

Thermodynamics – Heat motion: *Greek, Latin languages*

U - Internal Energy; **H** – Enthalpy, Heat content;

S – Entropy, on changes (entity): *Greek language- en tropos*

G – Free Energy: Gibbs Energy, freie Energie: *German language*

ΔH°_A – Standard heat content of Compound **A** kJ/mol

ΔS°_A – Standard Entropy content of Compound **A** kJ/mol

ΔG°_A – Standard Gibbs Energy content of Compound **A** kJ/mol

$\Delta H_r, \Delta S_r, \Delta G_r$ – Heat, Entropy, Gibbs Energy change in Reaction

$\Delta S_{\text{dispersed}} = -\Delta H_r / T$ heat dispersion; $\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}}$ total entropy change in reaction	$\Delta H_r = \sum \Delta H^\circ_{\text{product}} - \sum \Delta H^\circ_{\text{initial}};$ $\Delta S_r = \sum \Delta S^\circ_{\text{product}} - \sum \Delta S^\circ_{\text{initial}};$ $\Delta G_r = \Delta H_r - T \cdot \Delta S_r;$
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Bound energy

is calculated as $\Delta S_{\text{total}} \cdot T = -\Delta G_r$ is negative Gibbs Energy change in reaction

1) positive $\Delta S_{\text{total}} \cdot T > 0$ if in products is lost Free Gibbs Energy;

2) negative $\Delta S_{\text{total}} \cdot T < 0$ if Energy accumulated in reaction products

Compound **A** Chemical Potential μ_A per one mol as if $\Delta n_A = 1$ mol

$$\mu_A = \Delta G_A / \Delta n_A = \Delta G^\circ_A + R \cdot T \cdot \ln(X_A); \text{ kJ/mol with B, C, D in}$$

mixture $0 < X_A < 1$ always is negative value of $\ln(X_A) < 0$

Concentration Expression $X_A = n_A / n_{\text{total}}$ – Mole fraction

Reaction **Equilibrium** Constant $K_{\text{eq}} = \left(\frac{x_C^c \cdot x_D^d}{x_A^a \cdot x_B^b} \right)$ is constant value in

Equilibrium mixture Compound Concentrations X_C, X_D, X_A, X_B .

Free Energy change in Equilibrium forms minimum. It's forming

$\sum_{\text{product}} - \sum_{\text{initial}}$ difference zero $0 = \Delta G^\circ_{\text{eq}} + R \cdot T \cdot \ln(K_{\text{eq}})$ as well

Standard free energy change one calculates with negative natural logarithm at equilibrium K_{eq} : $\Delta G^\circ_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}})$.

Free energy change in human **homeostasis** is Prigogine

attractors driven as $\Delta G = \Delta G^\circ_{\text{eq}} + R \cdot T \cdot \ln \left(\frac{x_C^c \cdot x_D^d}{x_A^a \cdot x_B^b} \right) \neq 0$ not zero;

Attractors dissipative structure containing, irreversible working

Brownian molecular engines, evolution and surviving instruments.

Aris Kaksis **Chemical potential μ and Process Spontaneous Direction in Homeostasis**

Chemical potential show, how much change of **free energy** ΔG_A brings into reaction mixture adding of one 1 mole amount of compound **A**. In a fact: how great amount of **free energy** belongs to one **1 mol** of compound in mixture. If free energy ΔG_A amount included in Δn_A **moles of compound A**:

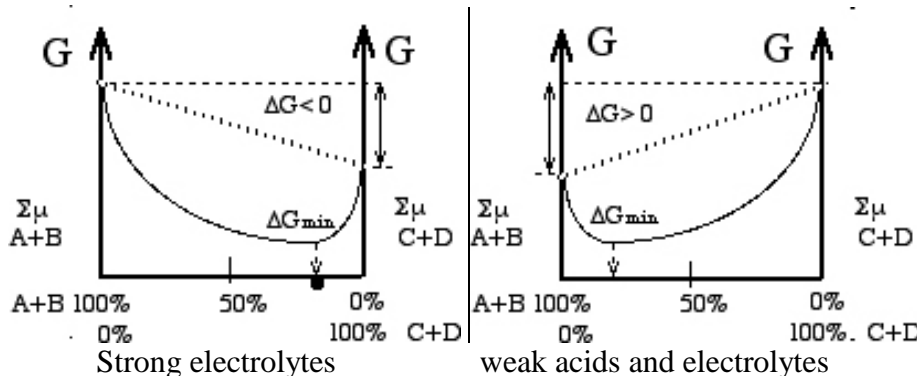
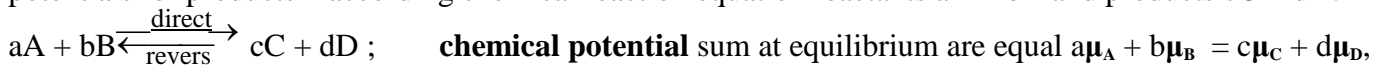
$$\mu_A = \frac{\Delta G_A}{\Delta n_A} = \Delta G^\circ_A + R \cdot T \cdot \ln(X_A) \quad (1-2)$$

chemical potential, where: ΔG°_A , **kJ/mol** - **standard chemical potential** for pure compound **A** at standard conditions **T = 298.16 K**, pressure **p = 101.3 kPa**; **R = 8.3144 J/mol/K** - universal gas constant; **ln(X_A)** - natural logarithmic function from argument **X_A** and **X_A**, unless - **molar fraction** concentration of compound **A** in mixture, expressed as **X_A = n_A/n_{total}** and laying between **0 < X_A ≤ 1** (absence, pure) compound **A** concentrations, where **n_A, mol** - **number of moles** for compound **A** and **n_{total}, mol** - total **number of moles** including water. Pure compound logarithmic zero **ln(1) = 0** yield **standard chemical potential** $\Delta G^\circ_A = \mu_A$ at **X_A = 1**, assuming **standard free energy of formation** G°_A from elements for compound **A** per one **1 mole**.

Chemical equilibrium and Thermodynamics of energy minimum

Free energy change-difference of pure products and reactants $\Delta G^\circ_{\text{reaction}}$ is criteria of process direction spontaneous for pure products 100% (negative $\Delta G^\circ_{\text{reaction}} < 0$) or thermodynamic forbidden, as products are absent 0%, but reactants are pure 100% (positive $\Delta G^\circ_{\text{reaction}} > 0$).

In state of equilibrium sum of chemical potentials for initial compounds is equal to sum of chemical potentials for products – according chemical reaction equation reactants **aA + bB** and products **cC + dD**:



The concentrations **X** of **reactants** and **products** at **equilibrium** mixture define the **equilibrium constant, K_{eq}**. **Chemical potential sum for reactants** $\Sigma\mu_{\text{reactant}}$ and **products** $\Sigma\mu_{\text{product}}$ at equilibrium are equal:

$$\Sigma\mu_{\text{reactant}} = \Sigma\mu_{\text{product}} ;$$

and free energy change for reaction is zero: $0 = \Delta G = \Sigma\mu_{\text{product}} - \Sigma\mu_{\text{reactant}}$ as minimum energy in mixture. Then

energy minimum $\Delta G^\circ_{\text{eq}}$ is calculated of mixture **chemical potential sum equivalence** $a\mu_A + b\mu_B = c\mu_C + d\mu_D$;

$$-\Delta G^\circ_{\text{eq}} = R \cdot T \cdot \ln \left(\frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b} \right) = R \cdot T \cdot \ln(K_{\text{eq}}) ; K_{\text{eq}} = \frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b} \quad (1-3)$$

In each sum a, b, c, and d are the number of molecules of A, B, C, and D participating in active mass law, the **equilibrium constant** is expressed by (1-3) where **X_A, X_B, X_C, and X_D** are the **molar fraction** concentrations of the reactants and products at the minimum point of **equilibrium** mixture. When the **equilibrium** is shifted out then start to work Le Chatelier principal toward reaching Prigogine **equilibrium** attractor the **free-energy** change minimum point ΔG_{\min} . At **standard conditions (298.15 K or 25 °C, p_{total} = 101.3 kilo-pascals (kPa))**, when reactants and products **molar fraction** concentrations in expression (1-3) reach equilibrium value, the Le Chatelier system driving forces toward equilibrium are defined as Prigogine

We must be careful to distinguish between two **2** different quantities: the **free-energy** change, ΔG , and the **standard free-energy** change, ΔG° . Each chemical reaction has a characteristic **standard free-energy** change per one **1 mol** of **reactant**, which maybe positive $\Delta G^\circ > 0$ unfavored with $0 < K_{\text{eq}} < 1$ values as well negative $\Delta G^\circ < 0$ favored with .1 hardly ever at special conditions zero $\Delta G^\circ = 0$ show in which direction and how far present reaction move reaching equilibrium minimum to right in direct reaction of products formation or to left reverse reaction as back restoring initial compounds.

ΔG° is a constant: it has a characteristic, unchanging value for a given reaction. But the actual **free-energy** change, ΔG , is a function of **reactant** and **product** concentrations **X** and of the temperature **T = 310.15 K** prevailing during the reaction in human body, which will not necessarily match the **standard conditions**. Moreover, the ΔG of any reaction proceeding \rightarrow spontaneously toward its **equilibrium** state is always negative $\Delta G < 0$, becomes less negative reaching equilibrium point and $\Delta G = 0$ is zero with $(X^d \cdot Y^c) / (X^a \cdot Y^b) = K_{eq}$, indicating constant value that no more work $W = -\Delta G = 0$ can be done by the reaction: $aA + bB = cC + dD$ according expression (1-3) $\Delta G = \Delta G^\circ_{eq} + R \cdot T \cdot \ln(K_{eq}) = 0$.

Studies in „Medical chemistry”, „Biochemistry”. Studies of Gibbs free energy change $\Delta G_{\text{reac}} = \Delta H_{\text{reac}} - T \cdot \Delta S_{\text{reac}}$

ΔH_{reac} Enthalpy	ΔS_{reac} Entropy	T Temperature	ΔG_{reac} Free energy	Spontaneous ability of reaction
Dispersed energy bound in surrounding and is lost as used free energy $\Delta G_{\text{reac}} < 0$	$T \cdot \Delta S_{\text{reac}} > 0$ is $\Delta S_{\text{reac}} > 0$ Positive entropy increases entropy change is positive	decomposition reaction	Biochemical $AB \rightarrow A + B$	catabolism organisms consume the free energy in spontaneous reactions maintain organisms living in Homeostasis .
1. Endothermic Positive $\Delta H_{\text{reac}} > 0$	Dispersed energy is forming greater measure of chaos $\Delta S_{\text{reac}} > 0$ Positive . Spontaneous catabolic reactions consume free energy change $\Delta G_{\text{reac}} < 0$ for life maintenances of organisms 37° C in human as well as to supply the heat for organisms.	low T ↓ $ \Delta H_{\text{reac}} > T \cdot \Delta S_{\text{reac}} $	Positive $\Delta G_{\text{reac}} > 0$ $\Delta H_{\text{reac}} - T \cdot \Delta S_{\text{reac}} > 0$	unfavorable reaction at low temperature
		high T ↑ $ \Delta H_{\text{reac}} < T \cdot \Delta S_{\text{reac}} $	Negative $\Delta G_{\text{reac}} < 0$ $\Delta H_{\text{reac}} - T \cdot \Delta S_{\text{reac}} < 0$	spontaneous reaction at high temperature
2. Exothermic Negative $\Delta H_{\text{reac}} < 0$		any T	Negative $\Delta G_{\text{reac}} < 0$ $\Delta H_{\text{reac}} - T \cdot \Delta S_{\text{reac}} < 0$	thermodynamically spontaneous reaction at any temperature
Living cell proliferations and existing conditions for Life	$\Delta S_{\text{reac}} < 0$ Negative entropy decreases entropy change is negative	synthesis reaction	Biochemical anabolism and organize in $A + B \rightarrow AB$	energy accumulates compounds as synthesized the higher order decreases measure of chaos $\Delta S_{\text{reac}} < 0$ negative
3. Endothermic Positive $\Delta H_{\text{reac}} > 0$	Synthesized as well as produced free energy $\Delta G_{\text{reac}} > 0$ Positive accumulates in photosynthesis , in ATP synthesis , in polypeptides as well as in proteins , in synthesized molecules , living cells live and proliferates	any T	Positive $\Delta G_{\text{reac}} > 0$ $\Delta H_{\text{reac}} - T \cdot \Delta S_{\text{reac}} > 0$	unfavorable reaction thermodynamically forbidden at any temperature
		high T ↑ $ \Delta H_{\text{reac}} < T \cdot \Delta S_{\text{reac}} $	Positive $\Delta G_{\text{reac}} > 0$ $\Delta H_{\text{reac}} - T \cdot \Delta S_{\text{reac}} > 0$	unfavorable reaction at high temperature
4. Exothermic Negative $\Delta H_{\text{reac}} < 0$		low T ↓ $ \Delta H_{\text{reac}} > T \cdot \Delta S_{\text{reac}} $	Negative $\Delta G_{\text{reac}} < 0$ $\Delta H_{\text{reac}} - T \cdot \Delta S_{\text{reac}} < 0$	spontaneous reaction at low temperature

In life important are negative change $\Delta S_{\text{reac}} < 0$ of **entropy** and positive increase $\Delta G_{\text{reac}} > 0$ of **free energy!**
Negative change $\Delta S_{\text{reac}} < 0$ dispersed energy $T\Delta S \downarrow$ decreases and into reaction accumulates supplied $+Q$ energy into compound macroergic bonds as increase the free energy $\uparrow \Delta G_{\text{reac}} > 0$.

$$\Delta H_{\text{reac}} = \uparrow \Delta G_{\text{reac}} + T \cdot \Delta S_{\text{reac}} \downarrow$$

Opposite to spontaneous reaction $\downarrow \Delta G_{\text{reac}} > 0$ negative change of free energy is lost energy.

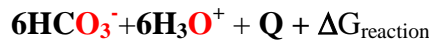
4th page <http://aris.gusc.lv/BioThermodynamics/BioThermodynamics.pdf>

Three Reaction examples studies of **Homeostasis** for students Medical Chemistry :

1. Glucose and oxygen **Green plants Photosynthesis**

← **Homeostasis**

red and **blue** light photons energy $E=h\nu$ absorption
 heat and free energy accumulates in glucose and **oxygen** n substance
 positive $\Delta H_{\text{reac}} > 0 = -Q$ **Endothermic** $\Delta H_{\text{reac}} = +2805,27 \text{ kJ/mol}$



photosynthetic process is **Endoergic** $\Delta G_r = +3040 \text{ kJ/mol}$

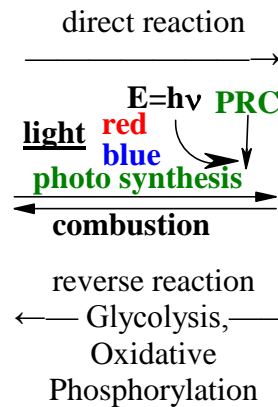
free energy accumulates in 1 mol cytosolic glucose molecules

$\text{C}_6\text{H}_{12}\text{O}_6$ biochemically in glycolise and Krebs cycle mitochondria

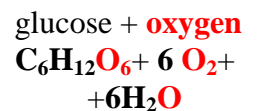
„**combusted**” by **oxygen** O_2 to **combustion** products HCO_3^-
 ($\text{CO}_{2\text{aqua}}$) and H_2O along oxidative phosphorylation pathway.

The Membrane potential 3rd page <http://aris.gusc.lv/BioThermodynamics/MembraneElektrodsAM.pdf>

(page 9 <http://aris.gusc.lv/BioThermodynamics/OxRedBiologicalW.pdf>)



Plant Enzymes
Photo synthetic
 ←/ **Reaction**
Center



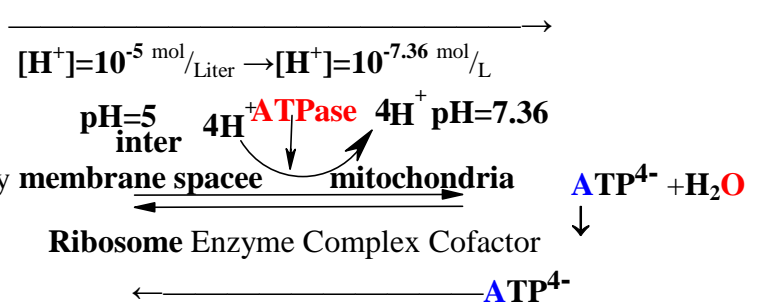
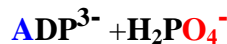
biochemical
 „**combustion**”
 Krebs cycle in
 mitochondria

2. **ATPase** driven **ATP synthesis** (**ATP** adenosine triphosphate ATP^{4-} anion $\text{pH}=7.36$ in mitochondria)

One mole of glucose $\text{C}_6\text{H}_{12}\text{O}_6$ produces glycolytical, $[\text{H}^+] 2290 \rightarrow$ Proton gradient over 1 $[\text{H}^+]$

mitochondrial totally **36 ATP** molecules. Membrane
 integral enzyme **ATPase** nano engine to transfer **free**
 energy $\Delta G_{\text{reac}} = +115,71 \text{ kJ/mol}$ for **Ribosome**

Enzyme Complex per produced **ATP** molecule under
 proton gradient drives in to **Ribosome** reaction energy



3. For free energy $\Delta G_{\text{reac}} = +57,3 \text{ kJ/mol}$ transfer

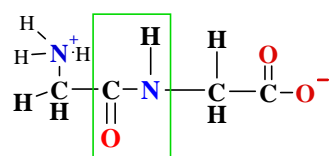
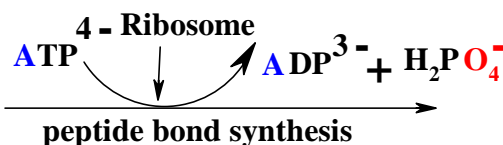
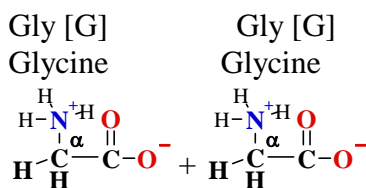
in Peptide Bond Formation Reaction is The **Ribosomal** protein synthesis: **gly+ gly→gly-gly+ H₂O**.

Ionic force = 1 M conditions in each reaction alone in separate pathways and as sum in one according Hes law.

to transfer from ATP^{4-} liberate and store **free energy** $\Delta G_{\text{reac}} = +57,3 \text{ kJ/mol}$ per one mole of **peptide bond**.

Ribosome joint **peptide** synthesis with **ATP** hydrolyze: **free energy** $\Delta G_{\text{hydrolyze}} = -115,71 \text{ kJ/mol}$ allows to

store $\Delta G_{\text{reac}} = +57,3 \text{ kJ/mol}$ free energy **in reaction per one mole peptide bond**.



ATP hydrolyze is **spontaneous**
 $\Delta G = -115,71 \text{ kJ/mol}$ and
 total **reaction** sum is \downarrow **spontaneous** too
 $\Delta G_{\text{reac}} = +57,3 - 115,71 = -58,41 \text{ kJ/mol}$
 $\Delta G_{\text{reac}} < 0$ negative

GlycinoGlycine
 Gly-Gly
 GG

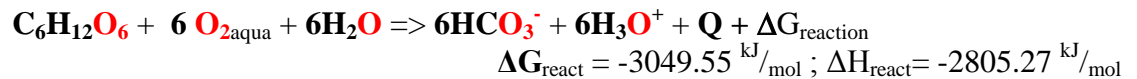
Biochemistry synthesis and decomposition reaction four types

Synthesis and decomposition (hydrolyse, biooxidation)

1. EXOTHERMIC, EXOERGIC DECOMPOSITION REACTION of HYDROLYSIS and BIOOXIDATION

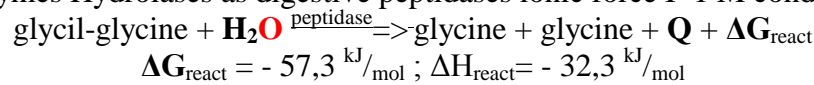
3rd and 4th page : <http://aris.gusc.lv/BioThermodynamics/BioThermodynamics.pdf>

Oxidoreductases E.1 classes enzymes, as oxidative phosphorylation summary Hess law according:



2nd and 3rd page : <http://aris.gusc.lv/BioThermodynamics/08ThGlyGlyH2OCRC10sol.pdf>

E.2 class degrading enzymes Hydrolases as digestive peptidases ionic force I=1 M conditions :



This type of reaction can be written in a general way as:



$$\Delta\text{G} = \Delta\text{H} - \text{T} \cdot \Delta\text{S} < 0,$$

one can see, that the first component of it (ΔH) is negative. ΔS itself is positive, but as there is a minus sign before it, the second component of it ($-\text{T} \cdot \Delta\text{S}$) is also negative. This means, that ΔG is always negative for this type of reactions..

Conclusion: an exothermic decomposition reaction is spontaneous at all conditions.

2. EXOTHERMIC REACTIONS OF SYNTHESIS

An EXOTHERMIC REACTION OF SYNTHESIS in a general way can be written as:



$$\Delta\text{G} = \Delta\text{H} - \text{T} \cdot \Delta\text{S}$$

the first component ΔH of the equation is negative, but the second one - positive (ΔS is itself negative, but there is a minus sign before it). As one of the components is positive, but the other negative, the result ΔG can be negative, if the negative component ΔH by its absolute value is greater, than the positive component ($-\text{T} \cdot \Delta\text{S}$):

$$|\Delta\text{H}| > |\text{T} \cdot \Delta\text{S}|$$

This is possible, if the temperature is low enough human body temperature 310.15 K

Conclusion: A synthesis reaction, that is exothermic, is spontaneous at low enough temperatures.

3. ENDOTHERMIC , EXOERGIC REACTION OF DECOMPOSITION

An example of an endothermic reaction of decomposition in a general form can be written as:



$$\Delta\text{G} = \Delta\text{H} - \text{T} \cdot \Delta\text{S}$$

Thus, the first component (ΔH) in the equation is positive, but the second one ($-\text{T} \cdot \Delta\text{S}$) - negative as entropy change itself is a positive value, but the minus sign in the equation turns the second component of equation negative.

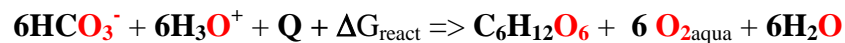
In such a way, the change of Gibbs's Energy ΔG can be negative (and the reaction can be spontaneous), if the negative component is greater, than the positive one: $|\text{T} \cdot \Delta\text{S}| > |\Delta\text{H}|$

An endothermic reaction of decomposition occurs spontaneously at high enough temperatures.

4. ENDOTHERMIC, ENDOERGIC REACTION OF SYNTHESIS.

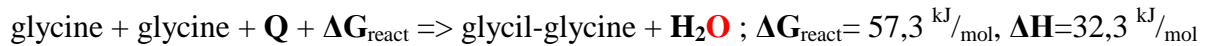
oxidoreductase class E.1 enzymes, as for photo synthesis: Hess law according:

$$\Delta G_{\text{react}} = 3049.55 \text{ kJ/mol} ; \Delta H_{\text{react}} = 2805.27 \text{ kJ/mol}$$



1st page : <http://aris.gusc.lv/BioThermodynamics/PhotoSynthesis15.pdf>

Protein peptide bond synthesis hydrolase class E.2 enzymes, as for Ribosomes ionic force I=1 M conditions:



4th page : <http://aris.gusc.lv/BioThermodynamics/08ThGlyGlyH2OCRC10sol.pdf>

This kind of reactions can be generally expressed as:



Thus, both components of ΔG are positive and therefore ΔG is positive at any temperature. It means, that this type of reaction can never be spontaneous alone- in other words, *an endothermic reaction of synthesis is thermodynamically forbidden.*

We can easily notice, that cases 1 and 4 and cases 2 and 3 are reverse reactions to each other.

Two more conclusions can be done:

1) *If the direct reaction is always spontaneous, the reverse one is forbidden.(cases 1 and 4).*

2) *If the direct reaction is spontaneous at high temperatures, the reverse one must be carried out at low temperatures.*