

МІНІСТЕРСТВО ОХОРОНИ ЗДОРОВ'Я УКРАЇНИ
ХАРКІВСЬКИЙ НАЦІОНАЛЬНИЙ МЕДИЧНИЙ УНІВЕРСИТЕТ

CHEMICAL THERMODYNAMICS

Methodical instructions for 1st year students' self-work
in Medical Chemistry

ХІМІЧНА ТЕРМОДИНАМІКА

Методичні вказівки для самостійної роботи студентів 1-го курсу
з медичної хімії

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Subject «CHEMICAL THERMODYNAMICS»

1. **Number of hours** 4

2. **Material and methodological support.**

Tables:

1. Scheme of structure of the subject.

2. Types of systems.

3. Hess's law and its corollaries.

4. I law of thermodynamics.

5. II law of thermodynamics.

6. Isobaric-isothermal potential.

1. Medical chemistry / V. A. Kalibabchuk, V. I. Halynska, V. I. Hryshchenko [et al.]. – Kyiv:AUS Medicine Publishing, 2010. – 224 p.

2. Fundamentals of medical chemistry: manual for students' self-work / A. O. Syrovaya, E. R. Grabovetskaya, L. G. Shapoval. – Kharkiv: KhNMU, 2015.– 196 p.

3. Medical chemistry. Adapted concise course: manual for students' self-work / A. O. Syrovaya, E. R. Grabovetskaya, L. G. Shapoval. – Kharkiv: KhNMU, 2013. – 160 p.

4. Medical chemistry: workbook for self-work of first-year students of medical and dentistry faculties / compiled by A. O. Syrovaya, V. N. Petunina, V. A. Makarov [et al.]. – Kharkiv : KhNMU, 2017. – 72 p.

5. Chemical thermodynamics : methodical instructions for 1st year students' self-work in Medical Chemistry / compiled by A. O. Syrovaya, L. V. Lukianova, O. A. Zavada [et al.]. – Kharkiv: KhNMU, 2017. – 38 p.

6. Individual tasks for students' self-control of knowledge in Medical Chemistry / A. O. Syrovaya, L. G. Shapoval, V. N. Petunina [et al.]. – Kharkiv : KhNMU, 2014. – 50 p.

7. Text of Lecture «Chemical thermodynamics».

3. Substantiation for the subject. One of the main specific properties of living beings is their ability to convert and store energy in various forms. All biological objects to support life require energy. Each cell and the entire human body as a whole is an open biological system. There are various processes associated with the transfer of energy: respiration, photosynthesis, muscle contraction, transport substances, etc. in biosystems. Thermodynamic methods are widely used in biology and medicine, because living organisms and all processes of life in it are closely related to changes in the energy balance in the system of "living organism–the environment". All processes of energy conversion in plants and animals occur within the limits of thermodynamic principles. The basic principles of thermodynamics are universal for living and inanimate nature.

4. The purpose of the subject:

- general: to explain chemical and biochemical processes in terms of their heat effects;

- specific: to be able to use thermodynamic functions for evaluating of directions of processes, to explain energy coupling in biological systems.

a) **to know:** laws of chemical processes, aggregative state of substances, the basic concepts and laws of chemical thermodynamics, physical and chemical principles of homeostasis.

b) **to be able to:** calculate the heat effect of chemical reaction using calorific values of the reactants and products, calculate calorificity of foods, use the thermodynamic functions for evaluating of directions of processes, to explain energy coupling in living systems.

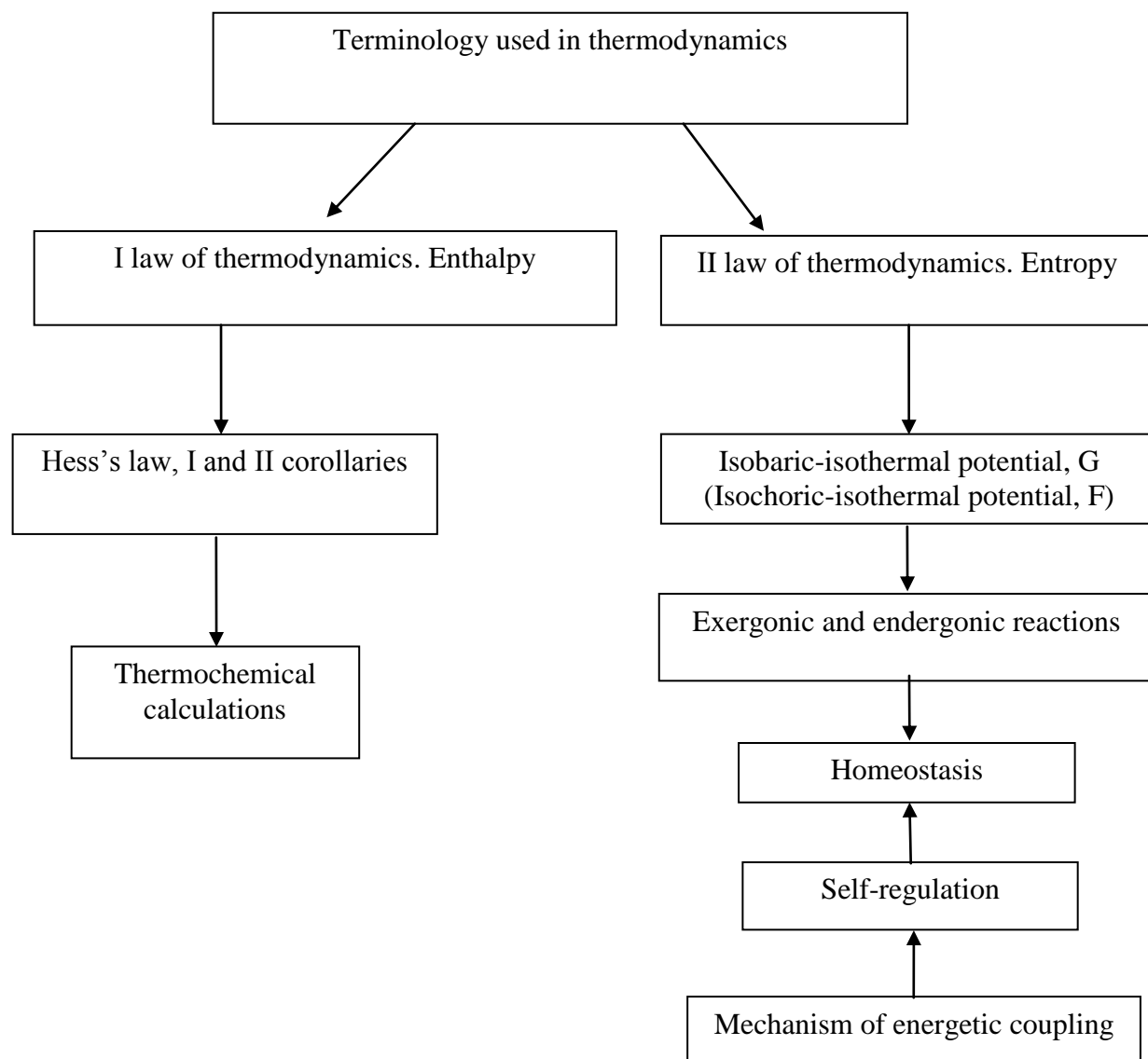
c) **practical skills:**

- to calculate heat effects of chemical reaction using the calorific values of the reactants and products;

- to calculate calorificity of foods;

- to use the thermodynamic functions for evaluating of directions of processes, to explain energy coupling in living systems.

5. Scheme of structure of the subject.



6. Plan of students' work.

№	Stage	Time, min	Training and visual aids	Location
1.	Motivational characteristic and plan of subject. Questions and answers	35	Manual, self-study guide for the 1 st year students	Class room
2.	Incoming control	20	Tests (Incoming control)	
3.	Independent work of students with methodological literature, the solution of educational problems, filling of self-study guide	35	Methodical instructions for students, text of lecture, manual for students' self-work, self-study guide, reference data, tables	
4.	Discussion of procedure of laboratory work	10	Text-book (work-book)	
5.	Performing of laboratory work and recording	35	Water, salt (anhydrous salt Na_2CO_3 and crystalhydrate $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)	
6.	Defence of laboratory work	15		
7.	Final control	25	Tests	
8.	Analysis and conclusions	4		
9.	Home-work	1		

7. Tasks for self-work:

- list of questions to be studied:

1. Basic concepts of chemical thermodynamics: system, thermodynamics parameters, thermodynamic state function.
2. First law of thermodynamics.
3. Enthalpy change. Standard heat effects.
4. Thermochemical equation. Heat of formation and combustion for compounds.
5. Laws of thermochemistry: Lavoisier and Laplace's law and Hess's law. Consequences of Hess's law.
6. Second law of thermodynamics. Entropy.

7. Criteria of spontaneous processes. Gibbs equation. Types of biochemical reactions according to the ΔG° values.

8. Application of laws of chemical thermodynamics to the living systems (stationary state, homeostasis, mechanism of energetical conjugation).

1. Basic concepts of chemical thermodynamics: system, thermodynamics parameters, thermodynamic state function

Chemical thermodynamics – a section of physical chemistry, studying energy conversions in chemical processes and energy characteristics of macroscopic systems based on the general laws of the relationship of heat, various types of work and energy. The essence of the thermodynamic approach is that it considers only initial and final states of the interacting objects, without taking into account the way in which the process takes place and time of transformation.

The tasks of thermodynamics are the study of:

- energy conversions from one body to another or from one form to another;
- energy effects of various physical and chemical processes that occur under different conditions;
- opportunities, directions and boundaries of these processes.

The object of the study of thermodynamics – a system.

A *thermodynamic system* is called any object of nature or a set of bodies separated by a real or imaginary surface of a partition (phase boundary), interacting with one another and with other objects (mass- and heat exchange). Under the notion of *the body* in thermodynamics understand that part of the space that is filled with matter. Nature objects that are not part of the system are called *the environment*.

Homogeneous is a system inside which there are no surfaces that separate parts of the system from others. An example is blood plasma, solution of various biogenic substances.

Heterogeneous – a system that consists of two or more parts, which have different physical properties or chemical composition and delimited by distribution surfaces. An example is a whole blood: blood with all its components (as white and

red blood cells, platelets, and plasma).

The phase is a homogeneous part of a heterogeneous system that has the same composition, physical and chemical properties, separated from other parts by the separation surface, in transition through which there is a spin-like change in its properties.

By way of interaction of the system with the environment distinguish types of systems:

Isolated system is a system which does not exchange neither mass nor energy with surroundings ($\Delta m = 0$, $\Delta U = 0$). In nature does not exist, the model is a thermostat.

Closed system exchanges only energy but not mass ($\Delta m = 0$, $\Delta U \neq 0$). An example is an ampoule with a medicinal substance.

Open system exchanges both mass as well as energy with surroundings ($\Delta m \neq 0$, $\Delta U \neq 0$). From the thermodynamics viewpoint, a living organism is an open system.

Each system is characterized by a number of properties that can be classified in two ways:

- intensive and extensive parameters;
- status and state functions.

Intensive parameters do not depend on the number of system particles and describe the general state of thermal motion in a substance (*pressure P, temperature T*).

Extensive parameters are determined by the total mass or number of particles of matter (*mass m, volume V*).

State parameters are the main characteristics that can be measured by instruments: *volume V, temperature T, pressure P, mass m, chemical composition*. If the thermodynamic parameters over time do not self-change, then the system is in a state of equilibrium, and the parameters at which such a state is observed, called *equilibrium*. *Stationary state* is a state of the system when the properties remain constant, but flows of matter and energy are observed.

State functions are properties that can not be measured (*internal energy, enthalpy, entropy, thermodynamic potential*), whose values depend only on the initial and final state of the system upon transition from one state to another and do not depend on the transition path.

The thermodynamic process is a phenomenon that occurs in a thermodynamic system and is associated with a change in its states.

In thermodynamics, the main types of processes are distinguished:

– *the reversible process* is a process in which the system at any given moment in a state is infinitely close to the thermodynamic equilibrium, and it is enough to change the conditions only so that the process is inversed;

– *the irreversible process* is a process in which the system changes in the direction of the final state (with involuntary flow of the process – to the state of equilibrium) at a certain speed.

Depending on the conditions of the flow there are the following types of processes:

- *isobaric* – the change in the state of the system occurs at constant pressure ($P = \text{const}$);

- *isothermal* – flows at a constant temperature ($T = \text{const}$);

- *isochronous* – goes with constant volume ($V = \text{const}$);

- *adiabatic* – a process in which there is no heat exchange with the environment ($U = \text{const}$).

2. First law of thermodynamics

The first law of thermodynamics (1850) is the law of conservation of energy in application to thermodynamic systems. This is a fundamental law of nature.

The energy of an isolated body system is a constant value, which does not depend on the nature of the processes occurring in the system, although these processes can be accompanied by the transition of energy from one part of the system to another. In other words, energy can neither be created nor destroyed, it can only transform from one form to another.

Energy is a measure of the movement and interaction of systems. There are *kinetic* (energy of motion of particles) and *potential* (energy of position and interaction of particles) energy. *The complete energy of the system* consists of the kinetic, potential and internal energy of the system.

The internal energy of the system (ΔU) is the energy of all continuously interacting moving particles of the system: the energy of the gradual and curvilinear motion of molecules; the energy of the oscillating atoms; the energy of intermolecular interaction; intranuclear energy, etc.

Basic forms of energy:

- *work (A)* – is a quantitative measure of the transfer of orderly motion;
- *heat (Q)* – is a quantitative measure of the transmission of chaotic motion.

These concepts relate not to the system, but to processes. The values of heat and work depend on the progress of the process (i.e. Q i A are not state functions).

The first law of thermodynamics is a fundamental law of nature: the energy of the isolated body system is a constant value that does not depend on the nature of the processes occurring in the system, although these processes may be accompanied by the transition of energy from one part of the system to another. In other words, *energy can neither be created nor disappear; it can only move from one form to another.*

Mathematical expression the first of the law of thermodynamics:

$$Q = \Delta U + A$$

– the heat brought to the system is spent on increasing the internal energy ΔU and performing work against external forces A .

The first law of thermodynamics denies the possibility of building a perpetual motion engine of the first kind, that is, a machine that would perform work from nothing, without the cost of any energy.

Expression of the first law of thermodynamics for different processes.

In the isothermal process, the transfer of heat from one body to another occurs at a constant temperature. Consequently, the internal energy does not change, $\Delta U = 0$, then the equation takes on the form:

$$Q = A, A = p\Delta V, Q = p\Delta V.$$

In the isochoric process, the transfer of heat from one body to another occurs when maintaining the system volume constant ($V = \text{const}$), respectively, $A = 0$, that is, all the heat provided to the system, is spent on the change of its internal energy. This leads to the following expression of the first law of thermodynamics:

$$Q = \Delta U.$$

In the adiabatic process there is no heat exchange ($Q = 0$) in the system, so the system can perform the work by reducing its internal energy:

$$\Delta U = - A.$$

In the isobaric process, constant pressure is observed ($p = \text{const}$):

$$Q = \Delta U + p\Delta V.$$

Since $\Delta U = U_2 - U_1$, $\Delta V = V_2 - V_1$, the equation takes on the form:

$$Q = (U_2 + pV_2) - (U_1 + pV_1) = H_2 - H_1 = \Delta H.$$

Expression of I law of thermodynamics to biological systems: the fulfillment of I of the law of thermodynamics for biological systems was proved in 1780 by Antoine Lavoisier and Pierre Laplace. They measured the amount of heat (at the rate of melting of snow) and carbon dioxide released by guinea pig during its life cycle, and compared these values with the thermal effect of combustion reactions to CO_2 consumption products. The results showed that there was no difference between the internal energy consumption of products and the heat that was allocated. This proves that living organisms are not independent energy suppliers, but only carry out the conversion of some types of energy to others.

The next stage in the study of the application of the I law of thermodynamics is the experiments of U. Etuoter, who constructed a calorimeter, which allowed studying the energy exchange of large animals and humans. The device had an oxygen supply system, a trap for released CO_2 , scales, and the measuring part of the calorimeter allowed to eliminate the loss of heat and to evaluate not only the amount of thermal energy, but also the respiratory factor.

Measurement of heat production in a calorimeter and the use of experimental data of indirect calorimetry allowed to accurately estimate the energy balance of man per day.

Thus, the I law of the thermodynamics of biological systems indicates that any biological system is an open thermodynamic system, living organisms can neither create energy from nothing nor destroy it, they can only transform one form of energy into another. In this case, organisms consume energy from the environment in the form in which they can use it in specific conditions of temperature and pressure, and then return to the environment an equivalent amount of energy in a different form that is less suitable for them. This law establishes a quantitative relationship between the amount of heat, the work and the change in the internal energy of the thermodynamic system, but does not determine the direction of thermodynamic processes.

The application of the first law of thermodynamics to living systems consists in the fact that the energy entering the living organisms with food is distributed in the process of consumption into two parts:

- is released in the environment in the form of heat and energy contained in products of life;
- deposited in cellular material.

The sum of these two parts is equal to the internal energy of the food entering the body.

In relation to living systems, the first law of thermodynamics can be formulated as follows: *all kinds of work in an organism occur at the expense of the equivalent amount of energy emitted during the oxidation of nutrients.*

The energy balance of an organism is studied by methods of *direct and indirect calorimetry*. In the first case, a person is placed in an isolated chamber in which the amount of heat emitted by a living organism in various processes of normal physiological activity is determined. Indirect calorimetry is based on calculation methods using respiratory factors and caloric oxygen equivalent.

Respiratory factor is the ratio between the amount of carbon dioxide emitted and the volume of absorbed oxygen. For carbohydrates it is equal to 1,0, proteins – 0,8, fats – 0,7.

The caloric equivalent of oxygen is equal to the amount of heat released at a flow of 1 liter of oxygen. For carbohydrates it equals 21,2 kJ, proteins – 20,09 kJ, fats – 19,6 kJ.

The caloric content of food products is also determined on the basis of thermochemical methods. The average value of physiological fuel (food products) of the three main classes is as follows: carbohydrates – 19,8 kJ/g, proteins – 16,8 kJ/g, fats – 37,8 kJ/g. Based on data on caloric content of food products, scientifically grounded norms of food needs for certain groups of population are made, taking into account energy costs. The standards take into account age, gender, the nature of its work and everyday life, as well as climatic features.

The internal energy of the system is a function of the state of the system, that is, its change is determined by the given initial and final states of the system and does not depend on the path of the process: $\Delta U = U_2 - U_1$. It is not possible to determine the absolute value of internal energy. Given the entire set of interactions in the system, it can be argued that it is impossible to imagine the state in which the internal energy of the system would be zero. Even at absolute zero temperatures, when virtually any motion in the system is stopped (the kinetic energy of individual molecules becomes zero), the energy of the interaction of particles does not disappear anywhere, and also does not stop, for example, the motion of electrons around nuclei, or the oscillation of atoms with the main frequency, etc. All this means that it is not advisable to speak of the absolute value (absolute reserve) of internal energy. However, its change in the transition from one state to another can be determined, and this is quite sufficient to solve many issues. The internal energy characterizes completely only the isochoric processes ($V = \text{const}$).

During the process of the isobaric process, in addition to changing internal energy, the expansion (or compression) of the system must also be taken into account, taking into account the thermodynamic function – enthalpy:

$$H = U + PV.$$

3. Enthalpy change. Standard heat effects

Enthalpy is often called *heat content of the system*.

Enthalpy (H), as well as internal energy, characterizes the energy state of substance, but it differs from the internal energy for the amount of energy expended in overcoming the forces of external pressure. It also depends on the state of the system and does not depend on the manner by which this state is reached. For gases, the difference between ΔH and ΔU during a given process can be very significant. This is due to the fact that for the chemical process proceeding at a constant pressure, the volume change is associated with the change of the number of moles of gaseous substances:

$$PV = nRT.$$

If n_1 moles of gaseous reagents is used up in reaction and n_2 moles of gaseous products is formed, then:

$$\Delta(p) = (n_2 - n_1) RT = \Delta nRT,$$

so,

$$Q_p = \Delta H = \Delta U + \Delta nRT, \quad Q_p = Q_v + \Delta nRT.$$

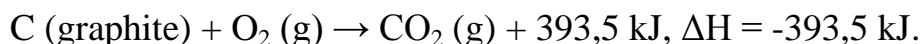
Comparing the values of Q_p and Q_v is easy to see that the thermal effect of the reaction proceeding at constant pressure, differs from that at constant volume by the value of expansion work. If reaction takes place in the condensed phase (solid or liquid), the differences between Q_v and Q_p and therefore between ΔU and ΔH are insignificant.

Thermal effects, assigned to 1 mole of the substance under standard conditions (temperature 298 K and pressure 101,3 kPa), are called *standard*. The standard state of matter will be: for solids – a stable at the standard temperature polymorphic form (graphite for carbon, rhombic sulfur, white phosphorus, etc.), for gases – the state of the ideal gas at a pressure of 1 atm, for substances in solutions – take the concentration, equal to 1 mole, while bearing in mind that the solution has properties, with its infinite dilution.

4. Thermochemical equation. Heat of formation and combustion for compounds

Thermochemistry is a section of thermodynamics that studies the thermal effects of chemical reactions and phase transformations.

The equation of chemical reactions, in which not only the formulas of substances are indicated, but also the thermal effects, are called *thermochemical equations*. Example:



Thermochemical equations, although very similar to the usual chemical equations, differ from the following features:

- specified aggregate (phase) states of all substances;
- all coefficients have dimension – mole;
- acceptable non-objective coefficients;
- with thermochemical equations one can perform arithmetical actions, as with algebraic equations, they can be composed, subtracted, multiplied by numbers.

Enthalpy of reaction in this case is called the heat effect of reaction. It is characterized not only by absolute value, but also by sign. The heat absorbed by the system (endothermic reaction) is considered to be positive ($\Delta H > 0$), and the heat evolved of the system (exothermic reaction) is considered to be negative ($\Delta H < 0$), so: $Q = -\Delta H$.

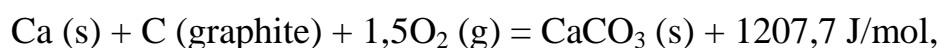
The thermal effect of a chemical reaction is a measure of changes in the energy reserve as a result of the process proceeding, which is released or absorbed when the reaction is irreversible, when the molar quantities of matter react between themselves, and the only work is only the expansion. The thermal effects of reactions in the general case depend on temperature and pressure, therefore, at their recording should clearly indicate the conditions under which the given thermal effect. The enthalpy of chemical reactions in the reference books is to be taken as *standard enthalpy changes*, which means that all the substances are participants of the reaction under standard conditions (pressure 1 atm (101,3 kPa) and temperature 298 K).

Enthalpy of simple substances in their most stable form at standard conditions

are zero.

The standard enthalpy of formation ($\Delta H_{f,298}^0$) is the thermal effect of the reaction of the formation of one mole of a substance from elements or simple substances under standard conditions. For elements and simple substances in a stable aggregate state, the standard enthalpy of formation is zero.

Example. If the substance is obtained by the reaction expressed Thermochemical equation:



its standard heat of formation is: $\Delta H_{298}^0(\text{CaCO}_3) = - 1207,7 \text{ J/mol}$.

The standard enthalpy of combustion ($\Delta H_{c,298}^0$) is the heat of combustion in an oxygen atmosphere of one mole of matter to the simplest oxides.

5. Laws of thermochemistry: Lavoisier and Laplace's law and Hess's law.

Consequences of Hess's law

Hess's law (and consequent law of thermodynamics) (1840): heat of chemical reactions occurring at constant volume or pressure does not depend on the number of intermediate stages and is determined only by the initial and final state of the system. The energy change accompanying any transformation is the same whether the process occurs in one step or many.

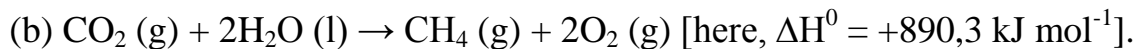
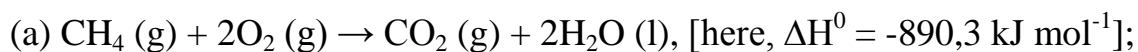
These statements preceded the first law of thermodynamics (1845) and helped in its formulation.

Lavoisier, Laplace and Hess also investigated specific heat and latent heat, although it was Joseph Black who made the most important contributions to the development of latent energy changes.

Lavoisier and Laplace's law (1782): This law may be stated in the general form as: the heat change accompanying a chemical reaction in one direction is exactly equal in magnitude, but opposite in sign, to that associated with the same reaction in the reverse direction. This law states that; the heat change (or enthalpy

change) of a chemical reaction is exactly equal but opposite in sign for the reverse reaction.

This is evident from the following two fractions:



Thus, it can be concluded that, $\Delta H_{\text{forward reaction}} = -\Delta H_{\text{backward reaction}}$.

A chemical equation when written along with enthalpy change for the reaction is termed a thermochemical equation. The two equations are examples of thermochemical equations. Laplace's law allows us to use thermochemical equations as algebraic equations.

Consequences of the Hess law:

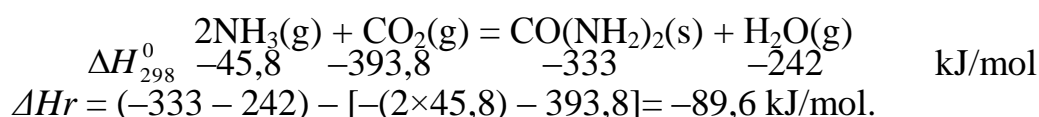
- *I consequences of the Hess law* – the heat of reaction (enthalpy) is the algebraic sum of enthalpy of formation of the reaction products with the exception of the algebraic sum of enthalpy of formation of precursors including stoichiometric ratios for the reaction is $n\text{AA} + n\text{BB} = n\text{CC} + n\text{DD}$, true:

$$\Delta H_r = \sum \Delta H_{(\text{products})} - \sum \Delta H_{(\text{reactants})}, \text{ where}$$

$$\sum \Delta H_{(\text{products})} = n\text{C}\Delta\text{HC} + n\text{D}\Delta\text{HD}$$

$$\sum \Delta H_{(\text{reactants})} = n\text{A} \Delta\text{HA} + n\text{B}\Delta\text{HB}.$$

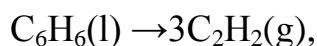
Example.



- *II consequences of the Hess law* – the heat of reaction is the difference amounts standard enthalpy of combustion of starting materials and standard enthalpy of combustion reaction products, taken in accordance with stoichiometric coefficients.

$$\Delta H_r = \sum \Delta H_{\text{comb}(\text{reactants})} - \sum \Delta H_{\text{comb}(\text{products})}.$$

Example.



$$\Delta H_r = \Delta H_{\text{comb}}(\text{C}_6\text{H}_6(\text{g})) - 3\Delta H_{\text{comb}}(\text{C}_2\text{H}_2(\text{g}))$$

$$\Delta H_r = -3268 - (-3 \times 1300) = 632 \text{ kJ/mol}.$$

Kirchhoff's Law: the temperature coefficient of the thermal effect of the reaction equals the change in heat capacity as a result of the process. The law establishes the dependence of the thermal effect of the reaction on temperature.

Exothermic chemical reactions are reactions in the course of which the enthalpy of the system decreases and heat is released to the external environment ($\Delta H < 0$).

Endothermic chemical reactions are reactions in the course of which the enthalpy of the system increases and the system absorbs heat from the outside ($\Delta H > 0$).

The heat capacity of the system (C) is the amount of heat needed to heat a unit amount of substance by one degree:

$$C = \Delta Q / \Delta T \text{ [J/K]}.$$

The term "*heat capacity*" actually means the capacity of heat – the ability of the body to accumulate, to absorb the energy supplied to it in the form of heat. Heat capacity is the extensive property of a substance, that is, it depends on the amount of matter.

There are several types of heat capacity, the criteria for division are:

- unit amount of substance;
- nature of the thermodynamic process;
- values of the temperature interval.

Depending on the unit amount of substance – 1 kg, 1 m³ and 1 mole, distinguish:

- specific, referenced to 1 kg of mass ($S_{\text{spec.}}$, J/(kg · K));
- bulk, assigned to 1 m³ of gas under normal physical conditions ($t = 0^\circ\text{C}$; $p = 760 \text{ mmHg}$) (S_{bulk} , J/(m³ · K));
- molar, assigned to 1 mole (S_{m} , J/(mole · K)).

Specific heat is a quantity that is numerically equal to the amount of energy in the form of heat, which is raised and absorbed by 1 kg of the body and causes a change in temperature by 1 K.

Depending on the nature of the thermodynamic process, the isobaric C_p and

isochoric C_v heat are distinguished.

Depending on the value of the temperature range, the average and true heat capacity are distinguished.

The average heat capacity of a homogeneous system corresponding to a finite temperature interval is determined by the ratio:

$$C_{av} = \Delta Q / T_2 - T_1,$$

where Q – amount of heat, at the expense of obtaining (return) of which The system temperature rises (decreases) from T_1 to T_2 .

Under the true heat capacity is understood the heat capacity, which corresponds to an infinitely small change in temperature.

6. Second law of thermodynamics. Entropy

The second law of thermodynamics is one of the general laws of nature, which is a postulate: *in an isolated system, spontaneously can occur only those processes in which there is an increase in entropy*. In other words: *"It is impossible to build a periodically operating car, the only result of which was only the execution of the work, or "perpetuum mobile" of the second kind is impossible"*.

There are several definitions of the second law of thermodynamics: "If heat flows by conduction from body A to another body B, then a transformation whose only final result is to transfer heat from B to A is impossible" (*Clausius's Postulate (1855)*), it is also equivalent to *Kelvin's postulate* or "impossible circular process, the only result of which would be the production of work at the expense of the cooling of the thermal reservoir" (*Thomson's postulate*):

$$\frac{A}{Q} = \frac{T_1 - T_2}{T_1} = \frac{Q_1 - Q_2}{Q_1},$$

where Q_1 is the amount of heat taken in a heater with a temperature T_1 ;

Q_2 – amount of heat given to the refrigerator (heat collector) with temperature T_2 ;

$Q_1 - Q_2 = A$ – is equal to the work carried out by the working body.

That is, the second law of thermodynamics states that it is impossible to obtain work at the expense of the energy of bodies in the thermodynamic equilibrium, and also it gives a limitation on the direction of the course of thermodynamic processes and determines the conditions for the independent flow of processes. The self-proclaimed processes are realized under the influence of two main factors: the desire of the system to achieve a minimum of energy and to increase its entropy, that is, to increase the chaos in it.

A positive process (self-destructive) is a process that takes place in a system without interference by external forces and brings the system closer to a state of thermodynamic equilibrium.

Negative process (self-supporting) – it removes the system from the state of thermodynamic equilibrium.

Equilibrium process – a process in which the system continuously passes a series of equilibrium states.

Entropy (Clausius definition) is a function of a state whose increment is equal to the heat of a summed system in a reversible isothermal process, divided by the absolute temperature at which the process is carried out:

$$\Delta S = \Delta Q/T \quad [\text{J/mole} \times \text{K}].$$

Ludwig Boltzmann (1844–1906) pioneered the concept that entropy could be calculated by examining the positions and energies of molecules. He developed an equation, known as the *Boltzmann equation*, which relates entropy to the number of *microstates* (W):

$$S = k \ln W,$$

where k is the Boltzmann constant ($1,38 \times 10^{-23}$ J/K), and W is the number of microstates.

Microstates is a term used to describe the number of different possible arrangements of molecular position and kinetic energy at a particular thermodynamic state. A process that gives an increase in the number of microstates therefore increases the entropy.

Entropy (molecular-kinetic definition) is a quantitative measure of disorder and the probability of a system being in a given state. Each system tries to move to the state with the most disorderly due to the fact that particles in nature are characterized by chaos. Entropy determines the direction of self-proclaimed process and does not depend on its path.

An involuntary process can run in an isolated system in the case when it is characterized by an increase in entropy, in an equilibrium system, the entropy is constant:

$$\Delta S \geq 0.$$

The amount of entropy depends on: aggregate state, allotropic form, temperature, pressure, complexity of the system. Any system aspires to transition to the most probable state (i.e. to increase the mess):

$$S(g) > S(l) > S(s).$$

The change in the entropy of the chemical process is equal to the difference between the amount of entropy of the reaction products and the amount of entropy of the starting substances (of course, taking into account the stoichiometric coefficients):

$$\Delta S_{\text{r-tion}} = \sum \Delta S_{(\text{products})} - \sum \Delta_{(\text{reactatns})}.$$

Expression II of the law of thermodynamics for biological systems: the suitability of the second law of classical thermodynamics to biological systems can be explained as follows. The living organism must be considered not isolated from the external environment, but in interaction with it. As is known, processes that occur independently in an isolated system lead it to a state of thermodynamic equilibrium. In this case, the gradients of energy are leveled, the system performance is zero, and its entropy is maximal. However, it is well known that biological systems, as long as they function, never reach such a state. They are always characterized by disability, and their entropy is not maximal. This is due to the fact that biosystems are not isolated, but are open systems. They constantly exchange energy with the environment. In this case, free energy enters the body in the form of food products, various radiations, etc., and is most often isolated in the degraded thermal form or in the form of low-energy compounds. Since the free energy flow contributes to

decreasing the entropy of the system, increasing energy gradients, decreasing the amount of degraded energy, it is said that the body consumes negative entropy and highlights positive entropy.

The body enters substances with low entropy (proteins, polysaccharides), and a large number of products that increase entropy of the environment (H_2O , CO_2 , NH_3 , etc.) are released. Processes with negative and positive values of S are interconnected: oxidation of glucose in the process of breathing and the synthesis of ATP due to the energy released during the oxidation of glucose. The processes of growth and development of the organism are accompanied by a decrease in entropy, however, it occurs so that the change in the total entropy ($S_{\text{human}} + S_{\text{medium}}$) is positive, but increases with minimal speed.

Because all processes occurring in living bodies are irreversible, their entropy is increasing during their time. At the same time, part of the energy is released into the environment in the degraded form (in the form of heat or in the form of energy-poor end-product metabolism). Therefore, when considering the suitability of the second principle of thermodynamics to biosystems, one should take the organism together with the area of the environment, which ensures its normal functioning for a certain time. Such a system was called a *conditionally isolated system*. To her the second principle of thermodynamics is fully applied. In some parts of this system, entropy, it would seem contrary to the second principle of thermodynamics, may even decrease (for example, in green leaves with photosynthesis). However, this decrease is due to the growth of entropy in another part of such a system (for example, in a light source from which light energy enters the leaves). As a result, the general entropy of such a system in accordance with the second principle of thermodynamics does not decrease, but tends to increase. Thus, the second principle of thermodynamics is applied to biosystems. The processes taking place in them occur in accordance with this principle, and entropy plays an important role here.

Living organisms maintain their inherent orderliness by increasing the entropy of the environment. Life is a constant struggle against the tendency to increase the entropy of the organism, but as it is impossible to avoid this growth, living organisms

have chosen the least "evil" – a steady state in which the rate of entropy growth is minimal.

Entropy, as one of the most important thermodynamic functions of biosystems. Among the thermodynamic functions characterizing the energy state of a biological object, the entropy plays an extremely important role. After all, a living organism is first of all an energy system, where the same laws of thermodynamics apply. Entropy characterizes the energy consumption of irreversible processes, which occur usually in the form of heat. Thus, the entropy reflects that part of the energy of the scattered, degraded system in a thermal form and can no longer be used to operate at a constant temperature. That is, under reversible processes, the change in entropy is zero, and if it is irreversible, it is positive. Therefore, the smaller the gradients of energy in the system and the more it is scattered in the form of heat of degraded energy, the greater is its entropy. The practical absence of reversible processes in biological systems is due to the fact that all processes that occur in them are accompanied by an increase in entropy. Consequently, in biosystems, not all free energy consumed in a certain process, becomes a useful work. Some of it dissipates in the form of heat. The ratio of the amount of work performed to the amount of free energy expended on it is called the coefficient of usefulness (efficiency) of the biological process. Thus, muscle contraction is carried out with an efficiency of ~30%, glycolysis ~ 36%. As can be seen, the loss of free energy in these processes is very large. There are, however, such processes that are close to reversible, i.e., the efficiency of which is high. For example, the glow of some tropical insects has an efficiency of 98-99 %, a discharge of electric fish – 98 %. The reason for this highly effective use of free energy is still not clear. Thus, the larger the increase in entropy in this process, the more probable is the irreversibility of this process.

7. Criteria of spontaneous processes. Gibbs equation. Types of biochemical reactions according to the ΔG° values

Depending on the type of system and the process, the role of the thermodynamic potential perform various state functions:

- in isolated systems – entropy;
- in the isothermal isochoric process – Helmholtz energy or isochoric isothermal potential F: $\Delta F = \Delta U - T\Delta S$;
- in isothermal-isobar processes – Gibbs energy or isobaric-isothermal potential G: $\Delta G = \Delta H - T\Delta S$.

The value of $T\Delta S$ characterizes the bound energy, that is, the part of the energy that dissipates to the environment. Thus, Gibbs energy characterizes that part of the energy in the corresponding systems, which can be transformed into work. This function is a state of the system and its absolute value can not be calculated. Changes in these functions are considered.

At constant temperature and pressure, only those processes for which the change in the energy of Gibbs (or Helmholtz) is negative can proceed only independently.

That is, based on the fact that the probability of the course of a chemical reaction depends on chemical affinity (the ability of substances to engage in chemical interaction with each other). The quantitative degree of chemical affinity is the thermodynamic potentials of the reaction ΔF and ΔG . The more negative the value of the corresponding potential, the more likely this reaction, that is, the greater the chemical affinity of the parent substance.

Example. Determine the possibility of a self-satisfactory flow of reaction $\text{Al}_2\text{O}_3 + 3\text{SO}_3 = \text{Al}_2(\text{SO}_4)_3$ under standard conditions.

Record thermochemical equation.

The reaction is self-propagating in the forward direction, if $\Delta G_{p,T} < 0$.

$$\Delta G = \Delta H - T\Delta S. \text{ Under standard conditions } \Delta G_{298}^0 = \Delta H_{298}^0 - T\Delta S_{298}^0.$$

$$\Delta H_{298}^0 = \Delta H_{f,298}^0(\text{Al}_2(\text{SO}_4)_3) - [\Delta H_{f,298}^0(\text{Al}_2\text{O}_3) + 3\Delta H_{f,298}^0(\text{SO}_3)].$$

According to tabular data, we have:

$$\Delta H_{298}^0 = -3434 - (-1675 - 3 \times 395,2) = -753,3 \text{ kJ}$$

$$\Delta S_{298}^0 = \Delta S_{298}^0(\text{Al}_2(\text{SO}_4)_3) - [\Delta S_{298}^0(\text{Al}_2\text{O}_3) + 3\Delta S_{298}^0(\text{SO}_3)]$$

$$\Delta S_{298}^0 = 239,2 - (50,94 + 3256,23) = -580,43 \text{ J/K} = -0,58 \text{ J/K}$$

$$\Delta G_{298}^0 = -753,3 - 298 \times (-0,58) = -580,46 \text{ kJ}.$$

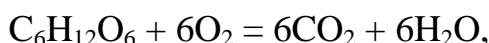
$\Delta G_{298}^0 < 0$, that is, the self-satisfactory flow of reaction in a forward direction is possible.

The thermochemical equation of reaction has the following form:



Hesse's law for Gibbs energy: the change in Gibbs energy in the formation of given products from these reagents at constant pressure and temperature does not depend on the number and type of reactions that result in these products.

Example. Changing the Gibbs energy for a glucose oxidation reaction



Defined outside the body is: $\Delta G_{\text{reaction}} = -2880 \text{ kJ/mol}$. In the cells of the body, this reaction is carried out through a number of successive stages, studied by biochemists. One can predict, based on Hess's law, that the sum of changes in the energies of Gibbs in all intermediate reactions is:

$$\Delta G_{\text{reaction}} = \Delta G1 + \Delta G2 + \Delta G3 + \Delta G4,$$

this is in good agreement with the experimental data.

Consequence of the Hess's law for Gibbs energy: the Gibbs energy of the reaction equals the algebraic sum of the Gibbs energies of the formation of the stoichiometric quantity of the reaction products minus the algebraic sum of the Gibbs energies of the stoichiometric number of reagents:

$$n\text{AA} + n\text{BB} = n\text{CC} + n\text{DD}; \Delta G_{\text{reaction}} = (n\text{C} \Delta G_{\text{C}} + n\text{D} \Delta G_{\text{D}}) - (n\text{A} \Delta G_{\text{A}} + n\text{B} \Delta G_{\text{B}}).$$

The standard energy of the Gibbs (Helmholtz) formation of a substance is the change in the energy of Gibbs (Helmholtz) in the reaction of the formation of 1 mol of complex matter from simple substances under standard conditions ($P_0 = 101325 \text{ Pa}$, $T = 298 \text{ K}$).

By the sign ΔG , the isothermal isobaric processes are divided into three groups:

- exogenous – $\Delta G < 0$, may go unintentionally;
- reversible – $\Delta G = 0$, occupy the frontier position;
- endogenous – $\Delta G > 0$, they can not pass themselves.

8. Application of the laws of chemical thermodynamics to living systems (stationary state, homeostasis, mechanism of energy conjugation)

First, classical thermodynamics studies isolated systems, and in the living nature of such systems there. Second, it considers equilibrium states, for living organisms their state is defined as non-equilibrium stationary. The stationary state is outwardly similar to equilibrium in that it maintains the constancy of pressure, volume, temperature, concentration of particles. However, this constancy is ensured by continuous, moving with constant velocity, outflow of matter from the system and the receipt of nutrients from it from the outside.

The property of living systems to maintain the constancy of parameters and the immutability in time of the rates of receipt and removal of substances and energy, which ensures the stability of physiological functions, is called homeostasis (from the Greek - "to remain the same"). The mechanism of homeostasis acts at all levels of the organization of living systems – molecular, cellular, at the level of the whole organism and even at the population level.

Stationary state is necessary for biosystems, because in this state they acquire the ability to self-regulate. If the stationary state is fairly stable, then, after deviating from it, caused by external influence, the system is able to return to its original state.

The energy exchange in living systems is organized in such a way that in it there are simultaneously possible thermodynamic reactions (for example, decomposition of carbohydrates into water and carbon dioxide) and impossible (biosynthesis of complex molecules, active transport through cell membranes, etc.). This is achieved At the expense of energy conjugation, the transition of the process to a multi-stage mode and the functioning of multi-enzyme systems. The mechanism of energy conjugation takes place when it is possible from the point of view of the entropy criterion, the reaction is combined with the reaction, thermodynamically impossible, and gives it energy. In this case, the free energy of the first must exceed the energy consumed by the second one. Reaction reactions should have a common component – a factor that combines, which is usually phosphate ion.

The transition of the biochemical process into a multistage regime allows the

living organism to easily control the synthesis of certain substances in the required quantities. This is explained by the fact that the difference between the free energies of the initial and final states for each of the individual stages is usually small, and therefore the probability of achieving a balance for it is greater than for the process as a whole.

The multisequence of passing chemical transformations in living systems is ensured by the operation of multi-enzyme systems operating on the principle of a molecular conveyor – the product of one enzymatic reaction serves as a substrate for the subsequent transformation.

EXAMPLES OF SOLUTION OF THE TASKS

Task 1. What has a greater entropy: 1 mole of crystalline substance or 1 mole of its vapor at the same temperature? Calculate the change in entropy at evaporation of 1 mole of water under standard conditions.

Solution: entropy is a measure of the disordered state of a substance. In a crystal, particles (atoms, ions) have an ordered arrangement and can only exist at certain points of space, and for gas there are no such restrictions. 1 mole of gas has a much larger volume than 1 mole of crystal, and the possibility of chaotic motion of gas molecules is greater. And since entropy can be regarded as a quantitative measure of the chaos of the atomic-molecular structure of matter, then the entropy of a mole of a mole of entropy is more molten than its crystals at the same temperature.

Method I: Using tabular data of enthalpy formation of liquid and vaporous water, we expect:

$$\Delta H_{\text{vap}}^0 = \Delta H_{\text{H}_2\text{O}(g)}^0 - \Delta H_{\text{H}_2\text{O}(l)}^0 = (-241,86) - (-285,84) = 44,01 \frac{\text{kJ}}{\text{mol}}.$$

$$\text{From here: } \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}} = \frac{44010}{373} = 118,0 \frac{\text{J}}{\text{mol} \times \text{K}}.$$

Method II: Using tabular data of the entropy of formation of liquid and vaporous water, we expect:

$$\Delta S_{\text{vap}} = \Delta S_{\text{H}_2\text{O}(g)}^0 - \Delta S_{\text{H}_2\text{O}(l)}^0 = 188,5 - 70,1 = 118,4 \frac{\text{J}}{\text{mol} \times \text{K}}.$$

Some divergence in the results is due to the fact that in different guides give the values of thermodynamic characteristics with different error.

Task 2. According to the thermochemical equation of reaction: $2\text{Cu} + \text{O}_2 = 2\text{CuO} + 311 \text{ kJ}$.

Calculate how much heat you get out of the oxidation of 1,5 moles of copper.

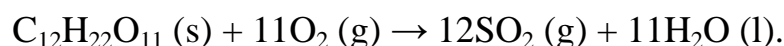
Solution: It is known from the equation of reaction that the oxidation of 2 mole of a substance corresponds to 311 kJ of heat, respectively:

$$2 \text{ mole} - 311 \text{ kJ}$$

$$1,5 \text{ mole} - X \text{ kJ}$$

$$\text{Hence, } X = 233,25 \text{ kJ.}$$

Task 3. Calculate the change in entropy, Gibbs energy and enthalpy in the process of assimilation of sucrose in humans (oxidation reaction):



Solution: it is necessary to use tabular data of the values of standard enthalpy, entropy, and free energy Gibbs for all substances involved in the reaction:

$$\Delta H_{f,298}^0 (\text{C}_{12}\text{H}_{22}\text{O}_{11}) = 2222 \text{ kJ/mol};$$

$$\Delta H_{f,298}^0 (\text{O}_2) = 0 \text{ kJ/mol};$$

$$\Delta H_{f,298}^0 (\text{CO}_2) = 393 \text{ kJ/mol};$$

$$\Delta H_{f,298}^0 (\text{H}_2\text{O}) = 286 \text{ kJ/mol};$$

$$\Delta S_{f,298}^0 (\text{C}_{12}\text{H}_{22}\text{O}_{11}) = +360 \text{ J/mol K};$$

$$\Delta S_{f,298}^0 (\text{O}_2) = + 205 \text{ J/mol K};$$

$$\Delta S_{f,298}^0 (\text{H}_2\text{O}) = +70 \text{ J/mol K};$$

$$\Delta S_{f,298}^0 (\text{CO}_2) = +214 \text{ J/mol K};$$

$$\Delta G_f^0 (\text{C}_{12}\text{H}_{22}\text{O}_{11}) = 1545 \text{ kJ/mol};$$

$$\Delta G_f^0 (\text{O}_2) = 0 \text{ kJ/mol};$$

$$\Delta G_f^0 (\text{CO}_2) = 394 \text{ kJ/mol};$$

$$\Delta G_f^0 (\text{H}_2\text{O}) = 237 \text{ kJ/mol}.$$

Using the I consequence of the Hess's law, we calculate the required values:

$$\Delta H_{\text{r-tion}} = [12 \Delta H_{f,298}^0 (\text{CO}_2) + 11 \Delta H_{f,298}^0 (\text{H}_2\text{O})] - [\Delta H_{f,298}^0 (\text{C}_{12}\text{H}_{22}\text{O}_{11}) + 11 \Delta H_{f,298}^0 (\text{O}_2)]$$

$$\Delta H_{\text{r-tion}} = [12(-393) + 11(-286)] - [-2222 + 11 \cdot 0] = -5676 \text{ kJ/mol};$$

$$\Delta S_{\text{r-tion}} = [12 \Delta S_{f,298}^0 (\text{CO}_2) + 11 \Delta S_{f,298}^0 (\text{H}_2\text{O})] - [\Delta S_{f,298}^0 (\text{C}_{12}\text{H}_{22}\text{O}_{11}) + 11 \Delta S_{f,298}^0 (\text{O}_2)]$$

$$\Delta S_{\text{r-tion}} = [12 \cdot 214 + 11 \cdot 70] - [360 + 11 \cdot 205] = +723 \text{ J/mol K};$$

$$\Delta G_p = [12 \Delta G_{\text{ym6}}^0 (\text{CO}_2) + 11 \Delta G_{298}^0 (\text{H}_2\text{O})] - [\Delta G_{\text{ym6}}^0 (\text{C}_{12}\text{H}_{22}\text{O}_{11}) + 11 \Delta G_{298}^0 (\text{O}_2)]$$

$$\Delta G_{\text{r-tion}} = [12 \Delta G_f^0 (\text{CO}_2) + 11 \Delta G_{298}^0 (\text{H}_2\text{O})] - [\Delta G_f^0 (\text{C}_{12}\text{H}_{22}\text{O}_{11}) + 11 \Delta G_{298}^0 (\text{O}_2)]$$

$$\Delta G_{\text{r-tion}} = [12(-394) + 11(-237)] - [(1545) + 11 \cdot 0] = -5790 \text{ kJ/mol}.$$

Task 4. The enthalpy of glucose combustion is -2802 kJ/mol at 298 K. How many grams of glucose should I spend on a person to climb the stairs of 3 m. Accept that 25 % of enthalpy can be transformed into useful work.

Solution: the maximum useful work that can be carried out by man as a result of oxidation of 1 g of glucose with oxygen (taking into account the efficiency of the organism) is:

$$A_{\text{max}} = n(\text{C}_6\text{H}_{12}\text{O}_6) \times H_{\text{comb}}(\text{C}_6\text{H}_{12}\text{O}_6) \times \eta$$

$$A_{\text{max}} = \frac{1 \text{ g}}{180 \frac{\text{g}}{\text{mol}}} \times 2802 \frac{\text{kJ}}{\text{mol}} \times 0,25.$$

The work required for lifting a person weighing 70 kg at a height of 3 m is:

$A = mgh = 70 \text{ kg} \times 9,8 \text{ kg/c}^2 \times 3 \text{ m} = 2058 \text{ J} = 2,058 \text{ kJ}$. So, if 1 g of glucose is oxidized, then the useful work is 3.89 kJ, and if the useful work is equal to 2058 kJ, then glucose is required by weight: $m(\text{C}_6\text{H}_{12}\text{O}_6) = 0,529 \text{ g}$.

Answer: It is necessary to spend 0,529 g of glucose.

Task 5. A person in a warm room eats 100 g of cheese (its energy value is 15,52 kJ/g). Assuming that there is no accumulation of energy in an organism, what

mass of water will it provide to establish an initial temperature?

Solution: Sweating cools the body, as energy is needed to evaporate water. The molar enthalpy of water vaporization is 44 kJ/mol. Evaporation of water occurs at constant pressure, therefore it is possible to equate the enthalpy of evaporation of water to the amount of heat that needs to be distinguished: $Q = n(\text{H}_2\text{O}) H_{\text{vap}}(\text{H}_2\text{O})$. The energy obtained during the assimilation of cheese is:

$$Q = m_{(\text{cheese})} \text{Cal}_{(\text{cheese})} = 100 \text{ g} \cdot 15,52 \text{ kJ/g} = 1552 \text{ kJ}.$$

Then the amount and weight of water to be allocated are:

$$n(\text{H}_2\text{O}) = \frac{Q}{H_{\text{vap}}} = \frac{1552 \text{ kJ}}{44 \frac{\text{kJ}}{\text{mol}}} = 35,3 \text{ mol}$$

$$m(\text{H}_2\text{O}) = n(\text{H}_2\text{O}) M(\text{H}_2\text{O}) = 35,3 \text{ mol} \cdot 18 \text{ g/mol} = 635 \text{ g}.$$

Answer: 635 g of water.

QUESTIONS FOR SELF-TESTING

1. What is thermodynamics and what phenomena does it study?
2. What is a system? What are the thermodynamic systems differ from each other?
3. Give definitions and give examples of thermodynamic processes: isothermal, isobaric, isochoric and adiabatic.
4. What physical quantities are called thermodynamic parameters, what is their peculiarity?
5. Give definitions of reversible and irreversible thermodynamic processes. Give examples. Can real natural processes be completely reversible?
6. Give the wording of the first law of thermodynamics known to you and prove that they do not contradict each other.
7. Write down the mathematical expression and the law of thermodynamics.
8. Give the definition of internal energy. What is its meaning in the expression of the first law of thermodynamics? List its properties.
9. Why does thermodynamics not consider the absolute value of internal

energy, but only its change?

10. Give the definition of enthalpy. Does enthalpy satisfy the properties of the state function of the system?

11. Applying the mathematical expression of the first law of thermodynamics, show that the thermal effect at constant pressure is a change in enthalpy, and the thermal effect at constant volume - the change in the internal energy of the chemical reaction.

12. Discuss the similarity and difference between the concepts of "equilibrium state of the system" and "stationary state of the system".

13. List the methods of transferring energy from one system to another. What is warmth and work? Is this a status or transition function?

14. What is the difference between exothermic and endothermic reactions?

15. What is the thermal effect of a chemical reaction?

16. Formulate Hesse's law. What are the consequences of Hess's law?

17. Explain why Hess's law is a special case of the law of thermodynamics?

18. Give the definition of "warmth of education", "heat of combustion".

19. Give the definition of heat capacity.

20. In what units is the heat capacity measured?

21. What formulation of the second law of thermodynamics do you know?

22. Write the mathematical expression of the second law of thermodynamics.

23. In what case, the change of entropy is a criterion for the equilibrium of self-proclaimed process?

24. What are the functions of state such as Helmholtz energy and Gibbs energy introduced into thermodynamics? Discuss their physical content.

TASKS

1. Determine the heat of combustion of one cubic meter (n. c.) of methane CH_4 and propane C_3H_8 . Which of these two gases is more profitable to use as a balloon gaseous fuel? (*Answer: -35813; -91241 kJ*).

2. Calculate the thermal effects of the combustion reactions of one mole of ethane C_2H_6 , ethylene C_2H_4 and acetylene C_2H_2 . Which of these three gases is more profitable to use for welding metals? (Answer: -1423; -1218; -802 kJ).

3. Is it possible to find a catalyst capable of causing water to decompose hydrogen and oxygen at room temperature? The answer is motivated by the calculation of the Gibbs energy change for the specified reaction under standard conditions. (Answer: +237,3 kJ/mol of H_2O).

4. A direct or reciprocal reaction may occur under standard conditions in the system: $2NO(g) + O_2(g) = 2NO_2(g)$. Answer motivate (it is necessary to calculate the direct reaction). (Answer: - 70.2 kJ)

5. Is the reaction possible: $Al_2O_3 + 3SO_3 = Al_2(SO_4)_3$ if the Gibbs energy of $Al_2O_3(k) = -1576,4$ kJ/mol, $SO_3 = -370,37$ kJ/mol, $Al_2(SO_4)_3 = -3091,9$ kJ/mol? (Answer: -404,39 kJ / mole, the reaction is possible)

6. Determine the Gibbs energy for the glycolysis reaction: $C_6H_{12}O_6 \rightarrow 2C_3H_6O_3$. If ΔG_f^0 lactic acid = 539 kJ/mol, and ΔG_f^0 glucose = -917 kJ/mol. (Answer: 161 kJ/mol)

7. Heat of formation of proteins in the human body is 4,1 kcal/g. The average daily protein requirement for female students is 96 g. Calculate the students' daily need for protein energy. (Answer: 393,6 kcal).

8. Check if there is a threat that the nitrogen (I) oxide used in Medicine as a narcotic will be oxidized by oxygen to the toxic nitrogen (II) oxide, if. ΔG_f^0 (N_2O) = 104 kJ/mol, ΔG_f^0 (NO) = 87 kJ/mol. (Answer: $\Delta G^0 = 140$ kJ/mol, respectively, the oxidation reaction is not possible).

9. In the Krebs cycle, isocitrate is converted into α -ketoglutarate: $Isocitrate + 1/2O_2(g) + H^+ \leftrightarrow \alpha\text{-ketoglutarate} + H_2O(g) + CO_2(g)$. Calculate ΔG of this reaction if ΔG_f^0 (isocitrate) = -1166,6 kJ/mol, ΔG_f^0 (α -ketoglutarate) = -796,8 kJ / mol, ΔG_f^0 (CO_2) = -394,4 kJ/mol; ΔG_f^0 (H_2O) = -237 kJ/mol. (Answer: - 267,2 kJ/mol)

10. Determine the thermal effect of the reaction of diethyl ether synthesis, which is used in medicine for anesthesia, at 298 K:



if the standard heat of combustion of the substances involved in the reaction

$$\Delta H_f^0(\text{C}_2\text{H}_5\text{OS}_2\text{N}_5) = -2727 \text{ kJ/mol}; \Delta H_f^0(\text{C}_2\text{H}_5\text{OH})(\text{l}) = -1371 \text{ kJ/mol. (Answer:}$$

-15kJ/mol)

11. One of the ways of glucose metabolism is the process: $\text{C}_6\text{H}_{12}\text{O}_6(\text{l}) \rightarrow \text{C}_3\text{H}_7\text{COOH}(\text{l}) + \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$. Calculate the ΔG reaction if $\Delta G_f^0(\text{C}_6\text{H}_{12}\text{O}_6(\text{l})) = -917,0 \text{ kJ/mol}$, $\Delta G_f^0(\text{C}_3\text{H}_7\text{COOH}(\text{l})) = -376 \text{ kJ/mol}$, $\Delta G_f^0(\text{CO}_2(\text{g})) = 394,4 \text{ kJ/mol}$. (Answer: $-247,8 \text{ kJ/mol}$).

12. Calculate the change in entropy ΔS when evaporating 250 g of water, if Molar heat of evaporation of water is 44,08 kJ/mole. (Answer: $612,2 \text{ kJ/mol}$).

13. For the following reactions, calculate the changes in enthalpy, entropy, and Gibbs energy (see the annex for details). Can a reaction in the forward direction be self-consistent in standard conditions at 298 K?

<i>Variant number</i>	<i>Reaction equation</i>
1	$2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH}(\text{r})$
2	$4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O}(\text{g}) + 2\text{Cl}_2$
3	$\text{NH}_4\text{Cl} = \text{NH}_3 + \text{HCl}$
4	$2\text{N}_2 + 6\text{H}_2\text{O}(\text{g}) = 4\text{NH}_3 + 3\text{O}_2$
5	$4\text{NO} + 6\text{H}_2\text{O}(\text{g}) = 4\text{NH}_3 + 5\text{O}_2$
6	$2\text{NO}_2 = 2\text{NO} + \text{O}_2$
7	$\text{Mg}(\text{OH})_2 = \text{MgO} + \text{H}_2\text{O}(\text{g})$
8	$\text{CaCO}_3 = \text{CaO} + \text{CO}_2$
9	$\text{Ca}(\text{OH})_2 = \text{CaO} + \text{H}_2\text{O}(\text{g})$
10	$2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$
11	$\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2(\text{g})$
12	$\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}(\text{g})$
13	$\text{CO} + \text{Cl}_2 = \text{COCl}_2(\text{g})$
14	$\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}(\text{g})$
15	$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}(\text{g})$
16	$2\text{CO}_2 = 2\text{CO} + \text{O}_2$
17	$\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$
18	$\text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{H}_2$
19	$\text{C}_2\text{H}_5\text{OH}(\text{r}) = \text{C}_2\text{H}_4 + \text{H}_2\text{O}(\text{g})$
20	$\text{CH}_3\text{CHO}(\text{r}) + \text{H}_2 = \text{C}_2\text{H}_5\text{OH}(\text{g})$
21	$\text{C}_6\text{H}_6(\text{g}) + 3\text{H}_2 = \text{C}_6\text{H}_{12}(\text{g})$
22	$1/2\text{S}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) = \text{SO}_2 + 2\text{H}_2$
23	$\text{N}_2\text{O}_4 = 2\text{NO}_2$
24	$1/2\text{S}_2(\text{g}) + 2\text{CO}_2 = \text{SO}_2 + 2\text{CO}$
25	$2\text{CO} + \text{SO}_2 = 1/2\text{S}_2(\text{g}) + 2\text{CO}_2$

Table 1. Values of thermodynamic functions at 298.15 K

Substance	Enthalpy ΔH^0, kJ/mol	Entropy S, J/mol·K	Gibbs free energy ΔG^0, kJ/mol
HCl (g)	92,2	186,7	-95,3
NaCl (s.)	411,0	72,4	-384,1
O₂ (g)	0	205,0	0
O₃ (g)	-142,0	238,8	162,8
H₂O (g)	-241,8	188,7	-226,6
H₂O (l.)	-285,8	69,9	-237,2
SO₂ (g)	296,9	248,5	-300,2
H₂S (g)	20,4	205,6	-33,5
NH₃ (g)	-46,2	192,5	-16,5
NH₃ (aq.)	-80,8		
HCN (g)	132,0	201,7	121,6
H₃PO₄ (s.)	-1281,1	110,5	-1119,2
C (graphite)	0	5,7	0
C (diamond)	+1,8	2,4	2,8
CO (g)	-110,5	197,9	-137,1
CO₂ (g)	-393,5	213,6	-393,4
CO₂ (aq.)	-699,6		
H₂ (g)	0	130,6	
Methane (g)	-74,8	186,2	-50,8
Ethylene (g)	52,3	219,4	68,1
Acetylene (g)	226,7	200,8	209,2
Benzene (l.)	49,0	173,2	-124,4
Glycerine (l.)	-670,7	20,5	-477,1

Substance	Enthalpy ΔH^0 , kJ/mol	Entropy S , J/mol·K	Gibbs free energy ΔG^0 , kJ/mol
Acetaldehyde (l.)	-166,0	264,2	-132,9
Aceton (l.)	-246,8	198,7	-155,4
Acetic acid (l.)	-487,3	159,8	-389,4
Butyric acid (l.)	-524,3	255,0	-376,7
Fumaric acid (s.)	-811,1	166,1	-653,6
Lactic acid (aq.)	-694,0	221,7	
Pyruvic acid (aq.)	-607,5		
Glycine (s.)	-524,7	109,2	-366,8
Urea (s.)	-333,2	104,6	-197,1
Urea (aq.)	-319,2	173,8	
Glucose (s.)	-1274,4		-919,5
Sucrose (s.)	-2222,0	360,3	-1544,7

Algorithm of the laboratory work «Determination of solution enthalpy of a salt»

Fill the weighted aluminum calorimeter ($m = 46$ g) with the 50 ml of water and measure temperature with the accuracy to 0.1°C . Dissolve 5 g of salt (anhydrous salt Na_2CO_3 and crystallohydrate $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) in calorimeter for 3 minutes and measure temperature of these solutions. Using the values of molecular heat capacities (C_p) of the substances, taken part in heat exchange, determine the solution enthalpy of a salts (ΔH) from the formula:

$$\Delta H = \left(C_{pc} \frac{m_c}{M_c} + C_{pw} \frac{m_w}{M_w} + C_{ps} \frac{m_s}{M_s} \right) \cdot \Delta T,$$

Where C_{pc} , C_{pw} , C_{ps} – molecular heat capacities of aluminum (from which made calorimeter), water and investigated salt;

ΔT – changing of temperature;

m_c , m_w , m_s – masses of calorimeter, water and investigated salt.

M_c , M_w , M_s – molar masses of aluminum, water and investigated salt.

Compound	C_{pc}	C_{pw}	C_{ps}	m_c	m_w	m_s
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	24.34	75.31	536	46	50	5

- **list of practical skills:** after studying the subject student should be able to:
 - calculate the heat effect of chemical reaction using the enthalpies of formation or combustion of the reagents and products;
 - use thermochemical calculations for energetic characteristics of biochemical processes;
 - calculate caloricity of food products;
 - use thermodynamic functions for estimation of the processes direction.

8. Tasks for knowledge control

1. What type of thermodynamic system does living organism belong to?

- A. Isolated;
- B. Open;
- C. Closed;
- D. Living organism is not a system.

2. Which one is a mathematical expression of the first law of thermodynamics?

- A. $H = U + pV$;
- B. $Q = \Delta U + A$;
- C. $\Delta S = Q/T$;
- D. $\Delta G = \Delta H - T\Delta S$.

3. Enthalpy is:

- A. Function which characterizes the direction of processes in a system;
- B. Function which characterizes the rate of processes in a system;
- C. Function characterizing the heat content in a system;
- D. Functions characterizing the possibility of processes in a system

Answers: 1 - B; 2 - B; 3 - C.

9. Recommendations for the work results design

Algorithms for solving educational problems of class work and self-work should be recorded in the workbook.

Навчальне видання

Хімічна термодинаміка

**Методичні вказівки для самостійної роботи студентів 1-го курсу
з медичної хімії**

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