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# *Thermodynamics*

# Plan

1. Basic terms and concepts.
2. The first law of thermodynamics.
3. Enthalpy.
4. Thermochemical equations.  
Thermochemistry.
5. Caloric content of food. Calorimetry.
6. Entropy.
7. Second law of thermodynamics.
8. Free energy of system and free energy changes. Gibbs's energy.
9. Criterion of a spontaneity of chemical processes.

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# **Basic terms and** **concepts**

# THE SUBJECT OF THERMODYNAMICS

- ***Energy*** is the capacity of a physical system to perform work. Energy exists in several forms such as heat, kinetic or mechanical energy, light, potential energy, electrical, or other forms.

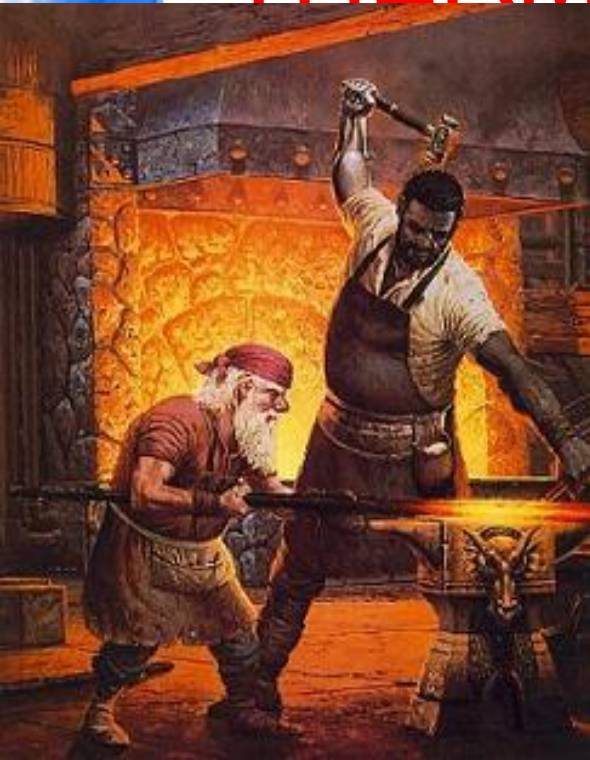
# THE SUBJECT OF THERMODYNAMICS

**Thermal energy** - form of energy associated with the motion of atoms, molecules or other particles from which the body is composed.

**Thermal energy** - is the total kinetic energy of the structural elements of the substance.

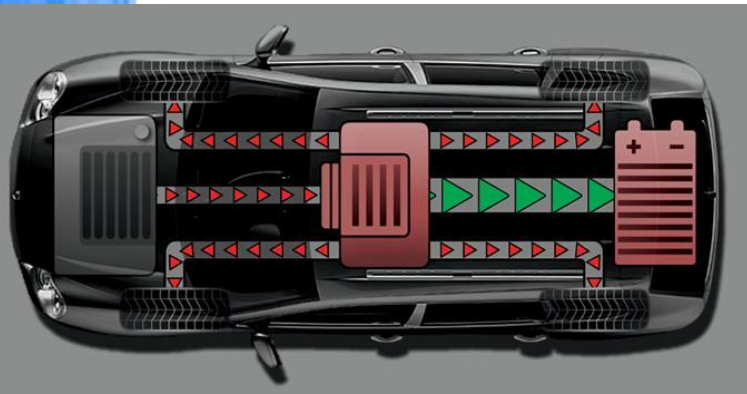


# THE SUBJECT OF THERMODYNAMICS



**Mechanical energy** can be converted into thermal energy and back.

*The conversion of mechanical energy into thermal energy and back is accomplished always strictly equivalent amounts.*



This is the essence of the first law of thermodynamics.

- **Work** is done when a force applied to some object moves the object. For example, lifting a heavy box is work.
- **Work** is the product of force and displacement.
- $A = Fx$

**A force** is that which causes a change in the motion of a body that is free to move.

- **Heat** ( $Q$ ) describes energy in transit from a warmer body to a cooler body.
- The **internal energy** ( $U$ ) of a substance is total energy the parts forming the substance.
- It consist of the **kinetic** and **potential** energies of the particles.
- The **kinetic** energy is energy of motion, objects in motion.
- The **potential** energy is stored energy. It is due to forces of attraction and repulsion acting between the particles.



- Generally in chemistry is not required to know the absolute value of ***internal energy*** . Most important to know value of change of ***internal energy*** in chemical processes.
- If the internal energy of a system of a system in the initial state is  $U_1$  and in the final state  $U_2$ , then the change of internal energy  $\Delta U$  may be given by:
  - $\Delta U = U_2 - U_1$
  - Similarly in chemical reaction,  $U_r$  is the internal energy of the reactants and  $U_p$  is the internal energy of products, then the change of internal energy  $\Delta U$ :
  - $\Delta U = U_p - U_r$

# *Thermodynamics*

**Thermodynamics** is the branch of physical science that studies all forms of energy and their mutual transformations.

Thermodynamics studies:

1) energy transitions from one form to another, from one part to another system;

2) energy effects accompanying the various processes and their dependence on the process conditions;

3) opportunity, direction and limits the flow of spontaneous flow of the processes themselves.

- **Chemical thermodynamics** is the study of the interrelation of heat and work with chemical reactions within the confines of the laws of thermodynamics.

## **Thermodynamics allows you to:**

**1) calculate the thermal effects of different processes;**

**2) predict whether the process is possible;**

**3) specify the conditions under which it will occur;**

**4) consider the conditions of chemical and phase equilibria;**

**5) form an idea of the energy balance of the body**

# Terms and concepts

**System** - a collection of physical objects , separated from the environment.

**Environment** - the rest of the space.

- **Isolated system** is a system which neither can exchange mass nor energy with the surrounding.
- **Closed system** is a system which can exchange energy but not mass with surroundings.
- **Open system** is a system which can exchange matter as well as energy with the surroundings.

**Homogeneous system** - all of the components are in a single phase and no interfaces ,

**Heterogeneous system** - consisting of several phases.

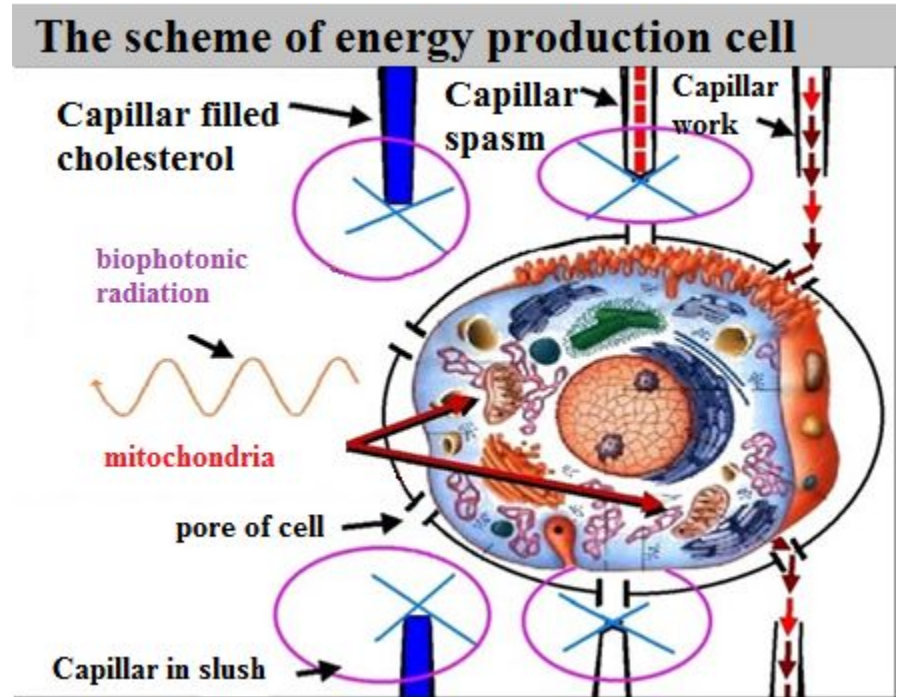
**Phase** - the part of the system with the same chemical and thermodynamic properties , separated by the interface .

**Energy** - a quantitative measure of a certain kind of motion.

# *Application of thermodynamics to biological matter*

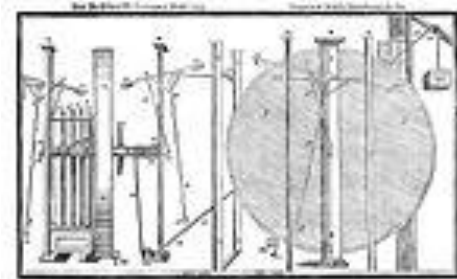
**Bioenergy** - section thermodynamics studying biosystems.

**Bioenergy** - section of biochemistry, studying energetic processes in the cell.





# Thermochemistry



**Thermochemistry** - is a branch of chemistry that studies the effects of thermal and chemical processes.

**Isobaric processes** - are under constant pressure ( $p = \text{const}$ ).

**Isochoric processes** called passing at constant volume ( $V = \text{const}$ ).

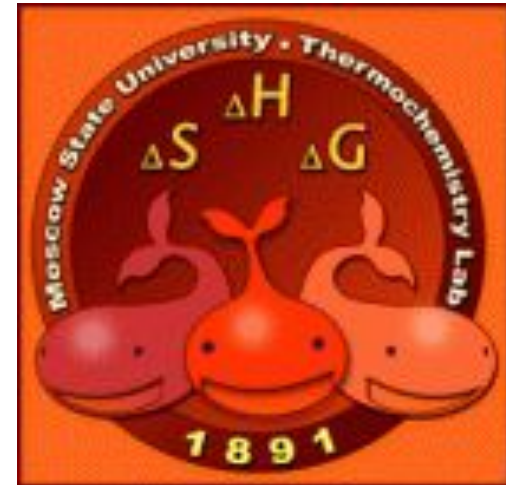
**Isothermal processes** is an area under constant temperature ( $T = \text{const}$ ).

## Thermodynamic parameters: extensive and intensive.

If the system changes its parameters, then it takes a thermodynamic process.

**Thermodynamic functions of condition** - functions depending on the state of the system and not by the way and the manner in which this state is reached.  
This is:

- internal energy (U),
- enthalpy (H),
- entropy (S)
- Gibbs free energy (G)
- Helmholtz free energy (F)



## *Types of processes*

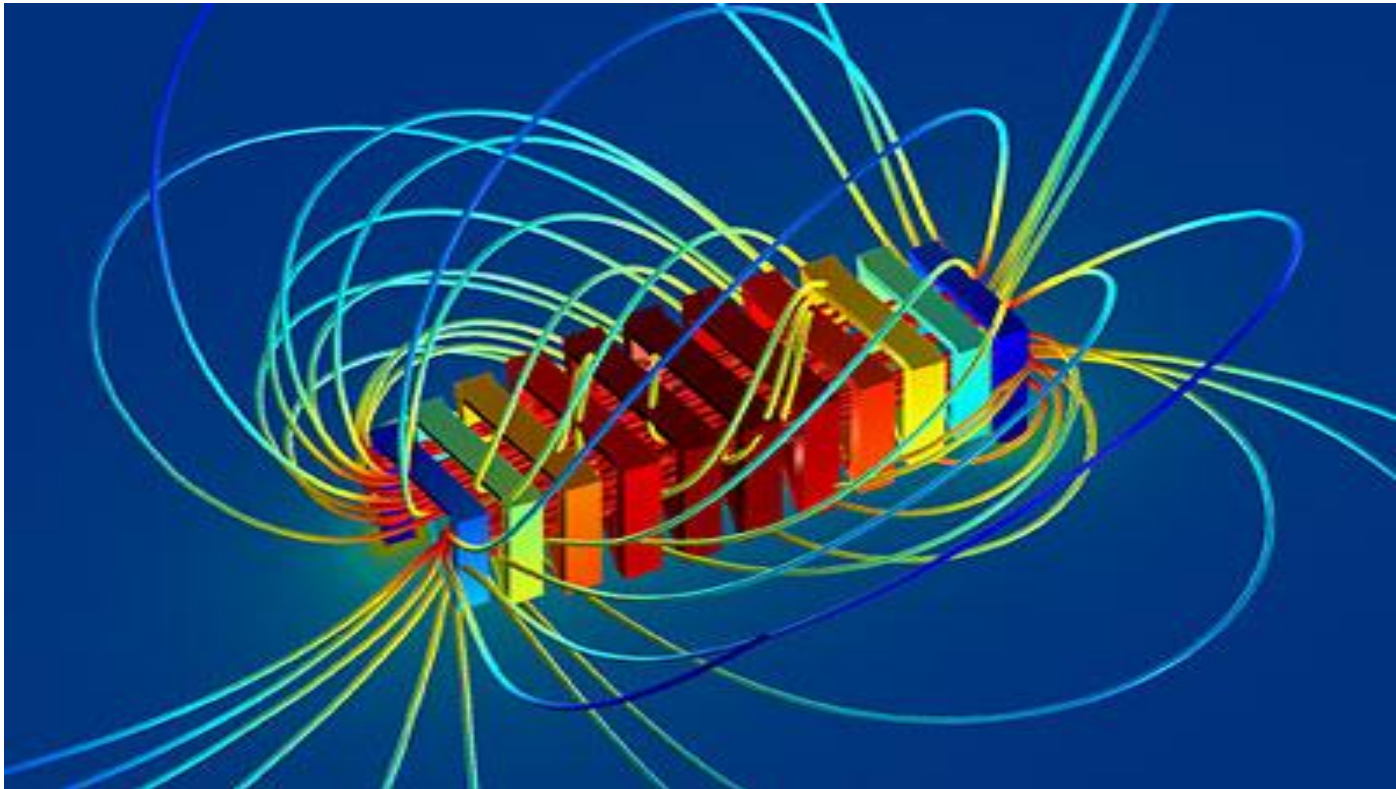
- ***Isothermal process*** is a process in which temperature remains constant.
- ***Isobaric process*** is a process in which pressure remains constant.
- ***Isochoric process*** is a process in which volume remains constant.



- ***Reversible process*** is a process that can be reversed by means of infinitesimal changes in some property of the system without loss or dissipation of energy, and can be reversed without causing change in the surroundings. The infinitesimal changes can be in temperature, pressure, etc.
- ***Irreversible process is*** a process which is not reversible.
- ***Spontaneous process*** is a process, which under particular conditions occurs by itself without extraneous source of energy.

# Zero law of thermodynamics

*If each of the two thermodynamic system is in thermal equilibrium with a third, they are in thermal equilibrium with each other.*



# ***1st law of thermodynamics***



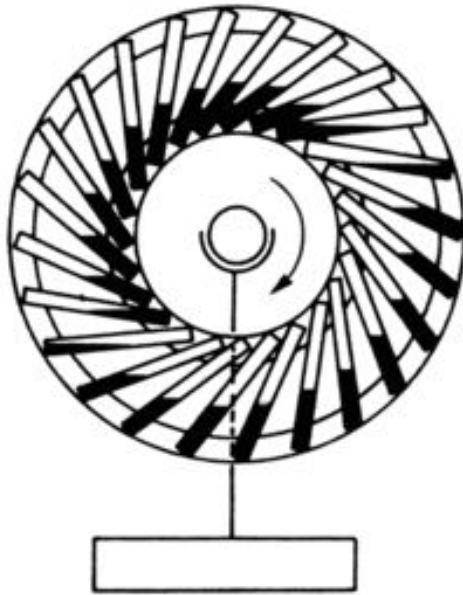
**1st law of thermodynamics - is the law of conservation of energy. It was first formulated by Lomonosov (1744g.) then confirmed the work of Hess (1836), Joule (1840), Helmholtz (1847).**

***The wording of the 1st law of thermodynamics:***

**I. Energy can not be created nor disappears, and converted from one form to another, without changing quantitatively.**

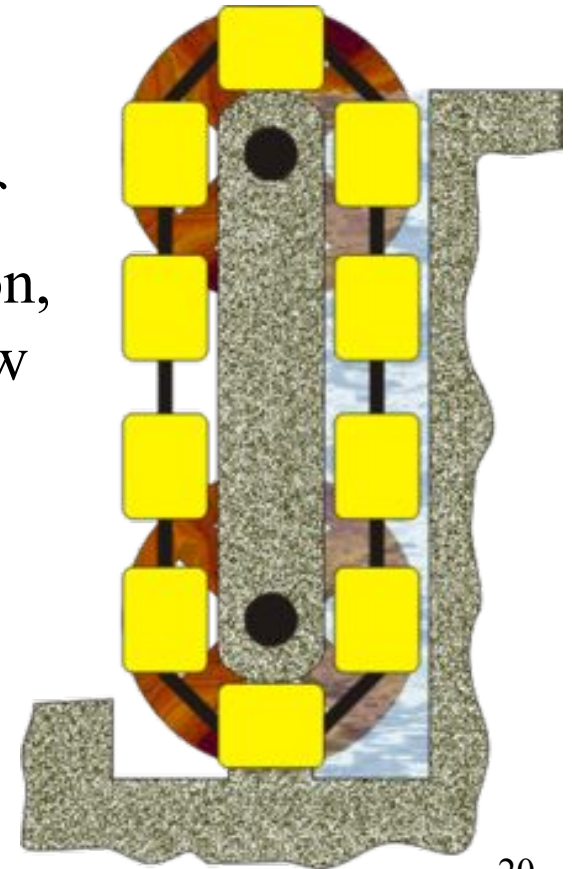
# *1st law of thermodynamics*

**II. Unable to create perpetum-mobile, or of the first kind, i.e. get the job done without wasting energy.**



Indian or Arabic perpetual motion with little obliquely fixed vessels partially filled with mercury

Construction of perpetual motion, based on the law of Archimedes



# ***1st law of thermodynamics***

**III. The heat supplied to the system (or leased by it) is spent on changing the internal energy of the system and commission work.**

$$**Q = \Delta U + A**$$

**where Q – amount of heat,  $\Delta U$  - the change in internal energy of the system, A - work.**

**The internal energy U - is the total energy of the system, which consists of the energy of motion of molecules, atoms, energy relations, etc.**

# ***1st law of thermodynamics***

**IV. Increase the internal energy of the system is equal to the heat that the system receives from the outside, except for the work that has made the system against external forces.**

**This is another formulation of the I-th law of thermodynamics.**

# 1st law of thermodynamics

$$A = p \Delta V$$

For isochoric process:

$$A=0 \quad \text{and} \quad Q_v = U_2 - U_1 = \Delta U$$

For isobaric:

$$Q_p = \Delta U + p\Delta V$$

$$\text{or } Q_p = (U_2 - U_1) + p(V_2 - V_1)$$

$$\text{or } Q_p = (U_2 + pV_2) - (U_1 + pV_1)$$

$$U + pV = H \text{ (enthalpy)}$$

$$\text{in this way } Q_p = H_2 - H_1 = \Delta H$$

heat content of the system

**$+\Delta H$**  - corresponds to the absorption system heat

**$-\Delta H$**  – heat release system

- In an isochoric process the ***heat of a reaction*** is equal to external energy change  $\Delta U$ :
- $Q_v = \Delta U$
- In isobaric process the ***heat*** is equal to a change of system's enthalpy  $\Delta H$ :
- $Q_p = \Delta H$



The positive value of ***enthalpy change*** ( $\Delta H > 0$ ) corresponds to enthalpy increase or to heat adsorbtion by a system (***an endothermic process***). The negative value of enthalpy change ( $\Delta H < 0$ ) corresponds to enthalpy decrease or to heate release by a system (***an exothermic process***).

# Nature of the thermal effects of chemical reactions. Thermochemical equations.

**Thermal effect of chemical reactions** - is the amount of heat that is absorbed or released during the reaction is related to the number of moles.

**The standard heat of reaction** is called a  $\Delta H_0$  effect which occurs under standard conditions

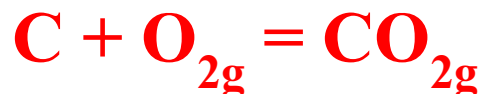
$p=101,3 \text{ kPa}$ ,  $T=298\text{K}$ ,  $(x) = \text{mole}$ .

**Heat of formation of a substance** is the heat of reaction is the formation of one mole of complex substances from simple:



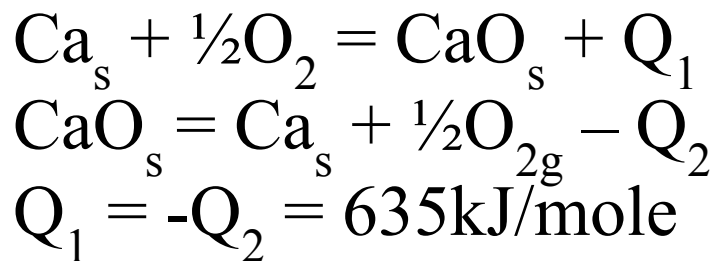
## Nature of the thermal effects of chemical reactions. Thermochemical equations.

*Enthalpy of combustion* is called the thermal effect of the reaction of one mole of a substance with oxygen to form stable higher oxides:



In 1780 the law was formulated **Lavoisier-Laplace** :

**Thermal effect on the decomposition of complex compound simple numerically equal to the thermal effect of the formation of this substance from simple substances with the opposite law.**

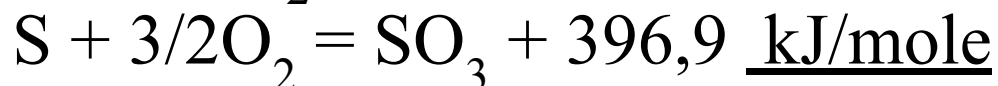
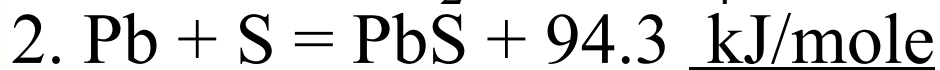


# Hess's Law

In 1840 N.G. Hess formulated the law of constancy of the sum of heat:

*The heat of reaction is independent of the transition reaction, but only on the initial and final state of the system.*

For example:  $\text{PbSO}_4$  can be obtained in different ways:



# Hess's Law

Thermal effects in thermochemical reactions are calculated using the consequences of the law of Hess.

**I consequence: the heat of reaction is the difference between the sum of the heats of formation of the reaction products and the sum of the heats of formation of the starting materials, combined with the corresponding stoichiometric coefficients.**

$$\Delta H_{\text{reaction}} = \sum n_i \Delta H^{\circ}_{\text{prod.}} - \sum n_i \Delta h^{\circ}_{\text{start.}}$$

# Hess's Law

**II consequence:** the heat of reaction is the difference between the sum of the heats of combustion of the starting materials and the amount of combustion heat of reaction products taken into account with the stoichiometric coefficients of the reaction:

$$\Delta H_{\text{reaction}} = \sum n_i \Delta H^{\circ} \text{comb.}_{\text{start.sub.}} - \sum n_i \Delta H^{\circ} \text{comb.}_{\text{prod.react..}}$$

For example, for the reaction :



$$\Delta H = (g\Delta H^{\circ} C + p\Delta H^{\circ} D) - (n\Delta H^{\circ} A + m\Delta H^{\circ} B)$$

$$\Delta H = (n\Delta H^{\circ}_{\text{comb}} A + m\Delta H^{\circ}_{\text{comb}} B) - (g\Delta H^{\circ}_{\text{comb}} C + p\Delta H^{\circ}_{\text{comb}} D)$$

# Hess's Law

**III consequence: The thermal effect of the forward reaction is equal to the thermal effect of the reverse reaction with the opposite sign:**

$$\Delta H_{\text{pr.}} = - \Delta H$$

In thermochemical equations indicate the state of matter:



# Research of thermochemical calculations for the energy performance of biochemical processes

Attached to the living organism the energy conservation law can be formulated as :

The quantity of heat  $Q$  liberated in an organism during food digestion is spent to compensate for heat loss  $q$  into the surroundings and work  $A$  performed by organism, i.e. , i.e.

$$Q = q + A$$



# The human requirement for energy during the 24 h

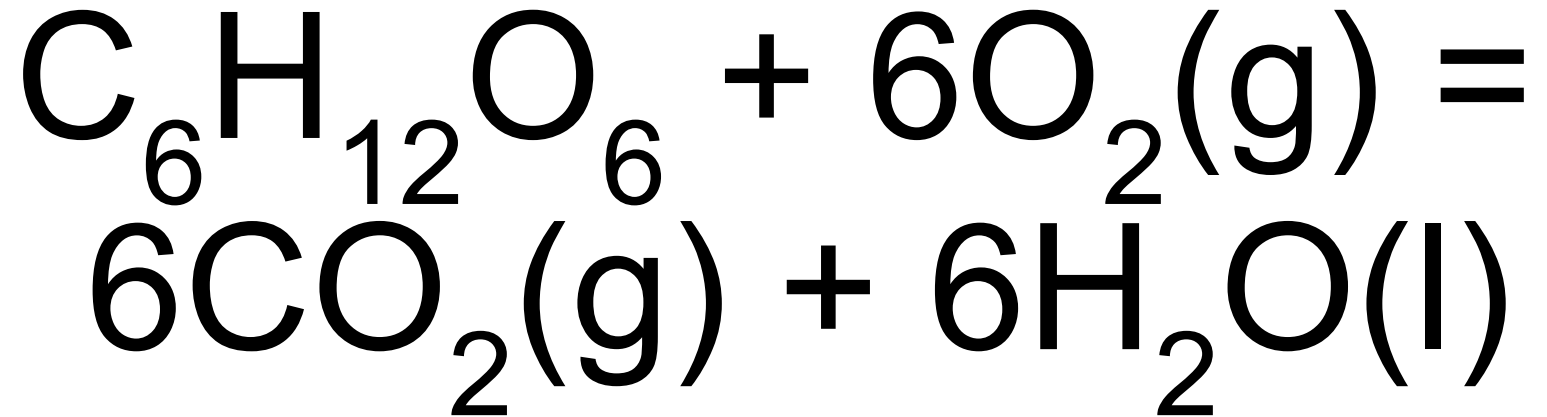
1. At easy work at sitting state (office managers) is 8400-11700 kJ.
2. At medium and hard work (doctors, postmen, students) is 12500-15100 kJ.
3. At hard physical labor (steel-maker, carpenter, etc.) is 16700-20900 kJ.
4. At special hard labor (sportsmen) is till 30100 kJ.

# Research of thermochemical calculations for the energy performance of biochemical processes

The energy is given mainly fats, proteins, carbohydrates: 39 kJ / g, 18 kJ / g, 22 kJ / g, respectively. Although they have different biochemical mechanism and thermochemical reactions produced the same quantity of products: CO<sub>2</sub> and H<sub>2</sub>O.

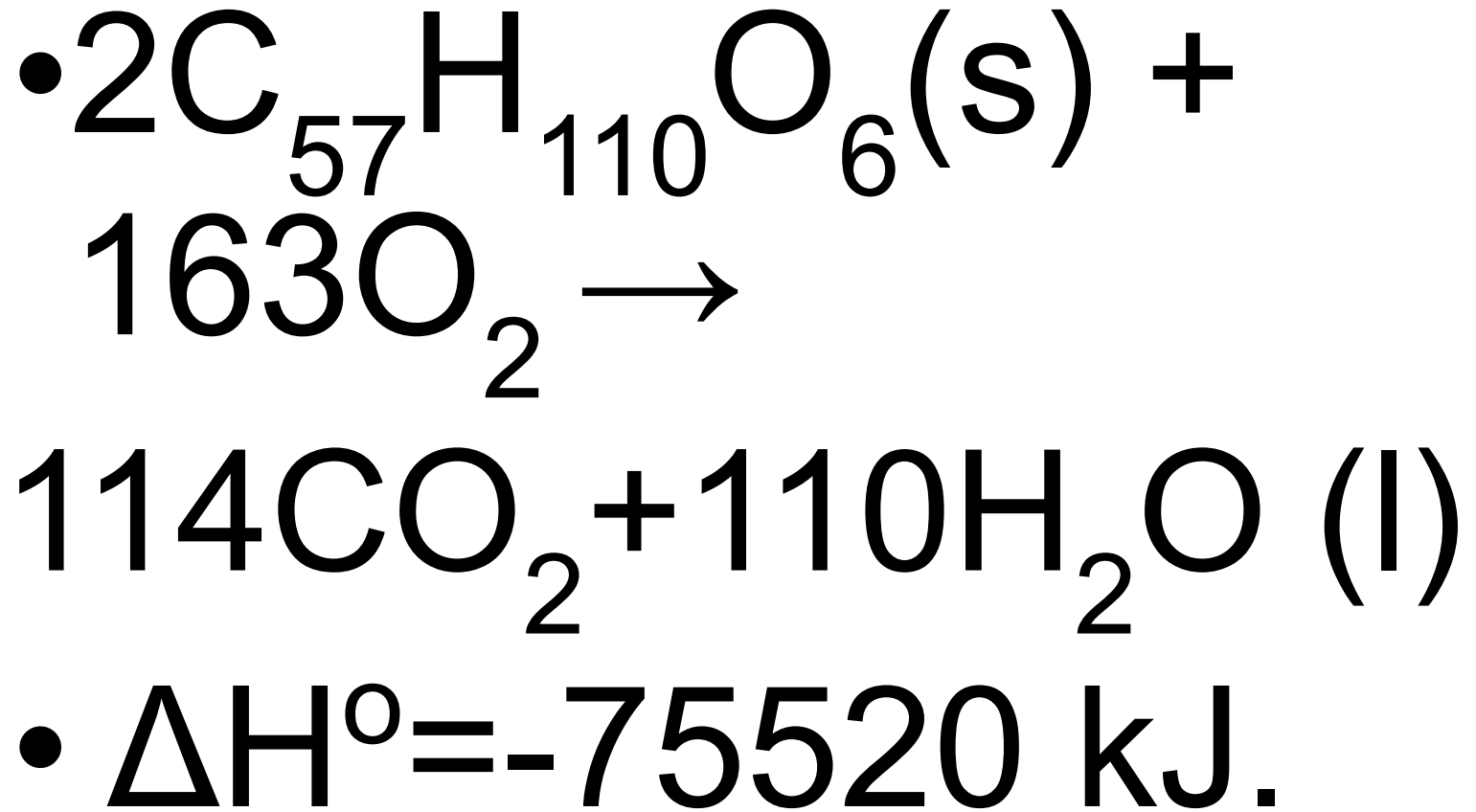


# ***CARBOHYDRATES***



$$\Delta H^\circ = -2816 \text{ kJ}$$

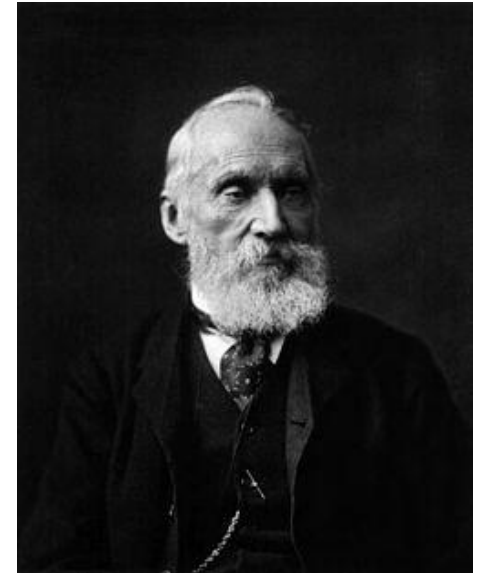
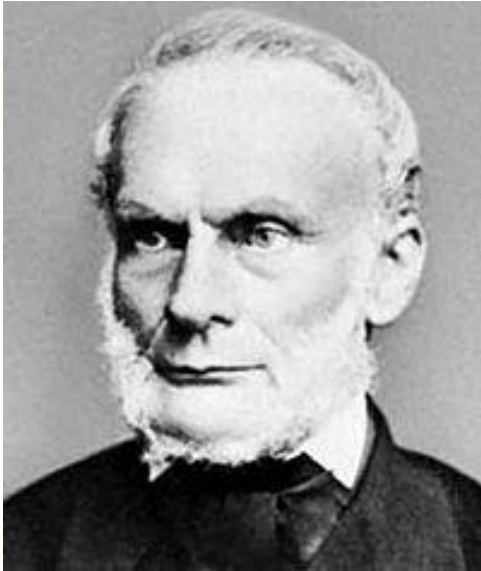
# FATS



# Table 1. Energy value of the food

Food	Energy value, kJ/g
Dairy butter	30.41
Cheddar cheese	16.82
Sugar	16.8
Rice	16.8
Beef meet	11.07
White bread	9.91
Chicken meat	9.54
Eggs	6.12
White fish	3.22
Apples	1.96

# 2nd law of thermodynamics



- 1) heat can not of itself pass from cold to hot heat, leaving no changes in the environment,
- 2) the heat can not be completely converted into work

Second law of thermodynamics sets limits the conversion of heat into work.

# *Entropy*

- *Entropy* is the property of a system which measures the degree of disorder or randomness in the system.

# 2nd law of thermodynamics

- 3) *In isolated systems, processes occur spontaneously on condition of entropy increase.*
- 4) *In other words: for a spontaneous processes in an isolated system, the change in entropy is positive.  $\Delta S > 0$ .*






# 2nd law of thermodynamics

All real spontaneous processes - irreversible. Invertible only ideal process.

In real systems, only the irreversible part of the energy is converted into useful work.

To characterize this energy related Clausius introduced a new state function, called entropy «S». Quantitative measure of entropy called internal disorder macrobody arbitrary state.

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$$\Delta S = S_2 - S_1$$

# 2nd law of thermodynamics

«Life - a struggle against entropy».

A. Schrödinger

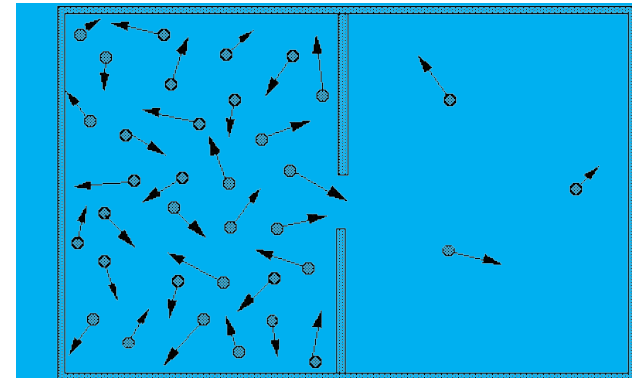
Entropy associated with the thermodynamic probability of realization of this system state **Boltzmann** equation:

$$\Delta S = K \ln W$$

**K** - Boltzmann constant,

**W** - thermodynamic probability or the number of possible microstates.

Entropy is measured in kJ / Mole·K or entropy units  
e. u. = 1 J / Mole·K



# 2nd law of thermodynamics

The more disordered system the greater its entropy.

Spontaneously reaching processes occur with an increase in entropy.

Non-spontaneous processes - crystallization, condensation - a decrease in entropy.



entropy

# 2nd law of thermodynamics

In isolated systems for reversible processes  **$S = \text{const}$ ,  $\Delta S = 0$** ;

Entropy associated with the thermal characteristics of the relationship:

$$\Delta S = \frac{Q}{T}$$

# Third law of thermodynamics

$\frac{Q}{T}$  called the reduced heat,  $TS = Q$  - bound energy.

The absolute value of the entropy can be calculated from Planck's postulate, which III law of thermodynamics.

*Entropy individual crystalline substance at absolute zero is zero—  $S_0 = 0$ .*

For him,  $W = 1$ , then  $S = K \ln 1 = 0$  Eto most orderly system.

# 2nd law of thermodynamics

**Consequence of the second law of thermodynamics:** the total entropy change required for the formation of a living organism and maintain his life, always positive.

**The entropy depends on several factors:**

- aggregate state :  $S_g > S_l > S_s$
- particle masses: more weight - more S
- hardness :  $S_{\text{amorph.}} > S_{\text{cryst.}}$
- fineness: the greater the greater the degree of dispersion S.
- density: the greater the density - the less S.

# 2nd law of thermodynamics

- nature of the relationship  $S_{cov.} > S_{met.}$
- the more complex chemical composition, the more S.
- the higher the temperature, the more S.
- the greater the pressure, the less S.

Entropy change  $\Delta S$  are on its standard values based on the consequences  $\Delta S^o$  law Hess:

$$\Delta S = \sum S^o_{prod.} - \sum S^o_{st.sub..} = K \ln \frac{W_{prod.}}{W_{st.sub.}}$$



*Free energy of system  
and free energy  
changes. The Gibbs's  
equation*

# Isobaric-isothermal potential or Gibbs energy.

The course of a chemical reaction can affect two factors:  $\Delta H$  enthalpy and entropy  $\Delta S$ . They are opposite in nature and the cumulative effect of their actions is described by Gibbs :

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

$\Delta G$  – Gibbs energy in J/mole

$\Delta H$  – maximum energy, which released or absorbed during chemical reaction

$T\Delta S$  – bound energy, which can not be converted into work.

If  $\Delta G < 0$  – process is spontaneous

$\Delta G > 0$  – process is impossible, the reverse process is spontaneous

$\Delta G = 0$  – the system is in a state of chemical equilibrium.

**Change  $\Delta G$  can be calculated by the law of Hess:**

$$\Delta G^0 = \sum \Delta G^0_{prod.} - \sum \Delta G^0_{st.sub..}{}^{50}$$

- $\Delta G < 0$  the process is possible, occurs spontaneously;
- $\Delta G > 0$  the process is impossible, the reverse process occurs spontaneously;
- $\Delta G = 0$  the system is an equilibrium state.

# Table 2. Spontaneity of chemical processes

Reaction	Sign of		$\Delta G$	Behavior
	$\Delta H$	$T\Delta S$		
Exothermic	-	+	-	Spontaneous
Exothermic	-	-	- at low T	Spontaneous
Exothermic	-	-	+ at high T	Nonspontaneous
Endothermic	+	-	+	Nonspontaneous
Endothermic	+	+	- at high T	Spontaneous

F – Helmholtz energy  
(isochoric - isothermal  
potential)

$$\Delta F^{\circ} = \Delta U^{\circ} - T\Delta S^{\circ}$$

**Application of the laws of thermodynamics to living systems.**

**Heat released from the body, heat is found by counting the oxidation of substances, i.e. I law applies to life processes .**

**It was long thought that the II law of thermodynamics does not apply to living systems .**

**Must be considered:**

**Biological systems are exchanged with the environment of energy and mass .**

**Processes in living organisms ultimately irreversible.**

**Living systems are not in equilibrium.**

**All biological systems are heterogeneous , multiphase**

**.**

**In a living organism (open system) instead of thermodynamic equilibrium steady state occurs , which is characterized not by equality of forward and reverse processes, and the constancy of the chemical changes and tap metabolites.**