

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 $0 = \Delta G^\circ_r + R \cdot T \cdot \ln(K_{\text{eq}})$ as well

Standard Free Energy change one calculates with negative natural

logarithm at equilibrium K_{eq} : $\Delta G^\circ_r = -R \cdot T \cdot \ln(K_{\text{eq}})$.

Free Energy Change if not equilibrium as human **Homeostasis**

distinguish from Zero value and Concentration Ratio $\left(\frac{x_C^c \cdot x_D^d}{x_A^a \cdot x_B^b} \right)$

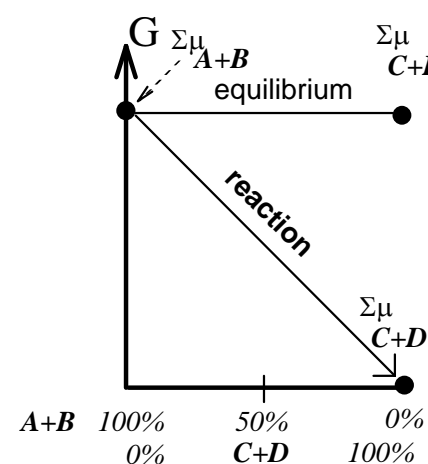
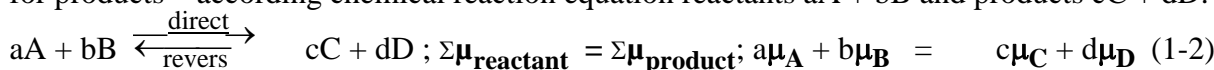
not Constant as well: $\Delta G_r = \Delta G^\circ_r + R \cdot T \cdot \ln \left(\frac{x_C^c \cdot x_D^d}{x_A^a \cdot x_B^b} \right) \neq 0$ not zero;

Aris Kaksis **Chemical potential μ and Process Spontaneous Direction in Homeostasis**
Chemical potential show, how much change of **free energy ΔG_A** brings into system-reaction adding of 1 mole amount of compound **A** . In a fact: how great amount of **free energy** belongs to one **1 mol** in mixture. It means how much free energy ΔG_A has itself per **1 mole** compound **A** , if amount of compound in molar numbers is $\Delta n_A = 1 \text{ mole} : \mu_A = \frac{\Delta G_A}{\Delta n_A} = \Delta G^\circ_A + R \cdot T \cdot \ln(X_A)$ (1-1)

chemical potential of compound **A**, where: ΔG°_A , **kJ/mol** - **standard chemical potential** 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**, expressed as **X_A = n_A/n_{total}** and laying between **0 < X_A ≤ 1** (absence and pure) compound **A** concentrations, where **n_A**, **mol** - **number of moles** for compound **A** and **n_{total}** , **mol** - total **number of moles** all present compounds **total** including water. Logarithmic function properties **ln(1) = 0** yield that **standard chemical potential $\Delta G^\circ_A = \mu_A$** at **X_A = 1** is pure **A** compound **1 mol** free energy content ΔG°_A , assuming **standard free energy of formation G°_A** from elements for compound **A** per one **1 mole**. Reaction proceeds completely forward until end only when **products** of reaction have hardly little disposition to reverse change back into **reactants**. In other words these **products** of reaction have trifling remarkable or zero value of chemical potential: **$\mu_{\text{products}} = 0$** , affinity turns back to **reactants: A ← x— products**.

Thermodynamics conditions of chemical equilibrium and Homeostasis

Provided chemical potential of reaction products is taking into consideration (it has anything remarkable level of value) , then reaction proceeds not completely until end, go not on completely 100% to reactants conversion to products, but one can observe the setting in equilibrium. 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**:



because compound factorials **a, b, c, and d** times **μ** . For compound **A** (**A+A+A+...**)=**aA**=> **$a\mu_A$** times **a**. For compounds **B, C, and D** as seen on equation of reaction expression(1-2), takes **a** part times **b, c** and **d**: (**B+B+B+...**)=**bB**=> **$b\mu_B$** ; (**C+C+C+...**)=**cC**=> **$c\mu_C$** ; (**D+D+D+...**)=**dD**=> **$d\mu_D$** Chemical potential **μ** like as amount of compound **n** in mols have additive properties, e.g. summing.

The concentrations **X** of **reactants** and **products** at **equilibrium** define the **equilibrium constant, K_{eq}** (see the Chemical Equilibrium). In the general reaction **chemical potential** sum for **reactants $\Sigma \mu_{\text{reactant}}$** and **products $\Sigma \mu_{\text{product}}$** at equilibrium are equal **and free energy change for reaction is zero $0 = \Delta G_{\text{react}} = \Sigma \mu_{\text{product}} - \Sigma \mu_{\text{reactant}}$** and expressed

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

Aris Kaksis 2016. Riga Stradin's University <http://aris.gusc.lv/BioThermodynamics/ChemicalPotential.pdf>

$$\Delta G_{\text{react}} = \Delta G^\circ_{\text{react}} + R \cdot T \cdot \ln \left(\frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b} \right) \neq 0; \text{ at equilibrium zero } \Delta G_{\text{react}} = \Delta G^\circ_{\text{react}} + R \cdot T \cdot \ln(K_{eq}) = 0 \quad (1-4),$$

in **Homeostasis** **$(X_D^d \cdot X_C^c) / (X_A^a \cdot X_B^b) \neq K_{eq}$** differs from equilibrium constant **$K_{eq} = \left(\frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b} \right)$**

We must be careful to distinguish between two 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 **$\Delta G^\circ > 0$** , negative **$\Delta G^\circ < 0$** , or some time zero **$\Delta G^\circ = 0$** , depending on the equilibrium constant **K_{eq}** of the reaction.

The **standard free-energy change** ΔG° tells us in which direction and how far a given reaction must go to reach **equilibrium** when the temperature is **25° C** as $T_0 = 298.15 \text{ K}$, and the pressure **p** is **101.3 kPa (1 atm)** and component concentrations at **equilibrium** are **X**. Thus 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** as defined above. Moreover, the ΔG of any reaction proceeding \rightarrow spontaneously toward its **equilibrium** state is always negative $\Delta G < 0$, becomes less negative as the reverse \leftarrow reaction proceeds, and is zero $\Delta G = 0$ at the point of **equilibrium** $(X^d \cdot X^c) / (X^a \cdot X^b) = K_{eq}$, indicating that no more work $W = -\Delta G_{react} = 0$ can be done by the reaction: $aA + bB = cC + dD$ according expression (1-4)

$$\Delta G_{react} = \Delta G^\circ_{react} + R \cdot T \cdot \ln(K_{eq}) = 0.$$

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

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

A.Kaksis 2017. Riga Stradin's University 4th page

<http://aris.gusc.lv/BioThermodynamics/BioThermodynamics.pdf>

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

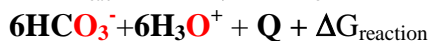
1. Glucose and oxygen **Green plants Photosynthesis**

← **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

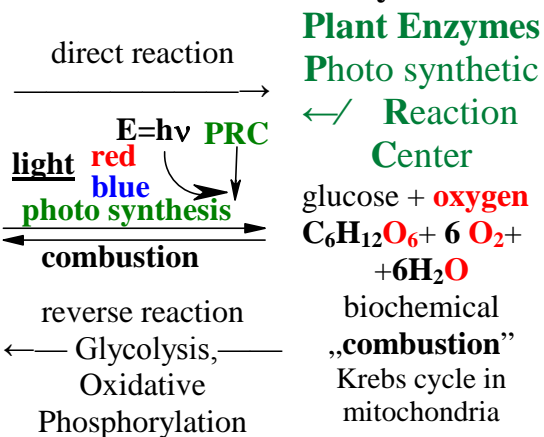
$\text{C}_6\text{H}_{12}\text{O}_6$ biochemically in glycolise and Krebs cycle mitochondria

„**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>)

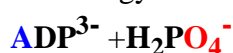


2. **ATPase** driven **ATP synthesis** (**ATP** adenosine triphosphate ATP^{4-} anion $\text{pH}=7.36$)

One mole of glucose $\text{C}_6\text{H}_{12}\text{O}_6$ produces glycolytical, **mitochondrial** totally **36 ATP** molecules. Membrane

integral enzyme **ATPase** nano engine to transfer **free** energy $\Delta G_{\text{reac}} = +30.5 \text{ kJ/mol}$ for **Ribosome** Enzyme

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



$[\text{H}^+] 2290 \rightarrow$ Proton gradient over 1 $[\text{H}^+]$

$[\text{H}^+] = 10^{-5} \text{ mol/Liter} \rightarrow [\text{H}^+] = 10^{-7.36} \text{ mol/L}$

$\text{pH}=5$ inter 4H^+ **ATPase** 4H^+ $\text{pH}=7.36$

membrane space mitochondria

$\text{ATP}^{4-} + \text{H}_2\text{O}$

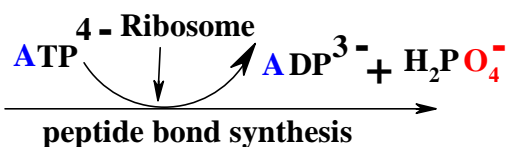
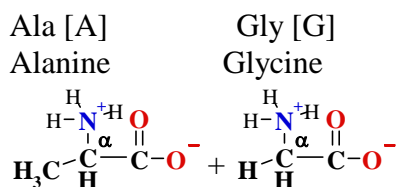
ATP^{4-}

3. For free energy $\Delta G_{\text{reac}} = +17.2 \text{ kJ/mol}$ transfer

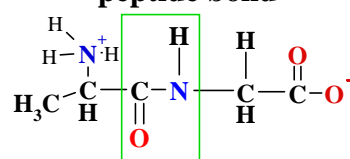
in Peptide Bond Formation Reaction is The **Ribosomal** protein synthesis: **ala + gly** → **ala-gly + H₂O**.

To transfer from ATP^{4-} liberate and store **free energy** $\Delta G_{\text{reac}} = +17.2 \text{ kJ/mol}$ per one mole of **peptide bond**.

Ribosome joint peptide synthesis with ATP hydrolyze: free energy $\Delta G_{\text{hydrolyze}} = -30.5 \text{ kJ/mol}$ allows to store $\Delta G_{\text{reac}} = +17.2 \text{ kJ/mol}$ **free energy** in reaction per one mole of **peptide bond**



ATP hydrolyze is spontaneous
 $\Delta G = -30.5 \text{ kJ/mol}$ and
 total **reaction** sum is \downarrow **spontaneous** too
 $\Delta G_{\text{reac}} = +17.2 - 30.5 = -13.3 \text{ kJ/mol}$
 $\Delta G_{\text{reac}} < 0$ negative



AlaninoGlycine
 Ala-Gly
 AG

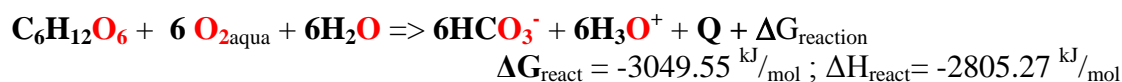
Biochemistry synthesis and decomposition reaction four types

Synthesis and decomposition (hydrolyse, biooxidation)

1. EXOTHERMIC, EXOERGIC DECOMPOSITION REACTION of HYDROLYSIS and BIOOXIDATION

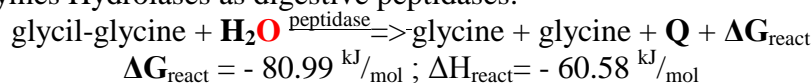
3rd and 4th page : <http://aris.gusc.lv/BioThermodynamics/BioThermodynamics.pdf>

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

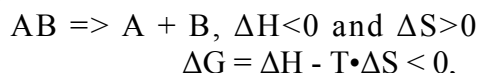


2nd and 3rd page : <http://aris.gusc.lv/BioThermodynamics/08ThGlyGlyH2OCRC10sol.pdf>

E.2 class degrading enzymes Hydrolases as digestive peptidases:



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



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:



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:



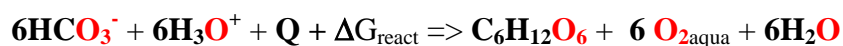
Thus, the first component (ΔH) in the equation is positive, but the second one ($-\text{T} \cdot \Delta\text{S}$) - negative as entropy change itself is a positive value, but the minus sign in the equation turns the second component of equation negative.

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.

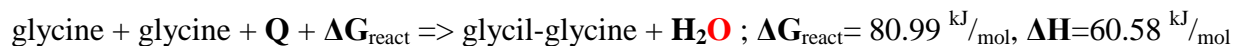
4. ENDOTHERMIC, ENDOERGIC REACTION OF SYNTHESIS.

oxidoreductase class E.1 enzymes, as for photo synthesis: $\Delta G_{\text{react}} = 3049.55 \text{ kJ/mol}$; $\Delta H_{\text{react}} = 2805.27 \text{ kJ/mol}$



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

Protein peptide bond synthesis hydrolase class E.2 enzymes, as for Ribosomes:



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 - 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.*