sigma 4\pi R_1^2 (T_2^4 - T_1^4)}{1 + (1-\varepsilon) R_1^2/R_2^2} \approx 1.78 \text{ W}$;
b) $\tau = \frac{4}{3} \pi \rho R^3 \lambda \mu / P \approx 36 \text{ h}$.
62. a) $N = -\frac{\ln \beta}{\alpha}$;
b) $A \approx N p_0 V \alpha = p_0 V |\ln \beta|$;
c) $T = T_0 \beta^{\frac{1}{\gamma}-1}$;
d) $A = 2p_0 V$.
63. a) $C \approx \frac{P\tau}{T_0 - T_1} = 350 \text{ J/}^\circ\text{C}$;
b) $Q = CT_c \approx 46 \text{ kJ}$.
64. 4689 K
65. $1 - \frac{T_1}{T_2}$.
66. a) $Q = q\nu \approx 546 \text{ J}$;
b) $v = \frac{Q}{3\rho a^3 c} \approx 0.22 \text{ mm/s}$ (an approximate answer, e.g. $v \approx 0.67 \text{ mm/s}$ is also OK);
c) $T = A \cdot e^{-Bt}$;
d) $v \sim \frac{Q}{\rho a^3} \sqrt{\frac{M_H}{RT}} \approx 180 \text{ m/s}$.
67. 135%.
68. $F = 7Sp_1 T_0 / T_1$.
69. $T = T_0 - (1 - \gamma^{-1}) \frac{\mu g}{R}$
70. a) $\frac{dT}{T} = (1 - \gamma^{-1}) \frac{dp}{p}$; b) $dp = -\frac{mg}{k_B T} dz$; c) $T_{\text{top}} = 20.6^\circ \text{C}$.
71. a) $U = \mu \frac{4}{3} \pi R^3 C (T_c - T_0) = 16768 \text{ J}$;
b) $J = \kappa (T_1 - T_0) / R = 2458 \text{ W} \cdot \text{m}^{-2}$;
c) $P = 4\pi R^2 J = 19.3 \text{ W}$; d) $\tau = U/P = 869 \text{ s}$ (these are estimates, so different numerical factors are acceptable).
72. $p = p_0 \frac{T}{T_0} \frac{w_0}{w_0 - V \alpha (T - T_0)}$; invalid if $T > 22^\circ \text{C}$.
73. Ai) $\alpha = gM_{\text{air}}/RT_0$; Aii) $P = P_0 - \rho g z$; Aiii) 88 kPa
Bii) $v = v_G r_G / r$; Biii) 141 m/s;
Biv) $r = r_G / \sqrt{1 - 2gz/v_G^2}$; Bv) Pipe-like ones.
Ci) $v = v_G r / r_G$; Cii) 76 kPa;
Ciii) between 5°C (at G) and -7°C (neglecting latent heat of condensation); Civ) heat released by condensation;
Di) 3.8; Dii) a close call.
74. Ai) $F_B = M_A n g \frac{P}{P + \Delta P}$; Aii) $\gamma = \rho_0 z_0 g / P_0 = 5.5$;
Bi) $\Delta P = \frac{4\kappa RT}{r_0} (\lambda^{-1} - \lambda^{-7})$; Bii) $a = 0.110$;
Ci) $z_f = 11 \text{ km}$, $\lambda_f = 2.1$.
75. $T_\odot = \sqrt{R_\odot} 2L \approx 289 \text{ K}$
76. $W_{\text{max}} = C(\sqrt{T_1} - \sqrt{T_2})^2$
77. $T_2 = \frac{T_0 \kappa}{\kappa + I \alpha} \approx 288 \text{ K}$
78. $T_0 \approx 212 \text{ K}$
79. 13.2°C
80. 1.2352 kg/m^3
81. a) $h \geq \frac{B^2}{A^2} \frac{1}{2g} \frac{T_{\text{air}}}{\Delta T}$; b) 45 m; c) $v = \sqrt{2gh \frac{\Delta T}{T_{\text{air}}}}$ is constant;
d) $p = p_0 - (\rho_{\text{air}} - \rho_{\text{smoke}})gh - \rho_{\text{smoke}}gz$; e) $\eta = \frac{gh}{cT_{\text{air}}}$;
f) linear; g) 0.64%; h) 45 kW; i) 360 kWh with 8 h;
j) $\Delta T = \left(\frac{G^2 S^2 T_{\text{air}}}{A^2 c^2 \rho_{\text{hot}}^2 2gh} \right)^{1/3} \approx 9.1 \text{ K}$; $w = 760 \text{ kg/s}$
82. $V_1 = 0.4721$, $p_1 = 1.06 \text{ atm}$; $V_2 = 0.3951$, $p_2 = 1.22 \text{ atm}$,
 $V_f = 0.1001$, $p_f = 1.22 \text{ atm}$
83. a) 14 g/mol; b) 3.3 km; c) 420 km; d) 2.6×10^{-3} ;
e) $7.5 \times 10^{11} \text{ 1/m}^2\text{s}$; f) 1.2×10^{38} ; g) 4500 years;
h) $9.6 \times 10^{11} \text{ years}$; i) supply as H_2O from oceans.

84. a) 8; b) $\frac{3mRT_0}{\mu} \ln \frac{r_0}{r_3}$; c) $T_0 \left(\frac{r_3}{r}\right)^{3\gamma-3}$;
 d) $r_4 \approx r_3 \left(\frac{RT_0 r_3}{\mu m G}\right)^{\frac{1}{3\gamma-4}}$, $T_4 \approx T_0 \left(\frac{RT_0 r_3}{\mu m G}\right)^{\frac{3\gamma-3}{4-3\gamma}}$
85. a) $R_m = 2.31 \mu\text{m}$, $T_m = 6.86 \times 10^4 \text{ K}$; b) $R_f = 2.98 \mu\text{m}$;
 c) $\tau \sim 3 \times 10^{-9} \text{ s}$; d) $a_0 \sim 0.01$
86. a) $\frac{3}{2}k_B T$; b) $\frac{3}{2}k_B T/E_F$, as the temperature grows, energy of a majority of the electrons will remain unchanged.
87. a) $-N\mu_B B \tanh(\mu_B B/k_B T)$ b) $N(\mu_B B)^2/k_B T$.
88. $m = 1.5RT\nu\rho/\sigma$ (proof of minimality required).