MINISTRY of HEALTH REPUBLIC of BELARUS
GOMEL STATE MEDICAL UNIVERSITY

Department of general and bioorganic chemistry

V.A. Philippova, A.V. Lusenkova, L.V. Chernishova

CHEMICAL THERMODYNAMICS

Laboratory manual

Gomel 2005

Рецензент: заведующий кафедрой биологической химии, доктор медицинских наук, профессор **А.И. Грицук**

Авторы-составители: В.А. Филиппова, А.В. Лысенкова, Л.В. Чернышева

Данные рекомендации призваны помочь студентам лечебного факультета, обучающихся на английском языке, овладеть теоретическими основами химической термодинамики, а также приобрести навыки по выполнению термодинамических расчетов, в том числе в биологических системах.

Утверждено и рекомедовано к изданию Центральным учебным научно-методическим Советом Учреждения образования «Гомельский государственный медицинский университет» 20 сентября 2005 г., протокол № 9.

*«**The energy of the universe is constant,
the entropy increases toward a maximum»***
Clausius

1. MAIN CONCEPTS OF CHEMICAL THERMODYNAMICS

Chemical thermodynamics is a branch of chemistry studying energy, heat and work transformation in the process of chemical reactions. It's a theoretical base of bioenergetics, thermochemistry, thermophisiology and other sciences dealing with energy exchange between biosystems and their surroundings.

Energy is defined as the capacity to do work or to produce change.

Heat is a process in which energy is transferred from one system to another as a result of temperature difference between them.

Work in mechanics is force times distance. In thermodynamics, the most common forms of work are gas expansion and electrical work carried out in an electrochemical cell.
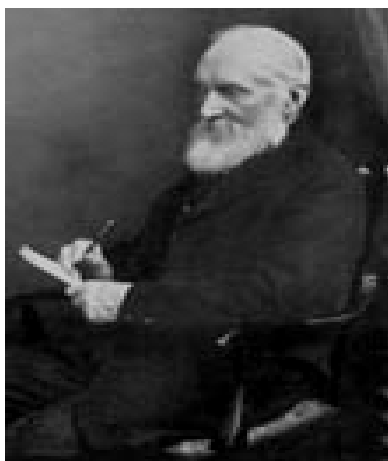
William Thompson, lord Kelvin
(26.VI. 1824 — 17.XII. 1907)

The kelvin (K) is defined so that the normal freezing point of water is 273.15 K and its normal boiling point is 373.15 K.

Thermodynamic systems are the objects of thermodynamic investigations. They defined as a part of Universe separated from its surroundings by a thermodynamics cover (real or abstract). There are three types of systems:

➢ **Isolated**, which exchange with the surroundings neither by energy, nor by mass;

➢ **Closed**, which exchange with the surroundings by energy only;

➢ **Open**, which exchange with the surroundings by energy and by mass.

The descriptions of a system include:

➢ A set of its **thermodynamic parameters**, such as temperature, pressure, volume, mass and others;

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

The most important **state functions** of a system are:

➢ **Internal energy (U)** — a total energy of a system composed of kinetic and potential energy of all its structural units;

➢ **Enthalpy** or **heat content (H)** — a part of system's internal energy available to be converted into heat;

➢ **Gibbs Free energy (G)** — a part of system's internal energy available to be converted into useful work;

➢ **Entropy (S)**, which characterizes on one side a heat of a system not available to be transformed into a useful work, and on the other side, randomness and disorder in a system.

2. THE FIRST LAW OF THERMODYNAMICS

Chemical thermodynamics is based upon its laws. Helmholts formulated **the first law of thermodynamics** in 1847: ***THE TOTAL QUANTITY OF ENERGY IN THE UNIVERSE IS ASSUMED TO REMAIN CONSTANT. THIS STATEMENT IS GENERALLY KNOWN AS THE LAW OF CONSERVATION OF ENERGY.***

For closed systems the first law is expressed by a following equation:

$$Q = \Delta U + p\Delta V + A' \qquad (1)$$

where Q — heat absorbed by a system, kJ, Δ

A′ — useful work produced in a system, kJ,

$p\Delta V$ — work of gas expansion, kJ.

For isobaric reactions (p = const) producing no useful work (A' = 0) the equation (1) may be rearranged as follows:

$$Q = \Delta U + p\Delta V \qquad (2)$$

where

$$\Delta H = \Delta U + p\Delta V \qquad (3)$$

Hence Q = ΔH, thus **ΔH has a sense of a heat of isobaric chemical reactions**.

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

Heat of the reactions may be determined experimentally or calculated on the base of the Hess law (1840): the heat of isobaric chemical reactions does not depend upon a number of intermediate steps, but depends upon the energy state of reactants and products.

Heat of a chemical reaction (Δ_rH) for a chemical reaction:

$$aA + bB \rightarrow cC + dD$$
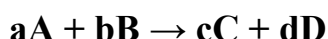
may be calculated as:

$$\Delta_r H = c \times \Delta_f H (C) + d \times \Delta_f H (D) - a \times \Delta_f H (A) - b \times \Delta_f H (B) \qquad (4)$$

where Δ_f H — a heat of formation of one mole of a complex substance from simple substances, kJ/moL

$$\Delta_r H = a \times \Delta_{com} H (A) + b \times \Delta_{com} H (B) - c \times \Delta_{com} H (C) - d \times \Delta_{com} H (D) \qquad (5)$$

where $\Delta_{com}H$ —a heat of combustion of one mole of a substance in pure oxygen up to the highest oxides, kJ/moL.

If $\Delta_rH < 0$, the reaction is exothermic (heat is released by a system), if $\Delta_rH > 0$, the reaction is endothermic (heat is absorbed by a system).

Thermochemistry is a scientific base of a dietology. Heat of combustion is an important characteristic of food products and their components: carbohydrates (16.7 kJ/g), lipids (37.6 kJ/g) and proteins (16.7 kJ/g). Various foods have different compositions and hence different energy contents.

Many labels on food packages show the calorie content of the food. The calorie (cal) is a non-SI unit of energy where

$$1 \text{ cal} = 4.184 \text{ J} \qquad (6)$$

In the context of nutrition, however, the calorie we speak of (sometimes called a "big calorie" is actually equal to a kilocalorie; that is,

$$1 \text{ Cal} = 1000 \text{ cal} = 4184 \text{ J}(7) \qquad (7)$$

Table 1

Fuel values of foods

Substance	$\Delta_{com}H$, kJ/g
Apple	–2
Beef	–8
Beer	–1.5
Bread	–11
Butter	–34
Cheese	–18
Eggs	–6
Milk	–3
Potatoes	–3

3. THE SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics deals with the spontaneity of processes in nature:

➢ Spontaneous processes proceed without absorbing energy from the surroundings up to the equilibrium state;

➢ Nonspontaneous processes proceed by absorbing energy from the surroundings.

The second law was developed by Carnot when he studied a heat engine work. (Fig. 1)

Carnot proved that heat engine's efficiency is always less than unit:

$$\text{Efficiency} = \frac{A}{Q_h} \leq \frac{T_1 - T_2}{T_1} \qquad (8)$$
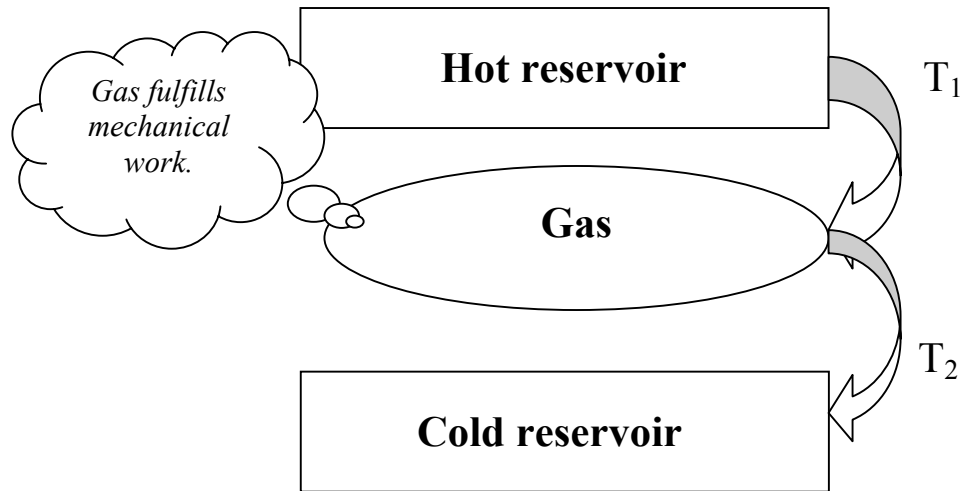

Fig. 1. The scheme of heat machine

The second law may be defined in several ways:

➤ *IT IS IMPOSSIBLE TO EXTRACT AN AMOUNT OF HEAT FROM A HOT RESERVOIR AND USE IT ALL TO DO WORK. SOME AMOUNT OF HEAT MUST BE EXHAUSTED TO THE COLD RESERVOIR* (Kelvin-Planck's 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* (Clausius's statement);

➤ *A PERPETUAL MOTION MACHINE IS IMPOSSIBLE;*

➤ *THE ENTROPY OF THE UNIVERSE INCREASES;*

➤ *TOTAL DISORDER INCREASES IN ANY SPONTANEOUS PROCESS* (Boltzmann's statement).

Two equations are considered to be the mathematical descriptions of the second law:

➤ $\Delta S \geq Q/T$ Clausius's inequality;   (9)

➤ $S = k \ln W$ Boltzmann's equation,   (10)

where **k** — the Boltzmann's coefficient (k= $1.38 \cdot 10^{-23}$ j/K);

W — thermodynamics probability, a number of microstates a system can be described.

The entropy change of a chemical reaction ($\Delta_r S$, J/K) may be calculated on the base of the Hess law, using standard molar entropy of reactants and products (S, J /moL $\times$ K):

$$\Delta_r S = c \times S\,(C) + d \times S\,(D) - a \times S\,(A) - b \times S\,(B) \qquad (11)$$

The combined review of the first and second laws gives opportunity to calculate free energy change in a closed system:

$$\begin{cases} Q = \Delta U + p\Delta V + A' \\ \Delta S = Q/T \end{cases}$$

Rearrange this to get $\Delta G = - A'$. Thus ΔG has a sense of a useful work fulfilled by a system or under a system. The sign of ΔG is a criterion of reactions' spontaneity.

Spontaneous process $A' > 0$ $\Delta G < 0$
Equilibrium state $A' = 0$ $\Delta G = 0$
No spontaneous process $A' < 0$ $\Delta G > 0$

Thus, we can make a conclusion that all spontaneous processes undergo with the decrease of free energy of a system.

In biochemistry spontaneous processes are known as exorgonic and nonspontaneous -as endorgonic. A process in which an endergonic reaction is made to proceed by coupling it to an exorgonic reaction is defined as a coupled reaction. Biological coupled reactions are usually mediated with the aid of enzymes.

4. CALCULATING FREE ENERGY CHANGES

1) Calculating free energy change of chemical reactions ($\Delta_r G$) on the base of the Hess law, using standard molar free energy of formation ($\Delta_f G$, kJ/moL):

$$\Delta_r G = c \times \Delta_f G\ (C) + d \times \Delta_f G\ (D) - a \times \Delta_f G\ (A) - b \times \Delta_f G\ (B) \qquad (12)$$

2) Calculating free energy change of chemical reactions ($\Delta_r G$) on the base of the equation:

$$\Delta_r G = \Delta_r H - T\Delta S \qquad (13)$$

3) Calculating free energy change of chemical reactions ($\Delta_r G$), using the equation known as a chemical reaction isotherm.

➢ for reactions running in liquid solutions:

$$\Delta_r G = \Delta_r G° + R \times T \times \ln \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \qquad (14)$$

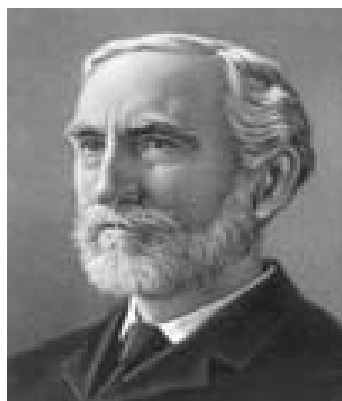➢ for reactions running in gaseous phases:

$$\Delta_r G = \Delta_r G° + R \times T \times \ln \frac{P^c(C) \times P^d(D)}{P^a(A) \times P^b(B)} \qquad (15)$$

4) Calculating free energy change in processes of substances transporting against their concentration gradient (ΔG):

$$\Delta_r G = \times R \times T \times \ln \frac{[A]ph2}{[A]ph1}, \text{ where } [A]\,ph2 > [A]\,ph1 \qquad (16)$$

Calculating free energy change is essential for biosystems since makes it possible to understand deeply the sense of biochemical reactions.


Gibbs J. W.
(11.II.1839 — 28.IV.1903)
The American physical chemist J. Willard Gibbs introduced free energy into chemical thermodynamics. A professor of mathematical physics at Yale University from 1871 until his death in 1903, Gibbs was the first to show how the laws of thermodynamics apply to chemical processes. Because Gibbs published in a little-known American journal at a time when most scientific work was being done in Europe, his outstanding contributions to chemical thermodynamics were not recognized until 13 years after they were first published. In the 1890s, however, his 400 pages of elegant mathematical development of this subject were translated into French and German, and European scientists quickly recognized the greatness of his work. To commemorate Gibbs, free energy is symbolized G and is sometimes called Gibbs free energy.

---

5. PROBLEMS

PROBLEM 1. Calculate the $\Delta_r H$ for the following reaction, using: standard heats of formation:

$$Al_2O_3 \text{ (c)} + 3\ SO_3 \text{ (g)} \rightarrow Al_2(SO_4)_3 \text{ (c)}$$
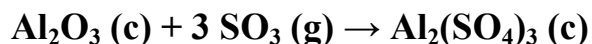
Substance	State	$\Delta_f H°_{298}$, kJ/mole
Al_2O_3	c	−1,675.1
SO_3	g	−395.2
$Al_2(SO_4)_3$	c	−3,434

Answer:

$\Delta_r H = \Delta_f H°_{298}\ (Al_2(SO_4)_3) - \Delta_f H°_{298}\ (Al_2O_3) - 3 \times \Delta_f H°_{298}\ (SO_3) =$
$= -3,434 - (-1,675.1) - 3 \times (-395.2) = -753.3$ kJ.

PROBLEM 2. Compute the $\Delta_r H$ for the following reaction using: standard heats of combustion:

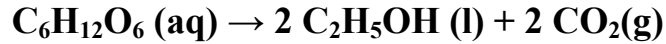$$C_6H_{12}O_6 \text{ (c)} \rightarrow 2\ C_2H_5OH \text{ (l)} + 2\ CO_2\text{(g)}$$

Substance	State	$\Delta_{com} H°_{298}$, kJ/mole
$C_6H_{12}O_6$	c	−2,810
C_2H_5OH	l	−1,370
CO_2	g	0

Answer:

$\Delta_rH = \Delta_{com}H°_{298}$ ($C_6H_{12}O_6$) $- 2 \times \Delta_{com}H°_{298}$ (C_2H_5OH) $= (-2{,}810) - 2 \times (-1{,}370)$ $= = -70$ kJ.

**EXAMPLE 3.** Calculate Δ_rG of a biochemical reaction under standard conditions:

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

Substance	State	$\Delta_fG°_{298}$, kJ/mole
$C_6H_{12}O_6$	aq	−917
C_2H_5OH	l	−175
CO_2	g	−394

Answer:

$\Delta_rG = 2 \times \Delta_fG°_{298}$ (C_2H_5OH) $+ 2 \times \Delta_fG°_{298}$ (CO_2) $- \Delta_fG°_{298}$ ($C_6H_{12}O_6$) $=$ $= 2 \times (-175) + 2 \times (-394) - (-917) = -221$ kJ.

This reaction runs spontaneously under standard conditions.

PROBLEM 4. Calculate Δ_rG of biochemical reaction under standard condition:

$$C_6H_{12}O_6 \text{ (aq)} + 6\ O_2 \text{ (g)} \rightarrow 6\ CO_2\text{(g)} + 6\ H_2O \text{ (l)}$$
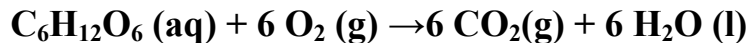
Substance	State	$\Delta_fH°_{298}$, kJ/mole	$S°_{298}$, J/mole×K
$C_6H_{12}O_6$	aq	−1,263	264
C_2H_5OH	g	0	205
CO_2	g	−394	214
H_2O	l	−286	70

Answer:

(a) $\Delta_rH = 6 \times \Delta_fH°_{298}$ (CO_2) $+ 6 \times \Delta_fH°_{298}$ (H_2O) $- \Delta_fH°_{298}$ ($C_6H_{12}O_6$) $=$ $= 6 \times (-394) + 6 \times (-286) - (-1{,}263) = -2{,}817$ kJ.

(b) $\Delta_rS = 6 \times S°_{298}$ (CO_2) $+ 6 \times S°_{298}$ (H_2O) $- S°_{298}$ ($C_6H_{12}O_6$) $- 6 \times S°_{298}$(O_2) $=$ $= 6 \times 214 + 6 \times 70 - 264 - 6 \times 205 = 210$ J/K

210 J/K or 0.210 kJ/K.

(c) $T \times \Delta_rS = 298 \times 0.210 = 62.58$ kJ.

(d) $\Delta_rG = \Delta_rH - T \times \Delta_rS = (-2{,}817) - 62.58 = -2{,}879$ **kJ.**

This reaction runs spontaneously under standard conditions.

PROBLEM 5. From the following equations and the enthalpy changes,

(a) C (graphite) $+ O_2$ (g) $\rightarrow CO_2$ (g) $\Delta_rH = -393.5$ kJ

(b) H_2 (g) $+ \frac{1}{2} O_2$ (g) $\rightarrow H_2O$ (L) $\Delta_rH = -285.8$ kJ

(c) $2\ C_2H_2$ (g) $+ 5\ O_2$ (g) $\rightarrow 4\ CO_2$ (g) $+ 2\ H_2O$ (L) $\Delta_rH = -2598.8$ kJ
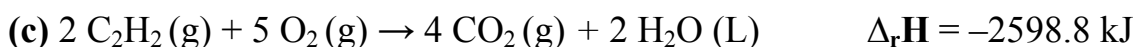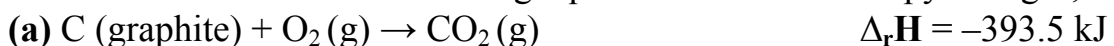
Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements: 2 C (graphite) $+ H_2$(g) $\rightarrow C_2H_2$(g)

Answer:
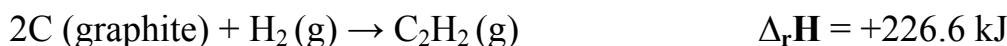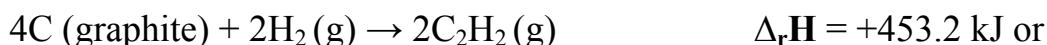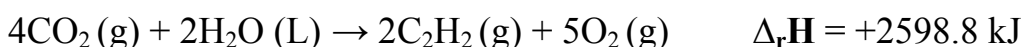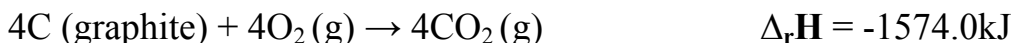Since we want to obtain one equation containing only C, H_2, and C_2H_2, we need to eliminate O_2, CO_2, and H_2O from the first three equations. We note that (c) contains 5 moles of O_2, 4 moles of CO_2, and 2 moles of H_2O. First we reverse (c) to get C_2H_2 on the product side:

(d) $4 CO_2(g) + 2 H_2O(L) \rightarrow 2 C_2H_2(g) + 5 O_2(g) \qquad \Delta_rH = +2598.8$ kJ
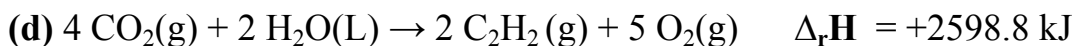
Next, we multiply (a) by 4 and (b) by 2 and carry out the addition of
$$4(a) + 2(b) + (d):$$

$4C \text{ (graphite)} + 4O_2(g) \rightarrow 4CO_2(g)$	$\Delta_rH = -1574.0$ kJ
$2H_2(g) + 4O_2(g) \rightarrow 2H_2O(L)$	$\Delta_rH = -571.6$ kJ
$4CO_2(g) + 2H_2O(L) \rightarrow 2C_2H_2(g) + 5O_2(g)$	$\Delta_rH = +2598.8$ kJ
$4C \text{ (graphite)} + 2H_2(g) \rightarrow 2C_2H_2(g)$	$\Delta_rH = +453.2$ kJ or
$2C \text{ (graphite)} + H_2(g) \rightarrow C_2H_2(g)$	$\Delta_rH = +226.6$ kJ

Since the above equation represents the synthesis of C_2H_2 from its elements, we have $\Delta_fH°_{298}(C_2H_2) = \Delta_rH /mol = +226.6$ kJ/mol.

PROBLEM 6. One of the biochemical reactions that produce ATP involves the conversion of acetyl phosphate to acetic acid and phosphoric acid:

Acetyl phosphate   Acetic acid
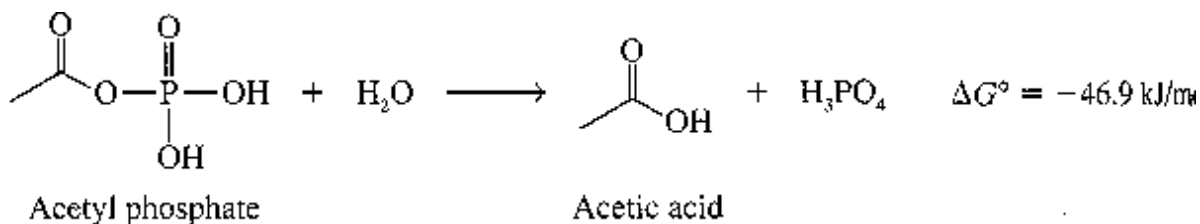
Answer:
Write the overall balanced equation, and show that the coupled reaction is spontaneous.

METHOD: A coupled process links a spontaneous reaction with a nonspontaneous one. In this case the energy released in the acetyl phosphate reaction provides the energy needed to drive the conversion of ADP to ATP.

Combining the two reactions gives the overall balanced equation:
Acetyl phosphate   Acetic acid
$CH_3CO_2PO_3H_2 + H_2O \rightarrow CH_3CO_2H + H_3PO_4$

$ADP + H_3PO_4 \rightarrow ATP + H_2O$

$CH_3CO_2PO_3H_2 + ADP \rightarrow CH_3CO_2H + ATP$
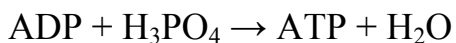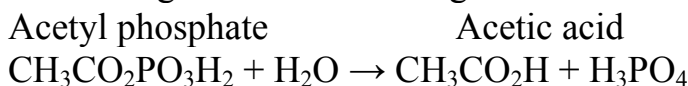
The net energy change for the coupled process is the sum of the Δ_rG values for the individual reactions:

$$\Delta_r G = \Delta_f G°_{\text{ acetyl phosphate}} + \Delta_f G°_{\text{ ATP}} = -46.9 \text{ kJ} + 30.6 \text{ kJ} = -16.3 \text{ kJ}$$

The negative value of $\Delta_r G$ shows that the free energy released in the ac re-action is more than enough to drive the conversion of ADP to ATP.

6. EXERCISES FOR THE SELF CONTROL

1. Compute the standard enthalpy change for the following reactions:

(a) $2 \text{ H}_2 \text{ (g)} + \text{O}_2 \text{ (g)} \rightarrow 2 \text{ H}_2\text{O (L)}$

(b) $\text{C (s)} + 2 \text{ H}_2 \text{ (g)} \rightarrow \text{CH}_4 \text{ (g)}$

(c) $\text{C}_2\text{H}_5\text{OH (L)} + 3 \text{ O}_2 \text{ (g)} \rightarrow 2 \text{ CO}_2 \text{ (g)} + 3 \text{ H}_2\text{O (L)}$

(d) $\text{Fe}_2\text{O}_3 \text{ (s)} + 2 \text{ Al (s)} \rightarrow \text{Al}_2\text{O}_3 \text{ (S)} + 2 \text{ Fe (s)}$

2. Compute the standard entropy change for the following reactions:

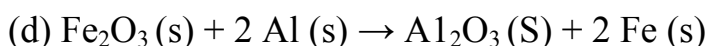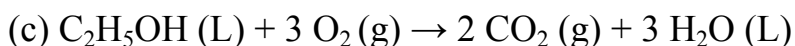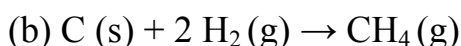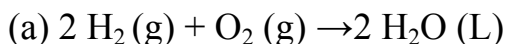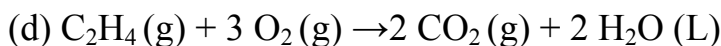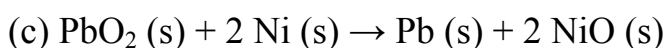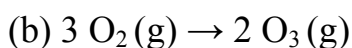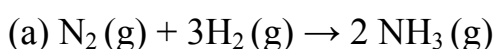(a) $\text{N}_2 \text{ (g)} + 3\text{H}_2 \text{ (g)} \rightarrow 2 \text{ NH}_3 \text{ (g)}$

(b) $3 \text{ O}_2 \text{ (g)} \rightarrow 2 \text{ O}_3 \text{ (g)}$

(c) $\text{PbO}_2 \text{ (s)} + 2 \text{ Ni (s)} \rightarrow \text{Pb (s)} + 2 \text{ NiO (s)}$

(d) $\text{C}_2\text{H}_4 \text{ (g)} + 3 \text{ O}_2 \text{ (g)} \rightarrow 2 \text{ CO}_2 \text{ (g)} + 2 \text{ H}_2\text{O (L)}$

3. For each reaction in Problem 2, explain what features of the disorder of reactants and products account for the magnitude and sign of $\Delta_r S$.

4. For each reaction in Problem 1, explain what features of the disorder of reactants and products account for the magnitude and sign of $\Delta_r S$.

5. Compute the standard free energy change for reaction in Problem 1, using the formula 13.

6. Compute the standard free energy change for reaction in Problem 2, using formula 13.

7. From the following data,

$\text{C(graphite)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$	$\Delta_r H = -393.5 \text{ kJ}$
$\text{H}_2 \text{ (g)} + \tfrac{1}{2}\text{O}_2 \text{ (g)} \rightarrow \text{H}_2\text{O (L)}$	$\Delta_r H = -285.8 \text{ kJ}$
$2\text{C}_2\text{H}_6 \text{ (g)} + 7 \text{ O}_2\text{(g)} \rightarrow 4\text{CO}_2 \text{ (g)} + 6\text{H}_2\text{O (L)}$	$\Delta_r H = -3119.6 \text{ kJ}$

calculate the enthalpy change for the reaction:

$2 \text{ C (graphite)} + 3\text{H}_2 \text{ (g)} \rightarrow \text{C}_2\text{H}_6 \text{ (g)}$

8. From the following heats of combustion,

$\text{CH}_3\text{OH (L)} + 2 \text{ O}_2\text{(g)} \rightarrow \text{CO}_2 \text{ (g)} + 2\text{H}_2\text{O (L)}$	$\Delta_r H = -726.4 \text{ kJ}$
$\text{C (graphite)} + \text{O}_2 \text{ (g)} \rightarrow \text{CO}_2 \text{ (g)}$	$\Delta_r H = -393.5 \text{ kJ}$
$\text{H}_2 \text{ (g)} + \tfrac{1}{2}\text{O}_2 \text{ (g)} \rightarrow \text{H}_2\text{O (L)}$	$\Delta_r H = -285.8 \text{ kJ}$

calculate the enthalpy of formation of methanol (CH_3OH) from its elements:

$\text{C (graphite)} + 2 \text{ H}_2 \text{ (g)} + \tfrac{1}{2} \text{ O}_2 \text{ (g)} \rightarrow \text{CH}_3\text{OH (L)}$

9. Calculate the standard enthalpy change for the reaction

$2 \text{ Al(s)} + \text{Fe}_2\text{O}_3 \text{ (s)} \rightarrow 2 \text{ Fe (s)} + \text{Al}_2\text{O}_3 \text{ (s)}$
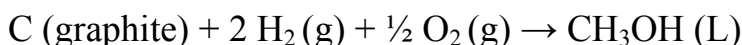
given that
$$2\,Al\,(s) + 3/2\,O_2(g) \rightarrow Al_2O_3(s) \qquad\qquad \Delta_r H = -1601\,kJ$$
$$2\,Fe(s) + 3/2\,O_2(g) \rightarrow Fe_2O_3\,(s) \qquad\qquad \Delta_r H = -821\,kJ$$
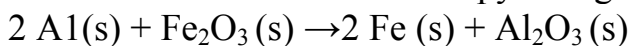
10. Calculate the standard enthalpy of formation of carbon disulfide (CS_2) from its elements, given that
$$C\,(graphite) + O_2\,(g) \rightarrow CO_2\,(g) \qquad\qquad \Delta_r H = -393.5\,kJ$$
$$S(s) + O_2(g) \rightarrow SO_2(g) \qquad\qquad \Delta_r H = -296.1\,kJ$$
$$CS_2\,(L) + 3\,O(g) \rightarrow CO_2\,(g) + 2SO_2\,(g) \qquad\qquad \Delta_r H = -1072\,kJ$$

11. The standard enthalpy of formation at 25°C of HF (aq) it is –320.1 kJ/mol; of OH⁻ (aq), it is –229.6 kJ/mol; of F⁻ (aq), it is –329.1 kJ/mol; and of H_2O (L), it is –285.8 kJ/mol.

(a) Calculate the standard enthalpy of neutralization of HF (aq):
$$HF\,(aq) + OH^-\,(aq) \rightarrow F^-\,(aq) + H_2O\,(L)$$
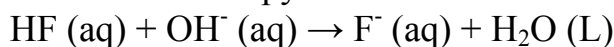
(b) Using the value of -56.2 kJ as the standard enthalpy change for the reaction:
$$H^+\,(aq) + OH^-\,(aq) \rightarrow H_2O\,(L)$$
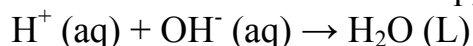
(c) Calculate the standard enthalpy change for the reaction
$$HF\,(aq) \rightarrow H^+\,(aq) + F^-\,(aq)$$
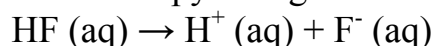
12. Nitrogen-fixing bacteria react N_2 with H_2O to produce NH_3 and O_2 using ATP as their energy source. Approximately 24 molecules at ATP are consumed per molecule of N_2 fixed. What percentage of the free energy derived from ATP is stored in NH_3?

13. The hydrolysis of ATP to ADP has $\Delta_r H = -21.0$ kJ/mol, whereas $\Delta_r G° = =-30.6$ kJ/mol at 298 K. Calculate $\Delta_r S$ for this reaction. What happens to the spontaneity of this reaction as the temperature is increased to 37°C?

14. In running a mile, an average person consumes about 500 kJ of energy:

(a) How many moles of ATP does this represent?

(b) Assuming 38% conversion efficiency, how many grams of glucose must be "burned"?

15. Each of the following statements is false. Rewrite that each makes a correct statement about free energy:

(a) In any process at constant T and P, the free energy of the universe decreases.

(b) When **T** changes during a process, the free energy of a system always decreases.

(c) $\Delta_r G > 0$ for any spontaneous process.

(d) $\Delta_r G = \Delta_r H + T \times \Delta_r S$.

16. Estimate $\Delta_r G_{425}$ for each reaction in Problem 1. (Assume no phase changes occur.)

17. Compute $\Delta_r H$, $\Delta_r S$, and $\Delta_r G$ for the production of NH_4NO_3 from ammonia and oxygen (t = 125°C), using the following reaction
$$2\,NH_3\,(g) + 2\,O_2\,(g) \rightarrow NH_4NO_3\,(g) + H_2O\,(L)$$
(This reaction is not feasible industrially because NH_3 combustion cannot be controlled to give NH_4NO_3 product.)
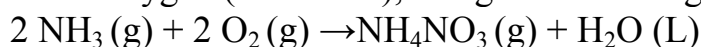
18. Compute $\Delta_r H$, $\Delta_r S$, and $\Delta_r G$ for the production of N_2 from N_2O_4 and N_2H_4 ($t = 100°C$):

$$N_2O_4 \text{ (L)} + N_2H_4 \text{ (L)} \rightarrow 3\,N_2 + 4\,H_2O \text{ (L)}$$
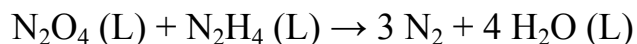
LITERATURE

1. *Chang Raymond*. Chemistry. — 4 th ed. — P. 219–261.
2. *Olmsted, John 111*. Chemistry, the molecular science. — P. 597–645.
3. *Leo J*. Malone. Basic concepts of chemistry. — 4 th ed.
4. *Chang Raymond*. Physical Chemistry for the Chemical and Biological Sciences. — 3rd ed. — P. 75–197

TEST ON CHEMICAL THERMODYNAMICS

Point out the correct answer or correct answers for the following test problems:

1. Entropy is a state function, which characterize:
a) Disorder or randomness in a thermodynamics system.
b) The amount of thermal energy not available to do work.
c) The efficiency of energy conversion in open systems.
d) The amount of thermal energy absorbed by a system.

2. Formulate the First Law of Thermodynamics:
a) The entropy of the Universe increases.
b) The total energy in the Universe remains constant.
c) The total energy in the Universe increases.
d) The total energy in the Universe decreases.

3. Which of the following are open systems?
a) A human being.
b) A helium — filled balloon.
c) The Universe.
d) An open glass with water.

4. The largest amount of heat is released at the result of the reaction:
a) $4 NH_3 + 3 O_2 \rightarrow 2 N_2 + 6 H_2O$, $\Delta_rH = -1530$ kJ.
b) $Fe_2O_3 + 3 CO \rightarrow 2 Fe + 3 CO_2$, $\Delta_rH = -26,8$ kJ.
c) $N_2 + O_2 \rightarrow 2 NO$, $\Delta_r H = 180$ kJ,
d) $C + O_2 \rightarrow CO_2$, $\Delta_r H = - 394$ kJ

5. Point out the mathematical definition of the second law of thermodynamics:
a) $S = k \ln W$
b) $\Delta G = \Delta H - T\Delta S$,
c) $Q = \Delta U + A$,
d) $\Delta S \geq Q/T$

6. Standard heats of combustion of graphite and diamond are equal correspondently –393.5 kJ/mol and –395.4 kJ/mol. The enthalpy of graphite to diamond transition is:
a) –1.9 kJ/mol.
b) +1.9 kJ/mol.
c) 0.
d) +3.8 kJ/mol.

7. What state function determines spontaneity of chemical reaction?
a) Internal energy.
b) Entropy.
c) Free energy.
d) Enthalpy.

8. An exothermic process proceeds with the increase of entropy. At what temperature it runs spontaneously?
a) At low temperature.
b) At high temperature.
c) At all temperatures.
d) At no temperatures.

9. An endothermic process proceeds with the decrease of entropy. At what temperature it runs spontaneously?
a) At low temperature.
b) At high temperature.
c) At all temperatures.
d) At no temperatures.

10. The hydrolyses of ATP to ADP has $\Delta H = -21$ kJ/mol, where as $\Delta G = -30.6$ kJ/mol at 298 K. Calculate ΔS for this reaction.
a) 32.2 J/K.
b) –32.2 J/K.
c) 0.0322 kJ/K.
d) 16.6 J/K.

SELECTED THERMADYNAMIC DATA AT 1 atm. AND 25ºC

Substance	ΔH_f^o (kJ/mole)	ΔG_f^o (kJ/mole)	ΔS^o (J/K·mole)
Ag (s)	0	0	42.7
Ag^+ (aq)	105.9	77.1	73.9
AgCl (s)	–127.0	–109.7	96.1
AgBr (s)	–99.5	–95.9	107.1
Agl (s)	–62.4	–66.3	114.2
$AgNO_3$ (s)	–123.1	–32.2	140.9
Al (s)	0	0	28.3
Al^{3+} (aq)	–524.7	–481.2	–313.38
Al_2O_3 (s)	–1669.8	–1576.4	50.99
As (s)	0	0	35.15
AsO_4^{3-} (aq)	–870.3	–635.97	–144.77
AsH_3 (g)	171.5	—	—
H_3AsO_4 (s)	–900.4	—	—
Au (s)	0	0	47.7
Au_2O_3 (s)	80.8	163.2	125.5
AuCl (s)	–35.2	—	—
$AuCl_3$ (s)	–118.4	—	—
B (s)	0	0	6.5
B_2O_3 (s)	–1263.6	–1184.1	54.0
H_2BO_3 (s)	–1087.9	–963.16	89.58
H_3BO_3 (aq)	–1067.8	–963.3	159.8
Ba (s)	0	0	66.9
Ba^{2+} (aq)	–538.4	–560.66	12.55
BaO (s)	–558.2	–528.4	70.3
$BaCl_2$ (s)	–860.1	–810.86	125.5
$BaSO_4$ (s)	–1464.4	–1353.1	132.2
$BaCO_3$ (s)	–1218.8	–1138.9	112.1
Be (s)	0	0	9.5
BeO (s)	–610.9	–581.58	14.1

Substance	ΔH_f° (kJ/mole)	ΔG_f° (kJ/mole)	ΔS° (J/K·mole)
Br_2 (*l*)	0	0	152.3
Br^- (*aq*)	−120.9	102.8	80.7
HBr (*g*)	−36.2	−53.2	198.48
C (graphite)	0	0	5.69
Cu^{2+} (*aq*)	64.39	64.98	98.7
CuO (*s*)	−155.2	−127.2	43.5
Cu_2O (*s*)	−166.69	−146.36	100.8
CuCl (*s*)	−134.7	−118.8	91.6
$CuCl_2$ (*s*)	−205.85	—	—
CuS (*s*)	−48.5	−49.0	66.5
$CuSO_4$ (*s*)	−769.86	−661.9	113.39
F_2 (*g*)	0	0	203.34
F^- (*aq*)	−329.1	−276.48	−9.6
HF (*g*)	−268.6	−270.7	173.5
Fe (*s*)	0	0	27.2
Fe^{2+} (*aq*)	−87.86	−84.9	−113.39
Fe^{3+} (*aq*)	−47.7	−10.5	−293.3
Fe_2O_3 (*s*)	−822.2	−741.0	90.0
$Fe(OH)_2$ (*s*)	−568.19	−483.55	79.5
$Fe(OH)_3$ (*s*)	−824.25	—	—
H (*g*)	218.2	203.2	114.6
H_2 (*g*)	0	0	131.0
H^+ (*aq*)	0	0	0
OH^- (*aq*)	−229.94	−157.30	−10.5
H_2O (*g*)	−241.8	−228.6	188.7
H_2O (*l*)	−285.8	−237.2	69.9
H_2O_2 (*l*)	−187.6	−118.1	?
Hg (*l*)	0	0	77.4
Hg^{2+} (*aq*)	—	−164.38	—
HgO (*s*)	−90.7	−58.5	72.0
$HgCl_2$ (*s*)	−230.1	—	—
Hg_2Cl_2 (*s*)	−264.9	−210.66	196.2
HgS (*s*)	−58.16	−48.8	77.8
$HgSO_4$ (*s*)	−704.17	—	—
Hg_2SO_4 (*s*)	−741.99	−623.92	200.75
I_2 (*s*)	0	0	116.7

Substance	ΔH_f° (kJ/mole)	ΔG_f° (kJ/mole)	ΔS° (J/K·mole)
I$^-$ (aq)	55.9	51.67	109.37
HI (g)	25.9	1.30	206.3
K (s)	0	0	63.6
K$^+$ (aq)	−251.2	−282.28	102.5
KOH (s)	−425.85	—	—
KCl (s)	−435.87	−408.3	82.68
KClO$_3$ (s)	−391.20	−289.9	142.97
KClO$_4$ (s)	−433.46	−304.18	151.0
KBr (s)	−392.17	−379.2	96.4
KI (s)	−327.65	−322.29	104.35
KNO$_3$ (s)	−492.7	−393.1	132.9
Li$_2$O (s)	−595.8	?	?
LiOH (s)	−487.2	−443.9	50.2
Mg (s)	0	0	32.5
Mg^{2+} (aq)	−461.96	−456.0	−117.99
MgO (s)	−601.8	−569.6	26.78
Mg(OH)$_2$ (s)	−924.66	−833.75	63.1
MgCl$_2$ (s)	−641.8	−592.3	89.5
MgSO$_4$ (s)	−1278.2	−1173.6	91.6
MgCO$_3$ (s)	−1112.9	−1029.3	65.69
Mn (s)	0	0	31.76
Mn^{2+} (aq)	−218.8	−223.4	−83.68
MnO$_2$ (s)	−520.9	−466.1	53.1
N$_2$ (g)	0	0	191.5
N$_3^-$ (aq)	245.18	?	?
NH$_3$ (g)	−46.3	−16.6	193.0
NH$_4^+$ (aq)	−132.80	−79.5	112.8
NH$_4$Cl (s)	−315.39	−203.89	94.56
NH$_3$ (aq)	−366.1	−263.76	181.17
N$_2$H$_4$ (l)	50.4	—	—
NO (g)	90.4	86.7	210.6
NO$_2$ (g)	33.85	51.8	240.46
N$_2$O$_4$ (g)	9.66	98.29	304.3
N$_2$O (g)	81.56	103.6	219.99
HNO$_2$ (aq)	−118.8	−53.6	—
HNO$_3$ (l)	−173.2	−79.9	155.6

Substance	ΔH_f° (kJ/mole)	ΔG_f° (kJ/mole)	ΔS° (J/K·mole)
NO_3^- (aq)	–206.57	–110.5	146.4
Na (s)	0	0	51.05
Na^+ (aq)	–239.66	–261.87	60.25
Na_2O (s)	–415.89	–376.56	72.8
NaCl (s)	–411.0	–384.0	72.38
NaI (s)	–288.0	—	—
Na_2SO_4 (s)	–1384.49	–1266.8	149.49
$NaNO_3$ (s)	–466.68	–365.89	116.3
Na_2CO_3 (s)	–1130.9	–1047.67	135.98
$NaHCO_3$ (s)	–947.68	–851.86	102.09
Ni (s)	0	0	30.1
Ni^{2+} (aq)	–64.0	–46.4	159.4
NiO (s)	–244.35	–216.3	38.58
$Ni(OH)_2$ (s)	–538.06	–453.1	79.5
O (g)	249.4	230.1	160.95
O_2 (g)	0	0	205.0
O_3 (aq)	–12.09	16.3	110.88
O_3 (g)	142.2	163.4	237.6
P (white)	0	0	44.0
P (red)	–18.4	13.8	29.3
PO_4^{3-} (aq)	–1284.07	–1025.59	–217.57
P_4O_{10} (s)	–3012.48	—	—
PH_3 (g)	9.25	18.2	210.0
HPO_4^{2-} (aq)	–1298.7	–1094.1	–35.98
$H_2PO_4^-$ (aq)	–1302.48	–1135.1	89.1
Pb (s)	0	0	64.89
Pb^{2+} (aq)	1.6	24.3	21.3
PbO (s)	–217.86	–188.49	69.45
PbO_2 (s)	–276.65	–218.99	76.57
$PbCl_2$ (s)	–359.2	–313.97	136.4
PbS (s)	–94.3	–92.68	91.2
$PbSO_4$ (s)	–918.4	–811.2	147.28
Pt (s)	0	0	41.84
$PtCl_4^{2-}$ (aq)	–516.3	–384.5	175.7
Rb (s)	0	0	69.45

Substance	ΔH_f° (kJ/mole)	ΔG_f° (kJ/mole)	ΔS° (J/K·mole)
Rb^+ (aq)	−246.4	−282.2	124.27
S (rhombic)	0	0	31.88
S (monoclinic)	0.30	0.10	32.55
SO_2 (g)	−296.1	−300.4	248.5
SO_3 (g)	−395.2	−370.4	256.2
SO_3^{2-} (aq)	−624.25	−497.06	43.5
SO_4^{2-} (aq)	−907.5	−741.99	17.15
H_2S (g)	−20.15	−33.0	205.64
HSO_3^- (aq)	−627.98	−527.3	132.38
HSO_4^- (aq)	−885.75	−752.87	126.86
H_2SO_4 (l)	−811.3	?	?
SP_6 (g)	−1096.2	?	?
Se (s)	0	0	42.44
SeO_2 (s)	−225.35	—	—
H_2Se (g)	29.7	15.90	218.9
Si (s)	0	0	18.70
SiO_2 (s)	−859.3	−805.0	41.84
Sr (s)	0	0	54.39
Sr^{2+} (aq)	−545.5	−557.3	39.33
$SrCl_2$ (s)	−828.4	−781.15	117.15
$SrSO_4$ (s)	−1444.74	−1334.28	121.75
$SrCO_3$ (s)	−1218.38	−1137.6	97.07
W (s)	0	0	33.47
WO_3 (s)	−840.3	−763.45	83.26
WO_4^- (aq)	−1115.45	—	—
Zn (s)	0	0	41.6
Zn^{2+} (aq)	−152.4	−147.2	106.48
ZnO (s)	−348.0	−318.2	43.9

SELECTED THERMADYNAMIC DATA
FOR ORGANIC SUBSTANCES AT 1 atm. AND 25ºC

Substance	Formula	ΔH_f^o (kJ/mole)	ΔG_f^o (kJ/mole)	ΔS^o (J/K·mole)
Acetic acid (*l*)	CH_3COOH	–484.2	–389.45	159.83
Acetaldehyde (*g*)	CH_3CHO	–166.35	–139.08	264.2
Acetone (*l*)	CH_3COCH_3	–246.8	–153.55	198.74
Acetylene (*g*)	C_2H_2	226.6	209.2	200.8
Benzene (*l*)	C_6H_6	49.04	124.5	124.5
Ethanol (*l*)	C_2H_5OH	–276.98	–174.18	161.04
Ethanc (*g*)	C_2H_6	–84.7	–32.89	229.49
Ethylene (*g*)	C_2H_4	52.3	68.1	219.45
Formic acid (*l*)	$HCOOH$	–409.2	–346.0	128.95
Glucose (*s*)	$C_6H_{12}O_6$	–1274.5	–910.56	212.1
Methane (*g*)	CH_4	–74.84	–50.8	186.19
Methanol (*l*)	CH_3OH	–238.7	–166.3	126.78
Zucrose (*s*)	$C_{12}H_{22}O_{11}$	–2221.7	–1544.3	360.24

GlOSSARY

Bioenergetics. The study of energy transformations in living organisms.

Closed system A system that allows the exchange of energy (usually in the form of heat) but not mass with its surroundings.

Coupled reactions. A process in which an endergonic reaction is made to proceed by coupling it to an exorgonic reaction. Biological coupled reactions are usually mediated with the aid of enzymes.

Endergonic process. A process that is accompanied by a positive change in Gibbs energy ($\Delta G > 0$) and therefore is thermodynamically not favored.

Endothermic reaction. A reaction that absorbs heat from the surroundings.

Energy. The capacity to do work or to produce change.

Enthalpy. A thermodynamic quantity used to describe heat changes taking place in at constant pressure.

Entropy. A thermodynamic quantity that expresses the degree of disorder and randomness in a system.

Exorgonic process. A process that is accompanied by a negative change in Gibbs energy ($\Delta G < 0$) and there for is thermodynamically favored.

Exothermic reaction. A reaction that gives off heat to the surroundings.

First law of thermodynamics. The law that states that energy can be converted from one form to another but cannot be created or destroyed.

Gibbs energy (G). A thermodynamic quantity defined by the equation G=H-TS.

Heat. Transfer of energy (usually thermal energy) between two bodies that are at different temperatures.

Hess's law. The law stating that when reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or a series of steps.

Internal energy. The internal energy of a system is the total energy of all its components.

Microstate. The state of a system as specified by the actual properties of each individual component (atoms or molecules).

Open system. A system that can exchange mass and energy with its surroundings.

Second law of thermodynamics. The entropy of the Universe increases in a spontaneous process and remains unchanged in an equilibrium process.

Spontaneous process. A process that occurs on its own accord under a given set of conditions.

State function. A property that is determined by the state of a system. The change in any state function in a process is path independent.

System. A specific part of the universe that is of interest to us.

Surroundings. The rest of the universe outside the system.

Thermodynamics. The scientific study of the interconversion of heat and other forms of energy.

Thermochemistry. The study of heat changes in chemical reactions.

Thermochemical equation. An equation that shows both the mass and enthalpy relations.

Work. In mechanics, work is force times distance. In thermodynamics, the most common forms of work are gas expansion and electrical work carried out in an electrochemical cell.

CONTENT

Department of general and bioorganic chemistry

V.A. Philippova, A.V. Lusenkova, L.V. Chernishova

CHEMICAL THERMODYNAMICS

Laboratory manual

Gomel 2005