

Theme 4. Physics basics specifying human body and environment energy exchange and internal processes of energy conversion

Problem

Test and metabolic processes intensities qualification at human body locations

Attendance prerequisite checklist. Note! Answer in writing to perform

1. Complete statements

- 1.1. A human body relates to _____ thermodynamic systems.
- 1.2. The internal energy of a thermodynamic system _____, if it carries out work.
- 1.3. Heat always flows spontaneously from a _____ body to a _____ body.
- 1.4. Any process is said to be thermodynamically _____ if the system participating in the process _____ to its initial state so that no change remains even in its surroundings.
- 1.5. The _____ is a measure of the disorder in a system.

2. Answer to the questions

- 2.1. What is meant by the word heat?
- 2.2. What is the internal energy?
- 2.3. If heat is added to a system and some work is done by the system, what is the difference between these quantities?
- 2.4. Discuss how the first law of thermodynamics can apply to metabolism in humans. In particular, note that a person does work W , but very little heat Q is added to the body (rather, it tends to flow out); why then doesn't the internal energy drop drastically in time?

Information resources

1. <https://www.sfu.ca/~mbahrami/ENSC%20388/Notes/Intro%20and%20Basic%20Concepts.pdf>
2. http://www.mhtlab.uwaterloo.ca/courses/ece309/lectures/notes/S16_chap1_web.pdf
3. <https://opentextbc.ca/physicstestbook2/chapter/the-first-law-of-thermodynamics/>
4. <https://courses.lumenlearning.com/physics/chapter/15-6-entropy-and-the-second-law-of-thermodynamics-disorder-and-the-unavailability-of-energy/>

Introduction

All living things require energy to sustain the life process. Green plants obtain their energy directly from the sun through the process of photosynthesis. Plants such as mushrooms, which do not utilise photosynthesis, as well as animals, require food capable of providing chemical energy. In all cases, living plants and animals operate within the constraints described by thermodynamics.

Thermodynamics was originated as the study of the relationship between mechanical and thermal energy associated with the disordered motions of the atoms and molecules within a substance. Today its scope is much broader, and it is important whenever temperature plays a role. It has major applications in virtually every field of basic and applied science.

Thermodynamics describes the behavior of matter in terms of a few macroscopic variables such as the temperature, volume, and pressure that define its **thermodynamic state**. This description is complete when there is equilibrium, and it provides a starting point for the study of nonequilibrium processes such as chemical reactions. In general thermodynamics defines a broad framework for relating changes in microscopic properties of a substance to its energy exchanges with the surroundings.

No direct reference is made in thermodynamics to the underlying atomic and molecular physics. Indeed, its principles were understood long before the development of our modern

picture of the microscopic world. **Statistical mechanics**, a much newer branch of physics, starts with the molecular interactions and calculates quantities that are taken from experiment in traditional thermodynamics.

A good deal of conventional jargon or terminology appears in discussions of thermodynamics. A **system** may refer to a single substance or object or to a more general situation involving several substances or components.

Heat is a popular but often poorly defined term. Historically, heat was thought to be a property of an object that could be transferred to another as a sort of fluid, called **caloric**. The caloric theory was long ago discarded after equivalence of heat and mechanical energy was realized. Today **heat flow** refers to energy transferred from one substance to another because of a temperature difference between them. The quantity of energy transferred in this way is an amount of heat entering or leaving a substance.

The first law of thermodynamics. The **first law of thermodynamics** generalizes the fundamental law of energy conservation to include thermal energy explicitly. It provides relationship between the heat transferred to a system, the work it performs, and the change in its **internal energy** associated with the motion of its molecules.

Mechanical work. Work can be done on or by a system in many ways. A gas may be compressed or allowed to expand against a piston. A liquid may be stirred, and a solid may be pounded with a hammer. Electric charges may be brought near a material, so that the electric forces alter the arrangements of charges inside the material. Thus the kinds of work that can be done are as varied as the forces that can be exerted on a system. In this section, we obtain an expression for the work done by a substance or system when its volume changes.

When a substance, or system expands or contracts, the work **W** done by the system can be related to the volume change of the material. It is conventional in thermodynamics to take **W** as positive when work is done by the system.

It is most convenient to develop our ideas using the example of gas.

The figure 1 shows a gas at a pressure **P** in a closed cylinder. A movable piston of cross-sectional area **A** forms one end of the enclosure. The gas exerts a force $\mathbf{F} = \mathbf{P} \mathbf{A}$ on the piston. When the piston moves a small distance $\Delta \mathbf{x}$ parallel to the force, the work done by the gas is $\Delta \mathbf{W} = \mathbf{F} \cdot \Delta \mathbf{x} = \mathbf{P} \cdot \mathbf{A} \cdot \Delta \mathbf{x}$. Since $\Delta \mathbf{V} = \mathbf{A} \cdot \Delta \mathbf{x}$ is a change in volume of the gas, the work done by the gas is $\Delta \mathbf{W} = \mathbf{P} \cdot \Delta \mathbf{V}$.

A large displacement can be regarded as composed of a series of very small displacements $\Delta \mathbf{x}_j$, so that during each displacement the force $\mathbf{F}_j = \mathbf{P}_j \cdot \mathbf{A}$ can be considered constant. The total work **W** done by the system is the sum of all the terms $\mathbf{P}_j \cdot \Delta \mathbf{V}_j$:

$$\mathbf{W} = \mathbf{P}_1 \Delta \mathbf{V}_1 + \mathbf{P}_2 \Delta \mathbf{V}_2 + \dots \quad (1)$$

The work done by the system is equal to the area under the **P(V) curve** (fig. 2). This result is valid for a gas in a container of any shape and also for volume changes in liquids and solids.

The equation 1 has a simple form if the work is done in an isobaric process, that is at constant pressure. If the initial and final volumes of the system are denoted by \mathbf{V}_i and \mathbf{V}_f , then the work done is $\mathbf{W} = \mathbf{P} \cdot (\mathbf{V}_f - \mathbf{V}_i)$. For an isobaric process, the work done by the system is positive if $(\mathbf{V}_f - \mathbf{V}_i)$ is positive; work is done on the system if $(\mathbf{V}_f - \mathbf{V}_i)$ is negative.

The internal energy. The internal energy **U** varies with the state of a system, as described by macroscopic variables such as the temperature, pressure, and volume. These variables are related for any system by an **equation of state**. For example, the equation of state for an ideal gas is $\mathbf{P} \cdot \mathbf{V} = \mathbf{n} \cdot \mathbf{R} \cdot \mathbf{T}$. For a given number of moles **n**, if **P** and **T** are known, then **V** is specified by this equation. Thus the internal energy for most substances depends on **T** and **P**. However, in ideal gases, **U** actually depends only on the temperature. The average translational kinetic energy of a molecule is $3\mathbf{k}_B \cdot \mathbf{T} / 2$ (\mathbf{k}_B is Boltzmann's constant). For **N** monatomic ideal gas molecules, the total internal energy is therefore $\mathbf{U} = 3\mathbf{N} \cdot \mathbf{k}_B \cdot \mathbf{T} / 2$. More generally, the internal energy of a substance includes the kinetic energies associated with translational, rotational, and

vibrational motions of the particles. It also includes the potential energy due to the interactions of the particles with one another. Only changes in internal energy affect the properties of the system.

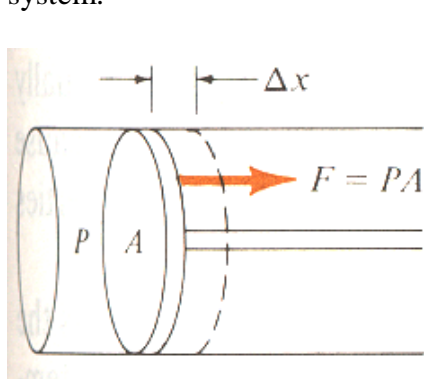


Figure 1

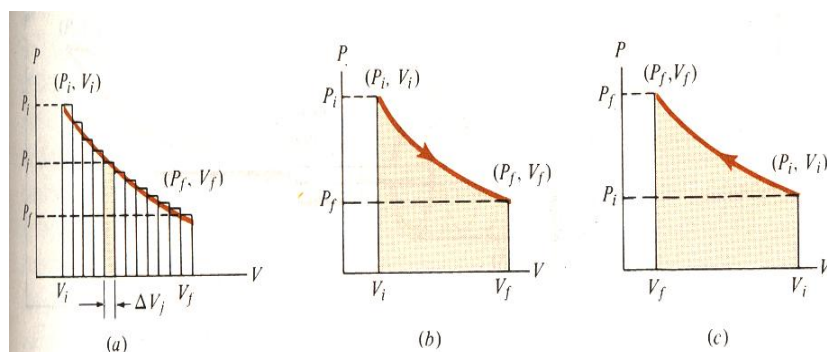


Figure 2

The **heat Q** added to or taken from a system is the amount of thermal energy transferred due to a temperature difference. For example, we may say that heat flows from a wood stove to the air and to objects in a room because they have the lower temperature than the stove.

The first law of thermodynamics. We now discuss the first law of thermodynamics, using a gas as an example. Consider a container of gas fitted with a movable piston (fig. 3). If we add heat **Q** to the system, but do not allow the piston to move, the temperature and hence the internal energy **U** of the gas will increase. We can also change the internal energy by doing work on the gas. Thus, if we insulate the container walls and push the piston in, we compress the gas. The work done on the system equals the change in internal energy, since no heat enters or leaves the gas.

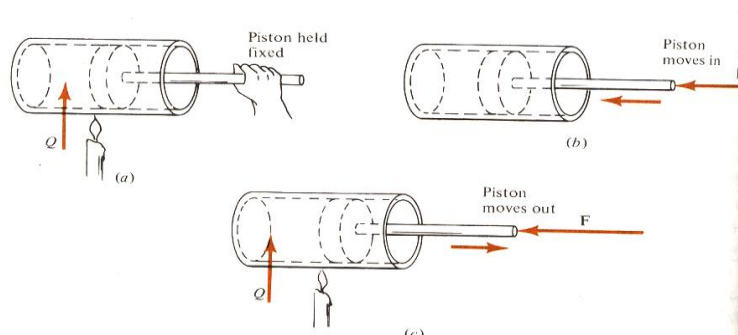


Figure 3

More generally we may add heat **Q** to the gas and have the gas do work. The difference is the change in internal energy of the gas, $\Delta U = U_f - U_i$. U_f and U_i are the final and initial energies of the gas, respectively. This is the **first law of thermodynamics**:

$$U_f - U_i = Q - W,$$

which means that **the change of the energy content in the process is equal to the algebraic sum of the heat exchanged and the work done during the process.**

Q is positive if heat is added to the system, and **W** is positive if work done by the system. Although we used a gas in this example, this result is generally true for all systems and does not depend on the presence of a gas.

Two statements about the physical world are contained in the first law. First, heat and work are equivalent; they are to be treated on the same basis. They are both forms of energy. Second, the same change in the internal energy can be achieved by adding heat, or by doing work, or by some of each, but the internal energy change is independent of how that change was achieved. This means that the internal energy depends only on the thermodynamic state of the system: its temperature, pressure, and volume in the case of gas. In other words, going from a given initial state to a particular final state does not require a definite amount of heat or work, but

rather a specific total of the two. It is meaningful to speak of the internal energy of a substance, but not of how much heat it contains.

The second law of thermodynamics. According to the first law, in Nature only processes in which the total energy remains unchanged take place. In reality, however, not all processes, being possible on the basis of the first law, occur. For instance, let us drop a stone from some height. On inelastic collision the mechanical energy of the stone will be transformed into heat. According to the first law, a process with opposite direction might also be possible, in which the heat is retransformed into mechanical energy, and its surroundings regain their initial position. However, this kind of process is never encountered. If a strong base reacts to a strong acid, a salt is produced spontaneously. The opposite process, however, never occurs; a salt never decomposes spontaneously into a base and an acid. The pressure, temperature and concentration differences in system without external influences tend to become equalized, and never increase. The second law of thermodynamics deals with problem, i.e. with the direction of spontaneous processes.

The factors determining the direction of spontaneous processes are related to heat, and in every case can be ascribed to the universal experience that **heat always flows spontaneously from a warmer body to a cooler body**. Various equivalent definitions of the second law are known, though perhaps the above is the simplest of all; its content can readily be followed as concerns atomic or molecular aspects. Heat is a form of energy, which has its origin in the random motion of atoms or molecules. When two systems come into contact, for instance, that in which the mean kinetic energy of the molecules is higher can transfer heat to the other. This seems to be quite natural. If billiard balls collide, it is more probable that the ball with higher energy will transfer some of its energy to the ball with lower energy, and not vice versa; the latter process may also occur, but with much lower probability. The situation is quite similar in case of molecular collisions. In principle it may be possible that the molecules of the warmer body gain energy from the molecules of the colder one, i.e. the warmer body obtains energy from the colder one, but this is so improbable that it does not occur spontaneously in practice. This type of process can take place only with some external aid. According to this concept, the second law of thermodynamics is a statistical one in character and simply expresses the fact that the thermodynamic processes progress spontaneously towards the more probable state. In principle the opposite processes may also occur but this is not probable spontaneously in practice. Processes in opposite direction can occur in reality only if they are accompanied by some other changes. In an isolated system, processes of any kind can be observed only until the system has reached thermodynamic equilibrium, from which it can be displaced only by some external effect.

The quantitative definition of the second law requires a state function, **entropy**. Entropy can be expressed by probabilities, more exactly by thermodynamic probabilities associated with the individual states. According to Boltzmann, the entropy S of a system in a given state is proportional to the logarithm of the thermodynamic probability w associated with this state. If natural logarithms are used the proportionality factor k_B is the Boltzmann's constant; thus, we have $S = k_B \ln w$. Let us denote the thermodynamic probability at the beginning of the process by w_A and the entropy by S_A , and in the final state let probability be w_B and the entropy S_B . With these notations the entropy change will be expressed by the relation

$$S_B - S_A = k_B \cdot \ln(w_B/w_A).$$

It is generally true that in any isolated system the processes progress in the direction of an increase in thermodynamic probability and hence in the entropy. The thermodynamic equilibrium is characterized by the maximum of the thermodynamic probability, and by that of the entropy.

In practice, entropy is usually determined via directly measurable quantities and not by calculating the thermodynamic probability. Before the phenomenological definition of entropy related to macroscopic quantities is given, a more profound analysis of the thermodynamic processes is necessary.

Thermodynamically reversible and irreversible processes. Any process is said to be thermodynamically **reversible** if the system participating in the process returns to its initial state so that no change remains even in its surroundings. In the opposite case the process is **irreversible**.

According to the second law, which is derived empirically, no **strictly reversible** process exists in Nature. In reality, processes proceed spontaneously in only one direction, and some external influence is necessary for the opposite direction to be taken. Though this external aid may cause the system to return to its initial state, some changes may be left over in the surroundings. The irreversible character of a process is related to heat phenomena, which are always present in practice. Mechanical, electric, and optical processes would be reversible if they were not accompanied by heat phenomena. For instance, the motion of a pendulum would be reversible if there were no friction, and similarly the motion of a falling and rebounding ball would be reversible if a perfectly elastic collision existed. Further, an electromagnetic field would propagate reversibly without the absorption phenomena associated with this propagation. Diffusion, evaporation, heat conduction, the volume change of gases, and chemical processes are typically irreversible processes. Though real processes are never reversible, all changes of state can be conceived of as reversible. The study of these idealized changes of state is important in practice, since the resulting knowledge provides an insight into the actual process. **The phenomenological definition of the entropy is also related to reversible processes. The processes associated with heat phenomena could be reversible only if they proceeded infinitesimally slowly in several steps through individual equilibrium states, i.e. quasi-statically.**

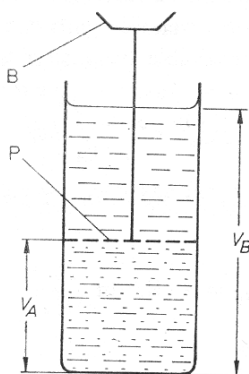


Figure 4

As an example, let us consider the **isothermal diffusion**. Consider a case when, at the beginning of the process, the lower half of a vessel is filled with an ideal solution, with above it a pure solvent (fig. 4). A volume of the solute in the initial state is V_A , while in final state it is V_B . Let us denote the initial concentration by c_A and the final concentration by c_B . The system can pass from its initial to its final state via various paths. It will be shown that in quasi-static osmotic process the diffusion too may proceed reversibly. For this purpose imagine the pure solvent to be separated from the solution by means of a piston which is permeable only for the pure solvent. The osmotic pressure may be compensated if an appropriate weight is placed on the balance.

Subsequently, we begin to decrease the force acting on the balance in infinitesimally small steps. During this process the piston gradually rises while the solution becomes continuously more dilute. The pressure acting on the balance at every moment is in quasi-equilibrium with the osmotic pressure

The work done by the system during the dilution W_{AB} can be calculated similarly as in the isothermal expansion of gases. From the analogy between the **universal gas law** $p = \nu \cdot R \cdot T / V$ and the **van't Hoff law** $p_{osm} = R \cdot T \cdot c$, the final result in case of ν moles of solute is

$$W_{AB} = - \nu \cdot R \cdot T \cdot \ln(V_B/V_A) \quad (2)$$

Since $c_A = \nu/V_A$ and $c_B = \nu/V_B$, instead of (2) we may write

$$W_{AB} = - \nu \cdot R \cdot T \cdot \ln(c_A/c_B) \quad (3)$$

Analogously, process opposite to diffusion or dilution, i.e. reversible concentration, may also be conceived. The solute distributed in the volume V_B may be collected in the volume V_A if the pressure on the balance is always larger than the actual osmotic pressure, and if it is finally equal to the pressure associated with V_A . With a quasi-static concentration increase the work done on the system is the same as the work done by it on dilution. This is valid for the exchanged heat too. Thus, by a cyclic process consisting of diffusion and subsequent concentration, the system can finally be brought back into its initial state so that no change remains in its surroundings.

Phenomenological definition of entropy. A development of the concept of the entropy is beyond the scope of this course. We merely give its definition. Let a thermodynamic system be transferred from a state **A** into a state **B**. From a given initial state, the system can be transferred into its final state via various paths. In reality every path is irreversible. The phenomenological definition of entropy is obtained by considering reversible processes. Let S_A be the entropy of the system in the **A** state, and S_B that in the **B** state. The entropy change in the process **A**→**B** is given by the relation

$$S_B - S_A = \int_A^B dQ_{\text{rev}}/T \quad (4)$$

The quantity dQ_{rev} denotes the heat exchanged between the system and its surroundings in an infinitesimal change of state at absolute temperature **T**, when the change of state is reversible. Instead of (4), the entropy can also be defined by its infinitesimally small change

$$dS = dQ_{\text{rev}}/T$$

If the system takes up heat in the course of the reversible change of state, its entropy increases, whereas a heat loss results in a decrease in entropy. It is again emphasized that entropy is a state function, whose value depends only upon the initial and final states, and is independent of the path along which the transformation of the state actually occurs. Its dimension is **J/K**.

At first sight the statistical and phenomenological interpretations of entropy differ considerably. However, Boltzmann showed the equivalence of these two relations, as long ago as the second half of the 19th century, and doing so connected phenomenological thermodynamics with molecular and statistical theory. The equivalence of the two relations is presented here in a simple case.

Consider the change of state of ν mol an ideal gas in a volume fraction V_A of a vessel when the gas expands at a constant temperature **T** until it fills the total volume V_B of the vessel. From (4), we have

$$S_B - S_A = \int_A^B dQ_{\text{rev}}/T = 1/T \int_A^B dQ_{\text{rev}} = Q_{AB}/T = \nu \cdot R \cdot \ln(V_B/V_A)$$

and by further transformation

$$S_B - S_A = N \cdot k \cdot \ln(V_B/V_A) = k \cdot \ln(V_B/V_A)^N$$

where **N** is the number of gas molecules. On the other hand, from the statistical interpretation we have

$$S_B - S_A = k \cdot \ln(w_B/w_A).$$

It must be proved that the relations derived from the two types of interpretation can be transformed into each other. This task is equivalent to providing the equality

$$w_B/w_A = (V_B/V_A)^N.$$

For this purpose let us investigate more closely the meaning of the quotient w_B/w_A ; this tells how many times the probability of uniform occupation of the volume V_B is greater than the probability that only the smaller volume V_A is filled. It is readily seen that this quotient is equal to the power expression on the right-hand side. Since the equation contains quotients, mathematical probabilities may be used instead of thermodynamic probabilities in the calculations. The mathematical probability of finding the **N** molecules in the total volume V_B is equal to 1, i.e. certainty. On the other hand, the probability of finding **N** molecules in the volume V_A smaller than V_B is V_A/V_B for the case $N = 1$, $(V_A/V_B)^2$ for $n = 2$, and $(V_A/V_B)^N$ for the case $n = N$. Thus the above equivalence is proved.

We can now give the macroscopic form of the second law. For any process, **the total entropy of a system plus its surroundings may never decrease: $\Delta S_{\text{total}} \geq 0$.**

The total entropy change is zero for a reversible process and positive for an irreversible process. Microscopically this is equivalent to saying that the molecular disorder of a system and its surroundings remains constant if the process is reversible and increases if it is not.

Direction and equilibrium of isothermal processes Enthalpy. In practice the different physical and chemical processes take place at constant pressure, usually under atmospheric conditions. This statement is also valid for living processes.

Processes at constant pressure can be described in a simple way, if a new state function, called **enthalpy (H)** is introduced: $\mathbf{H} = \mathbf{U} + \mathbf{pV}$, where \mathbf{U} is the internal energy of the system, \mathbf{V} is the volume and \mathbf{p} the pressure of the system in **equilibrium** at a given volume and temperature. It follows from the definition that the equilibrium pressure is always equal to the external pressure (for instance, the atmospheric pressure) acting on the system. For processes at constant pressure the change in the enthalpy due to the changes in \mathbf{U} and \mathbf{V} will be $\mathbf{H} = \Delta\mathbf{U} + \mathbf{p}\Delta\mathbf{V}$ and $\mathbf{dH} = \mathbf{dU} + \mathbf{pdV}$, respectively. Thus, the enthalpy change is given by sum of the internal energy change and the volumetric work. This allows the change in internal energy and the volumetric work in **isobaric** processes to be expressed as the change in a single quantity. For instance, after appropriate rearrangement the last equation can be written in the form $\Delta\mathbf{H} = \mathbf{Q}_p$. It is generally true that in **isobaric** processes, where there is only volumetric work, the exchanged heat is equal to the change in the enthalpy, and in those **isosteric** processes where, other than the naturally missing volumetric work, no work is involved, the exchanged heat is equal to the change in the internal energy $\Delta\mathbf{U} = \mathbf{Q}_v$.

In practice, situations are fairly frequently encountered where the temperature of the system is the same at the beginning as at the end of a process. Such processes may be regarded as isothermal from the viewpoint of their direction as well as their equilibrium. The chemical reactions in laboratory experiments are of this type, as are the life processes. In order to study isothermal processes, the use of the internal energy (enthalpy) and the entropy allows the introduction of state functions which give the direction and equilibrium of the processes directly. The state function which can be used in processes at constant volume (isochoric processes) is called the **free energy**, and the concept of **Gibbs free energy** is used to describe **isobaric** processes at constant pressure. The free energy function is also termed the Helmholtz function and the Gibbs free energy is sometimes called free enthalpy.

The free energy is defined by the state function $\mathbf{F} = \mathbf{U} - \mathbf{TS}$. In isothermal processes, where \mathbf{T} is constant

$$\mathbf{dF} = \mathbf{dU} - \mathbf{TdS} \quad (5)$$

From experience it may be said that **isothermal processes proceed spontaneously in direction of a decrease in the free energy. The end of the change of state, i.e. the equilibrium state, is characterized by the minimum free energy attainable in the given situation.** The decrease means a negative change, and the minimum attained refers to zero change. These statements can be briefly expressed by the relation

$$\mathbf{dF} \leq 0 \quad (6)$$

\mathbf{dF} has a simple physical meaning. To illustrate this, let us write the first law for a reversible process $\mathbf{dU} = \mathbf{dQ}_{\text{rev}} + \mathbf{dW}_{\text{rev}}$. Since the volume is constant in our case no volumetric work is done and \mathbf{dW}_{rev} may denote some other, e.g. electric work. However, by definition $\mathbf{dQ}_{\text{rev}} = \mathbf{TdS}$, and, thus, can be rewritten to yield

$$\mathbf{dW}_{\text{rev}} = \mathbf{dU} - \mathbf{TdS} \quad (7)$$

From a comparison of (5) and (7) we have $\mathbf{dF} = \mathbf{dW}_{\text{rev}}$ which means that the change in the free energy in a case of isothermal-isochoric processes is equal to the work done in a reversible process, so that condition (6) can be put into the form

$$\mathbf{dW}_{\text{rev}} \leq 0 \quad (8)$$

The work is less than zero if it is done by the system. **According to (8) the isothermal-isochoric processes proceed spontaneously in the direction in which work is done by the system, or more exactly in the direction in which the system can do work.** This correction is necessary, since in reality the process may proceed without doing any work, only heat exchange occurring. However, in the determination of the direction of the spontaneous process information must be obtained about the possibilities. The maximum work that can be done by a system is that performed reversibly as expressed in (8). The system attains thermodynamic equilibrium, even if in principle no more work can be gained.

Lab test

Human body surface temperatures measurements and analyses

NOTE! Copy diagram below

1. Measure temperatures at areas surfaces shown by non-contact thermometer.
2. What are the physical processes causing the heating of the body surface?
3. Compare data and explain results obtained.
4. How is temperature interpreted as a diagnostic test of a patient state?

