Subject 8. Thermodynamic basics of biochemical processes

1. Importance

Bioenergetics studies transformations of energy in the organism. The chemical energy of food products is the main source of energy for the organism. It is used in the internal processes: respiration, blood circulation, metabolism, secretion, temperature control, as well in doing external work. Chemical thermodynamics is the theoretical base for bioenergetics despite lots of specific characteristics of energy metabolism in the organism. Thermochemistry renders it possible to measure energy values of food products, which is important in nutritiology. Laws and methods of thermochemistry are used to study heat effects of biochemical reactions.

Competencies of learning that are promoted by study subject.

Capacity for abstract thinking, analysis and synthesis, capacity to learn.
Ability to apply knowledge in practical situations.
Ability to communicate in native language both orally and in writing.
Ability to choose strategy of communication; ability to work in a team; skills of interpersonal interaction.
Ability to exercise self-control and healthy life style, adaptability and ability to perform in a new situation.
Confidence and persistence on tasks.
Ability to use information and communication technologies.
Ability to assess and ensure the quality of work.
Motivation to preserve the environment.
Ability to solve common problems and practical problems in the learning process.
Ability to interpret chemical and biochemical processes from the standpoint of their thermal effects.

2. Concrete aims

Explain heat effects of chemical and biochemical processes.

Be able to use thermodynamical functions for evaluation of directions of processes, explain energy coupling in living systems.

Be able to perform thermochemical calculations.

3. Basic knowledge, skills necessary for studying the subject (interdisciplinary integration)

Previous subjects	Obtained skills

1. Chemistry and Physics (school course)	- Have an understanding of endo- and exothermic reactions.
2. Medical and Biological Physics	- Understand thermodynamics of open biomedical systems. - Have an understanding of importance of thermodynamics for environmental protection.
3. Medical Biology	- Be able to describe macroergic bonds. - Have an understanding of macroergic compounds.
4. Ukrainian language for professional purposes	- Possess knowledge of the native language. - Be able to communicate in native language both orally and in writing.
5. Safety, basics of bioethics and biosafety	- Strive to protect the environment.

4. Tasks for independent work during preparation for the class and in class.

4.1. The list of key terms, parameters, characteristics which the student is to learn while preparing for classes:

Term	Definition
1. Chemical thermodynamics	A branch of physical chemistry that studies transformations of various forms of energy in chemical processes.
2. Thermodynamic system	A body or several interacting bodies that are separated from the environment with a real or imaginary boundary. Types of systems: isolated, open, closed.
3. The First Law of thermodynamics	1) In an isolated system the sum of all forms of energy is constant. 2) It is impossible to create a perpetual motion machine of the first kind that does work without using energy. 3) Various forms of energy are transformed into each other in equivalent proportions. 4) Energy does not disappear or be created.
4. Hess Law	The heat effect of a reaction is independent of the path of the reaction, and is only determined by the initial and final states of the system
5. The Second Law of Thermodynamics	1) It is impossible to build a perpetual motion machine of the second kind that completely transforms heat into work.

	2) It is impossible to transfer heat from a cold body to a hot body, without doing work
6. Gibbs equation	$\Delta G = \Delta H - T\Delta S$
7. Macroergic compounds	Oxidation of carbohydrates, fats and proteins in the body releases energy that accumulates in macroergic compounds rich in energy. - ATP - adenosine triphosphate - ADP – adenosine diphosphate - phosphoenolpyruvate - creatine - acetyl-CoA

4.2. Theoretical questions to the lesson:

1. Chemical thermodynamics as a science. Basic ideas:
   - thermodynamic systems and their types;
   - parameters of the state of the system (extensive, intensive);
   - processes (reversible, irreversible).
2. The First Law of Thermodynamics. Internal energy.
3. Enthalpy. Standard enthalpies (heats) of formation and combustion.
4. Thermochemistry. Hess' Law. Thermochemical transformations.
5. Thermochemical calculations and their applications for energy characteristics of biochemical processes.
6. The Second Law of Thermodynamics.
7. Entropy and its change in spontaneous processes.
8. The Gibbs energy and its change as the criteria of the spontaneous process.
9. Macroergic compounds. ATP as the universal source of energy for biochemical processes. Properties of macroergic bonds.
10. Enery conjugation in living systems: exergonic and endergonic processes in the organism.

4.3. Practical work (task) done by students in class

1. Calculate the possibility of a spontaneous process at $T^o = 298$ K, if $\Delta H^o = 300$ kJ, $\Delta S^o = 26$ J/K.
2. Calculate the energy value of 200 g margarine that contains 0.3% protein, 82.3% fat and 1% carbohydrate, if 1 g protein or 1 g carbohydrate releases 17.18 kJ in the organism, and 1 g fat releases 38.97 kJ.

3. Calculate the amount of heat that is released in the reaction:
$C_{(s)} + 2N_2O_{(g)} = CO_{2(g)} + 2N_{2(g)}$, if the mass of N_2O is 22 g, and enthalpies of formation are: $\Delta H^0_{\text{formation}}(N_2O_{(g)}) = 81.55$ kJ/mol, $\Delta H^0_{\text{formation}}(CO_{2(g)}) = -393.51$ kJ/mol:

a) 475.1 kJ; b) 139.2 kJ; c) 278.3 kJ; d) 556.61 kJ.

Contents of the subject:

Chemical thermodynamics as a science. Concepts:

- Thermodynamic systems and their types;
- Parameters of systems (extensive, intensive);
- Processes (reversible, irreversible).

Chemical thermodynamics is a branch of physical chemistry that studies transformations of various forms of energy in chemical processes.

Thermodynamic system is a body or several interacting bodies that are separated from the environment with a real or imaginary boundary.

Types of systems: isolated, open, closed.

Isolated system is a system that exchanges neither matter or energy with the environment.

Closed system exchanges energy with the environment and does not exchange matter.

Open system exchanges both energy and matter with the environment.

Parameters of systems:

a) **extensive** that depend on the size of the system (volume, mass, heat capacity).

b) **intensive** that do not depend on the size of the system (temperature, pressure, concentration, potential)

Reversible and irreversible processes:

Transition of a system from one state to another is called a process. The processes that can proceed in forward and reverse directions through the same intermediate stages without any change in the system and in the environment are called reversible.

If during the course of the process changes in the system or its environment occur the process is called irreversible.

2. The First Law of Thermodynamics. Internal energy.

The First Law of Thermodynamics

1) In an isolated system the sum of all forms of energy is constant.
2) It is impossible to create a perpetual motion machine of the first kind that does work without using energy.
3) Various forms of energy are transformed into each other in equivalent proportions.
4) Energy does not disappear or be created.

Mathematical equation of The First Law of Thermodynamics:

$$\mathbf{Q = \Delta U + A}$$

Q – amount of heat,

ΔU – change of internal energy,

A – work.

Internal energy is the total energy that consists of the kinetic energy of motion of its components (molecules, atoms, ions) and the potential energy of their interaction, without the kinetic and potential energy of the system as a whole.

3. Enthalpy. Standard heats (entalpies) of formation and combustion of substances.

Enthalpy is the energy of a system at constant pressure. It is numerically equal to the amount of internal energy and the product of the volume of the system and external pressure. $H = U + pV$

Standard heat (enthalpy) of formation is the heat of a reaction of formation of one mole of a complex substance from simple substances at standard conditions.

Standard heat (enthalpy) of combustion is the heat of a reaction of combustion of one mole of a substance in oxygen with a formation of a stable higher oxide.

4. Thermochemistry. Hess Law. Thermochemical transformations.

Thermochemistry is the branch of chemistry that studies heat effect of reactions.

Hess Law:

The heat effect of a reaction is independent of the path of the reaction, and is only determined by the initial and final states of the system.

Thermochemical equations are equations of chemical reactions, where enthalpies and aggregative states of products and reactants are indicated.

5. Thermochemical calculations and their applications for energy characteristics of biochemical processes.

Consequences of the Hess Law are important in thermochemical calculations.

Consequences of the Hess Law

1. Heat effect of the forward reaction is equal to heat effect of the reverse reaction with an opposite sign.

2. Heat effect of a reaction of formation is equal to the difference of sums of enthalpies of formation of the products and reactants.

3. Heat effect of a reaction of combustion is equal to the difference of sums of enthalpies of combustion of the products and reactants in the reaction.

6. The Second Law of Thermodynamics.

The Second Law of Thermodynamics:

1) It is impossible to build a perpetual motion machine of the second kind that completely transforms heat into work.
2) It is impossible to transfer heat from a cold body to a hot body, without doing work.

7. Entropy and its change in a spontaneous process.

Entropy is the measure of disorder in a system. A greater disorder means greater entropy.

Entropy increases spontaneously in isolated systems.

Factors that effect entropy:

- aggregative state,
- mass of particles in the substance,
- density,
- dispersion,
- temperature,
- pressure.

8. Gibbs energy and its change as the criterion of a spontaneous process.

Both the enthalpy factor and entropy factor effect a chemical process.

Gibbs energy is the total effect of the enthalpy factor and entropy factor.

Gibbs equation: $\Delta G = \Delta H - T\Delta S$

where ΔG – Gibbs free energy, kJ/mol;

ΔH – enthalpy (heat that is released or absorbed in the reaction);

ΔS – entropy (a measure of disorder of the system);

$T\Delta S$ – bound energy that cannot be used to do work.

A process is spontaneous if $\mathbf{\Delta G < 0.}$

9. Macroergic compounds. ATP as the universal source of energy for biochemical reactions. Characteristics of macroergic bonds.

Oxidation of carbohydrates, lipids and proteins releases energy. The energy is stored in energy-rich **macroergic compounds**.

- ATP – adenosine triphosphate
- ADP – adenosine diphosphate
- Phosphoenolpyruvate
- Creatine phosphate
- Acetyl CoA

ATP is the universal source of energy for the biochemical reactions:

- synthesis of nucleic acids;
- synthesis of lipids;
- synthesis of cholesterol;
- synthesis of glucose;
- active transport of substances through the cell membrane;
- muscle contraction.

10. Energy conjugations in living systems: exergonic and endergonic processes in the organism.

Biochemical reactions that proceed with a decrease of Gibbs energy ($\Delta G_{reaction} < 0$) are spontaneous, i.e. **exergonic**.

If ΔG is positive ($\Delta G_{reaction} > 0$), the reaction only proceeds upon absorption of external energy and is **endergonic**.

Materials for self control:

A. Tasks for self control:

1. What reactions are exergonic (catabolic) and endergonic (anabolic) in biochemistry as indicated by the free energy change (ΔG) in isobaric-isothermic processes?

2. When a reaction is endothermal:

a) when the energy of products is equal to the energy of initial substances;

b) when the energy of products is higher than the energy of initial substances;

c) when the energy of products is lower than the energy of initial substances;

d) it is possible to determine only when it is known whether energy is absorbed or released.

3. Choose exothermal reactions:

a) $O_2 + 1/2O_2 = O_3$, $\Delta H = 142$ kJ;

b) $1/2O_2 + H_2 = H_2O$, $\Delta H = -242$ kJ;
c) $H_2O + 1/2O_2 = H_2O_2$, $\Delta H = 98.2$ kJ;
d) $H_2 + 1/2O_2 = H_2O$, $\Delta H = -285.8$ kJ.

3. Choose the substance with zero standard enthalpy of formation:
a) Br_2 (g); b) Br_2 (l); c) Br_2 (s); d) HBr (g).

4. What is the subject of bioenergetics?
a) transformation of different types of energy in the organism;
b) transformation of energy of nutrients into muscle work;
c) transformation of one type of energy into another;
d) transformation of heat in the organism.

5. Which is the equation of the First Law of Thermodynamics:
a) $Q = \Delta U + A$;
b) $Q = \Delta U - A$;
c) $\Delta U = Q - A$;
d) $\Delta U = Q + A$.

B. Calculation tasks for self control:

1. Under certain conditions, 120 g carbon is oxidized to carbon monoxide. The reaction produces 1105 kJ of heat. Write a thermochemical equation of the reaction.

2. For the thermochemical equation of combustion of carbon monoxide

$2CO\ (g) + O_2\ (g) = 2CO_2\ (g)$, $\Delta H = -566$ kJ.

calculate the amount of heat produced at combusion of:
a) 4 mol carbon monoxide;
b) 4 g carbon monoxide;
c) 4 L (STP) carbon monoxide.

3. Decide about the changes of enthalpy and entropy at which the reaction is spontaneous at any temperature.

a) $\Delta H>0$, $\Delta S>0$; b) $\Delta H<0$, $\Delta S<0$; c) $\Delta H>0$, $\Delta S<0$; d) $\Delta H<0$, $\Delta S>0$

Literature

Main:

1. Medical Chemistry: textbook / V.O. Kalibabchuk, V.I. Halynska, V.I. Hryshchenko et al.; edited by Prof. V.O. Kalibabchuk – Kyiv: "Medicine", 2010 – 224 p. (P. 24 – 36).

Informational resources:

2. www. pdmu, edu.ua
https://med-chemistry.pdmu.edu.ua/

(Web page of Poltava State Medical University).