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METHODOLOGICAL MANUAL
for conducting the laboratory class with the first-year students
of the Faculty of International Students
studying in the specialty 7-07-0911-01 "Medical business" (FIS)
English-speaking students
in the discipline "Medical chemistry"

Topic 6: **CHEMICAL THERMODYNAMICS AND BIOENERGETICS**

Time: 2 hours

Gomel, 2023

THE TRAINING AND EDUCATIONAL GOALS, MOTIVATION TO STUDY THE TOPIC

The purpose of the class:

1. To familiarize students with how to perform thermodynamic calculations of changes in the most important thermodynamic functions: ΔH, ΔS, ΔG; as well as thermochemical calculations of the heat effects of chemical reactions using the Hess' Law.

2. To teach the use of thermodynamic methods for determining the caloric content of food products and preparing diets.

3. To estimate the possibility of spontaneous running of processes.

The tasks of the class:

As a result of the class, the student *must know:*

1) basic definitions of chemical thermodynamics: energy, heat, work, thermodynamic system and types of systems (isolated, closed, open), thermodynamic parameters, thermodynamic functions (state functions and path functions);

2) formulation of the First Law of Thermodynamics and its mathematical description for all types of systems;

3) the concept of enthalpy, and its physical meaning;

4) the concept of heat effects of chemical reactions, the heats of formation and the heats of combustion of individual substances; Hess' Law as a consequence of the First Law of Thermodynamics;

5) specific enthalpies of the main food components (proteins, fats, carbohydrates), the concept of dietology;

6) the concept of spontaneous and non-spontaneous, reversible and irreversible processes;

7) statements of the Second Law of Thermodynamics; the mathematical description of the Second Law (Clausius' inequality and Boltzmann's equation); the concept of entropy, thermodynamic and statistical interpretations of entropy; calculations of entropy changes for chemical reactions;

8) the concept of Gibbs' Free Energy; the sign of ΔG is a criterion for reactions' spontaneity; methods for calculation of Gibbs' Free Energy change;

9) the concept of bioenergetics; exergonic and endergonic reactions.

The student *must be able to:*

1) make calculations using the First Law and the Second Law of Thermodynamics;

2) make calculations using Hess' Law.

Motivation to study the topic:

Thermodynamics is a branch of physical chemistry that studies the laws of mutual transformations of various types of energy associated with the transfer of energy between systems in the form of heat and work. Chemical thermodynamics is a branch of chemistry that describes the energy changes that occur in the process of chemical reactions, phase changes, formation of solutions. It is the theoretical basis of bioenergetics − the science of energy transformations in living organisms and the specific features of the transformation of some types of energy into others in the process of vital activity.

In a living organism there is a close connection between the processes of metabolism and energy transformation. Metabolism is the source of energy for all life processes. Performing any physiological functions (movement, maintaining a constant body temperature, secreting digestive juices, etc.) requires energy. The source of all types of energy in the body are nutrients (proteins, fats, carbohydrates), the potential chemical energy of which in the process of metabolism is converted into other types of energy. The use of thermodynamic methods makes it possible to quantify the energy of structural transformations of proteins, nucleic acids, lipids.

In the practice of a doctor, thermodynamic methods are most widely used to determine the intensity of metabolism in various physiological and pathological conditions of the body, as well as to determine the calorie content of food products.

NECESSARY EQUIPMENT

1. Methodological manual for students on the topic "Chemical thermodynamics and bioenergetics".

2. Reference materials of physico-chemical constants for the 1st year education international students.

3. Chemical reagents and equipment necessary for laboratory work.

CONTROL QUESTIONS ON THE TOPIC OF THE CLASS

1. Basic terms and definitions.
2. The First Law of Thermodynamics.
3. Thermochemistry.
4. The Second Law of Thermodynamics.
5. Gibbs' Free Energy.
6. Bioenergetics.

COURSE OF THE CLASS

The theoretical part

1. BASIC TERMS AND DEFINITIONS

Chemical thermodynamics is a branch of chemistry that describes the energy changes that occur in the process of chemical reactions, phase changes, formation of solutions.

The tasks of chemical thermodynamics are:

− to determine the heat effects of chemical and physico-chemical processes;

− to establish criteria for spontaneous flow of processes;

− to establish criteria for equilibrium states of thermodynamic systems.

Energy (E, kJ (kcal), 1kcal = 4.184 kJ) can be defined as the capacity to do work or to produce changes.

The main types of energy are:

▪ **potential energy** is the energy that an object has because of the relative positions or orientations of its components;

▪ **kinetic energy** is the energy that an object has due to its motion.

Heat (Q) and **work (A)** are two forms of energy exchange between a system and its surroundings.

Heat (Q) is a measure of the energy that is transferred to or from the system due to temperature differences.

Work (A) is a measure of energy transferred by the orderly movement of particles under the action of some forces. In thermodynamics all types of work except work of gas expansion ($p \times \Delta V$) are assumed to be **useful work (A$'$)**.

The most important types of useful work in a human body are:
− mechanical work of muscles;
− osmotic work of kidneys;
− electrical work of nerve tissue.

Thermodynamic system is a part of Universe separated from its surroundings by a thermodynamics cover (real or abstract). In other words, thermodynamic system is the part of the physical Universe which is under study, while the rest of the Universe is surroundings.
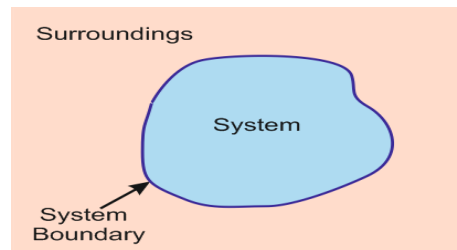

Figure 1 — Thermodynamic system

There are three types of thermodynamic systems:

▪ **isolated** systems are systems which can exchange neither matter nor energy with the surroundings (an ideal Thermos bottle).

In practice perfectly isolated systems cannot exist and they are used as simplified models of real processes.

▪ **closed** systems are systems which can exchange energy but not matter with the surroundings (an ampoule with a drug; a cup of soup with a lid).

▪ **open** systems are systems which can exchange both energy and matter with surroundings (a cup of tea that is open to the air; plants, animals, human beings).
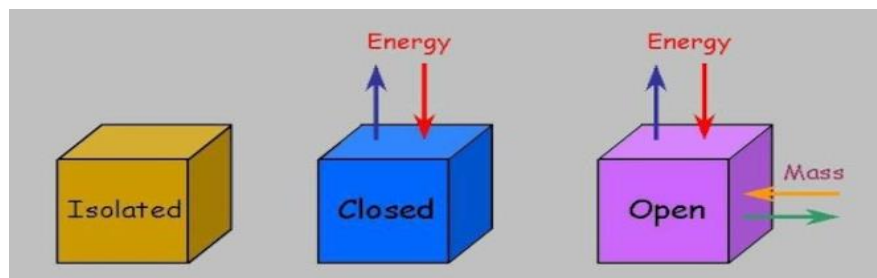

Figure 2 − Types of thermodynamic systems: isolated, closed, open

State of thermodynamic system may be described by:

▪ a set of its **thermodynamic parameters:** temperature, pressure, volume, mass and others;

▪ a set of **thermodynamic functions** which characterize energy of a system and its ability to do work.

Thermodynamic functions are:
▪ state functions;
▪ path functions.

For state functions (path independent): their changes depend only upon initial and final energy states and don't depend upon a number of intermediate steps.

The most important state functions of a system are:

1) Internal Energy (U) – a total energy of a system composed of kinetic and potential energy of all its structural units;

2) Enthalpy (H) – a total heat content of a system available to be converted into heat or work;

3) Gibbs' Free Energy (G) – a part of system's internal energy available to be converted into useful work;

4) Entropy (S) characterizes on one side an energy of a system not available to be transformed into a useful work, and on the other side, disorder in a system.

For path functions (path dependent): their changes depend upon a number of intermediate steps. For example: heat (Q) or work (A).

Any change in the state of the system is a **thermodynamic process.**

A **reversible thermodynamic process** is defined as a process in which the system reverts to its initial state without having caused any changes in its surroundings. If changes do take place in the surroundings, then the process is **irreversible**. Spontaneous processes are irreversible [1-4].

2. THE FIRST LAW OF THERMODYNAMICS

The First Law of Thermodynamics states: **the total energy of the Universe remains constant.** This statement is generally known as the Law of Energy Conservation.

In other words, **energy is neither created nor destroyed in any process, although it may be converted from one form into another or transferred from a system to the surroundings or vice versa.**

The First Law can't be proved theoretically but it was confirmed by all experience of people humanity. For example, *perpetual motion machines of the first kind are impossible.* A perpetual motion machine of the first kind is a machine that performs work without absorbing energy from the surroundings.

Mathematical description for the First Law for 3 types of thermodynamic systems:

1. The internal energy of an **isolated system** is constant: $U = const$, $\Delta U = 0$

2. Heat absorbed by a **closed system** increases its internal energy and is used to do work: $Q = \Delta U + A$ or $Q = \Delta U + A' + p \times \Delta V$

For isobaric processes (p = const) producing no useful work (A' = 0) the equation may be rearranging:

$Q_p = \Delta U + p \times \Delta V = (U_2 - U_1) + p \times (V_2 - V_1) = (U_2 + p \times V_2) - (U_1 + p \times V_1)$;

$U + p \times V = H$;   H is a state function named enthalpy (heat content);

$Q_p = H_2 - H_1 = \Delta H$, ΔH (the enthalpy change) is heat gained or lost by the system under constant pressure.

3. Internal energy of an **open system** is increased by heating and adding some amount of a substance into it: $\Delta U = Q \pm \mu \times \Delta n - A$.

μ − proportionality coefficient named a chemical potential, kJ/mol;

n − chemical amount of substances, mol.

3. THERMOCHEMISTRY

Thermochemistry is a branch of chemical thermodynamics dealing with the heat of chemical reactions.

The heat of a reaction can be defined as the heat change in the transformation of reactants at some temperature and pressure to products at the same temperature and pressure. For an isobaric process, the heat of a reaction is equal to the enthalpy change of the reaction:

$\Delta_r H$ — heat of a reaction, kJ (the subscript r denotes reaction).

$\Delta_r H^0_{298}$ — heat of a reaction under *standard conditions:*

T = 298 K, p = 101.3 kPa, C_M = 1 mol/l, pH = 7.

Thermochemical equations are balanced chemical equations where heat of reactions, physical states of all reactants and products are indicated.

For example, thermochemical equations an endothermic reaction:

$N_2O_4(l) \rightarrow 2NO_2(g)$, $\Delta_r H^0_{298} = + 58{,}4$ kJ   or $N_2O_4(l) \rightarrow 2NO_2(g) - 58{,}4$ kJ
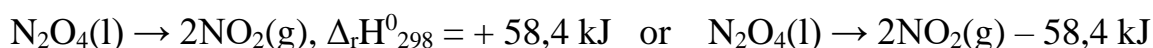
The heat of reactions may be determined experimentally or calculated on the base of the Hess' Law: **the heat of an isobaric chemical reaction does not depend upon a number of intermediate steps but depends upon the energy state of reactants and products.**

Applications of the Hess' Law are calculations of a heat of chemical reactions:

a) using the standard enthalpies of formation (heats of formation) of individual substances;

The standard enthalpy of formation of substance ($\Delta_f H^0_{298}$, kJ/mol) is an amount of heat absorbed or released when 1 mole of the substance is formed from the simple substances at their reference state. The standard enthalpies of formation of simple substances at their stable states is equal zero.

In general, heat of a reaction under standard conditions equals to the sum of the standard enthalpies of formation of the products minus the sum of the standard enthalpies of formation of the reactants taking into account the proper stoichiometric coefficients:

$$\Delta_r H^0_{298} = \sum (m \times \Delta_f H^0_{298(products)}) - \sum (n \times \Delta_f H^0_{298(reactants)})$$

m and n are the proper stoichiometric coefficients in an equation of a reaction;

$\Delta_f H^0_{298}$ − a heat of formation of individual substance, kJ/mol.

Problem 1. Calculate the standard enthalpy (heat of chemical reaction under standard conditions) for the following reaction:

$$Al_2O_3(s) + 3SO_3(g) \rightarrow Al_2(SO_4)_3(s)$$
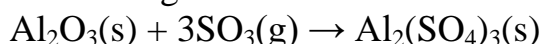
using the standard enthalpies of formation of individual substances:

Substance	State	$\Delta_f H^0_{298}$, kJ/mol
Al_2O_3	s	−1670
SO_3	g	−395
$Al_2(SO_4)_3$	s	−3434

Solution:

$\Delta_r H^0_{298} = \Delta_f H^0_{298}(Al_2(SO_4)_3) - \Delta_f H^0_{298}(Al_2O_3) - 3 \times \Delta_f H^0_{298}(SO_3) =$

$= -3434 - (-1670) - 3 \times (-395) = -579\ kJ. \quad As\ \Delta_r H < 0,\ the\ reaction\ is\ exothermic.$

b) using the standard enthalpies of combustion (heats of combustion) of individual substances.

The standard enthalpy of combustion of a substance ($\Delta_{com}H^0_{298}$, kJ/mol) is an amount of released heat when 1 mole of a substance is oxidized in pure oxygen up to the highest oxide. The standard enthalpies of combustion of the highest oxides and oxygen are defined as zero.

In general, heat of a reaction under standard conditions can be calculated as the total standard enthalpy of reactants' combustion minus the total standard enthalpy of products' combustion:

$$\mathbf{\Delta_r H^0_{298} = \sum (m \times \Delta_{com}H^0_{298(reactants)}) - \sum (n \times \Delta_{com}H^0_{298(products)})}$$

m and n are the proper stoichiometric coefficients in an equation of a reaction;

$\Delta_{com}H^0_{298}$ − a standard heat of combustion of individual substance, kJ/mol.

Problem 2. Calculate the standard enthalpy (heat of chemical reaction under standard conditions) for the following reaction:

$$C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$$

using the standard enthalpies of combustion of individual substances:

Substance	State	$\Delta_{com}H^0_{298}$, kJ/mol
$C_6H_{12}O_6$	s	−2810
C_2H_5OH	l	−1370
CO_2	g	0

Solution:

$\Delta_r H^0_{298} = \Delta_{com}H^0_{298}(C_6H_{12}O_6) - 2 \times \Delta_{com}H^0_{298}(C_2H_5OH) =$
$= (-2810) - 2 \times (-1370) = -70\ kJ. \quad As\ \Delta_r H < 0,\ the\ reaction\ is\ exothermic.$

Thermochemistry is a theoretical base for a **dietology** is the science of rational nutrition. Thermochemical characteristic of food products and their components are discussed in terms of their *specific enthalpy,* the magnitude of the enthalpy of combustion per gram of matter.

Specific enthalpies of the main food components are: for lipids ~ 9 kcal/g (37.6 kJ/g), for proteins, carbohydrates ~ 4 kcal/g (16.7 kJ/g).

The daily energy requirement depends on physical activity, gender and age of a person. Energy requirements are increased by serious diseases of patients. Thus, rheumatoid artrite gives increase in energy requirements up to ~10 %.

Increase in energy of food products and decrease in muscular activity is responsible in obesity [2, 3].

$$Body\ Mass\ Index = mass\ (kg) / height^2\ (m)$$

If BMI > 30 a person suffers on obesity. Obesity increases the risk of developing cardiovascular diseases, cancer, and diabetes.

4. THE SECOND LAW OF THERMODYNAMICS

A large number of processes occurring in the world around us − in nature, technology, etc. − can be divided into two groups:

▪ **non-spontaneous processes** run by absorbing energy from the surroundings. Examples of non-spontaneous processes are: photosynthesis, electrolysis and some others.

▪ **spontaneous processes** proceed without absorbing energy from the surroundings. Examples: the mixing of gases, dissolving, diffusion, osmosis, the neutralization of a strong acid by a strong base, all types of explosion and many other reactions and processes. The spontaneous processes lead to an equilibrium in a system as the final result.

Thermodynamic equilibrium is a state of a system characterized by constant thermodynamic parameters (T, p, V and others) in all the points of its volume. The system in equilibrium state is not able to produce useful work. Equilibrium state is maintained only in isolated and closed systems. It can't be achieved in open systems because of permanently changing outer conditions.

Stationary state of an open system is an analogue for its equilibrium state. Stationary system is characterized by thermodynamic parameters which remain constant for a long period of time with simultaneous ability to produce useful work. The balanced flows of heat and substances inside and outside a system is responsible for stationarity of an open system. All biological systems including human body, are defined as open systems at their stationary state.

A type of a process (spontaneous or nonspontaneous) can be predicted within the Second Law of Thermodynamics.

Statements of the Second Law:

1) Kelvin-Planck's statement: **it is impossible to convert all heat into useful work;**

2) Clausius' statement: **it is impossible for heat to flow from a colder body to a warmer body without any work having been done to accomplish this flow;**

3) Tompson's statement: **a perpetual motion machine of the second type is impossible (it is a heat engine of which efficiency is equal to unity).**

The mathematical description of the Second Law involves a state function named **entropy (S, J/К).** Entropy is defined as heat absorbed by a system, divided by the absolute temperature of the system at the time the heat was absorbed: **S = Q/T.**

Entropy is the only state function which can be defined in two different ways:
▪ thermodynamic;
▪ statistical.

Thermodynamic interpretation of entropy: *entropy is a measure of the heat loss of a system.* In other words, entropy is a measure for «waste energy» which dissipates to the surroundings. The higher the entropy, the lower the efficiency of the process.

The Clausius' inequality is considered to be the mathematical description of the Second Law: **ΔS ≥ Q/T.**

Statistical interpretation of entropy was proposed by the Austrian physicist Boltzmann: *entropy is a measure of disorder or randomness in a system.*
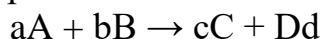
▪ Comparison of entropies: gases > liquids > solids.
▪ Entropy is greater for larger atoms and molecules with larger number of atoms.
▪ More configurations (different geometries), more will be the entropy.

Statistical thermodynamics derives energy state of a system from energy state of its structural units. **Boltzmann's equation** is considered to be another mathematical description of the Second Law: **S = k × lnW**

k − the Boltzmann's coefficient (k = 1.38×10^{-23} J/K); k = R/ N_A
W − thermodynamics probability or a number of microstates a system can be described.

The entropy changes for a hypothetical chemical reaction ($\Delta_r S^0_{298}$, J/K):
$$aA + bB \rightarrow cC + Dd$$
may be calculated using *the standard molar entropies (S^0_{298}, J/mol×K)* of reactants and products:

$$\Delta_r S^0_{298} = c \times S^0_{298} (C) + d \times S^0_{298} (D) - a \times S^0_{298} (A) - b \times S^0_{298} (B)$$

When $\Delta_r S > 0$ a reaction proceeds with increase in disorder;
When $\Delta_r S < 0$ a reaction proceeds with decrease in disorder.

Problem 3. Calculate the standard entropy change for the following chemical reaction: $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
using the standard molar entropies of reactants and products:

Substance	State	S^0_{298}, J/mol×K
$CaCO_3$	s	93
CaO	s	40
CO_2	g	214

Solution:
$\Delta_r S^0_{298} = S^0_{298} (CaO) + S^0_{298} (CO_2) - S^0_{298} (CaCO_3) = 40 + 214 - 93 = 161$ J/K.
As $\Delta_r S > 0$, the reaction proceeds with increase in disorder.

5. GIBBS' FREE ENERGY

The behavior of chemical reactions is influenced by two factors: enthalpic and entropic. The reactions are promoted by a combination of tendencies: decrease in enthalpy (H → min) and increase in entropy (S → max). The total effect of these two opposite tendencies in processes taking place at constant T and p is reflected by a state function **Gibbs' Free Energy** (Gibbs' potential or isobaric-isothermal potential):

$$G = H - T \times S$$

The Gibbs' Free Energy is a measure of the amount of energy available to do work at constant temperature and pressure in thermodynamic system. Since H and S are state functions, so is G. Thus, for any change in state, we can write the extremely important relation:

$$\Delta G = \Delta H - T \times \Delta S$$

G physical sense becomes clear by the combined First and Second Laws of Thermodynamics: $Q = \Delta U + p \times \Delta V + A'$;

$$Q = T \times \Delta S$$

Rearrange this to get:

$A' = T \times \Delta S - \Delta U - p \times \Delta V = T \times \Delta S - (\Delta U + p \times \Delta V)$,   where $\Delta U + p \times \Delta V = \Delta H$

Thus, $A' = - (\Delta H - T \times \Delta S)$,   where $\Delta H - T \times \Delta S = \Delta G$

Hence, $A' = - \Delta G$, ΔG has a sense of a useful work fulfilled by a system or under a system.

The change in Gibbs' Free Energy (ΔG) is a very important parameter: the sign of ΔG (+ or –) is a criterion for reactions' spontaneity:

spontaneous process	$A' > 0$	$\Delta G < 0$
equilibrium state	$A' = 0$	$\Delta G = 0$
nonspontaneous process	$A' < 0$	$\Delta G > 0$

Thus we can make a conclusion that **all spontaneous processes proceed with the decrease of Free Energy of a system** [2, 3].

The methods to calculate Gibbs' Free Energy change:

1) according to the Gibbs' equation:
$$\Delta_r G = \Delta_r H - T \times \Delta_r S,$$
    $T \times \Delta_r S$ − entropy factor of a chemical reaction;

2) according to the Hess' Law using standard Free Energy of formation ($\Delta_f G^0_{298}$, kJ/mol):

$$\Delta_r G^0_{298} = \sum (m \times \Delta_f G^0_{298(products)}) - \sum (n \times \Delta_f G^0_{298(reactants)})$$
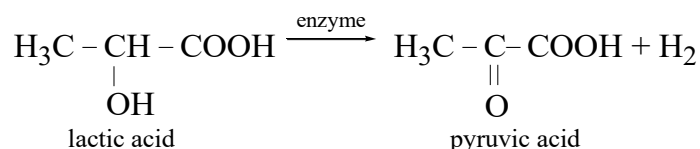
m and n are the proper stoichiometric coefficients in an equation of a reaction;

$\Delta_f G^0_{298}$ − a standard Free Energy of formation is the change of Free Energy during the formation of a substance in its standard state from the simple substances in their standard states.

3) calculation of Free Energy change in the processes of substances transporting against their concentration gradients:

$$\Delta G = - n \times R \times T \times \ln[A]_{ph2}/[A]_{ph1}, \quad \text{where} \quad [A]_{ph2} > [A]_{ph1}$$

Problem 4. Make a conclusion about the possibility of spontaneous course of the chemical reaction at T = 298 K:

$$H_3C - CH - COOH \xrightarrow{\text{enzyme}} H_3C - C - COOH + H_2$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad ||$$
$$\quad\quad\quad OH \quad\quad\quad\quad\quad\quad\quad\quad\quad O$$
$$\quad\quad\text{lactic acid} \quad\quad\quad\quad\quad\quad\quad\text{pyruvic acid}$$

using the following data:

Substance	$\Delta_f H^0_{298}$, kJ/mol	S^0_{298}, J/mol×K
lactic acid ($C_3H_6O_3$)	–673	192
pyruvic acid ($C_3H_4O_3$)	–586	179
H_2	0	130

Solution:

1) $\Delta_r H^0_{298} = \Delta_f H^0_{298}(C_3H_4O_3) - \Delta_f H^0_{298}(C_3H_6O_3) = -586 - (-673) = 87\ kJ;$
   as $\Delta_r H > 0$, the reaction is endothermic;

2) $\Delta_r S^0_{298} = S^0_{298}(C_3H_4O_3) + S^0_{298}(H_2) - S^0_{298}(C_3H_6O_3) =$
   $= 179 + 130 - 192 = 117\ J/K = 0.117\ kJ/K;$
   as $\Delta_r S > 0$, the reaction proceeds with increase in disorder;

3) $\Delta_r G^0_{298} = \Delta_r H^0_{298} - T \times \Delta_r S^0_{298} = 87 - 298 \times (0.117) = 52\ kJ;$
   as $\Delta_r G^0_{298} > 0$, the reaction is nonspontaneous at standard conditions.

Sometimes it is possible to change a character of a reaction by altering thermodynamic parameters of a system: temperature, pressure, concentration of substances. The analysis of Gibbs' equation $\Delta G = \Delta H - T \times \Delta S$ show the effect of temperature on spontaneity of different processes (Table 1).

Table 1 – Temperature effect on ΔG of a reaction

ΔH	ΔS	ΔG	Possibility (impossibility) spontaneous course of the reaction
+	+	±	reaction spontaneous at high temperatures
+	–	+	reaction nonspontaneous at all temperatures
–	+	–	reaction spontaneous at all temperatures
–	–	±	reaction spontaneous at low temperatures

6. BIOENERGETICS

Bioenergetics is thermodynamics of biological systems. It deals with energy, heat and work exchange in plants, animals and human bodies. A human body is an open stationary system. Its main source of energy is chemical energy of food products. Carbohydrates are responsible for 55-60 %, lipids – 20-25 %, and proteins – 15-20 % of energy.

In general efficiency of converting the chemical energy of food into useful work in the human body is ~ 25 %, and its entropy losses are ~ 75 %.
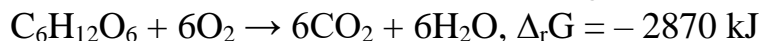
The energy accumulated by a body is used:
1) to do useful work of internal organs and tissues,

2) to fulfill all types of labor activity including migration of a body in space,

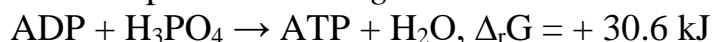3) for heating of atmospheric air, water and food products consumed by a person.

Biochemical reactions are chemical reactions which proceed *in vivo*. They are:

- **exergonic (spontaneous)** $\quad\quad$ **$\Delta_r G < 0$**
- **endergonic (nonspontaneous)** $\quad$ **$\Delta_r G > 0$**

The most important *exergonic reactions* are oxidation reactions of carbohydrates and fats which occur with the release of a large amount of energy:

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O, \Delta_r G = - 2870$ kJ

$C_{15}H_{31}COOH + 23O_2 \rightarrow 16CO_2 + 16H_2O, \ \Delta_r G = - 9790$ kJ

An example of an *endergonic reaction* is ATP synthesis:

$ADP + H_3PO_4 \rightarrow ATP + H_2O, \Delta_r G = + 30.6$ kJ
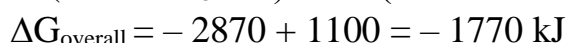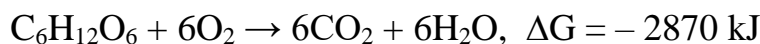
Some biochemical reactions are endergonic but they can be carried out by coupling them with exergonic reactions.

Coupled reactions are reactions, one of which occurs due to the energy released during the other reaction. As a rule, coupled reactions are catalyzed by a common enzyme.

A scheme of a coupled reaction can be represented as follows:

$A + B \rightarrow C + D, \quad\quad\quad\quad \Delta G_1 \ll 0$

$L + M \rightarrow P + Q, \quad\quad\quad\quad \Delta G_2 > 0$

$\Delta G_{overall} = \Delta G_1 + \Delta G_2 < 0$

In cells ATP production is coupled with glucose oxidation. The energy released during the oxidation of 1 glucose molecule is sufficient for the synthesis of 36 ATP molecules.

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O, \ \Delta G = - 2870$ kJ

$36(ADP + H_3PO_4) \rightarrow 36(ATP + H_2O), \quad \Delta G = + 1100$ kJ

$\Delta G_{overall} = - 2870 + 1100 = - 1770$ kJ

Although 1100 kJ of energy is stored in this coupled process, 1770 kJ of energy is «wasted». Efficiency of the process is: efficiency = 1100/2870 = 0.38 (38 %). The remaining 62 % of energy is dissipated as heat [2].

Control over the assimilation of the topic

It is conducted in the form of written independent work of students.

QUESTIONS FOR SELF-CONTROL OF KNOWLEDGE

1. Thermodynamic systems and types of systems (isolated, closed, open). Energy, heat, work. The internal energy of system. Thermodynamic parameters and thermodynamic functions (state functions and path functions).

2. The First Law of thermodynamics and its mathematical description for all types of systems. Enthalpy.

3. Thermochemistry. Heat effects of chemical reactions. Hess' Law as a consequence of the First Law of thermodynamics. Heats of formation of individual substances. Standard heats of formation. Heats of combustion of individual substances. Standard heats of combustion.

4. Thermochemistry as the basis of dietology. Specific enthalpies of the main food components (proteins, fats, carbohydrates). Daily requirements in energy of a person. Diseases associated with eating disorders.

5. Characteristics of processes: spontaneous and non-spontaneous; reversible and irreversible. The Second Law of thermodynamics: formulations and its mathematical description (Clausius' inequality and Boltzmann's equation). Entropy. Thermodynamic and statistical interpretation of entropy.

6. Gibbs' Free Energy. Gibbs' Free Energy change as a criterion of equilibrium and the possibility of spontaneous processes in isobaric-isothermal conditions. Methods for calculation the change in Gibbs' Free Energy. The concept of bioenergetics; exergonic and endergonic reactions.

Exercises for the self – control

1. Specify which processes are exothermic and which are endothermic:
a) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$, $\Delta_r H = -891$ kJ
b) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g) + 185$ kJ
c) $N_2(g) + O_2(g) \rightarrow 2NO(g)$, $\Delta_r H = 180.5$ kJ
d) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g) - 178$ kJ
e) $H_2(g) + I_2(s) \rightarrow 2HI(g)$, $\Delta_r H = 52.2$ kJ
f) $2NO(g) \rightarrow N_2(g) + O_2(g)$, $\Delta_r H = -180.5$ kJ

2. Calculate the heat of chemical reaction under standard conditions for the reaction of obtaining ethyl ether of aminobenzoic acid (a semi-product in the preparation of anesthesine) in accordance with the following reaction:
$4C_2H_5OCOC_6H_4NO_2(l) + 9Fe(s) + 4H_2O(l) \rightarrow 4C_2H_5OCOC_6H_4NH_2(l) + 3Fe_3O_4(s)$,
using the standard heats of formation of individual substances:

Substance	State	$\Delta_f H^0_{298}$, kJ/mol
$C_2H_5OCOC_6H_4NO_2$	l	–463.2
H_2O	l	–273.2
$C_2H_5OCOC_6H_4NH_2$	l	–1759.0
Fe_3O_4	s	–1068.0

Answer: –7294.4 кJ

3. Without making calculations, specify the sign $\Delta_r S$ in the following processes:
a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$
b) $H_2O(l) \rightarrow H_2O(g)$
c) $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$
d) $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$
e) $2CH_3OH(g) + 3O_2(g) \rightarrow 4H_2O(g) + 2CO_2(g)$

4. Without making calculations, specify whether the processes can occur spontaneously and under what conditions:
a) $2N_2(g) + O_2(g) \rightarrow 2N_2O(g)$, $\Delta_r H > 0$
b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta_r H < 0$
c) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, $\Delta_r H > 0$
d) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$, $\Delta_r H < 0$

5. Calculate $\Delta_r G^0_{298}$ for the following reaction: $CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$ using the following data:

Substance	$\Delta_f H^0_{298}$, kJ/mol	S^0_{298}, J/mol×K
CO(g)	−110.5	197.4
H$_2$(g)	0	130.6
CH$_3$OH(l)	−238.7	126.7

Can this reaction proceed spontaneously under standard conditions?

Answer: −29.29 kJ; the reaction is spontaneous under standard conditions

QUESTIONS FOR INDEPENDENT WORK OF STUDENTS (IWS)

1. The concept of chemical equilibrium. Equilibrium constant and ways of its expressing (K_c, K_p, K_{sp}, K_{ins}, K_a, K_b, K_w) in specific types of reactions.

2. Factors that affect chemical equilibrium: concentration, temperature, and pressure. Le Chatelier's Principle.

3. The equation of the isotherm of a chemical reaction used for the thermodynamic description of a reversible process.

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2. Основы химии для иностранных студентов = Essential chemistry for foreign students : учебно-методическое пособие / С. В. Ткачёв [и др.]. – 5-е изд. – Минск : БГМУ, 2018. – С. 34-58. – Режим доступа: http://rep.bsmu.by:8080/handle/BSMU/21054

3. Филиппова, В. А. Общая химия : учеб. пособие для студентов лечеб. факта, обуч. на англ. яз. : в 2 ч. = General Chemistry : Educational guaidance for students medical department in English medium / В. А. Филиппова, А. В. Лысенкова, Л. В. Чернышева. – Гомель : ГомГМУ, 2009. – Ч. 1. – 192 с. URI: https://elib.gsmu.by/handle/GomSMU/2679

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