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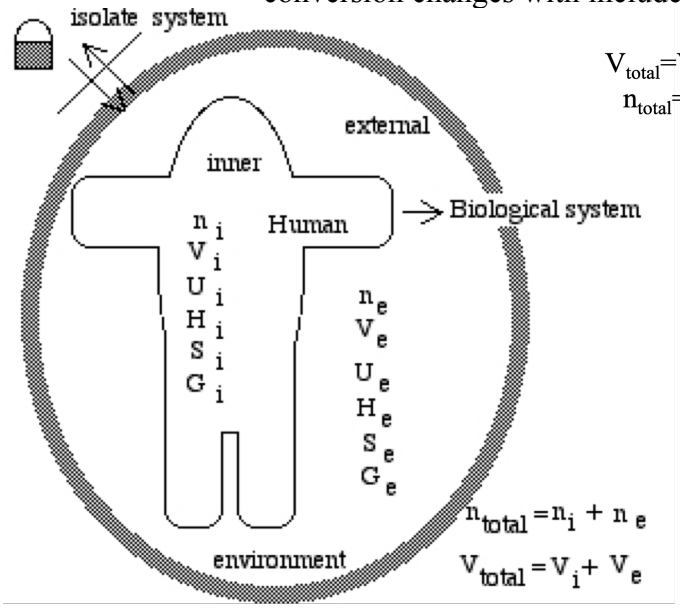
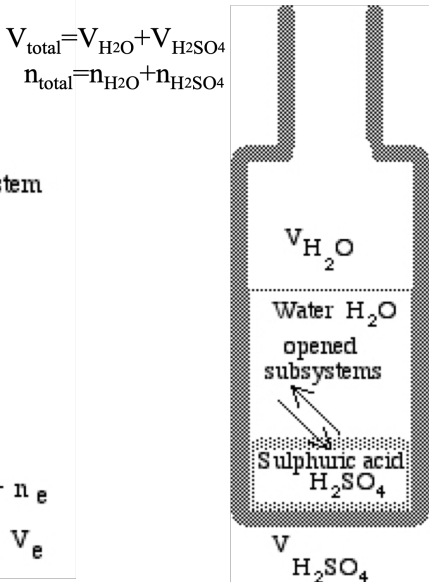
Thermodynamics – Equilibrium - Homeostasis

Method for studies of energy and mass exchange in Nature, Human and Cells .
Meanings of: **Thermodynamics** – **Heat motion**: *Greek, Latin -English languages*

Homeostasis – even - equal staying: *Greek-English language*

Inside Isolate **System** (n=const, V=const, U=const, H=const, S=const, G=const) study interactions of conversion changes with included at least two and more open sub **systems**.

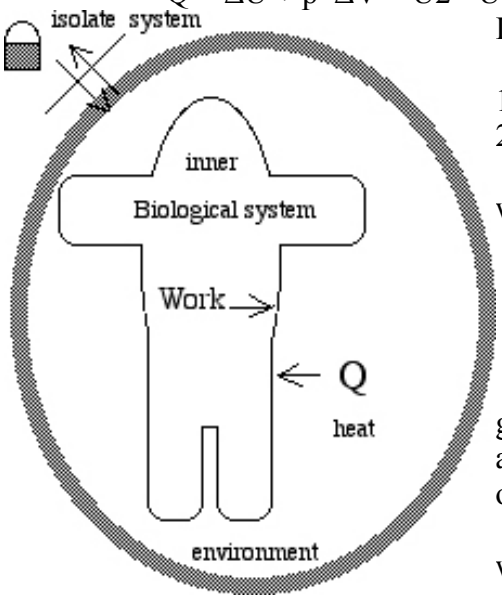




Are two shapes of sub **systems**: homogeneous and heterogeneous
Biological sub **systems** (Humans) are to environment organic regulated opened sub **systems** for mass and energy exchange (metabolism) inhaled osmosis O_2, H_2O, food (carbohydrates, proteins, fats) and remove homeostasis products of metabolic wastes zero free energy $G_{H2O}=G_{CO2gas}=0$ $^{kJ}/_{mol}$.

Enthalpy H = U +p*V heat content of system

Heat Q of environment supplied is growth the heat content ΔH of biological sub system:
Q = ΔU + p*ΔV = U2 - U1 + p(V2 - V1) = U2 + pV2 - (U1 + pV1) = H2 - H1 = ΔH



If environment sub system adds heat Q to the biological sub system, heat Q is used:
1.) for increasing of the ΔU internal energy and
2.) for a work W, that does against environment thus:

Q = ΔU + W

where Q is heat amount of environment and
W=p*Δ V is the work of biological sub system and
ΔU is a internal energy change of biological sub system.

Biochemistry Thermodynamics

Living cells and organisms must perform **work W** to stay alive, to grow, and to reproduce. Biochemistry thermodynamics account the accumulate and dispersed energy **G** in products. That the living organisms fundamental property for accumulation and dispersion.
Iļya Prigogine 1977 declare **attractors** for quantitative studies to which trend driven irreversible free energy **G** transfer processes.

Organisms are compartmented complex reactions clusters of compounds mixture, dissipative structure containing, irreversible trends to minimum working free energy change, with certain **attractors** driven Brownian molecular engines, evolution and surviving instruments of non equilibria being homeostasis.

Chemical energy **G** of fuels create concentration **C** gradients, electrical **E** gradients, ***motion*** work **W**, ***heat*** **H** and some organisms as fireflies the ***light*** **~hv**. Photosynthetic organisms accumulate photon energy **~hv** into glucose, oxygen, water $C_6H_{12}O_6+6O_{2aqua}+6H_2O$ with free **energy** $\Delta G_{Lehninger}$=2840 $^{kJ}/_{mol}$ 6th page Biochemistry amount of free energy $G_{C6H12O6}$=**1857.7** $^{kJ}/_{mol}$ and reduction potential $E^{\circ}_{C6H12O6}$=0,157 V; 1st page.

Hess Law and free energy change minimization Prigogine attractor for reaction

Hess Law ΔH_{Hess}, ΔS_{Hess}, ΔG_{Hess} of standard formation products minus reactants for standard enthalpy ΔH°, entropy ΔS° and free energy ΔG° of compound molecule are change in a reaction, in which one mole of the compound is formed from free elements at standard conditions I= 0,25 M, T=298 K, p=101.3 kPa: **Hess** Standard enthalpy change for reaction: $\Delta H_{Hess} = \Sigma\Delta H^\circ_{products} - \Sigma\Delta H^\circ_{reactant}$;

Hess Standard entropy change for reaction: $\Delta S_{Hess} = \Sigma\Delta S^\circ_{products} - \Sigma\Delta S^\circ_{reactant}$;

Hess Standard free energy change for reaction: $\Delta G_{Hess} = \Sigma\Delta G^\circ_{products} - \Sigma\Delta G^\circ_{reactant}$;

Change obtained as products minus reactants has equal parity in equivalent amounts.

Note: Human metabolism daily uptake 15,6 mol O_2, 2 liter H_2O, carbohydrates, proteins, fats and equal in five type complex reactions eliminate 15,6 mol CO_2, 2 liter H_2O, metabolic wastes as products.

Combustion heat of compound is the enthalpy change in a reaction, in which 1 mole of the compound is completely combusted to CO_2 and H_2O $\Delta H_{Hess} = \Sigma\Delta H^{\mathbf{combustions}}_{\mathbf{reactants}} - \Sigma\Delta H^{\mathbf{combustions}}_{\mathbf{products}}$

ΔG_{Hess} free energy change as products minus reactants in reaction aA+bB<=>cC+dD minimized reaching equilibrium constant: $K_{equilibrium} = \frac{k_{\rightarrow}}{k_{\leftarrow}} = \frac{[C]^c \bullet [D]^d}{[A]^a \bullet [B]^b} = K_{eq}$; $\Delta G_{eq} = -R\bullet T\bullet \ln\left(\frac{[C]^c \bullet [D]^d}{[A]^a \bullet [B]^b}\right) = -R\bullet T\bullet \ln(K_{eq})$.

Minimum $|\Delta G_{eq} = \Delta G_{min}|$ is Prigogine attractor $|\Delta G_{Hess}| > |\Delta G_{eq} = \Delta G_{min}|$ to what trend reaction.

Water protolysis - ionization and neutralization inverse attractors of reverse reactions:

Energy minimum of free energy change $\Delta G_{min} = \Delta G_{eq}$

1. equilibrium $H_2O+H_2O+Q+\Delta G=H_3O^+ + OH^-$; **2.** equilibrium $H_3O^+ + OH^- = H_2O+H_2O+Q+\Delta G$

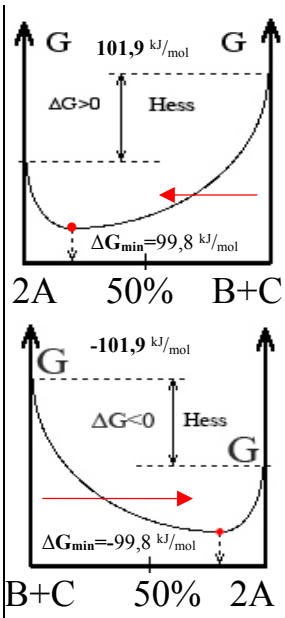
Free energy change for Hess law 1st and 2nd reaction is positive and negative unfavored and favored, endoergic and exoergic, in direct and in reverse reaction :

$\Delta G_{ionisationHess} = \Delta H_{ionisationHess} - T\Delta S_{ionisationHess} = +101.9\ ^{kJ}/_{mol}$.

$\Delta G_H = \Delta H_H - T*\Delta S_H = 55.89+298.15*0.154305 = 101.9\ ^{kJ}/_{mol}$ **endoergic**.

$\Delta G_{neutralizationHess} = \Delta H_{neutralizationHess} - T\Delta S_{neutralizationHess} = -101.9\ ^{kJ}/_{mol}$;

$\Delta G_H = \Delta H_H - T*\Delta S_H = -55.89-298.15*0.154305 = -101.9\ ^{kJ}/_{mol}$ **exoergic**.



Reaching mixture 1 and 2 equilibrium constants values are inverse:

$K_{eq1} = \frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]} = 3.26\bullet 10^{-18}$; $K_{eq2} = \frac{[H_2O]\cdot[H_2O]}{[OH^-]\cdot[H_3O^+]} = 3.068\bullet 10^{17}$;

$\Delta G_{eq1} = -R\bullet T\bullet \ln(K_{eq1}) = -8.3144\bullet 298.15\bullet \ln(3.26\bullet 10^{-18}) = +99.8\ ^{kJ}/_{mol}$,

$\Delta G_{eq2} = -R\bullet T\bullet \ln(K_{eq2}) = -8.3144\bullet 298.15\bullet \ln(3.068\bullet 10^{17}) = -99.8\ ^{kJ}/_{mol}$,

Hess Free energy change ΔG_{Hess} is greater, but minimizes reaching equilibrium mixture $|\Delta G_{eq}| = 99.8\ ^{kJ}/_{mol} < 101.9\ ^{kJ}/_{mol} = |\Delta G_{Hess}|$.

Water protolysis increases free energy content for water molecules $2H_2O$ from zero 0 to $99.8\ ^{kJ}/_{mol}$ for protolysis products $H_3O^+ + OH^-$, what have lost in neutralization.

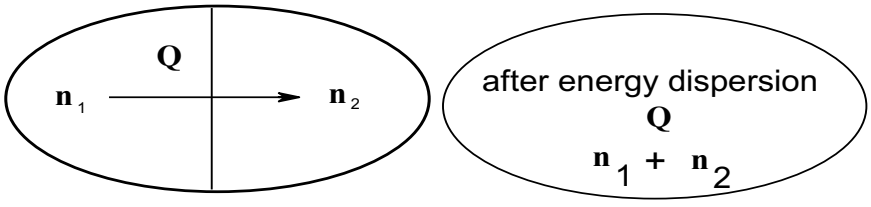
All reactions trend to Prigogine attractor minimum of free energy change $\Delta G_{min} = \Delta G_{eq}$ at equilibrium mixture with reverse reactions inverse constants $K_{eq1} = \frac{1}{K_{eq2}}$ for.

In 1977 declared Ilya Prigogine attractors claim perfect order trends of Universe for each process to energy change minimum in mixture of reacting compounds.

See page 15th

Thermodynamics II Law. Measure of **energy dispersion** for one mol per one unit **T** (298,15 K) degree is **entropy amount S** value sum of 1st Heat dispersion and 2nd of **entropy change** in reaction

1. The amount of heat dispersed from warmer body $\mathbf{n}_1$ to cooler surroundings body.
Energy of system is dispersed on more great count of particles sum $\mathbf{n}_1 + \mathbf{n}_2$.

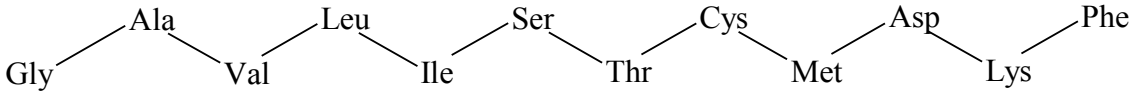


$\mathbf{T_1} > \mathbf{T_2}$ =>Energy dispersion=> $\mathbf{T_1} > \mathbf{T} > \mathbf{T_2}$

Heat dispersion of reaction $-\Delta\mathbf{H}_{Hess}$ per temperature **T** unit is **entropy growth positive** into environment as surrounding $\Delta\mathbf{S}_{\mathbf{dispersed}} = -\Delta\mathbf{H}_{Hess}/\mathbf{T}$

2. Polypeptide chain protein molecule own united dissipative system of 12 amino acids:

Glycine, Alanine, Valine, Leucine, Isoleucine. Serine,
Threonine, Cysteine, Methionine, Aspartate, Lysine and Phenylalanine.



After hydrolysis (decomposition) reaction => to separate in to 12 small molecules :
H1 H2 H3 H4 H5 H6 H7 H8 H9 H10 H11 H12:
Gly + Ala + Val + Leu + Ile + Ser + Thr + Cys + Met + Asp + Lys + Phe

Energy dispersion on temperature **T** unit is dissipative system decomposition. Hess law calculates entropy growth positive for Polypeptide dissipation into 12 free amino acids sum $\Sigma\Delta\mathbf{S}^\circ_{amino\_acids\_12}$:

$$\Delta\mathbf{S}_{Hess}=\Sigma\Delta\mathbf{S}_{product}-\Sigma\Delta\mathbf{S}_{reactant}=\Sigma\Delta\mathbf{S}^\circ_{amino\_acids\_12}-\Delta\mathbf{S}^\circ_{Polypeptide}>0.$$

Total entropy $\Delta\mathbf{S}_{\mathbf{total}}$ is energy dispersion sum of heat plus dissipation the structures in reaction of hydrolysis decomposition : $\Delta\mathbf{S}_{\mathbf{total}} = \Delta\mathbf{S}_{\mathbf{dispersed}} + \Delta\mathbf{S}_{Hess} > 0$ growth positive.

Note: Synthesis reaction alone is impossible $\Delta\mathbf{S}_{\mathbf{total}} < 0$ as negative because chaos decreases in polymer and energy accumulates from dissipated reactants, monomers: mono sacharides, amino acids, nucleic acids, ect.

II Law of thermodynamics spontaneous Energy dispersion Law

Internal energy U or enthalpy H of system has two summing parts:
$U = F + S\bullet T$; at constant volume V=const
$H = G + S\bullet T$; at constant pressure p=101,3 kPa on see level.
1. free energy F (Helmholtz's energy) or G (Gibbs's free energy) and 2. lost energy $S\bullet T$,
where S entropy of lost energy in surrounding per temperature T unit degree multiplied by T temperature in Kelvin grades is "bound" dispersed as lost energy in environment:

1. G free Gibbs's energy at constant pressure is more appropriate, because most processes on Earth occur at acceptable for life constant pressure p=101,3 kPa (at see level).

For <u>isolate</u> <u>system</u>, where U and H are constant, unchanged. It means enthalpy change $\Delta H_{\mathbf{total}}=0$ is zero as H is constant: $\Delta H_{Hess} = \Delta G_{Hess} + \Delta S_{Hess}\bullet T = 0$.

Spontaneous process always take a place and free energy $\Delta G_{Hess}<0$ growth smaller that compensates with a growth of entropy $\Delta S_{\mathbf{total}}>0$, so that sum of the free Energy and bound energies changes compensate each other. In other word's growth of entropy $\Delta S_{\mathbf{total}}>0$ in bound energy $\Delta S_{\mathbf{total}}\bullet T>0$ is compensated with free Energy $\Delta G_{Hess}<0$ decrease as sum is zero: $0=\Delta G_{Hess}+\Delta S_{\mathbf{total}}\bullet T$.

So free energy decrease in spontaneous process converts to free energy "bound" : $G\downarrow=>\uparrow S\bullet T$
and dispersion in surrounding as well as "lost free energy ΔG_{Hess}" change is negative value and converts equal increased to bound energy $\Delta S_{\mathbf{total}}\bullet T$, at constant pressure p = const. the change of value ΔH_{Hess} determine character of reaction: exothermic $\Delta H_{Hess} <0$ or endothermic $\Delta H_{Hess} >0$ $\Delta G_{Hess} = \Delta H_{Hess} - \Delta S_{Hess}\bullet T$

At this can conclude :
1. Exoergic process spontaneous, favored if free energy has negative value $\Delta G_{Hess}=\Delta H_{Hess}-\Delta S_{Hess}\bullet T<0$ or
2. Endoergic process unfavored, forbidden if free energy has positive value $\Delta G_{Hess}=\Delta H_{Hess}-\Delta S_{Hess}\bullet T>0$.

The chemical mechanisms that underlie energy **G** transductions => have fascinated and challenged scientist for centuries. **Antoine Lavoisier** (1743-1794), before he lost his head in the French Revolution, recognized that animals somehow transform chemical fuels (foods) into heat **H** and that this process of respiration is **essential** to **life**. He observed that …in general, respiration O_2 is nothing but a slow **combustion** of carbon **C** and hydrogen **H**, which is entirely similar to that which occurs in a lighted lamp or candle, and that, from this point of view, animals that respire are true **combustible** bodies that **burn** and consume themselves.

…One may say that this analogy between **combustion** and **respiration** has not escaped the notice of the poets, or rather the philosophers of antiquity, and which they had expounded and interpreted. This fire stolen from heaven, this torch of Prometheus, does not only represent an ingenious and poetic idea, it is a faithful picture of the operations of **nature**, at least for animals that breathe O_2; one may therefore say, with the ancients, that the torch of life lights itself at the moment the infant breathes for the first time, and it does not extinguish itself except at death. **Biochemical** studies have revealed much of the chemistry underlying that "torch of life".

Biological energy G transductions => obey the same **physical laws** that govern all other natural processes. However **Biology** do not have data for Hess law and Prigogine attractors calculation, what do **biochemistry**.

It is therefore essential for a student of bio-medical-sciences to understand these **biochemistry** laws and how they apply to the flow => of **energy G** in the biosphere. In this chapter we first review the laws (Hess law and Prigogine attractors) of thermodynamics and the quantitative relationships among free **energy G**, **enthalpy H** (**internal heat content** of substance), **bound energy T•S** (**temperature** and **entropy** factorial) and Prigogine attractors. What the role of **ATP** in **biochemical energy G** exchanges play for biochemical environment forming fast equilibria, what drive life processes with attractors of molecules functional activity:
water concentration $[H_2O]$=55.3457 M, generate concentration gradients, air 20.95% $[O_2]$,
osmolar concentration 0,305 M, ionic strength 0,2 M,
pH=7,36 hydroxonium cations concentration $[\mathbf{H_3O^+}]=10^{-7,36}$ M, temperature 310,15 K degree.

Finally, we consider the importance of *oxidation-reduction* free energy change minimization decrease driven *reactions* in homeostasis of cells, the thermodynamics of **electron e^- transfer** reactions, and the **electron e^- carriers** commonly employed as cofactors of the enzymes that catalyze these **reactions**.

*From a memoir by Armand Seguin and Antoine Lavoisier, dated 1789, quoted in Lavoisier, A. (1862) Oeuvres de Lavoisier, Imprimerie Imperiale, Paris.

Biochemistry synthesis and decomposition reaction four types

1. EXOTHERMIC, EXOERGIC DECOMPOSITION REACTION of hydrolysis and bio oxidation Oxidoreductases E.1 classes enzymes, as oxidative phosphorylation summary:

$\mathbf{C_6H_{12}O_6+ 6O_{2aqua}+6H_2O=>6HCO_3^-+6H_3O^+}+\Delta G+Q$; ΔG_{Hess}= **-3765** $^{kJ}/_{mol}$;ΔH_{Hess}= **-2812,6** $^{kJ}/_{mol}$

E.3 class degrading enzymes Hydrolases-digestive peptidases : exoergic exothermic

$\mathbf{Gly\text{-}Gly_{aqua}+H_2O} \xrightarrow{peptidase} \mathbf{Gly_{aqua}+Gly_{aqua}}+ Q+\Delta G$; $\Delta G_{Lehninger}$= **- 9,2** $^{kJ}/_{mol}$; ΔH_{Hess}= **-25,92** $^{kJ}/_{mol}$

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

AB => A + B, $\Delta G = \Delta H - T\bullet\Delta S < 0$, **ΔS>0 and ΔH<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 (**- T•ΔS**) 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:

A + B => AB, ΔH<0 and ΔS<0 ; $\Delta G = \Delta H - T\bullet\Delta S$

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 (**- TΔS)**:

$$|\Delta H| > |T\bullet\Delta S|$$

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:

AB => A + B ΔH>0 and ΔS>0 ; **ΔG = ΔH - T•ΔS**

Thus, the first component (**ΔH**) in the equation is positive, but the second one (**-T•ΔS**) - 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: **| T•ΔS | > | ΔH |**

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

4. ENDOTHERMIC, ENDOERGIC REACTION OF SYNTHESIS.

Oxidoreductase class E.1 enzymes, as for photosynthesis: endoergic endothermic:

$6HCO_3^- + 6H_3O^+ + \Delta G + Q \Rightarrow C_6H_{12}O_6 + 6O_{2\,aqua} + 6H_2O$; $\Delta G_{Hess} = +3765\ ^{kJ}/_{mol}$; $\Delta H_{Hess} = +2812{,}6\ ^{kJ}/_{mol}$

Protein peptide bond synthesis hydrolase class E.3 enzymes, as for Ribosomes: endoergic endothermic:

$Gly_{aqua} + Gly_{aqua} + Q + \Delta G \xrightarrow{ribosome} Gly\text{-}Gly_{aqua} + H_2O$; $\Delta G_{Lehninger} = +\,9{,}2\ ^{kJ}/_{mol}$; $\Delta H_{Hess} = +\,25{,}92\ ^{kJ}/_{mol}$

This kind of reactions can be generally expressed as: **A + B => AB** ; **ΔS<0** and **ΔH>0** .
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.

Biochemical Thermodynamics

Thermodynamics is the quantitative study of the energy **G** transductions in living organisms the pathways and functions of the **chemical** processes by Ilya Prigogine defined dissipative structure consisting complex systems. Irreversible processes working, with certain attractors driven Brownian molecular engines.

Enzymes and its complexes .

Biochemical Energy Transformation based on irreversible dispersion (Prigogine)

Many quantitative observations made by physicists and chemists on the inter-conversion of different forms of energy led, in the nineteenth **19th** century, to the formulation of two **2** fundamental **laws** of thermodynamics.

The first **1st law** is the principle of the conservation of energy and mass: *for any physical or chemical change, the total amount of energy* **U = const** (**internal** energy) *in the* **isolate system** *remains constant*. Dissipative subsystems *energy may change form or it may be transported between such regions* (**open subsystems** as total **isolate system**)*, but it cannot be created or destroyed* (as **system** total is **isolate**).

The second **2nd law** of thermodynamics state spontaneous dispersion of energy. The **isolate system** always tends to use own **free** energy **G** content toward increasing **bound** energy **T•S**:

in all natural processes, the total entropy **S** *increases* .

Living organisms synthesise molecules with much more high order. From apparent chaos of Prigogine mixture attractor creates order as polymers or composite materials-clusters of water soluble and water insoluble mediums membranes. These surrounding materials from constructions for organism maintenance and building produce the perfect order of Biochemistry, sciences and universe. Prigogine dissipative structures thermodynamic often designed as chaos theory for perfect order of universe.

Organisms are compartmented complex reactions clusters of compounds mixtures, dissipative structure containing, irreversible free energy change to minimum working, with certain **Attractors** driven Brownian molecular engines, evolution and surviving instruments of non equilibria being homeostasis.

Second **2nd law** operate strictly collaborate with **surroundings** (**environment**). The **reacting systems** and its **surroundings** compartmented complex reactions clusters of compounds mixtures are irreversible non equilibria energy **U**, **H**, **G** dispersing systems in to **surroundings** trends reach the minimum of energy change at equilibrium mixture.

They convert the chemical energy **G** of fuels into concentration **C** gradients, electrical **E** gradients and into ***motion*** work **W**, ***heat*** **H** and some organisms as fireflies into ***light*** **~hv**. Photosynthetic organisms accumulate light energy **~hv** into life resources $C_6H_{12}O_6+6O_{2aqua}+6H_2O$ free **energy** $\Delta G_{Lehninger}=2840\ ^{kJ}/_{mol}$ amout 6th page and reduction potential $E^{\circ}_{C6H12O6}=0,157$ V; 1st page:.

Defined three **3** thermodynamic quantities that describe the energy changes **ΔG**, **ΔH**, and **ΔS•T** occurring in a chemical reaction. **Gibbs free** energy (**G**) expresses the amount of energy capable of doing work **W** during a reaction at constant pH=7,36, osmolar concentration C_{osm}=0,305 M, ionic strength I=0,2 M, temperature **T** and pressure **p**. When a reaction from **1** => to **2** proceeds with the release of **free** energy **ΔG** (i.e., when the system changes so as to possess less **free** energy G_2 difference of change will be negative $\Delta G=C_2-G_1$), the **free**-energy change, **ΔG<0**, has a negative value and the reaction is said to be **exoergic**. In **endoergic** reactions, the system gains **free** energy and **ΔG>0** is positive. **Enthalpy**, **H**, is the **heat content** of the reactant **system**. It reflects the number and kinds of chemical bonds in the **reactants** and **products**. When a chemical reaction releases **heat** **ΔH<0**, it is said to be **exothermic**; the **heat content** of the **products** is less than that of the **reactants** and $\Delta H=H_2-H_1$ has, by convention, a negative value. **Reacting systems** that take up heat **ΔH>0** from their **surroundings** are **endothermic** and have $\Delta H=H_2-H_1$ positive values. Entropy, **S**, is a quantitative expression for the loosing-dispersion of **free energy** **ΔG<0** in a system products. When the **products** of a reaction are decomposed more complex **reactants** and has more dispersed or dissipated **free energy** than the **reactants**, the reaction is said to proceed with a gain in **bound** energy **T•ΔS** as rises entropy **ΔS>0** of products.
The units of **ΔG** and **ΔH** are $^{joules}/_{mole}$ or **calories/mole** (recall that **1 cal** equals **4.184 J** units)
of **entropy** are $^{joules}/mole/_{Kelvin}$ ($^{J}/mol/_{K}$).

Under the conditions existing on the see level of Earth surface (including standard conditions), changes in **free** energy **ΔG**, **enthalpy** **ΔH**, and **entropy** **ΔS** are related to each other quantitatively by the equation (1-1) according Hess law: $\Delta G_{Hess} = \Delta H_{Hess} - T\bullet\Delta S_{Hess}$ (1-1)
in which $\Delta G_{Hess}=G_2-G_1$ is the change in **Gibbs free** energy of the reacting **system**, $\Delta H_{Hess}=H_2-H_1$ is the change in **enthalpy** of the **system**, **T** is the absolute temperature, and $\Delta S_{Hess}=S_2-S_1$ is the change in **entropy** of the **system**. By convention, **ΔS>0** has a positive (+) sign when **entropy** **S** increases. **ΔH<0**, as noted above, has a negative (-) sign when **heat** is released by the **system** to its **surroundings** as well **system** has lost the **heat content H.** Either of these conditions, which are typical of **favorable** processes, tend to make **ΔG<0** negative. In fact, **ΔG** of a spontaneously reacting system is always negative **ΔG<0**.

Table 1-1. Some Physical Constants and Units Used in Thermodynamics

Boltzmann constant, **k = 1.381 • 10^{-23} $^{J}/_{K}$**

Avogadro's number, **N_A = 6.022 • 10^{23} mol^{-1}** ; Faraday constant, **F = 96 485 J/V/mol**

Gas constant, **R = 8.3144 $^{J}/mol/_{K}$ (= 1.987 $^{cal}/mol/_{K}$)**

Units of **ΔG** and **ΔH** are $^{kJ}/_{mol}$ (or $^{kcal}/_{mol}$)

Units of **ΔS** are $^{J}/mol/_{K}$ (or $^{cal}/mol/_{K}$); **1 cal = 4.184 J**

Units of absolute temperature, **T**, are Kelvin, **K**; **25 °C => 298,15 K** ; **37 °C** => **310,15** K;

Ionic strength, **I**, **mol/L=M**(molarity); standard conditions **I**=0,2 M human, **I**=0,1 M plants.

Concentrations: water [H_2O]= **55.3457 M**, hydroxonium [H_3O^+]=$10^{-7,36}$ M pH=7,36, $C_{osmolar}$=0,305 M blood.

The second **2nd law** of thermodynamics states that the **bound** energy **T•ΔS** and **entropy** to the **isolate system** increases during all chemical and physical processes behalf of free energy **G** decrease, but it does not require that the **entropy** increase take place in the **reacting system** itself as member of **sub-systems** included into **isolate system**. The **synthesized** products within cells as they grow and divide **free** energy **ΔG>0** increase on second than more exoergic compensated for by the decomposition they create **free** energy losing **ΔG<0** in their **surroundings** in the course of growth and division. In living organisms preserve their internal **free** energy **ΔG>0** increase by taking from the **surroundings free** energy **ΔG<0** which is lost in the form of high nutrients **free** energy G_n or sunlight **free** energy **~hv = G_s**, and returning to their **surroundings** an equal amount of
energy as **heat H** and **entropy S**.

Entropy: Energy dispersion measure per one mole one Kelvine degree

The term **entropy S**, which literally means a " **change within**"(*Greek* **en** - in, **tropos** - turning), was first used in 1851 by Rudolf Clausius, one of the formulators of the second **2nd law** of thermodynamics. A rigorous quantitative definition of **entropy S** involves statistical and probability considerations. However, its nature can be illustrated qualitatively by three **3** simple examples using **bound** energy **T•S** terms, each demonstrating two aspect of **entropy S**. **Entropy S** are ***randomness*** *of thermal motion* and *dissipation* of energy in **products**, manifested in two (reaction and heat dispersion) ways over one unit of Kelvine degree temperature.

Case I - The Teakettle and the Dispersion of Heat Entropy growth as **enthalpy** increases**.** We know that steam generated from boiling water can do useful work **W**. But suppose we turn off the burner under a teakettle full of water at **100 'C** (the "**system**") in the kitchen (the "**surroundings**") and allow the teakettle to cool. As it cools, no work is done, but heat disperses from the teakettle to the surroundings, raising the temperature **T** of the **surroundings** (the kitchen) by an infinitesimally small amount until complete equilibrium is attained. At this point all parts of the teakettle and the kitchen are at precisely the same temperature **T**. The **heat** energy dispersion $-\Delta\mathbf{H}_{tea}$ that was once concentrated in the teakettle of hot water at **100 °C** for number of moles only $\mathbf{n}_{tea}$, *potentially* capable of doing work **W**, has lost as dispersed among total number of moles $\mathbf{n}_{tea}+\mathbf{n}_{kitch}$ including surroundings. Its equivalent in **heat** energy is still present commonly in the teakettle + kitchen (i.e., the '**isolate system**') but has become completely randomized throughout. This energy is no longer available to do work =x=>**W** because there is no temperature differential within the kitchen and teakettle. Moreover, the increase in **entropy** $\Delta\mathbf{S}_{dispersion}$ and **bound** energy $\mathbf{T}\bullet\Delta\mathbf{S}_{dispersion}$ of the teakettle + kitchen (the **isolate system**) is irreversible because the **heat** $-\Delta\mathbf{H}_{tea}$ dissipation to all members among total number of moles $\mathbf{n}_{tes}+\mathbf{n}_{kitch}$. We know from everyday experience that **heat** $-\Delta\mathbf{H}_{tea}=\mathbf{T}\bullet\Delta\mathbf{S}_{dispersion}$ never spontaneously passes back from the kitchen into the teakettle to raise the temperature **T** of the water to **100 °C** again because **bound** energy $\mathbf{T}\bullet\Delta\mathbf{S}_{total}$ is lost energy within dissipation of **heat** and loose of heat content – enthalpy negative change $-\Delta\mathbf{H}_{tea}$.
Case 2: The decomposition of Glucose by the Oxidation of Glucose. Entropy $\Delta\mathbf{S}_{total}$ has a sum of two processes **bound heat** energy $\mathbf{T}\bullet\Delta\mathbf{S}_{dispersion}$ and **matter chemical reaction** energy change dispersion $\mathbf{T}\bullet\Delta\mathbf{S}_{react}$. Aerobic (hetero-tropic) organisms extract **free** energy $\Delta\mathbf{G}_{react}$ from **glucose** obtained from their **surroundings** by **oxidizing** the **glucose** with molecular oxygen $\mathbf{O}_{2aqua}$ in water solutions also inhale from the air . The end products of this oxidative metabolism, $\mathbf{CO}_{2aqua}$ and $\mathbf{H_2O}$, are released and returned to the surroundings. In this process the **surroundings** undergo an increase in **bound** energy $\mathbf{T}\bullet\Delta\mathbf{S}_{total}$ and entropy $\Delta\mathbf{S}_{total}$, whereas the organism itself remains in a steady state and undergoes to homeostasis (no change) in its internal state $\mathbf{G}_{in}$, $\mathbf{H}_{in}$, and $\mathbf{T}\bullet\mathbf{S}_{in}$. The oxidative decomposition reaction, illustrated by the equation for the oxidation of **glucose**. Biochemical amount of glucose free energy and reduction potential in cells are $\mathbf{G}_{C6H12O6}$**=1857.7** $^{kJ}/_{mol}$ and $\mathbf{E}^{\circ}_{C6H12O6}$=0,157 V; 1st page

$\mathbf{C_6H_{12}O_6}+\mathbf{6O_{2aqua}}+\mathbf{6H_2O}=>\mathbf{6HCO_3^-}+\mathbf{6H_3O^+}+\Delta G+\mathbf{Q}$; $\Delta\mathbf{G}_{Lehninger}$=2840 $^{kJ}/_{mol}$ 6th page; $\Delta\mathbf{H}_{Hess}$= **-2812,6** $^{kJ}/_{mol}$
Glucose $\Delta\mathbf{S}_{Hess}$= **3194,1** $^{J}/_{mol/K}$ **exoergic** **exothermic**

$-\Delta\mathbf{H}_{Hesst}/\mathbf{T}=\Delta\mathbf{S}_{dispersion}$ = **9433,5** $^{J}/_{mol/K}$; $\Delta\mathbf{G}_{bound}=\mathbf{T}\bullet\Delta\mathbf{S}_{total}$= 298.15 ***12,6276** =**-3764,9** $^{kJ}/_{mol}$;

$\Delta\mathbf{S}_{total}=\Delta\mathbf{S}_{dispersion}+\Delta\mathbf{S}_{Hess}$= **9433,5** $^{J}/_{mol/K}$ + **3194,1** $^{J}/_{mol/K}$ = **12627,6** $^{J}/_{mol/K}$

We can represent this schematically as

7 molecules	and 12 ionic molecules of products in water medium (aqua)	
$\mathbf{O_{2aqua}}$ $\mathbf{O_{2aqua}}$	$\mathbf{HCO_3^-}$ $\mathbf{HCO_3^-}$ | **6** $\mathbf{HCO_3^-}$ |	The atoms contained in **1** molecule of **glucose**
(aqua)$\mathbf{O_{2aqua}}$ $\mathbf{O_{2aqua}}$	$\mathbf{HCO_3^-}$ $\mathbf{HCO_3^-}$ |	plus **6** molecules of oxygen $\mathbf{O_{2aqua}}$,a total of **7** molecules,
$\mathbf{O_{2aqua}}$ $\mathbf{O_{2aqua}}$	=> $\mathbf{HCO_3^-}$ $\mathbf{HCO_3^-}$ | | (aqua)	are more randomly dispersed by the **oxidation**
Glucose ◊	$\mathbf{H_3O^+}$ $\mathbf{H_3O^+}$ $\mathbf{H_3O^+}$ |	reaction and produce in a total of
$\mathbf{C_6H_{12}O_6}$ (aqua)	$\mathbf{H_3O^+}$ $\mathbf{H_3O^+}$ $\mathbf{H_3O^+}$ | (aqua) |	**12** ionic molecules (**6**$\mathbf{HCO_3^-}$+**6**$\mathbf{H_3O^+}$).

Whenever a chemical reaction results in an increase in the number **n** of molecules-of moles or when a solid substance is converted into **liquid** or **gaseous** products, which allow more freedom of molecular movement and take up more volume than solids in decomposition reaction ,and thus **bound** energy $\mathbf{T}\bullet\Delta\mathbf{S}_{total}$ as well entropy of Hess reaction $\Delta\mathbf{S}_{Hesst}$= **3194,1** $^{J}/_{mol/K}$ and heat dispersion $\Delta\mathbf{S}_{dispersion}$ = **9433,5** $^{J}/_{mol/K}$ increases.

Case 3- Information the Entropy Julius Caesar, Act IV, Scene 3, is spoken by Brutus, when he realizes that he must face Mark Antony's army. It is an information-rich non random arrangement of **129** letters or **163** characters including space **28** and punctuation **6** marks of the English alphabet: **163-28-6**

There is a tide in the affairs of men,
Which, taken at the flood, leads on to fortune;
Omitted, all the voyage of their life
Is bound in shallows and in miseries.

voy inThie tide irs affof meoes.dlin, lem
bou aWis ch, takat t ahe fl ono,isads
ted, all t shalhe theenage ofir d infe tone;
Is nherd inlowOmi thets a fortun eri

In addition to what this passage says overtly, it has many hidden meanings. It not only reflects a complex sequence of events in the play, it also echoes the play's ideas on conflict, ambition, and the demands of leadership. Permeated with Shakespeare's understanding of human nature, it is very rich in information.

However, **129** letters making up this quotation to fall into a completely random, chaotic pattern. They would have no meaning what's ever. **129** letters contain no **information**, but they are rich in entropy **S** as random dispersion. That **information** carrying **letters** or **molecules** are a form of **free** energy **G** accumulation; **information carriers** have bring "small **bound** energy **T•S** or entropy **S**." The mathematics information theory, which is basic to the programming logic of computers, is closely related to thermodynamic theory. Living organisms are homeostasis order, non-random and **polymer** structures, rich in **information**, **free** energy **ΔG**

and thus **bound** energy **T•ΔS** or entropy-poor.

Cells Require Nutrition-Sources of Free Energy and **protolytic activation with water**.

Cells are **isothermal** systems-they function at essentially optimal **attractors** temperature 310.15 K (298.15 K), water concentration [$\mathbf{H_2O}$]=**55.3457 M**, hydroxonium cations pH=7.36 [$\mathbf{H_3O^+}$]=$10^{-7,36}$ M, $C_{osmolar}$=0,305 M, ionic strength 0.2 M. **Heat ΔQ** compensate endothermic protolytic activation of $\mathbf{CO_2}$+2$\mathbf{H_2O}$ from zero $G_{CO2+2H2O}$=0 $^{kJ}/_{mol}$ to $G_{H3O++HCO3-}$=68.38 $^{kJ}/_{mol}$ and from zero G_{2H2O}=0 $^{kJ}/_{mol}$ to G_{H3O+OH}=99.8 $^{kJ}/_{mol}$. The energy that cells use is **free** energy change **ΔG**, as the **Gibbs free** energy content change of reactants $\mathbf{G_1}$ and products $\mathbf{G_2}$, which trend to reach reaction the equilibrium state. Thousands of protolytic equilibria and Biochemical quasi equilibria have been studied as the homeostasis complex reactions order.

The **equilibrium** position, and the amount of work **W** is calculated at standard conditions. Hetero-trophic cells accumulate **free** energy from nutrient and heat **ΔQ** sources molecules, but photosynthetic cells accumulate it from absorbed solar heat **ΔQ** and radiation **~hν = ΔG**. Both kinds of cells transform this **free** energy into **ATP**$^{4-}$, **NADH**, $\mathbf{FADH_2}$ e.c. **energy-rich**, protolytic water activate soluble compounds free energy **ΔG** transporters for homeostasis work **W=-ΔG** at standard temperature **T**.

Hess law Standard Free-Energy Change at complete product formation**:** $\Delta G_{Hess} = \Delta H_{Hess} - T \cdot \Delta S_{Hess}$

Equilibrium mixture in expression of **Constant** minimizes **Free Energy Change:** $-\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq})$;

Absolut numbers always are positive and minimum is les value $|\Delta G_{eq}| < ||\Delta G_{Hess}|$ **:**

$|\Delta G_{eq}| = |-R \cdot T \cdot \ln(K_{eq})| < |\Delta G_{Hess}| = |\Delta H_{Hess} - T \cdot \Delta S_{Hess}|$;

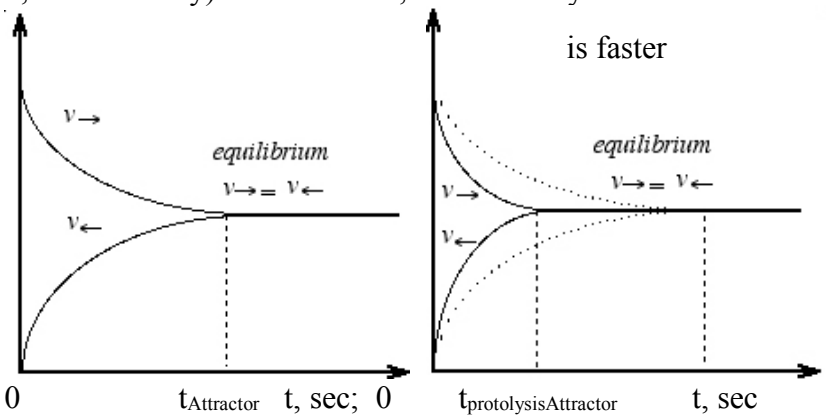
The homeostasis composition order of enzymatic **reactants** and **products** trends to reach **equilibrium** state, but never reaches as is non equilibrium state (Y. Prigogine 1977th). The exception is attractor Carbonic Anhydrase high rate protolysis which stay at equilibrium. Water protolysis activate molecules and keep attractors at equilibrium state with high rate protolysis mechanism support, however homeostasis is continue.

Living organisms thousands of Biochemical reactions have been studied as at equilibria.

Water high rate protolysis support the activation of molecules and keep Attractors at equilibrium state constant value because direct reaction velocity fast become equal to reverse reaction $\mathbf{v} = \overrightarrow{\mathbf{v}} = \overleftarrow{\mathbf{v}}$:

Direct reaction forwards => aA + bB <=> cC + dD <=Reverse reaction backwards.

Mass action Law for Direct $\overrightarrow{\mathbf{v}} = \overrightarrow{\mathbf{k}} \cdot C_A^a \cdot C_B^b$ <=$\overset{\text{direct}}{\underset{\text{revers}}{\rightleftarrows}}$=> $\overleftarrow{\mathbf{v}} = \overleftarrow{\mathbf{k}} \cdot C_C^c \cdot C_D^d$ for Reverse reaction .



Velocity of reaction for Direct reaction decreases and for Reverse reaction increases.

Protolytic Attractor reaching is faster for high rate protolysis at least thousand times $t_{protolysisAttractor} * 1000 = t_{Attractor}$ because homeostasis reactions velocity is slower.

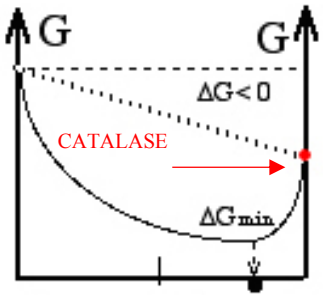
Carbonic dioxide 0,04% of air solubility endoergic accumulate in one mol solute CO_{2aq}: $\Delta G_{spCO2aq}$=8.379 $^{kJ}/_{mol}$; CO_{2gas}= Q+CO_{2aq}; with concentration for constant K_{spH2O} is $[CO_{2aqua}]=K_{spH2O}*[CO_{2air}]$=0,00075125 M.

Carbonic Anhydrase CA increases free energy content from $G_{CO2+2H2O}$=0 $^{kJ}/_{mol}$ to $G_{H3O+HCO3-}$=68.5 $^{kJ}/_{mol}$.

Free energy content is $G_{H3O+HCO3}=\Delta G_{spCO2aq}+\Delta G_{eqCO2aqua}$=8.379+60.14=68.52 $^{kJ}/_{mol}$. [1,8,14]

Enzyme carbonic anhydrase **CA** drive irreversible water solute carbonic dioxide protolysis with two water molecules: $CO_{2aq}+2H_2O+Q = \underline{CA} \rightarrow H_3O^+ + HCO_3^-$, so increase ratio $[CO_{2aq}+HCO_3^-]/[CO_{2air}]$=30,6 times. Limestone, dolomite, chalk and marble rocks formation favors CA $[CO_{2air}]$=0,04% protolysis with water. Distinction of Carbonic Anhydrase on Earth the assimilation of CO_2 in aqua sphere decreases 30,6 times. 4th, 45th, 46th pages .

H_2O_{2aqua} conversion to life resources is slow $k_{\rightarrow}$=1.191•10^{-8} Ms^{-1}, but CATALASE peroxide consume thirty million times 30•10^6 faster. Irreversible CATALASE reactivity for peroxide consuming is Prigogine attractor. In peroxisomes that indispensible for essential unsaturated fatty acid elongation to C20:4 by ethyl group **-CH₂-CH₂-** conversion to cis double bond **H>C=C<H** by ● 100% efficiency of dehydrogenase erasing H_2O_{2aqua} molecules.: 57th, 58th pages .



$$K_{eq}=10^{8,43}=\frac{[Fumarate^{2-}]\cdot[H_2O_2]}{[Succinate^{2-}]\cdot[O_2]}\ \text{CATALASE}$$, as

peroxide consumed to zero $[H_2O_2]^2$=0 $^{mol}/_{liter}$ and process velocity limits only dehydrogenase enzyme. It favors of peroxide **2H-O-O-H** conversion in to life resources $O_{2aqua}+2H_2O+Q$ thirty million times 30•10^6.

CATALASE reactivity and enzymes irreversibility for homeostasis are indispensible Brownian molecular engine for evolution and survival.

Irreversible enzymes reactivity reaching energy minimum as Le Chatelier principle are Ilya Prigogine declared attractors for organism composite complex reaction five types, which inactive compounds convert to following favored irreversible process, that works as Brownian molecular engine so drive organism to evolution, homeostasis, survival.

Attractor of reaction mixture the logarithm of expressed equilibrium constant ratio for products over reactants is Free energy change minimum value:

$$aA+bB<=>cC+dD;\ \mathbf{K_{eq}}=\frac{\mathbf{k_{\rightarrow}}}{\mathbf{k_{\leftarrow}}}=\frac{[C]^{c}\bullet[D]^{d}}{[A]^{a}\bullet[B]^{b}};\ \mathbf{\Delta G_{eq}=-R\bullet T\bullet \ln}\left(\frac{[C]^{c}\bullet[D]^{d}}{[A]^{a}\bullet[B]^{b}}\right)=\mathbf{-R\bullet T\bullet \ln(K_{eq})=\Delta G_{min}}.$$

The homeostasis order composite complex reactions Biochemistry rules Prigogine thermodynamic equilibrium state Attractor with high rate protolysis activate molecules in water.

Attractor stays at equilibrium , while homeostasis continues.

Non equilibria free energy change $\mathbf{\Delta G_{Homeostasis}}$ of Biochemical processes is dependent on ratio products over reactants concentrations factorials $\mathbf{([C]^{c}\bullet[D]^{d})/([A]^{a}\bullet[B]^{b})=K_{Homeostasis}}$, which different from zero $\mathbf{\Delta G_{Homeostasis}=0}$ equilibrium value because different is non equilibrium ratio versus equilibrium constant $\mathbf{K_{eq}}$:

$$\mathbf{\Delta G_{Homeostasis}=\Delta G_{eq}+R\bullet T\bullet \ln}\left(\frac{[C]^{c}\bullet[D]^{d}}{[A]^{a}\bullet[B]^{b}}\right)=\mathbf{\Delta G_{eq}+R\bullet T\bullet \ln(K_{Homeostasis})}\neq 0\ .$$

Established equilibrium free energy change for $\mathbf{\Delta G_{Homeostasis}}$ is zero, because equivalence of $\mathbf{K_{Homeostasis}=K_{eq}}$:

$$0=\mathbf{\Delta G_{Homeostasis}=0=\Delta G_{eq}+R\bullet T\bullet \ln}\left(\frac{[C]^{c}\bullet[D]^{d}}{[A]^{a}\bullet[B]^{b}}\right)=\mathbf{\Delta G_{eq}+R\bullet T\bullet \ln(K_{eq})=0}\ \text{and}$$

calculates free energy change minimum $\mathbf{\Delta G_{eq}=\Delta G_{min}}$ at equilibrium state from constant $\mathbf{K_{eq}}$ value

$$\text{for reaction: }\mathbf{\Delta G_{eq}=-R\bullet T\bullet \ln}\left(\frac{[C]^{c}\bullet[D]^{d}}{[A]^{a}\bullet[B]^{b}}\right)=\mathbf{-R\bullet T\bullet \ln(K_{eq})}\ .$$

Versus **Hess Law** 2nd page for five complex reactions calculation order and standard difference values formation $\mathbf{\Delta H_{Hess}}$, $\mathbf{\Delta S_{Hess}}$, $\mathbf{\Delta G_{Hess}}$ of molecule from reactants and from elements are pure products $\mathbf{\Delta H^{\circ}_{Hess}}$, $\mathbf{\Delta S^{\circ}_{Hess}}$, $\mathbf{\Delta G^{\circ}_{Hess}}$ (molecule formation from elements $\mathbf{\Delta H^{\circ}_{Hess}}$, $\mathbf{\Delta S^{\circ}_{Hess}}$, $\mathbf{\Delta G^{\circ}_{Hess}}$) minus pure reactants $\mathbf{\Delta H^{\circ}_{Hess}}$, $\mathbf{\Delta S^{\circ}_{Hess}}$, $\mathbf{\Delta G^{\circ}_{Hess}}$ (elements for molecule $\mathbf{\Delta H^{\circ}_{element}}$, $\mathbf{\Delta S^{\circ}_{element}}$, $\mathbf{\Delta G^{\circ}_{element}}$):

Favored and unfavored equilibrium constant calculate with exponent $\mathbf{K_{eq}=exp(-\Delta G_{eq}/R/T)=e^{-\Delta Geq/RT}}$

Favored reaction constant grater about one $\mathbf{K_{eq}}>1$ forms negative free energy change $\mathbf{\Delta G_{eq}}<0$,

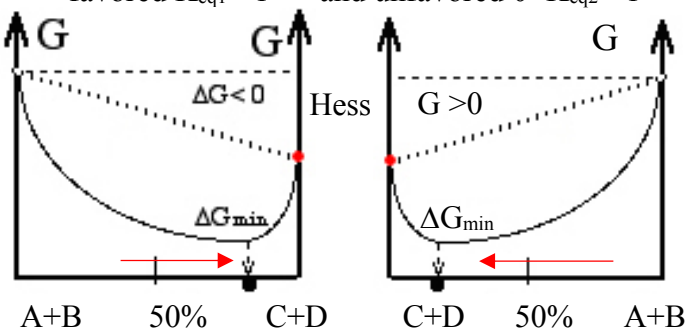
Unfavored reaction constant les of one $0<\mathbf{K_{eq}}<1$ forms positive free energy change $\mathbf{\Delta G_{eq}}>0$,

At equilibrium being compounds concentration constant $\mathbf{K_{eq}}$ is independent on concentrations.

For mixture of compounds at equilibrium free energy change $\mathbf{\Delta G_{eq}=-R\bullet T\bullet \ln(K_{eq})=\Delta G_{min}}$ at minimum as Free energy change in mixture is smaller versus complete conversion with **Hess law** 2nd page in reaction:

$|\mathbf{\Delta G_{eq}}|=|\mathbf{\Delta G_{min}}|<|\mathbf{\Delta G_{Hess}}|$ Hess law calculation order is greater as minimum:

favored $K_{eq1}>1$ and unfavored $0<K_{eq2}<1$



Le Chatelier's principle erase made changes after chemical equilibrium disruption with product or initial compound concentration change as well heat supply.

Free energy change minimum $\mathbf{\Delta G_{min}}$ is Ilya Prigogine declared attractor to which trend reaction inverse nor favored Direct forwards nor reverse unfavored backwards direction.

Inverse equilibrium constants for Direct $K_{eq1}=1/K_{eq2}$ and reverse reaction.

Water attractors protolysis and neutralization inverse constants of equilibrium:

1. equilibrium $\mathbf{H_2O+H_2O+Q+\Delta G=H_3O^++OH^-}$; **2.** equilibrium $\mathbf{H_3O^++OH^-=H_2O+H_2O+Q+\Delta G}$

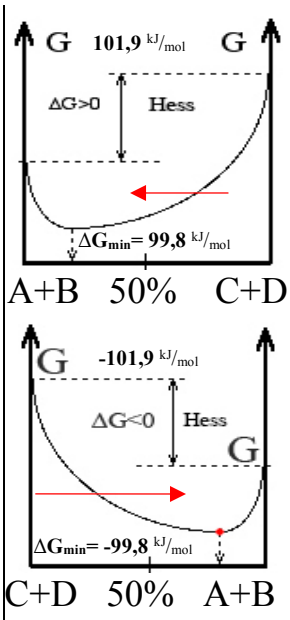
Free energy standard change for Hess law 1st and 2nd reaction is positive and negative unfavored and favored, endoergic and exoergic, in direct and in reverse reaction :

$\Delta G_{HessProtolysis}=\Delta H_{HessProtolysis}-T\Delta S_{HessProtolysis}= +101,9\ ^{kJ}/_{mol}$.

$\Delta G_H = \Delta H_H - T*\Delta S_H = 55,89+298,15*0,154305=101,9$.....$^{kJ}/_{mol}$ **endoergic**.....

$\Delta G_{neutralizationHess}=\Delta H_{neutralizationHess}-T\Delta S_{neutralizationHess}= -101,9\ ^{kJ}/_{mol}$;

$\Delta G_H = \Delta H_H - T*\Delta S_H = -55,89-298,15*0,154305= -101,9$.....$^{kJ}/_{mol}$ **exoergic**.....



Reaching mixture 1 and 2 equilibrium constants values are inverse:

$K_{eq1}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=3.26\bullet10^{-18}$; $K_{eq2}=\frac{[H_2O]\cdot[H_2O]}{[OH^-]\cdot[H_3O^+]}=3,068\bullet10^{17}$;

$\Delta G_{eq1}=-R\bullet T\bullet\ln(K_{eq1})=-\ 8,3144\bullet298,15\bullet\ln(3.26\bullet10^{-18})=+99,8\ ^{kJ}/_{mol}$,

$\Delta G_{eq2}=-R\bullet T\bullet\ln(K_{eq2})=-\ 8,3144\bullet298,15\bullet\ln(3,068\bullet10^{17})=-99,8\ ^{kJ}/_{mol}$,

Pure compounds Free energy change ΔG_{Hess} by Hess law is greater, than equilibrium mixture of compounds Free energy change ΔG_{eq} minimizes :

$$|\Delta G_{eq}| = 99,8\ ^{kJ}/_{mol} < 101,9\ ^{kJ}/_{mol} = |\Delta G_{Hess}|\ .$$

All reactions trend to Prigogine attractor minimum of Free energy change $\Delta G_{min} = \Delta G_{eq}$ at equilibrium mixture with inverse constants $K_{eq1}=\frac{1}{K_{eq2}}$.

In 1977 declared Ilya Prigogine attractors create order in apparent chaos of universe.

It claims that our Universe was created in perfect order and show that each process trends to Prigogine attractor – energy change minimum in mixture of reacting compounds.

pages 15th and 14th

$\mathbf{CH_3COOH}$ protolysis raaction with water: $\mathbf{CH_3COOH+H_2O+\Delta G \Leftrightarrow H_3O^++CH_3COO^{-}+Q}$

Free energy standard change from Hess law is positive so than unfavored, endoergic reaction: $\Delta G_{protolysisHess} = \Delta H_{protolysisHess} - T\Delta S_{protolysisHess} = 42,36\ ^{kJ}/_{mol}$.

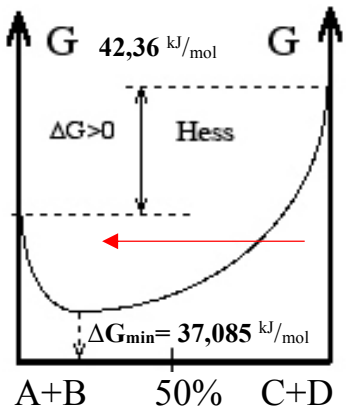
Equilibrium reaches free energy minimum in mixture of compounds ratio for constant expression: $K_{eq}=\frac{[H^+]\cdot[CH_3COO^-]}{[H_2O]\cdot[CH_3COOH]_{nedis}}=K_a/[H_2O]=1,76*10^{-5}/55,3=10^{-6,497}$

$\Delta G_{eq}= -R\bullet T\bullet\ln(K_{eq})= -8,3144\bullet298,15\bullet\ln(10^{-6,497}) = 37,085\ ^{kJ}/_{mol}$,

Endothermic and endoergic acetic acid protolysis reaction free energy is $\Delta G_{protolysis}$ positive $42,36\ ^{kJ}/_{mol}$, but minimized $\Delta G_{min}= \Delta G_{eq}= 37,085\ ^{kJ}/_{mol}$ in mixture reaching equilibrium

Reaction trends to Prigogine attractor free energy change minimum ΔG_{min}. Free energy change minimum reaching establish equilibrium mixture of compounds.

in mixture reactants $CH_3COOH+H_2O$ products. $\mathbf{H_3O^++CH_3COO^-}$



Ions from crystalic Na^+Cl^- ⇄ Na^++Cl^- solubility product dissociation Hess process

$\Delta G_{dissociation} = \Delta H_{dissociation} - T\Delta S_{dissociation}$ = -9.15 $^{kJ}/_{mol}$ favored reaction.

At equilibrium reached free energy change minimum on solubility products concentration factorial in mixture: $K_{sp}=K_{eq}=[Na^+_{aq}]*[Cl^-_{aq}]/[NaCl_{aq}]$= =4.0952*4.0952/1.3482=12.4393;

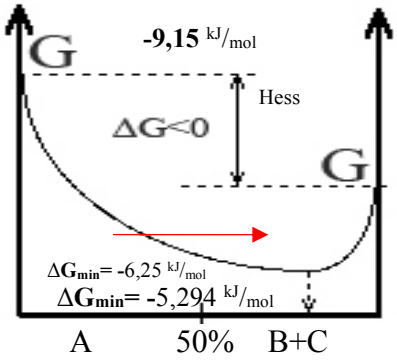
ΔG_{sp}= -R•T•ln(K_{sp})=-8.3144•298.15•ln(12.44)=-6.25 $^{kJ}/_{mol}$,

Physiologic solution 0.9 % $K_{0.9\%}=K_{eq}=[Na^+_{aq}]*[Cl^-_{aq}]/[NaCl_{aq}]$= 8.46

ΔG_{eq}=-R•T•ln(K_{eq})=-8.3144•298.15•ln(8.46)=-5.294 $^{kJ}/_{mol}$,

Endothermic and exoergic crystals $Na^+Cl^-_s$ dissociations reaction free energy $\Delta G_{dissociation}$ negative -9.15 $^{kJ}/_{mol}$ as favored reaction, but minimized up to ΔG_{sp}= -6.25 $^{kJ}/_{mol}$ and ΔG_{min}= $\Delta G_{0.9\%}$= -5.294 $^{kJ}/_{mol}$ in mixture reaching equilibrium $K_{sp}=K_{eq}$=**12.44** and $K_{0.9\%}=K_{eq}$=8.46.

Le Chatelier principle is Prigogine attractor free energy change minimum ΔG_{sp} for crystalline sodium chloride Na^+Cl^- solubility product and physiologic solution 0.9 % . Free energy change minimum reaching established equilibrium mixture of compounds.



9th NaCl, 12th CH_3COONa, 53rd pages.

Sodium acetate solubility products equilibrium CH_3COONa_s ⇄ Na^+_{aqua}+$CH_3COO^-_{aq}$

$\Delta G_{dissociation} = \Delta H_{dissociation} - T\Delta S_{dissociation}$ = 23.6 $^{kJ}/_{mol}$ favored dissociation reaction.

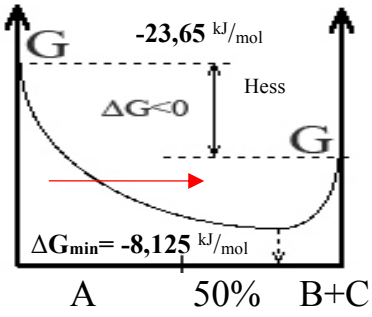
At equilibrium reached frees energy minimum according compound concentration $C_{CH3COONa}$= 5.1493 $^{mol}/_{L}$ in expression for mixture components factorial:

$K_{eq}=[Na^+_{aqua}]•[CH_3COO^-_{aq}]$=5.1493*5.1493=26.515

ΔG_{eq}=-R•T•ln(K_{eq})=-8.3144•298.15•ln(26.515)= -8.125 $^{kJ}/_{mol}$,

Exothermic and exoergic CH_3COONa_s dissociations reaction free energy change $\Delta G_{dissociation}$ negative -23.65 $^{kJ}/_{mol}$ as favored reaction, but minimized up to ΔG_{min}= ΔG_{eq}= -8.125 $^{kJ}/_{mol}$ in mixture reaching equilibrium K_{eq}=26.515 .

The reactant CH_3COONa_s mol fraction one $[CH_3COONa_s]_{solid}$=1 and Na^+_{aqua} +$CH_3COO^-_{aqua}$ B+C are products.



Reaction trends to Prigogine attractor free energy change minimum ΔG_{min} .

Free energy change minimum reaching established mixture equilibrium of compounds.

O_2↑gas solubility products equilibrium O_2↑$_{gas\ AIR}$+H_2O<$\overset{Aquporin}{=>}$ H_2O_{Blood} +$O_{2aqua\text{-}Blood}$;

$\Delta G_{dissociation} = \Delta H_{dissociation} - T\Delta S_{dissociation}$ = 77.55 $^{kJ}/_{mol}$ unfavored reaction.

ELSEVIER, Rotating Electrode Method and Oxygen reduction Electrocatalysts, 2014, p.1-31,

1. WeiXingaMinYinbQingLvbYangHubChangpengLiubJiujunZhangc. As pure mol fraction is $[O_{2gas}]$=1 . Solubility at 25° C 298,15 K is ratio $K_{O2}=[O_{2aqua}]/[O_{2gas}]=[O_{2aqua}]/0.2095=1.22*10^{-3}$ M as distribution between gas and water. Solubility from AIR 20.95% $[O_{2aqua}]=1.22*10^{-3}*0.2095=2.556*10^{-4}$ M:

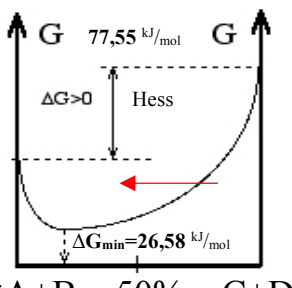
Prigogine attractor equilibrium constant $K_{eq}=\frac{[O_{2\ aqua}]}{[O_{2\ gas}]\cdot[H_2O]}$ =$K_{O2}/[H_2O]$=$1.22*10^{-3}/55.333= 2.205*10^{-5}$;

$\Delta G_{min}=\Delta G_{eq}$=-R•T•ln($K_{eq}$)=-8.3144*298.15*ln($2.205*10^{-3}$)=-8.3144•298.15•6.414=26.58 $^{kJ}/_{mol}$

Prigogine attractor unfavored equilibrium by Hess law solution **is** exothermic and endoergic free energy change positive $\Delta G_{solubility}$ =77.55 $^{kJ}/_{mol}$, but minimized by Prigogine attractor unfavored equilibrium constant free energy change minimum value ⟶ ΔG_{min}= ΔG_{eq} = 26.58 $^{kJ}/_{mol}$ reaching equilibrium mixture:

$K_{eq}=[O_{2aqua}]/[H_2O]/[O_{2gas}]$ =$2.205*10^{-5}$= $10^{-4.66}$.

Reactant O_2↑$_{gas}$+ H_2O A+B and C+D products H_2O_{Blood} +$O_{2aqua\text{-}Blood}$.



Reaction trends to Prigogine attractor free energy change minimum ΔG_{min} .

Free energy change minimum reaching establish equilibrium mixture of compounds.

cAmmonium chloride $NH_4Cl_{(s)} \Rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{aqua}$

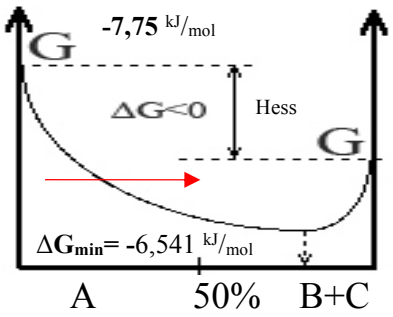
electrolyte dissociations process equilibrium

$\Delta G_{dissociation} = \Delta H_{dissociation} - T\Delta S_{dissociation} = -7.75\ ^{kJ}/_{mol}$ favored, exoergic reaction.

At equilibrium reached frees energy minimum according compound mixture in expression:

$$K_{eq} = \frac{[NH_4^+]_{aqua} \cdot [Cl^-]_{aqua}}{[NH_4Cl]_{aqua}} = 3.97651*3.97651/1.13 = 13.9935$$

$\Delta G_{eq} = -R \bullet T \bullet \ln(K_{eq}) = -8.3144 \bullet 298.15 \bullet \ln(13.9935) = -6.541\ ^{kJ}/_{mol}$,



Endothermic and exoergic $NH_4Cl_{(s)}$ dissociations reaction free energy $\Delta G_{dissociation}$ negative $-7.75\ ^{kJ}/_{mol}$ as favored reaction, but minimized up to $\Delta G_{min} = \Delta G_{eq} = -6.541\ ^{kJ}/_{mol}$

in mixture reaching equilibrium $K_{eq} = \frac{[NH_4^+]_{aqua} \cdot [Cl^-]_{aqua}}{[NH_4Cl]_{aqua}} = 13.9935$.

Reactant is non dissociate $NH_3 \bullet HCl_{aqua}$ ammonium chloride NH_4Cl_{aqua} (A) and products are $NH_4^+{}_{aq} + Cl^-{}_{aqua}$ (B+C) .

Reaction trends to Prigogine attractor free energy change minimum ΔG_{min} .

Free energy change minimum reaching established equilibrium mixture of compounds.

13th NH_4Cl solubility, 16th NH_4^+ protolysis pages:

Ammonium water in physiologic medium pH=7.36 $NH_4^+{}_{aq} + H_2O + \Delta G + Q \Rightarrow NH_{3aq} + H_3O^+$

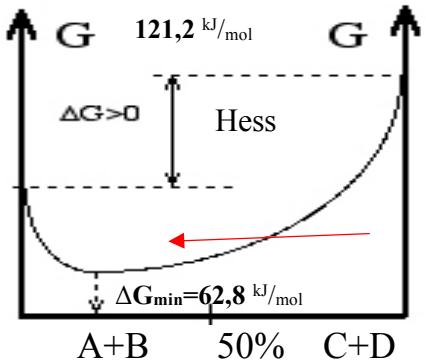
as weak acid $NH_4^+{}_{aq}$ protolysis - dissociations thermodynamics

$\Delta G_{protolysis} = \Delta H_{protolysis} - T\Delta S_{protolysis} = 121.2\ ^{kJ}/_{mol}$ unfavored reaction. Protolysis reached equilibrium frees energy minimum according compound mixture in expression:

$$K_{eq3} = \frac{[NH_3]_{aqua} \cdot [H_3O^+]}{[NH_4^+] \cdot [H_2O]} = 1.014*10^{-11}\ ;\ K_a = \frac{[H^+] \cdot [NH_3]_{aqua}}{[NH_4^+]} = [H_2O]*K_{eq3} = 10^{-9.25} = 10^{pKa}\ ;$$ Classic $pK_a = 9.25$

acid dissociation constant $K_a = 55.34*1.014*10^{-11} = 5.61176*10^{-10} = 10^{-9.25} = 10^{pKa}$.

$\Delta G_{eq3} = -R \bullet T \bullet \ln(K_{eq3}) = -8.3144 \bullet 298.15 \bullet \ln(1.014*10^{-11}) = 62.76\ ^{kJ}/_{mol}$,



Endothermic and endoergic $NH_4^+{}_{(aq)}$ protolysis reaction free energy $\Delta G_{protolysis}$ positive $121.2\ ^{kJ}/_{mol}$ as unfavored reaction, but minimized up to $\Delta G_{min} = \Delta G_{eq} = 62.76\ ^{kJ}/_{mol}$

in mixture reaching equilibrium $K_a = \frac{[NH_3]_{aqua} \cdot [H_3O^+]}{[NH_4^+]_{aqua} \cdot [H_2O]} = \mathbf{1.013*10^{-11}}$

Mixture reactant compounds are $NH_4^+{}_{(aq)} + H_2O$ (A+B) and products are $NH_{3(aq)} + H_3O^+$ (C+D) .

Reaction trends to Prigogine attractor free energy change minimum ΔG_{min} .

Free energy change minimum reaching established equilibrium mixture of compounds.

Chemical potential μ

Professor Ilya Prigogine **chemical potential μ** of compound **A** shows, how much change of **free energy** ΔG_A brings into system of our interest when adding the **1 mol** amount of compound **A** in the mixture.
In a fact: how great amount of free energy belongs to one **1 mol** of compound in mixture.
Hess Free energy $\Delta G°_A$ has the pure compound **A** itself per **1 mol** amount, no mixture of compounds,
the **chemical potential** μ_A of compound **A** if amount with in mixture others for molar number is Δn_A **= 1 mol**

$\mu_A = \frac{\Delta G_A}{\Delta n_A}$; $\mu_A = \Delta G°_A + R•T•\ln(X_A)$, where X_A is concentration of **A** unit less **mol fraction** $X_A = \frac{n_A}{n_{total}}$ (5)

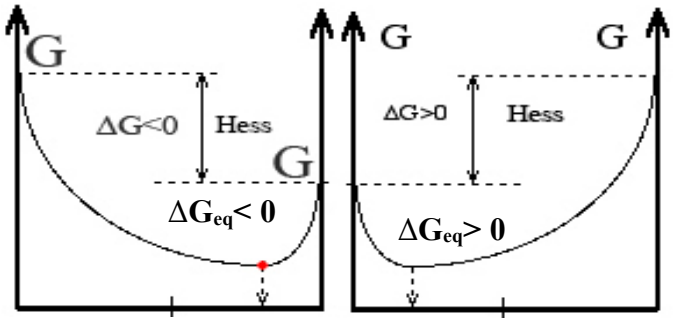
For pure compound **A** when $n_A = n_{total}$ **mol fraction** is $X_A = 1$ so **ln(1) = 0** and $\mu = \Delta G°_A$ that present **standard free energy** of formation the **1 mol** pure compound **A** from elements. Conflict in consideration pure compound absolute $|\Delta G°_A|$ is greater as mixture amount for one mole absolute $|\mu_A| < |\Delta G°_A|$. As value is $0 < X_A \leq 1$.
Minimization in mixture I. Prigogine, R. Defey. "Chemical Thermodynamics".1954, Longmans Green & co ©.

Equilibrium state minimum of energy is attractor for non equilibrium state

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

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

$aA + bB \underset{revers}{\overset{direct}{\rightleftarrows}} cC + dD$; **chemical potential** sum at equilibrium are equal $a\mu_A + b\mu_B = c\mu_C + d\mu_D$,



Strong electrolytes weak acids and electrolytes

The concentrations **X** of **reactants** and **products** at **equilibrium** mixture define the **equilibrium constant**, K_{eq}. **Chemical potential** sum for **reactants** $\Sigma\mu_{reactant}$ and **products** $\Sigma\mu_{product}$ at equilibrium are $\Sigma\mu_{reactant} = \Sigma\mu_{product}$ equal: and chemical potential change at equilibrium is zero: $0 = \Delta G\mu = \Sigma\mu_{product} - \Sigma\mu_{reactant}$ as minimum energy in mixture. Hess Free energy change is greater:

$|\Delta G_{Hess}| > |\Delta G_{eq}| = |\Delta G_{min}|$ than

Prigogine attractor value at equilibrium ΔG_{eq} .
energy minimum ΔG_{eq} is calculated of mixture **chemical potential** sum equivalence $a\mu_A + b\mu_B = c\mu_C + d\mu_D$;
$a•(\Delta G°_A + R•T•\ln(X_A)) + b•(\Delta G°_B + R•T•\ln(X_B)) = c•(\Delta G°_C + R•T•\ln(X_C)) + d•(\Delta G°_D + R•T•\ln(X_D))$.
In contrast non equilibrium are Biochemistry conditions :

$$\Delta G_{Homeostasis} = \Delta G_{eq} + R•T•\ln\left(\frac{X_C^c • X_D^d}{X_A^a • X_B^b}\right) \neq 0 \quad (1\text{-}4)$$

At equilibrium chemical potential change is zero: $\Delta G\mu = \Delta G_{eq} + R•T•\ln\left(\frac{X_C^c • X_D^d}{X_A^a • X_B^b}\right) = 0$ and calculates ΔG_{eq}

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

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 reaction components (reactants and products) at the minimum point of **equilibrium** mixture.

When the **equilibrium** is shifted out then start to work Le Chatelier's principal toward reaching **equilibrium** as Prigogine attractor the **free**-energy change minimum point ΔG_{min}. Under **standard conditions** (**298.15 K** or **25 °C**), when reactants and products are present in **molar fraction** concentrations, at partial pressures for total pressure as sum p_{total} **= 101.3 kilo-Pascals** (**kPa**), the force driving the system toward equilibrium is defined as Prigogine attractor **free**-energy change minimum point ΔG_{eq}. By this definition the **attractor state** for reactions maintains equilibrium constant value in ratio $(X_C^c • X_D^d)/(X_A^a • X_B^b) = K_{eq}$. High rate protolysis equilibrium protonate water molecules are hydrogen ions $X_{H3O}+$ as **pH** with water concentration as Prigogine attractors, values **pH=7.36** and $[H_2O]$**=55.3** M . Both the **pH** and the concentration of water $[H_2O]$ are equilibrium being Attractor values for calculations, while homeostasis as non equilibrium state continues.

Classic biochemistry in **standard state** calculations do not include water [H_2O] and hydroxonium [H_3O^+]=$10^{-7.36}$ **M** (**pH=7.36**) concentrations , comprising its in to equilibrium constant values, usually designed as Lehninger equilibrium constant instead thermodynamic equilibrium constants ΔG_{eq} , K_{eq}, E°_{RedOx}:

$\Delta G_{eqLehninger} = -R \bullet T \bullet \ln(K_{eqLehninger})$ and $K_{eqLehninge} = K_{eq}/[H_2O]$ or $K_{eqLehninger} = K_{eq} * [H_2O]$

For reactions that involve Mg^{2+} (including most reactions for which **ATP** is a substrate), its concentration in solution is commonly taken to be constant at **1 mM**. Equilibrium constant calculates as direct and reverse reaction velocity constant ratio: aA + bB <=> cC + dD ; $K_{equilibrium} = \frac{k_{\rightarrow}}{k_{\leftarrow}} = \frac{[C]^c \bullet [D]^d}{[A]^a \bullet [B]^b} = K_{eq}$.

Recommended by an international committee of chemists and biochemists, that the **equilibrium free** energy ΔG_{eq} change is Prigogine attractor for equilibrium. According Lehninger biochemistry H_2O, H_3O^+ (Mg^{2+} catalyzed direct reaction velocity constant $k_{\rightarrow}$ increase) are **reactants** or **products**, their concentrations as constants are included in new constant $K_{eqLehninge}$, so are integrated, incorporated into Lehninger constants.

K_{eq} is a thermodynamic constant for equilibrium, so too is thermodynamic ΔG_{eq} a constant. As is noted in General Chemistry course Hess **standard free**-energy ΔG_{Hess} change of a chemical reaction is greater by absolute value of ΔG_{eq} minimized at equilibrium with constant K_{eq}: $\Delta G_{eq} = -R \bullet T \bullet \ln(K_{eq})$.

If **equilibrium** constant for reaction is K_{eq} = **1.0**, than Prigogine attractor minimized energy to zero and is equal to Hess **standard free energy** change as zero $0 = \Delta G_{eq} = \Delta G_{Hess}$.

If K_{eq} of a reaction is greater than **>1.0**, its $\Delta G_{Hess} < \Delta G_{eq} < 0$ is negative.

If K_{eq} is less than **<1.0**, $0 < \Delta G_{eq} < \Delta G_{Hess}$ is positive.

Prigogine attractor is free energy change minimum reaching at equilibrium mixture of compounds.

Hess **standard free**-energy change ΔG_{Hess} have to calculate as the difference between the pure 100% **products**, and the pure 100% **reactants** under **standard conditions** : $\Delta G_{Hess} = \Sigma \Delta G^\circ_{product} - \Sigma \Delta G^\circ_{reactant}$.(1-3a)

When $\Delta G_{Homeostãasis}$ **?** $\Delta G_{Hess} < \Delta G_{eq} < 0$ is negative, but at equilibrium point in mixture of chemical potential expressions logarithmic value shows smaller by absolute number but so ever negative value $\Delta G_{eq} < 0$. All chemical reactions tend to go in the conversion direction that results in a decrease in the **free** energy of the **system**. A positive value of $0 < \Delta G_{eq} < \Delta G_{Hess}$ means that the **products** of the reaction contain more **free** energy than such reaction trend to reach the equilibrium minimum conversion in reverse $\xleftarrow{\text{reverse}}$ direction.

Free-Energy changes ΔG are additive

In the case of two **2** sequential chemical reactions, **A⇔B** and **B⇔C**, each reaction has its own **equilibrium** constant K_{eq1}, K_{eq2} and each has its characteristic **equilibrium free**-energy change, ΔG_{eq1} and ΔG_{eq2}. As the two reactions are sequential, **B** cancels out to give the overall reaction **A⇔C**, which has its own **equilibrium** constant $K_{eq} = K_{eq1} * K_{eq2}$ and thus its own **equilibrium free**-energy change, ΔG_{total} The **ΔG** values of sequential chemical reactions are additive. For the overall reaction **A⇔C**, $\Delta G_{eq\_total} = \Delta G_{eq1} + \Delta G_{eq2}$ is the algebraic sum of the individual **equilibrium free**-energy changes, ΔG_{eq1} and ΔG_{eq2}, and the overall **equilibrium** constant $K_{eq} = K_{eq1} K_{eq2}$ is the factorial of the **equilibrium** constant K_{eq1} and K_{eq2} of the two **2** sequential reactions.

As an example, let us make a simple calculation of Hess **standard free**-energy change ΔG_{Hess} of the reaction catalyzed by the enzyme **phosphogluco-mutase** (**glucose** symbol is **Glc** of three letters):

37th , 38th pages:

Glc 1-P^{2-} => Glc6-P^{2-};$\Delta G_{totalHess} = \Delta G^\circ_{H66} + \Delta G^\circ_{H1} = \mathbf{38{,}55 - 68{,}25 = -29{,}7}$ $^{kJ}/_{mol}$ **exoergic**.....$^{kJ}/_{mol}$

$\Delta G_{Lehninger} = 13{,}8$ $^{kJ}/_{mol}$; **Glc+HPO_4^{2-} => Glc6P^{2-}+H_2O**; pH=7,36; $\Delta G_{H66} = 38{,}55$ $^{kJ}/_{mol}$;

$K_{Lehninger} = EXP(-13800/8{,}3144/298{,}15) = 0{,}0038223$;

$K_{a22} = K_{Lehninger} * [H_2O] = 0{,}003822314 * 55{,}3457339 = 0{,}211548774$;

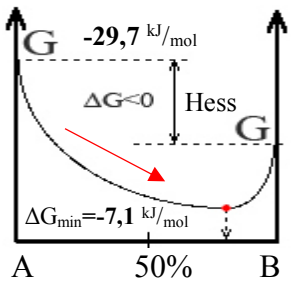
$\Delta G_{a22} = -8{,}3144 * 298{,}15 * \ln(0{,}211548774)/1000 = 3{,}850534$ $^{kJ}/_{mol}$;

$K_{eq} = [Glc6fosfãts]/[Glc1fosfãts] = 17$ mM/1 mM=17; $\Delta G_{eq} = -R \bullet T \bullet \ln(17{,}54) = -7.02$ $^{kJ}/_{mol}$;

$\Delta G_{Lehninger} = -20{,}9$ $^{kJ}/_{mol}$; **Glc1P^{2-}+H_2O=>Glc+HPO_4^{2-}**; pH=7,36; $\Delta G_{H1} = -68{,}25$ $^{kJ}/_{mol}$;

$K_{Lehninger} = EXP(20900/8{,}3144/298{,}15) = 4587{,}215687$;

$K_{a2} = K_{Lehninger}/[H_2O] = 4587{,}215687/55{,}3457339 = 82{,}90153826$;



$\Delta G_{a2} = -8{,}3144 * 298{,}15 * \ln(82{,}90153826) = -10{,}95$ $^{kJ}/_{mol}$; $K_{eq} = K_{a22} K_{a2} = 0{,}211548774 * 82{,}90153826 = \mathbf{17{,}54}$;

$\Delta G_{eq} = -R \bullet T \bullet \ln(K_{eq}) = -8{,}3144 * 298{,}15 * \ln(17{,}537719)/1000 = -7{,}1$ $^{kJ}/_{mol}$; $\Delta G_{eq} = 3{,}85 - 10{,}95 = \mathbf{-7{,}1}$ $^{kJ}/_{mol}$ **exoergic**

Pure reagents change in table 1-1 $\Delta G_{Hess} = -29{,}7$ $^{kJ}/_{mo}$ is greater as attractor minimum $\Delta G_{eq} = -7.1$ $^{kJ}/_{mol}$.

For the reverse reaction **glucose 1-phosphate <=** from **glucose 6-phosphate** .

The conversion to **+7.1** $^{kJ}/_{mol}$ is the same number but the opposite sign. Reverse reaction is thermodynamic forbidden. Actual Free-Energy Changes Depend on Reactant and Product mixture

Concentrations in **Homeostasis**. Table 1-1 gives Hess **standard free**-energy changes ΔG_{Hess} for some representative chemical reactions in Hess law thermodynamic calculations. $\Delta G_{Hess} = \Delta H_{Hess} - T\,\Delta S_{Hess}$. (1-3b) Note that **hydrolysis** of simple **esters**, **amides**, **peptides**, and **glycosides**, as well as **rearrangements** and **eliminations**, proceed with relatively small **free**-energy changes ΔG_{Hess}, whereas **hydrolysis** of **acid anhydrides** occurs with relatively large decreases in **free**-energy ΔG_{Hess}. The complete **oxidation** of organic compounds such as **glucose** or **palmitate** to CO_2 and H_2O, which in cells occurs in many complex enzyme reaction step wises, results in very large decreases in **standard free** energy ΔG_{Hess}. However, **free**-energy changes ΔG_{Hess} such as those in Table 1-1 indicate how much **free** energy is available from a reaction under **standard conditions** for one **1 mol** of pure compound. To describe the energy released under the **homeostasis** mixture **conditions** for cells one has to use chemical potential 1-4. The expression for the **actual homeostasis free**-energy change ΔG_{eq} calculation at equilibrium position as Prigogine attractor minimum is essential.

$\Delta G = \Delta G_{eq} + R \cdot T \cdot \ln(XD^{d} \cdot XC^{c})/(XA^{a} \cdot XB^{b}) \neq 0$; $0 = \Delta G_{eq} + R \cdot T \cdot \ln(K_{eq})$ at equilibrium zero (1-4)

Table 1-1. Standard Free-Energy Changes for pure compounds hydrolise ΔG_{Hess} at I=0.2 M (298.15 K)

Hydrolysis reactions free energy change ΔG_{eq} at equilibrium and in Hess calculation law	ΔG_{Hess}	$^{kJ}/_{mol}$
$CH_3COOOCCH_3+H_2O=2CH_3COOH$; $\Delta G_{Leninger}$= -91.1 $^{kJ}/_{mol}$; $K_{Leninger}=10^{15.96}$;	**-97.4**	pH<4.5
$CH_3COOOCCH_3+3H_2O=>2CH_3COO^{-}+2H_3O^{+}$; K_{eq}=0.0056732; ΔG_{eq}=12.82 $^{kJ}/_{mol}$	223	pH=7.36
$H_2PO_4^{-}+H_2O=>HPO_4^{2-}+H_3O^{+}$;$\Delta G_{Lehninger}$=64.96 $^{kJ}/_{mol}$; K_{eq2}= **1.143•10^{-9}**;ΔG_{eq}=51.04 $^{kJ}/_{mol}$;ΔG_{Hess}=	70	pH=7.199
$ATP^{3-}+H_2O=>ADP^{2-}+H_2PO_4^{-}$; $K_{bLehninger}$=3984,1; $\Delta G_{bLeningeH}$=-20.55 $^{kJ}/_{mol}$; bez pH=?	**-37,854**	pH=?
$ATP^{4-}+2H_2O=>ADP^{3-}+HPO_4^{2-}+H_3O^{+}$; $\Delta G_{bLeninger}$=-30,5 $^{kJ}/_{mol}$; $K_{bLeninger}$=220500,2;	**-99,58**	pH=7.36
$ATP^{4-}+2H_2O=>AMP^{3-}+2HPO_4^{2-}+2H_3O^{+}$; $\Delta G_{Leninger}$=-64.8 $^{kJ}/_{mol}$;	-	pH=7.36
$ATP^{3-} + H_2O =>AMP^{1-}+ \mathbf{H_2P_2O_7^{2-}}$; $K_{mppL}=K_{mppLehninger}/[H_2O]$=1760968; ΔG_{mppL}=-35.65 $^{kJ}/_{mol}$;	**-63.15**	pH<6.72
$ATP^{4-}+2H_2O=>AMP^{2-}+\mathbf{HP_2O_7^{3-}}+\mathbf{H_3O^{+}}$; $K_{mppLeninger}$=97462087; $\Delta G_{Leninger}$=-45.6 $^{kJ}/_{mol}$	**-111.45**	pH=7.36
$\mathbf{H_2P_2O_7^{2-}}+H_2O=>H_2PO_4^{-}+H_2PO_4^{-}$; $K_{pp}=K_{Lehningerpp}/[H_2O]$=41.748; ΔG_{ppL}=**-9,251** $^{kJ}/_{mol}$;	**-70.94**	pH=?_
$\mathbf{HP_2O_7^{3-}}+2H_2O=>2HPO_4^{2-}+\mathbf{H_3O^{+}}$; $K_{app}=K_{Leningepp}$=2310.57; $\Delta G_{Leningerpp}$=-19.2 $^{kJ}/_{mol}$;	**-85.6**	pH=7.36
$UDPGlc^{2-}+H_2O=>UMP^{1-}+Glc1P^{1-}$; $K_{Leninger}=10^{7.75333}$; $\Delta G_{Leninger}$=-43;$\Delta G_{aLeninger}$=-33.05 $^{kJ}/_{mol}$;	-128.64	pH<7.199
Esters ↓; $UDPGlc^{2-}+3H_2O=>UMP^{2-}+Glc1P^{2-}+2H_3O^{+}$;$K_{eq}=10^{-12.4}$; ΔG_{eq}=70.868 $^{kJ}/_{mol}$; 424 or	**113**	pH=7.36
CH_3CH_2-O-$OCCH_3+H_2O=>CH_3CH_2OH+HOOCCH_3$;$K_L$=2715; ΔG_L=-19.6; ΔG_{eL}=-9.65 $^{kJ}/_{mol}$;	**-19.745**	pH<4.76
$CH_3CH_2OOCCH_3+H_2O=>CH_3CH_2OH+^{-}OOCCH_3$; K_{eL}=49.07; $K_{ee}=10^{-7.41}$; ΔG_{eL}=42.3 $^{kJ}/_{mol}$;	87.757	pH=7.36
$Glc6P^{2-}+H_2O=>Glc+HPO_4^{2-}$;$\Delta G_L$=-13.8 $^{kJ}/_{mol}$;K_{a2L}=261.62; ΔG_{aL}= -3.851 $^{kJ}/_{mol}$	-38.55	I=0.2 M
$Glc1P^{2-}+H_2O=>Glc+HPO_4^{2-}$;$\Delta G_L$=-20.9 $^{kJ}/_{mol}$;K_{a2L}= 48.07;	**-36.1**	I=0.2 M
Glc+ATP^{4-}+H$_2$O=>Glc6P^{2-}+ADP^{3-}+H$_3$O^{+}; K_{a22b}=48.07; ΔG_{eq}=**-R•T•ln(K_{eq})**= -9.6 $^{kJ}/_{mol}$	**-25.2**	pH=7.36
Amīdi un peptīdi		
$Gln+ \mathbf{H_2O} =>Glu^{-}+NH_4^{+}$; $\Delta G_{aLehninger}$=-14.2 $^{kJ}/_{mol}$; $K_{aLeninger}$=307.43;	**-183.65**	7.36≥pH
$Glu^{-}+NH_4^{+}+ATP^{4-}+H_2O=>Gln+ADP^{3-}+HPO_4^{2-}+\mathbf{H_3O^{+}}$; ΔG_{ab}=**35.66** $^{kJ}/_{mol}$; K_{ab}=0,0000005657	**254.9**	pH=7.36
GlyGly+H_2O=>2Gly; $K_{0.2Mhydrolyse}=1/K_{0.2M}$ =1/**0.07146**=13.994; $\Delta G_{0.2M}$=**-6.54** $^{kJ}/_{mol}$; I=0.2 M	**-16.2**	pH=7.36
Glycosides;	-	-
Maltose+H_2O=>2Glc; $K_{eq}=K_{Leninger}$=519.4; $\Delta G_{Leninger}$=-15.5 $^{kJ}/_{mol}$;	**-155**	pH=7.36
Lactose+H_2O=>Glc+Gal; $K_{eq}=K_{Lehninger}$; $\Delta G_{Leninger}$=-15.9 $^{kJ}/_{mol}$;	**-20.334**	pH=7.36
Group transfer (transferases)		
$Glc1P^{2-}$=>$Glc6P^{2-}$;K_{eq}=[Glc6P]/[Glc1P]=17;ΔG_{eq}=-RTln(K_{eq})=-7.02 $^{kJ}/_{mol}$**;** BioThermodyn06	**-7.04**	I=0.2 M
$Fruc6P^{2-}$=>$Glc6P^{2-}$; $K_{Leninger}$=1.98531; $\Delta G_{Leninger}$=-1.7 $^{kJ}/_{mol}$	**-3.173**	pH=7.36
Water H_2O elimination		I=0.2M
Malate=>Fumarate+H_2O; $\Delta G_{Leninger}=\Delta G_{eq}$=3.1 $^{kJ}/_{mol}$; $K_{eq}=K_{Leninger}$=0.28635	**3.6165**	pH=7.36
Oxidation with molecular oxygen O_2 ; Glucose+6O_2=>6CO_2+6H_2O; $\Delta G_{Leninger}$=-2840 $^{kJ}/_{mol}$**;**	-	-
$C_6H_{12}O_6$+6O_{2aqua}+6H_2O<=>6HCO_3^{-}+6H_3O^{+};$K_{Lehninger}=10^{497.55}$; =>6$CO_{2aqua}$+12$H_2O$;	**-2921.5**	aqua
Palmitic acid+23O_{2aqua}=>16CO_{2aqua}+16H_2O;$\Delta G_{Leninger}$=-9770 $^{kJ}/_{mo}$; $K_{Lehninger}=10^{1711.6428}$;		
$C_{16}H_{32}O_{2s}$+16H_2O+23O_{2aqua}=16HCO_3^{-} |+16H_3O^{+}=16CO_{2aqua}+32H_2O=16CO_{2gas}↑+32H_2O	**-12020**	aqua

ΔG_{eq} is a constant: as Prigogine attractor free energy change minimum for equilibrium. ΔG homeostasis **reactant**, **product** generate ratio in reaction of human body, which irreversibly out of **equilibrium** position. Moreover, the ΔG of any reaction proceeding => spontaneously toward its **equilibrium** state with change $\Delta G<0$, minimized by absolute value about ΔG_{eq} , but shift to **equilibrium** position zero $\Delta G=0$. Expression indicating $(X_D^d \bullet X_C^c)/(X_A^a \bullet X_B^b)=K_{eq}$, no possible work $W=-\Delta G=0$ with zero in reaction: (1-3).

$\Delta G_{Homeostasis}$ and ΔG_{eq} connected in the equation (1-4), in which the terms are actually dominating at homeostasis. The concentration **X** ratio in the equation expression reflects **mass action**. As an example, let us write general reaction a**A**+b**B**=c**C**+d**D** which works at the **standard conditions** of temperature T_o = **298.15 K** (**25 °C**) and pressure (**101.3 kPa**) but we simply enter the equilibrium concentrations of X_A, X_B, X_C, and X_D in Equation 1-4; the values of **R**, T_o, and calculate the ΔG_{eq} . Actual concentrations of X_A, X_B, X_C, and X_D in Equation 1-4 with negative $\Delta G_{non\_equilibrium}$ **<0** changes to reach zero =>**0** as substrate concentrations of X_A and X_B decrease and products concentrations of X_C, and X_D increase.

Notice that when a reaction is at **equilibrium**-when there is no **force** driving the reaction in either direction and ΔG is zero-Equation 1-4 to calculate ΔG_{eq} = - **R•T•ln**(K_{eq}) as **0** = ΔG_{eq} + **R•T•ln**(K_{eq}) the equation relating the **equilibrium free**-energy change with **equilibrium** constant K_{eq} as noted above (1-4).

Water molecules in Biochemistry for homeostasis have activate value per one mol:

$$G_{H2O\_Biochemistry}=\Delta G°_{H2O\_Biochemistry}-\Delta G°_{H2O\_distilled}=\mathbf{-151,549}-(-237,191)=\mathbf{85.65}\ {}^{kJ}/_{mol}.\ [1,8]$$

Water protolysis activate with protonation and deprotonation $H_2O+H_2O<=>H_3O^+ + OH^-$ one mol of ions:.

$$G_{H3O++OH-}=\Delta G_{H3O++OH-}+\Delta G°_{2H2O}=-R\bullet T\bullet \ln(K_{H3O++OH-}) - 0=99.8\ {}^{kJ}/_{mol}\ .$$

Concentration is exponent of **pH** $[H_3O^+]=10^{-pH}$ for: blood plasma and cytosol **pH=7.36** and specific for inter membrane space of mitochondria **pH=5.0**; of saliva juice **pH=6.8**; stomach juice **pH=1.2** (before meals). Extracting from **equilibrium** mixture constant K_{eq} as expression **R•T•ln**($X_{H3O}{}^{+n}$) by mathematical separation of logarithm ratio in (1-4) may correct **equilibrium free**-energy ΔG_{eq} value to **conditions** for **pH** of medium of $[H_3O^+]$ = 10^{-pH} **M** solution where **n** is the number of hydrogen ions H_3O^+ involved in reaction **equilibrium** mixture according given reaction equation. Addition or subtraction to **standard free**-energy ΔG_{eq} value yield $\Delta G_{pH} = \Delta G_{eq} \pm$ **R•T•ln**($X_{H3O}{}^{+n}$) **free**-energy **pH conditions** at given medium **-R•T•ln**($X_{H3O}{}^{+n}$) agree for **reactant** and/or **+R•T•ln**($X_{H3O}{}^{+n}$) for **product**.

The criterion for spontaneity of a reaction is the value of equilibrium ΔG_{eq} . Equilibrium with a positive $\Delta G_{eq}>0$ can go in the forward direction if $\Delta G_{Homeostasis}$ **<0** is negative. This is possible if the expression in equation 1-4 is negative (-) **R•T•ln**([**products**]/[**reactants**]) and has a larger absolute value greater **>** than ΔG_{eq}. For example, the immediate removal of the **products** of a reaction can keep the ratio well below **<1**, so expression has a large, negative value.

CATALASE erase H_2O_2 molecules in peroxisomes for fatty acid elongation C20:4 at dehydrogenation ethyl groups **-CH_2-CH_2-** about cis double bonds **H**>C=C<**H** in ω=6, ω=3 fatty acids products with 100% efficiency.

ΔG_{eq} and $\Delta G_{Homeostasis}$ are expressions of the maximum amount of **free** energy per one **1 mol** of compound that a given reaction can theoretically deliver an amount of energy that could be realized only if a perfectly efficient device were available to trap or harness it. Given that no such device is possible (some **free** energy ΔG is always lost to **bound** energy **T•**Δ**S** with entropy ΔS during any process), the amount of work $W\leq-\Delta G$ done by the reaction at constant temperature **T=const** and pressure is always less than the theoretical amount ΔG.

Another important point is that some thermodynamically favorable reactions (that are, reactions for which ΔG_{eq} **<0** is large and negative) do not occur at measurable rates. For example, **combustion** of firewood to CO_2 and H_2O is very favorable thermodynamically, but firewood remains stable for years.

Oxygen O_{2aqua} decreased power for functional active isooxia Norma solution in blood so in cytosol too driven with four Attractors: water triplet state of oxygen, water concentration $[H_2O]=55.3\ {}^{mol}/_{Liter}$, air oxygen level 20.95 % for five hundred million Years, pH=7.36 for the concentration $[H_3O^+]=10^{-7.36}$ M. [14] Protolytic free energy content created from $G_{O2aqua}=329.7\ {}^{kJ}/_{mol}$ to $G_{O2Biochemistry\_arterial}=78.08\ {}^{kJ}/_{mol}$.

All **enzymes** reactivity lowering the activation energy E_a and increase reactions velocity constant about million times 10^6. **Hess law** in living cells show **free**-energy change ΔG_{Hess} for a reaction is independent of the **pathway** by which the reaction occurs; it depends only on the reactants and products. **Enzymes** decrease equilibrium reaching time $t_{Attractor}$. Equilibrium remains constant K_{eq} and independent on concentrations X.

Biochemical thermodynamics explains how unfavorable **endoergic** reaction can be driven in favorable by coupling it to a **exoergic** reaction in complex sequential order through a **common intermediate**. The **Glc 6-phosphate**$^{-}$ formation attractor intermediate concentration **pH = 7.36** make reaction **a** endoergic:

a Glucose+HPO_4^{2-} =>**glucose-6-phosphate**$^{-}$ +H_2O; $\Delta G_{aLehninger}$=13.8 $^{kJ}/_{mol}$; $K_{aaLehninger}$=0.003822314;

Cellular **hydrolysis** of ATP^{4-} to ADP^{3-} producing HPO_4^{2-} +H_3O^+ in **endoergic b** $\Delta G_{bLeninger}$=-30.5 $^{kJ}/_{mol}$ driven by hydrogen ion concentration [**H3O**$^+$]=$10^{-7.36}$ **M** in blood **pH = 7.36 exoergic b**:

b ATP^{4-}+2 H_2O => ADP^{3-}+HPO_4^{2-}+H_3O^+ **;** $\Delta G_{bLeninger}$=-30.5 $^{kJ}/_{mol}$ **(pH = 7.36)** (1-5)

Homeostasis share Biochemistry constants for H_3O^+ and H_2O concentrations and for Attractor pH=7.36.

37th , 38th pages:

$$K_{bLeninger}=\exp(-\Delta G_{bLehninger}/R/T)=\exp(30500/8.3144/298.15)=220500=\frac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_2O]^2[ATP^{4-}]}$$

$\Delta G_{bLeninger}$=-**R**•**T**•**ln**($K_{bLeninger}$)= -8.3144•298.15•**ln**(220500.2)= -30.5 $^{kJ}/_{mol}$;

a **Glc** + HPO_4^{2-} => **Clc6P**$^{2-}$ + H_2O; $\Delta G_{aLehninger}$=13.8 $^{kJ}/_{mol}$;

b ATP^{4-}+2 H_2O => ADP^{3-}+HPO_4^{2-} + H_3O^+; $\Delta G_{bLehninger}$=-30.5 $^{kJ}/_{mol}$**;**

Sum: **Glc** + ATP^{4-} + H_2O => **Glc6P**$^{2-}$ + ADP^{3-} + H_3O^+ ; $\Delta G_{totaleq}$ =13.8 + -30.5 $^{kJ}/_{mol}$= -16.7 $^{kJ}/_{mol}$;.

Reactions iis **exoergic**. Such a way ATP^{4-} molecules are used for **glucose 6-phosphate** synthesis driving, even formed from **glucose** and **phosphate** at attractor **pH=7.36** affected **a exoergic**. Any way the **pathway** of **glucose 6-phosphate** formation by **phosphoryl transfer** from ATP^{4-} through paths (**a**) and (**b**)**.** Both pathways sum give the free energy changes according Hess law calculation order products minus reactants.

Equilibrium ΔG_{eq} is a way of expressing the **equilibrium** constants K_{a1eq} for a reaction. For reaction (**a**) above at standard **T=298.15K** or human body temperature **T=310.15K** unfavored:

$$K_{a298}=\frac{[Glc6P^{2-}]\cdot[H_2O]}{[Glc]\cdot[HPO_4^{2-}]}=\text{EXP(-13800/8.3144/298.15)= 0.003822314 ; } K_{a310}=0.004741\ .$$

Notice concentration [H_2O]= 55.3457 **M** constant is included in its value, To calculate **standard equilibrium** constants in tables is to divide by, but at cell temperature **T=310.15 K** by [H_2O] =55.1398 **M**.

The **equilibrium** constants K_b for the **hydrolysis** of ATP^{4-} are at attractor pH=7.36 favored :

$$K_{b298}=\frac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_2O]^2\cdot[ATP^{4-}]}=220500.2 \text{ or } K_{b310}=136983.25\text{; favored .}$$

The equilibrium constant for the two coupled reactions **T=298.15K** or human body temperature **T=310.15K** is

$$K_{eq298}=\frac{[Glc6P^{2-}]\cdot[H_2O]}{[Glc]\cdot[HPO_4^{2-}]}\ \frac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_2O]^2\cdot[ATP^{4-}]}=\frac{[Glc6P^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[Glc]\cdot[H_2O]\cdot[ATP^{4-}]}=842.82 \text{ or } 649.438=K_{eq310}$$

Equilibrium ΔG_{eq} value are additive for two **2** reactions that sum to a third **3rd**, Constant K_{total} for a reaction of two **2** reactions is the commutative K_a•K_b of values favored largest yielding with medium attractor value pH=7.36 K_{eq298}=842.82 or K_{eq310}=649.438 at human body temperature **T=310.15K** (**37°C**) respectively. **Equilibrium** constants are commutative in joined (tandem) reactions as ATP^{4-} **hydrolysis** to glucose 6-phosphate^{-} synthesis.. In coupling (tandem) reactions **common intermediate** employed is living cells strategy in metabolic synthesis as **photosynthesis**, poly condensation reactions (proteins, nucleic acids, polysaccharides, muscle contractions. This strategy works only if reactant ATP^{4-} is continuously available. In have to study this important cellular **pathways** for producing ATP^{4-}.

Phosphoryl Group $^{+}PO_3^{2-}$ Transfers with metabolic intermediate ATP^{4-}

Thermodynamic of energy change minimisation under attractors rule controle the **energy cycle** in cells and the role of ATP^{4-} as the **energy expences** that drive homeostasis of catabolism and anabolism. Heterotrophic cells obtain **free** energy in a chemical form by the catabolism of **nutrient** molecules to generate concentrations gradients for metabolism and for osmosis of homeostasis. ATP^{4-} ions to **endoergic synthesis** of metabolic **macromolecules** from **smaller precursors**, the **transport** of metabolits across membranes by concentration gradients, and mechanical motion. Accumulation in and donation of energy from ATP^{4-} involves the covalent participation of ATP^{4-} in the reverse reactions are converted to ADP^{3-} and $\mathbf{HPO_4^{2-}+H_3O^{+}}$ or in some reactions to AMP^{2-} and 2 $\mathbf{HPO_4^{2-}}$+2 $\mathbf{H_3O^{+}}$. The large **free**-energy changes $\Delta G_{Homeostasis}$ that accompany **hydrolysis** of ATP^{4-} and other **high-energy phosphate** compounds. Energy donation by ATP^{4-} involve nucleophilic group transfer to electrophilic acceptor groups.

The **Free-Energy** Change for **ATP^{4-} Hydrolysis** is large

The chemical basis for the relatively large **free** energy ΔG_{Hess}=**-99,58** $^{kJ}/_{mol}$ and at equilibrium minimum $\Delta G_{bLeninger}$=-30.5 $^{kJ}/_{mol}$ of **hydrolysis** at pH=7.36 . The **hydrolysis** of the terminal **phosphoric acid anhydride** bond in ATP^{4-} separates one of the three **3** negatively charged **phosphates** and thus relieves some of the electrostatic repulsion. HPO_4^{2-} stabilize high rate protolysis deprotonate water molecule $\mathbf{H_2O}$ =>$\mathbf{H^{+}}$+OH^{-}. Electrophilic $\mathbf{OH^{-}}$ ion stabilize nucleophilic phosphoryl group $\mathbf{^{+}PO_3^{2-}}$ covalently:$\mathbf{OH^{-}+{}^{+}PO_3^{2-}}$=>H-**O**-$\mathbf{PO_3^{2-}}$ binding. Anhydride oxygen direct **protolysis** product ADP^{2-} immediately deprotonates about ADP^{3-}, adding $\mathbf{H^{+}}$ to $\mathbf{H_2O}$ water in medium with low ions concentration $[\mathbf{H_3O^{+}}]=\mathbf{10^{-7.36}}$ **M**. As direct products of ADP^{3-} **hydrolysis** are far below the concentrations at **equilibrium**, than mass action favors the hydrolysis reaction due to high rate protolytic attractors pH=7.36 $[\mathbf{H_3O^{+}}]=10^{-7.36}$ and high water influence $\mathbf{2H_2O}$ two $[\mathbf{H_2O}]$=55.3 M.

Joined tandem complex enzyme poly condensation reactions drive 3rd class hydrolases, which work under rules of high rate protolysis attractors: I=0.2 M, $[\mathbf{H_2O}]$=55.3 M, $[\mathbf{H_3O^{+}}]=10^{-7.36}$ M and T=310.15 K. Rapid protonation rate **v** of the **phospho anhydride** bonds occurs only with an **enzyme** reactivity what decrease activation energy $\mathbf{E_a}$ 10^6 times. **Enzyme** reactivity optimizes Prigogine attractors as high rate protolysis staying at equilibrium while homeostasis continues for life process driving.

The **free**-energy change $\Delta G_{eq}=\Delta\mathbf{G_{bLeninger}}$=**-30.5** $^{kJ}/_{mol}$ for ATP^{4-} hydrolysis equilibrium:

$$\mathbf{K_{eq}=K_{bLeninger}=exp(-\Delta G_{bLeninger}/R/T)}=\exp(30500/8.3144/298.15)=\exp(12.304)=220500.2,$$

but in living cells ATP^{4-} **free** energy of hydrolysis $\Delta G_{Homeostasis}$ is very different: at cellular 310 K, pH=7.36, ATP^{4-}, ADP^{3-}, HPO_4^{2-} are much lower than **1.0 M** Table 1-2. Enzymes bind $\mathbf{Mg^{2+}}$ coordinative to ATP^{4-} and ADP^{3-} (Fig. 1-1b), it let's protonate electrophilic **anhydride** bond oxygen atom $^{18}\mathbf{O}$, what bound opened nucleophilic **phosphoryl** group $\mathbf{^{+}PO_3^{2-}}$ for transfer to electrophilic $\mathbf{OH^{-}}$.group: forming $\mathbf{OH^{-}+{}^{+}PO_3^{2-}}$ => H**O**-$\mathbf{PO_3^{2-}}$ hydrogen phosphate with negative charge. Value ΔG_{eq}=**-30,5** $^{kJ}/_{mol}$ is for **MgATP^{4-} hydrolysis**. That shown how ΔG for ATP^{4-} **hydrolysis** in the erythrocyte can be calculated from the data in Table 1-2. Cellular ATP^{4-} **hydrolysis**, usually designated is much more negative than ΔG_{eq}, ranging from -111 to **-117** $^{kJ}/_{mol}$. $\Delta G_{Homeostasis}$ is often called the **phosphorylation potential.** In Biochemistry studies use the **equilibrium free**-energy change for ATP^{4-} **hydrolysis**, because this allows comparison, on the same basis, with the energetic of other cellular reactions. Remember, however, that in living cells $\Delta G_{Homeostasis}$ is the relevant quantity for ATP^{4-} **hydrolysis** and are different from ΔG_{eq}.

First **1st**, **hydrolysis**, by causing charge separation, relieves **electrostatic repulsion** among the four negative (-) charges on **ATP^{4-}**. Second **2nd**, **phosphate HPO_4^{2-}** released by **hydrolysis** is stabilized by formation of a resonance hybrid, in which each of the four **P-O** bonds has the same degree of double-bond character and **protonate H^{+}** is not permanently associated with any one of the oxygen =**O**. Some degree of resonance stabilization also occurs in phosphates involved in **ester** or **anhydride** linkages, but fewer resonance forms are for $\mathbf{PO_4^{3-}}$ too. Third **3rd**, ADP^{2-} protolytic deprotonates about ADP^{3-} and H_3O^{+}. A fourth **4th** factor ATP^{4-} greater degree of **hydration** of the products $\mathbf{HPO_4^{2-}}$ and **ADP^{3-}** relative to **ATP^{4-}** . That stabilizes the **products** relative to the **reactants**.

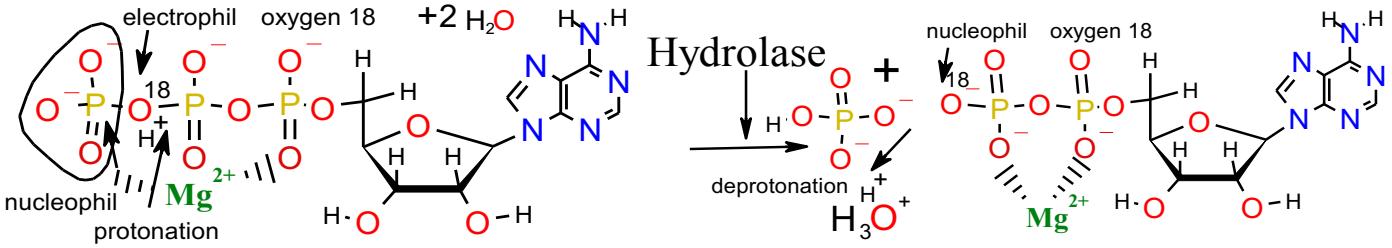


Figure 1-2. Mg^{2+} and ATP^{4-}. Mg^{2+} coordination let's protonate electrophilic **anhydride** bond oxygen atom, erase negative charges **2-** with **2+ conformation** of Mg^{2+} **phosphate** groups in such as ATP^{4-} and ADP^{3-}.

Ingested foods with catabolic **exoergic** reactions ♦ in photonsynthetic reactions accumulate energy attractors drive homeostasis with generate concentration gradients ATP^{4-} => ADP^{3-}=> AMP^{2-}=> $HP_2O_7^{3-}$=> HPO_4^{2-}; => Osmosis => Transport=> Mechanical work => Composite materials => **endoergic synthesis** reactions

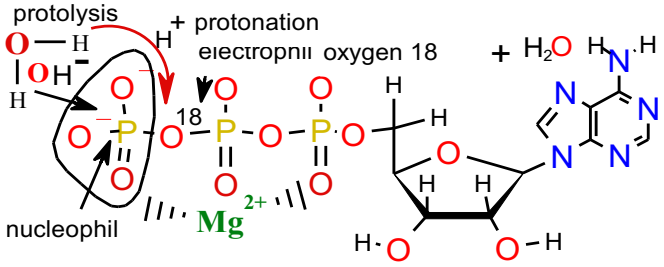


Figure 1-1a. ATP^{4-} is the shared chemical intermediate linking energy releasing anabolism to energy requiring catabolism cell processes. Its role in the cell is analogous to that of money in an economy it is "earned/produced" in **exoergic** reactions and "spent/consumed" **endoergic** accumulating in synthesis products, favored by constants [H_2O], [H_3O^+] and temperature T=298.15 K

Electrophilic OH^- to nucleophilic attack, protonation H^+ deprotonation of $H\text{-}^{18}O\text{-} = H^+ + {}^{18}O^-$.

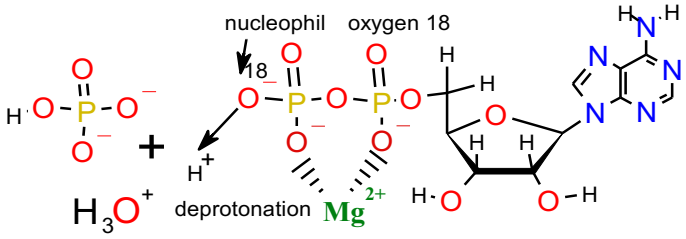


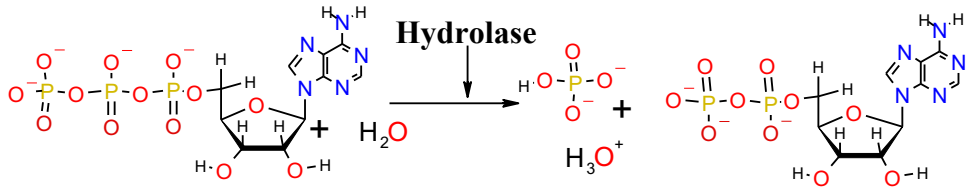
Figure 1-1b. Enzymatic reactivity basis for the large **free-energy change** tandem coupling with **ATP** hydrolysis to

$ATP^{4-} + 2\ H_2O \Rightarrow ADP^{3-} + HPO_4^{2-} + H_3O^+$;

$\Delta G_{bLehninger}$=-30.5 $^{kJ}/_{mol}$; ΔG_{Hess}=**-99.58** $^{kJ}/_{mol}$;

ATP driven FORBIDDEN REACTIONS in Homeostasis

Synthesis for **gly+gly=>glygly+H_2O;** is thermodynamically forbidden $\Delta G_{0.2M}$=6.54 $^{kJ}/_{mol}$. In hydrolysis of ATP^{4-} molecules with water is formed adenosine diphosphate ADP^{3-} and phosphate: Favor conditions create homeostasis attractors: water [H_2O]=55.3 M , physiologic pH=7.36 for hydroxonium ions [H_3O^+]=$10^{-7.36}$ M and temperature 298.15 K thermodynamic, which included in Lehninger



equilibrium constant. ATP^{4-} hydrolysis at homeostasis conditions are greater: up to **-117** $^{kJ}/_{mol}$.

$ATP^{4-}+2H_2O=>ADP^{3-}+HPO_4^{2-}+H_3O^+$; $\Delta G_{Leninger}$=-30.5 $^{kJ}/_{mol}$;

33rd pages : $K_{bLeninger}=\exp(-\Delta G_{bLeninger}/R/T)=\exp(30500/8.3144/298.15)=220500.2=\frac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_2O]^2[ATP^{4-}]}$

$2gly=>glygly+H_2O$; $\Delta G_{Leninger}$=9.2 $^{kJ}/_{mol}$; in homeostasis unfavored synthesis

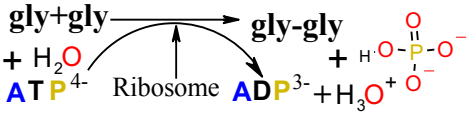
48th pages : $\Delta G_{0.2M}$=**6.54** $^{kJ}/_{mol}$; $K_{0.2M}$ **<1** $K_{0.2M}=\exp(-6541/8.3144/298.15)=0.07146=\frac{[H_2O]\cdot[H_3N^+GlyGlyCOO^-]Gly}{[H_3N^+CH_2COO^-]Gly^2}$

49th pages : $\Delta G_{a0.2Mb}=\Delta G_{0.2M}+\Delta G_{bLeninger}$=**6.54**-30.5=-23.96 $^{kJ}/_{mol}$;

ab) $Gly_{aq}+Gly_{aq}+ATP^{4-}+H_2O=>GlyGly_{aq}+ADP^{3-}+HPO_4^{2-}+H_3O^+$;

$K_{a0.2Mb}=K_{0.2M}K_b$= **0.07146***220500.2=[GlyGly]*[ADP^{3-}]*[HPO_4^{2-}]*[H_3O^+]/[Gly]^2/[ATP^{4-}]/[H_2O]= 15756.9.

The forbidden processes are combined with hydrolysis of ATP^{4-}. Liberated water is used for hydrolysis of ATP^{4-}. Join two reactions together in tandem the reaction becomes in $\Delta G_{a0.2Mb}$=**6.54**-30.5=-23.96 $^{kJ}/_{mol}$ spontaneous up to $\Delta G_{Homeostasis}$=**6.54-117=-110.46** $^{kJ}/_{mol}$ -; Joined tandem complex enzyme poly condensation reactions drive 3rd class hydrolases, which use in reactions homeostasis attractors: I=0.2 M, [H_2O]=55.3 M, [H_3O^+]=$10^{-7.36}$ M and thermodynamic temperature T=310.15.



Medical Chemistry show functional active molecules formation ruled attractors. Irreversible enzyme reactivity in organisms, which activate inactivate compounds with Biochemistry medium high rate protolysis, are Ilya Prigogine declared attractors: water concentration [H_2O]=55.3 M, generate concentration gradients [C_2]/[C_1], 0.305 M osmolarity, ionic strength 0.2 M, air oxygen 20.95% [O_2], pH = 7.36 concentration [H_3O^+]=$10^{-7.36}$ M, temperature 310.15 K degree. Following favored irreversible processes work as Brownian molecular engines driving organism for evolution, homeostasis, survival .

Five types complex ordered reactions versus chaos and pollution of non Enzymatic reactions:

5 complex Enzyme reactions

Versus non Enzymatic reactions

chaos and contamination

Enzyme governed complexe reactions drive the LIFE in 5 ways

7th page : Velocity KINETICS of REACTION dependence on Attractors create molecules functional Activity

1. GRADUAL-CONSECUTIVE organized favored reaction sequence of **ENZYME** complexes for Glycolysis, Krebs cycle; Polycondensation: Replication, Polymerisation, Proteins Translation Synthesis

1. Chaotic

2. ENZYMES specificity 100% efficiency of product **singularity**

2. PARALLEL reaction preseeding in chemistry as side products

3. JOINT-TANDEM SYNTHESIS Ribosomes for polypeptides, proteins Photosynthesis glucose and oxygen

3. Thermodynamic forbidden, impossible reaction unfavored has positive free energy change $\Delta G=\Delta H-\Delta S \bullet T>0$

1 st 5 th page:
Thermodynamic attractor with functionally active O_{2aqua}, CO_{2aqua}

4. COMPETITIVE regulation as **inhibition** and **allostery** sensitive to concentration O_{2aqua}, HCO_3^-, H^+ (**Le Chatelier** principle)

4. Chaotic

His63,58 as for hemoglobin, His64 as for myoglobin as regulated back response prevent (hypo amount) deficiency and (hyper amount) overproduction

so stabilises Physiologic pH=7.36, arterial [O_{2aqua}]=$6 \cdot 10^{-5}$ M and venous [O_{2aqua}]=$0{,}426 \cdot 10^{-5}$ M.

Photosynthesis global stabilises oxygene concentration [O_{2AIR}]= 20,95% in Earth Atmosphere.

5. Enzyme radical driven reactivity the process for maintanance of homeostasis producing resources

5. Contamination destructive chemistry with the chaotic radical chain reactions in multiple parallel products

Prigogine irreversible reactivity attractors in mixture of non-equilibrium compartmented complex reactions clusters create organic regulated order of homeostasis. With enzyme specificity as selectivity attractors organized order: gradual-consecutive, joint-tandem, competitive regulation allostery and inhibition, enzyme driven radical reactions. Organisms are compartmented five type complex reactions in enzyme clusters of dissipative structure containing compounds mixture, irreversible free energy change to minimum working, with certain **Attractors** rule Brownian molecular engines, evolution and surviving instruments of non-equilibrium being homeostasis.

The **equilibrium free energy** change $\Delta G_{bLeninger}$ of **ATP^{4-} hydrolysis** is favored -30,5 $^{kJ}/_{mol}$ with equilibrium constant $K_{bLeninger}$=220500,2. The Attractors: [H_2O]=55,3 M and buffer with pH 7.36 [H_3O^+]=$10^{-7,36}$ M drive **ATP^{4-} hydrolyse** activation to favored homeostasis value in erythrocytes $\Delta G_{Homeostasis}$=**-117,07** $^{kJ}/_{mol}$:

pH=7.36 ATP^{4-} + 2 H_2O => ADP^{3-} + HPO_4^{2-} + H_3O^+ ; $\Delta G_{eq}=\Delta G_{bLeninger}$=**-R•T•ln**($K_{bLeninger}$)=30,5 $^{kJ}/_{mol}$;

$$K_{eq}=K_{bLeninger}=\frac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_2O]^2\cdot[ATP^{4-}]}=\exp(-\Delta G_{bLeninger}/R/T)=\exp(30500/8,3144/298,15)=220500,2.$$

pH<7.199 $K_{Lehninger}=K_{bLehninger}*[H_3O^+]/[H_2O]$=220500,2*10^(-7,36)/55,3457=0,0001739= $\frac{[H_2PO_4^-]\cdot[ADP^{2-}]}{[H_2O]\cdot[ATP^{3-}]}$;

$\Delta G_{eq}=\Delta G_{bLehninger}$=**-R•T•ln**($K_{bLehninger}$)=-8,3144*298,15***ln**(220602)/1000= **-30,5** $^{kJ}/_{mol}$; favored equilibrium .

Human **erythrocyte** generate concentration gradient attractor [ATP^{4-}]/[ADP^{3-}]=2,25/0,25=9 increasing activity for reaction nine times: $K_{Leninger[ADP3-]/[ATP4-]}$=220602*9=1985418 . With concentration gradients of **ATP^{4-}**, **ADP^{4-}**, **HPO_4^{2-}**, **2.25**, **0.25**, **1.65 mM** in ratio and attractor value [H_3O^+]=$10^{-7,36}$ obtains favored homeostasis constant value: $K_{Homeostasis}$=2,63215•10^{-15}=2,5*10^(-4)*1,65*10^(-3)*10^(-7,36)/2,25/10^(-3)/55,1398^2= $K_{erythrocytes}$:

$$K_{Homeostasis}=2,63215\bullet10^{-15}=\frac{2.50\bullet10^{-4}\bullet1.65\bullet10^{-3}\bullet10^{-7.36}]}{2.25\bullet10^{-3}\bullet55.1398^2}$$ and free energy change favored :

$$\Delta G_{Homeostasis}=-30.5\ ^{kJ}/_{mol}+(8.3144\ J/mol/K\bullet310.15\ K)\bullet\ln\frac{2.50\bullet10^{-4}\bullet1.65\bullet10^{-3}\bullet10^{-7.36}]}{2.25\bullet10^{-3}\bullet55.1398^2}=-117,07\ ^{kJ}/_{mol}\ ;$$

$\Delta G_{Homeostasis}$=-30,5+8,3144 *310,15*ln(2,63215*10^(-15))/1000=-30,5+8,3144 *310,15*-0,03357=**-117,07** $^{kJ}/_{mol}$;

at temperature 310,15 **K** ; in homeostasis **2,6322•10^{-15}** = $K_{erythrocytes}$ and equilibrium :

$K_{bLeninger}$=**exp(-**$\Delta G_{bLeninger}$**/R/T)**=exp(30500/8,3144/298,15)=exp(12,304)=220500,2 .

Thus the **free energy** change required to **synthesize ATP^{4-}** from **ADP^{3-}** and **HPO_4^{2-}** under the conditions prevailing in the **erythrocyte** would be accumulate **-117,07** $^{kJ}/_{mol}$ in **ATP^{4-}** one mole.

Table 1-2. Adenin Nucleotide, **phosphate** and **phospho creatine concentrations** in **cells***

Concentration C (mM) or -pH **ATP^{4-}** -30;5 $^{kJ}/_{mol}$ **PCr -12,5**; **-13** $^{kJ}/_{mol}$ 310,15 K 298,15 K; 310,15 K

	ATP^{4-}	ADP^{3-}	AMP^{2-}	P_i	PCr	pH	$\Delta G_{HomeostasisATP}$	$\Delta G_{HomeostasisPCr}$	$\Delta G_{HomeostasisPCr}$
Rat hepatocyte	3.38	1.32	0.29	4.80	0.0	7.36	-111,07	**-60,065**	-60,565
Rat myocyte mitochondria	8.05	0.93	0.04	8.05	28.0	7.36	-112,88	**-72,995**	-73,495
Rat myocyte	8.05	0.93	0.04	8.05	28.0	7.36	-112,88	**-68,18**	-68,680
Rat neuron	2.59	0.73	0.06	2.72	4.7	7.36	-113,38	**-67,41**	-67,910
Human erythrocyte	2.25	0.25	0.02	1.65	0.0	7.36	**-117,07**	**-66,06**	-66,560
E. coli cell	7.90	1.04	0.82	7.90	0.0	7.36	-112,59	**-64,33**	-64,830

* For **erythrocytes** the concentrations **C** are those of the cytosol (human **erythrocytes** lack a nucleus and mitochondria). In the other types of cells the data are for the entire cell contents, although **the cytosol** and the mitochondria have very different concentrations **C** of **ADP^{3-}**. **PCr** is **phospho creatine**, discussed on above. **This value** reflects total concentration; the true value for **free ADP^{3-}** may be much lower (see above).

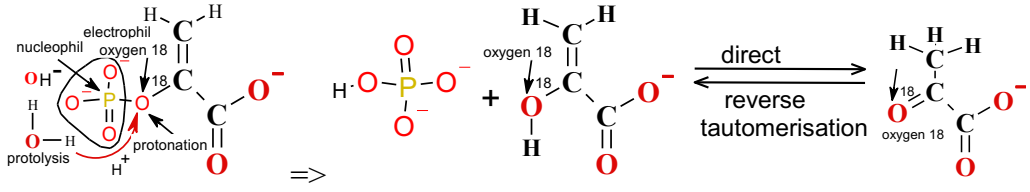
Because the concentrations **C** of **ATP^{4-}**, **ADP^{3-}**, and [HPO_4^{2-}] differ from one cell type to another (see Table 1-2), ΔG for **ATP^{4-} hydrolysis** likewise differs among cells. Moreover, in any given cell, ΔG can vary from time to time, depending on the **metabolic conditions** in the cell and how they influence the concentrations **C** of **ATP^{4-}**, **ADP^{3-}**, [HPO_4^{2-}], high rate protolysis attractors: [H_2O]=55,3 M and buffer with pH 7.36 [H_3O^+]=$10^{-7,36}$ M. We can calculate the actual **free energy** change ΔG for any given metabolic reaction as it occurs in the cell, providing we know the concentrations **C** of all the reactants and products of the reaction and attractors (**pH**, **T**, H_2O and concentration gradients) that affect the ΔG and thus the calculated **free energy** ΔG change.

Prigogine attractors concentrations **:** ATP^{4-}, ADP^{3-}, HPO_4^{2-} and H_3O^+ reaching trend is organisms self organizing properties of dissipative structures, which create perfect order non-equilibrium homeostasis. Molecules protolytic high rate functional activate attractors staying at equilibria are accompanied indispensably for **specific binding** to proteins in perfect order homeostasis as irreversible non equilibrium state. For example, the concentration **C** of **free ADP** in resting muscle has been variously estimated at between **10** and **370 µM**. Using the value **250 µM** in the calculation outlined above, we get a $\Delta G_{Homeostasis}$ of **-117.07** $^{kJ}/_{mol}$. Attractors, water $[H_2O]$=55.3 M , pH 7.36 $[H_3O^+]=10^{-7.36}$ M , $[ATP^{4-}]/[ADP^{3-}]$=2.25/0.25=9 generate concentration gradient increase activity of reaction nine times and totally accumulate in ATP^{4-} **hydrolysis** exoergic homeostasis free energy change $\Delta G_{Homeostasis}$**=-117.07** $^{kJ}/_{mol}$ more as for reaching equilibrium ΔG_{eq}=-30.5 $^{kJ}/_{mol}$ or Hess **free energy** change ΔG_{Hess}= **-99.58** $^{kJ}/_{mol}$ for pure reactants and pure products.

Other **Phosphorylated Compounds, Thio-esters also have Large Free Energies of Hydrolysis** and others

Phospho enol pyruvate (Fig. 1-3) contains a **phosphate ester** bond. Attractors, water $[H_2O]$=55.3 M concentration increase activity of favored reaction to yield the **enol** form of **pyruvate**,. Protolytic attractors are the greatest contributing factors to the high **free** energy of **phospho enol pyruvate hydrolysis**: Hess law value $\Delta G_{Hess}=\Delta G°_{H3CC=OCOO-}+\Delta G°_{HPO42-}-\Delta G°_{PyruvEnolP3-}-\Delta G°_{H2O}$**=-190.3** $^{kJ}/_{mol}$ is greater change as equilibrium value

phospho enol pyruvate^{3-}+H_2O=>pyruvate$^-$+HPO_4^{2-}**;** $\Delta G_{eqLehninger}$=-61.9 $^{kJ}/_{mol}$; I=0.20 M, pH=7.36 :



pyruvate

Figure 1-3. Hydrolysis of phospho enol pyruvate (**PEP**). **Pyruvate kinas** protonate electrophilic **ester** bond oxygen atom ^{18}O. Opened nucleophilic **phosphoryl** group $^+PO_3^{2-}$ transfer to electrophilic OH^-.group: forming $OH^-+{}^+PO_3^{2-}$ => $HO\text{-}PO_3^{2-}$ hydrogen phosphate with negative charge and spontaneous **tautomerization** of the **product**, **pyruvate**. **Tautomerization** is not possible in **PEP**, and thus the products of **hydrolysis** are stabilized relative to the **reactants**. Resonance stabilization of **Pi** = HPO_4^{2-} also occurs, as shown in Figure 1-1b.

Another three-carbon C_3 compound, **1,3-bis-phosphoglycerate** (Fig. 1-4), contains an **anhydride** bond between the carboxyl group $-CO-{}^{18}O-PO_3^-$ at C_1 and **phosphate**. **Hess** law: at ionic force I=0,20 M and pH=7,36 free-energy change ΔG_{Hess}==**-107.75** $^{kJ}/_{mol}$ is grater as minimized equilibrium $\Delta G_{aLehninger}$=-49,3 $^{kJ}/_{mol}$. Attractors, water $[H_2O]$=55,3457 M and pH 7.36 $[H_3O^+]=10^{-7,36}$ M increase functional activity in homeostasis ATP^{4-} synthesis process favored $\Delta G_{Homeostasis}<\Delta G_{abb}$=-18,8 $^{kJ}/_{mol}$. on pages. 21st , 19th , 20th :

$\Delta G_{Hess}=\Delta G°_{H3O+}+\Delta G°_{Glyc3P}+\Delta G°_{HPO42-}-\Delta G°_{Glyc31P}-2\Delta G°_{H2O}$**=-107.75** $^{kJ}/_{mol}$; $\Delta G_{Lehninger}$=-49,3 $^{kJ}/_{mol}$;

a 1,3-bis-phospho-glycerate^{4-}+2H_2O => 3-phospho-glycerate^{3-} + HPO_4^{2-}+ H_3O^+ ; pH=7,36

$\Delta G_{aLehninger}$=-49,3 $^{kJ}/_{mol}$;$K_{aLehninger}$**=exp(-**$\Delta G_{Lehninger}$**/R/T)**=exp(49300/8,3144/298,15)=433562158,5;

bb ADP^{3-}+ HPO_4^{2-} + H_3O^+ => ATP^{4-}+2 H_2O **;** $\Delta G_{bbLehninger}$=30,5 $^{kJ}/_{mol}$

---

abb : **Glyc31P**$^{4-}$ + ADP^{3-} => **Glyc3P**$^{3-}$ + ATP^{4-}; $\Delta G_{abb}=\Delta G_{aLehninger}+\Delta G_{bbLehninger}$=-49,3+30,5= -18,8 $^{kJ}/_{mol}$**;**

When H_2O is added across the anhydride bond of **1,3-bis-phospho-glycerate**, one **1** of the direct products, **3-phospho-glyceric acid**, immediately deprotonated H^+ give the **carboxylate ion**, **3-phosphoglycerate**, which has two **2** equally probable resonance forms (Fig. 1-4). Deprotonate the direct **product** and formation of the resonance-stabilized ion favors the forward reaction.

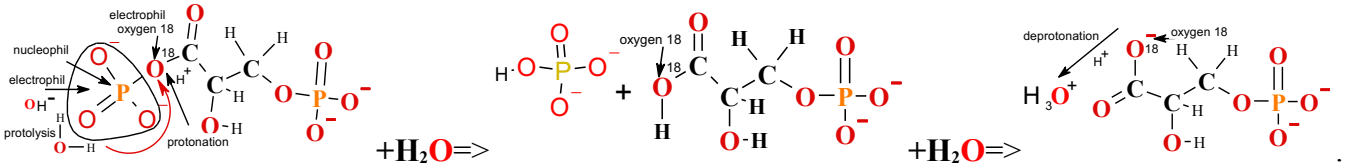


Figure 1-4. Hydrolysis of **1,3-bis-phospho-glycerate.** Biochemistry constants for water $[H_2O]$=55,3 M , physiologic pH=7,36 for hydroxonium ion concentration $[H_3O^+]=10^{-7,36}$ M at temperature T-298,15 K activate favored homeostasis constant $K_{Homeostasis}>K_{abb}$. The direct product of **hydrolysis** is **3-phospho-glyceric acid** with **carboxylic acid** group high rate protolysis **deprotonation** to **carboxylate** stabilize the **product** relative to the **reactants**. Resonance stabilization of **Pi** = HPO_4^{2-} further contributes to the negative **free**-energy change $\Delta G_{Homeostasis}<\Delta G_{abb}$**= -18,8** $^{kJ}/_{mol}$ and constants $K_{Homeostasis}>K_{abb}$.

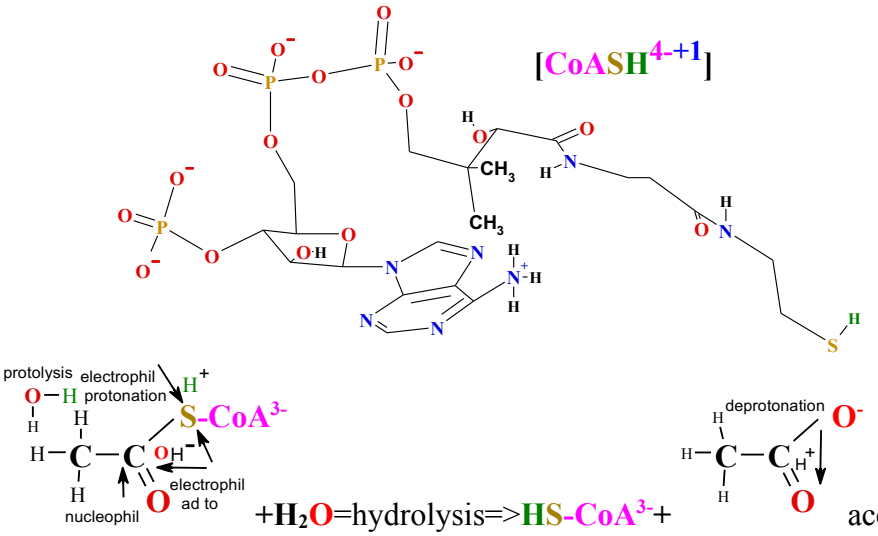


Figure 1-5. Hydrolysis of **acetyl-coenzyme A**. **Acetyl-CoA** is a **thio-ester** with a large, negative (-), **standard free** energy $\Delta G_{Hess} < 0$ of **hydrolysis**. **Thio-esters** contain a sulfur **S** atom in the position occupied by an
oxygen **O** atom in **esters**. on page.23rd :

Thio-esters, in which a sulfur atom replaces the usual oxygen **O** in the **ester** bond, also have large, negative (-), **free** energies Δ**Gc** of **hydrolysis**. **Acetyl-coenzyme A**, or **acetyl S-CoA**$^{3-}$ (Fig. 1-5), is one of many **thio-esters** important in metabolism. The **acyl** group in these compounds is activated for **trans-acylation**, **condensation**, or **oxidation-reduction** reactions. **Thio-esters** undergo much less resonance stabilization than do oxygen **-O- esters** (Fig. 1-6); consequently, the difference in free energy Δ**G** between the **reactants** and its **hydrolysis products**, which are resonance- stabilized, is greater for **thio-esters** than for comparable oxygen **O esters**. In both cases, **hydrolysis** of the **ester** generates a **carboxylic acid**, which can ionize and assume several resonance forms (Fig. 1-6). Attractors, water [$\mathbf{H_2O}$]=55.3 M , pH=7.36
concentration [$\mathbf{H_3O^+}$]=$10^{-7.36}$ M , T=298.15 K activate Lehninger equilibrium constant favored reaction :

$\mathbf{K}_{Leninger}=\mathbf{K_{eq}}$=317017.6 with negative free energy change $^{-}\Delta G_{Lehninger}$=-31.4 $^{kJ}/_{mol}$;.

Les favored at pH<4.76 ;$AcetylCoA^{2-}+H_2O \Rightarrow CH_3COOH+HSCoA^{2-}$; $^{-}\Delta G_{aLehninger}$=-21.45 $^{kJ}/_{mol}$;

$\Delta G_{Leninger}=-R \bullet T \bullet \ln(K_{Leninger})$=-8.3144*298.15*ln(5732.69)= -21.45$^{kJ}/_{mol}$;

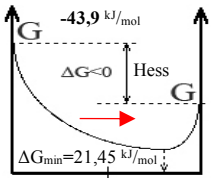
$$K_{aLeninger}=K_{Leninger}/[H_2O]=317017.6/55.3=5732.69=\frac{[CH_3COOH]\cdot[HSCoA^{2-}]}{[H_2O]\cdot[Acetyl\text{-}CoA^{2-}]}$$

$\Delta G_{Hess} = \Delta G°_{CH3COOH}+\Delta G°_{CoA2-}-\Delta G°_{Acetyl\text{-}CoA2-}-\Delta G_{H2O}$ = **-43.9** $^{kJ}/_{mol}$;

Exoergic **AcetylCoA**$^{2-}$ Hess free energy change is negative ΔG_{Hess}= **-43.9** $^{kJ}/_{mol}$,

but minimized $\Delta G_{min}=\Delta G_{eq}$= -21.45 $^{kJ}/_{mol}$ reaching equilibrium mixture:

$$K_{aLeninger}=K_{Leninger}/[H_2O]=317017.6/55.3=5732.69=\frac{[CH_3COOH]\cdot[HSCoA^{2-}]}{[H_2O]\cdot[Acetyl\text{-}CoA^{2-}]};$$

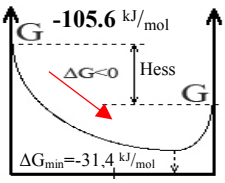


A+B 50% C+D
$AcetiilCoA^{2-}+H_2O$
$CH_3COOH+HSCoA^{2-}$

Prigogine attractor is free energy change minimum ΔG_{min};.
Free energy change minimum established equilibrium mixture of compounds.
$Acetyl\ CoA^{3-}+2H_2O \Rightarrow CH_3COO^{-}+HSCoA^{3-}+H_3O^{+}$; pH=7.36; $^{-}\Delta G_{Lehninger}$=-31.4 $^{kJ}/_{mol}$;.

$\Delta G_{Hess}=\Delta G°_{CH3COO-}+\Delta G°_{CoA3-}+\Delta G°_{H3O+}-\Delta G°_{Acetyl\text{-}CoA3-}-2*\Delta G_{H2O}$=**-105,6** $^{kJ}/_{mol}$;

$$K_{eq}=K_{Lehninge}=\exp(31400/8.3144/298.15)=\frac{[CH_3COO^{-}]\cdot[HSCoA^{3-}]\cdot[H_3O^{+}]}{[H_2O]^2\cdot[Acetyl\text{-}CoA^{3-}]}=317017.6;$$



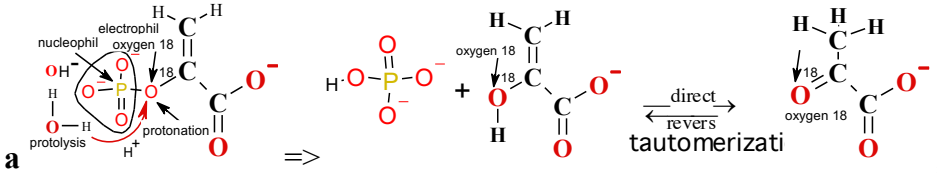
A+2B 50% C+D+E
Acetyl CoA$^{3-}+2H_2O$
$CH_3COO^{-}+HSCoA^{3-}$

Exoergic **AcetylCoA**$^{3-}$ Hess free energy change negative ΔG_{Hess}=**-105.6** $^{kJ}/_{mol}$, but minimized $\Delta G_{min}=\Delta G_{Lehninger}$= -31.4 $^{kJ}/_{mol}$ reaching equilibrium mixture.
Prigogine attractor is free energy change minimum ΔG_{min} .

Reaching free energy change minimum established equilibrium mixture of compounds.

Reactions with large, negative (-) **free**-energy changes ΔG have more stable **products** than the **reactants.** (**1**) The bond strain in **reactants** due to **electrostatic repulsion** are relieved by protolytic **charge separation**, as for **ATP**$^{4-}$ (described earlier); (**2**) **Products** stabilize high rate protolysis protonation of **acyl phosphates** and

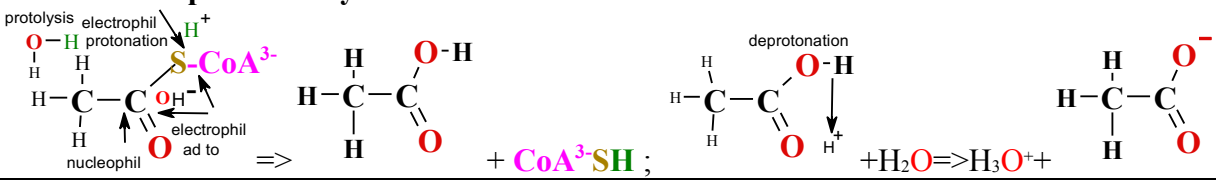
thio-esters, like as for **ATP**$^{4-}$; (**3**) Products are stabilized by **isomerisation** (**tautomerization**), as for **phospho-enol-pyruvate**, **acyl phosphates** and **thio-esters**; (**4**) **Products** release protonate **creatine** and nucleophilic phosphoryl group from **phosphor creatine carboxylate** ion. Phosphate linkages protolysis rule attractors water [**H_2O**]=55.3 M , pH=7.36 [**H_3O^+**]=$10^{-7.36}$ M concentrations, T=298.15 K activating **anhydride** and **ester** linkages.



a => ;

PEP enol form Pyruvate Pyruvate

Thio-S-ester **Phospho Enol Pyruvate** keto form salt form



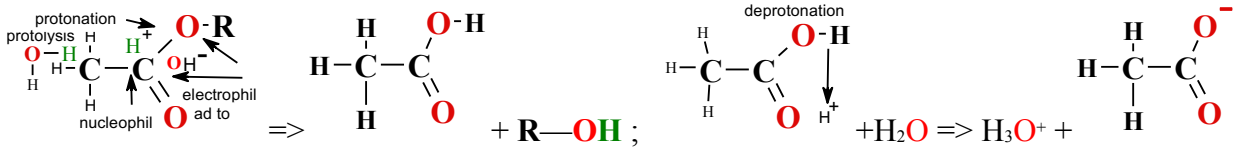
=> + $CoA^{3-}SH$; $+H_2O => H_3O^+ +$

+ **H_2O** => Extra stabilization by resonance and deprotonation in water

ΔG_S for thio-ester ΔG_O for **Oxygen -O- acid**

acetate

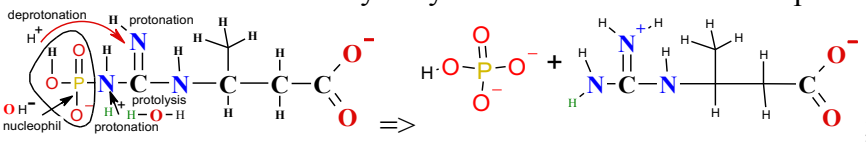
Oxygen -O- ester hydrolysis deprotonation .



=> + **R—OH** ; $+H_2O => H_3O^+ +$

+ **H_2O** => Extra stabilization by resonance and deprotonation in water

ΔG_O for ester hydrolysis ΔG_O for **Oxygen -O- acid** protolysis acetate

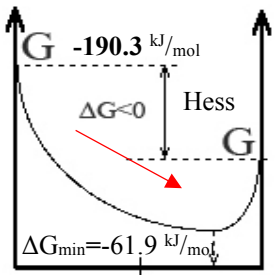


=> ;

Figure 1-6. Free energy ΔG of **hydrolysis** for **thio-esters** and oxygen **O esters**. The **products** of both types of **hydrolysis** reaction have about the same **free**-energy content (**G**), but the **thio-ester** has a higher free-energy G_t content than the oxygen **O ester**. Orbital overlap between the **O** and **C** atoms allows resonance stabilization in oxygen **O esters**, but orbital overlap between **S** and **C** atoms is poorer and little resonance stabilization occurs. **Thio-ester** yield **free energy change** is much more negative $-\Delta G_S > -\Delta G_O$ as oxygen **O ester.**

$K_{Leninger}=\exp(-\Delta G_{Lehninger}/R/T)=\exp(61900/8,3144/298,15)=K_a=69902464988=\frac{[CH_3C{=}OCOO^-]\cdot[HPO_4^{2-}]}{[H_2O]\cdot[PyruvEnolP^{3-}]}$.

Exothermic and exoergic **PyruvEnolP**$^{3-}$ hydrolyze free energy change negative at pH=7,36 negative $\Delta G_{hydrolise}$=**-190,3** $^{kJ}/_{mol}$, but minimizes ΔG_{min}= -61,9 $^{kJ}/_{mol}$ reaching equilibrium mixture $K_{Leninger}=K_a$= 69902464988 .



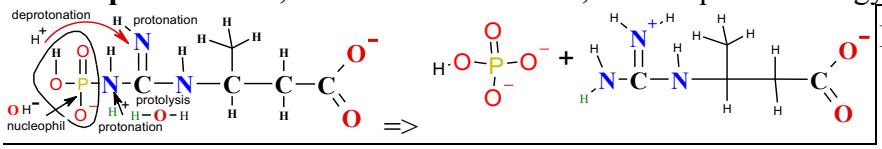
Equilibrium reaching is Prigogine attractor free energy change minimum ΔG_{min} .

Free energy change minimum reaching establishes equilibrium.

$PyruvEnolP^{3-}+H_2O$ reactants $H_3CC{=}OCOO^-+HPO_4^{2-}$ products A+B 50% C+D

Phospho Creatine hydrolysis

Phospho creatine, derived from **creatine**, is an important energy **E** store in skeletal muscle.



Hydrolyses of Phosphorylated Compounds.
a) hydrolysis with H_2O at equilibrium
$\Delta G_{Lehninger}$=**-43** $^{kJ}/_{mol}$ $K_{Lehninger}$=34145290,3;

Biosynthesis of creatine and **phospho creatine**. **Creatine** is made from three amino acids **AA** glycine **Gly**, Arginine **Arg** and methionine **Met**. Thus pathway shows the combinatory of amino acids **AA** versatility as precursor of other nitrogenous molecules.

a) $Pcreatine^{2-}+H_2O$=creatine+HPO_4^{2-}; $\Delta G_{Lehninger}$=-43 $^{kJ}/_{mol}$; $\Delta G_{Ellington}$=**-44,46** $^{kJ}/_{mol}$; J.exp.Biol.143,177-194,1989;308 K:

$$K_{Ellington}=\frac{[creatine]\cdot[HPO_4^{2-}]}{[Pcreatine^{2-}]\cdot[H_2O]}=\exp(44454,47/8,3144/308)=36400000;$$

b $ADP^{3-}+HPO_4^{2-}+H_3O^+ \Rightarrow ATP^{4-}+2H_2O$; $\Delta G_{Lehninger}$=30,5 $^{kJ}/_{mol}$ =ΔG_{bb}; K_{bb}=0,000004535142;

Phospho creatine , also called **creatine phosphate**, serves as a store of **phosphoryl** groups for the synthesis of ATP^{4-} from ADP^{3-}. The **phospho creatine** (**PCr**) concentration **C** in skeletal muscle is **30 mM**, ten times the concentration **C** of ATP^{4-}, and in smooth muscle, brain, and kidney is **5** to **10 mM**. The **enzyme creatine kinase** catalyzes the irreversible reaction: $ADP^{3-}+PCr^{2-}$ $\xrightarrow{Mg^{2+}\text{creatine kinase}}$ $ATP^{4-}+Cr$;

$\Delta G_{Lehninger}=\Delta G_{abb}=\Delta G_a+\Delta G_{bb}$=-43+30,5= **-12.5** $^{kJ}/_{mol}$ Lehninger 2000; ΔG=**-13** $^{kJ}/_{mol}$(310,15 K);

Attractors **pH** ($[H_3O^+]$) and on the concentration of water $[H_2O]$ rule equilibrium constant and energy minimum $\Delta G_{abb}=\Delta G_a+\Delta G_{bb}$=-43+30,5= -12,5 $^{kJ}/_{mol}$;298,15 K.

$$\frac{[creatine]\,[ATP^{4-}]\cdot[H_2O]}{[Pcreatine^{2-}]\cdot[ADP^{3-}]\,[H_3O^+]}$$

=154,854= $K_a \bullet K_{bb}=K_{abb}$;

$\Delta G_{eq}=-R\bullet T\bullet \ln(K_a\bullet K_b)$=-8,3144•298,15•ln(154,854)= -13 $^{kJ}/_{mol}$; (310,15 K)

$$\Delta G=\Delta G_{eq}+R\bullet T\bullet \ln K=-13+8.3144*310.15*\ln\frac{28\bullet 10^{-9}\bullet 8.05\bullet 10^{-5}\bullet 55.1398}{28\bullet 10^{-3}\bullet 9{,}3\bullet 10^{-3}\bullet 10^{-7.36}}=-6{,}832\ {}^{kJ}/_{mol};$$

$$\Delta G=\Delta G_{eq}+R\bullet T\bullet \ln K=-13+8.3144*310.15*\ln\frac{28\bullet 10^{-8}\bullet 8.05\bullet 10^{-5}\bullet 55.1398}{28\bullet 10^{-3}\bullet 9{,}3\bullet 10^{-3}\bullet 10^{-7.36}}=-0{,}8943\ {}^{kJ}/_{mol};$$ (pages 35th-36th)

Attractors, $[H_2O]$=55,3 M, with $[H_3O^+]=10^{-7,36}$ M pH 7.36 spent ATP^{4-} and generate concentration gradient $[ADP^{3-}]/[ATP^{4-}]$ form 1000000 to 100000 times so trend from ΔG -6,83 to -0,8943 $^{kJ}/_{mol}$.

Poly-phosphates (**polyP**) are a linear polymers composed of hundreds **100** of P_i residues linked through **phospho anhydride** bonds. This polymer, present in cells of all organisms, has about the same **phosphoryl** group transfer potential PP_i with following favored hydrolysis to 2 P_i. In *Escherichia coli*, **polyP** accumulation confers a survival advantage during periods of nutritional or oxidative stress. The enzyme **poly-phosphate kinas** catalyzes the reaction :

polyphosphate $HP_2O_7^{3-}+ADP^{3-}$ $\xrightleftharpoons{Mg^{2+}}$ polyphosphate $HPO_4^{2-}+ATP^{4-}$; $\Delta G_{Lehninger2000}$=**20.0** $^{kJ}/_{mol}$

by a mechanism involving an enzyme-bound **phospho Histidine** intermediate (recall the mechanism of **nucleoside diphosphate kinas**, described above). Because the reaction is reversible, **polyP** (like **PCr**) could serve as a reservoir of **phosphoryl** group donor analogous to ATP^{4-} for **kinas**-catalyzed transfers. The shortest **poly-phosphate**, PP_i (**n = 2**) can serve as the energy **E** source for active transport of H^+ in plant vacuoles. PP_i is also the usual **phosphoryl** group donor for at least one **1** form of the enzyme **phospho fructo-kinas** in plants, a role normally played by ATP^{4-} in animals and microbes. The finding of high concentration of **polyP** in volcanic condensates and steam vents suggests that it could have served as an energy **E** source in pre-biotic and early cellular evolution.

Protolytic hydrolysis attractors of ATP^{4-} the concentration $[H_3O^+]=10^{-7,36}$ M, pH=7,36 are indispensible foe homeostasis. ATP^{4-} **hydrolyze** at **pH 7.36**, with specific kinas Mg^{2+} increase irreversible velocity. Constant $K_{bLehninger}$ yield exoergic $\Delta G_{bLehninger}=-R\bullet T\bullet \ln(K_{bLehninger})$ =-8.3144•298.15•ln(220500.2)=-30.5 $^{kJ}/_{mol}$.

$ATP^{4-}+2H_2O \Leftrightarrow ADP^{3-}+HPO_4^{2-}+H_3O^+$; $220500=K_{bLehninger}=[ADP^{3-}]\bullet[HPO_4^{2-}]\bullet[H_3O^+]/[ATP^{4-}]/[H_2O]^2$

ATP^{4-} Provides Energy by Group Transfers Kinases (Hydrolases)

Throughout the **Biochemistry** reactions are for tandem coupled ATP^{4-} energy. The contribution of Kinases tandem coupled ATP^{4-} indicates irreversible high rate protolysis attractors ruled conversions of ATP^{4-} to **ADP^{3-}** and **P$_i$**=HPO$_4^{2-}$ or of ATP^{4-} to AMP^{2-} and **PP$_i$= HP$_2$O$_7^{3-}$** (**pyro-phosphate**). Work paper: Work sheet:

Table 3. Hess, Lehninger, equilibrium Free Energies of hydrolysis, Phosphoryl, Acetyl-CoA compounds

Hydroxonium ions H_3O^+, H_2O present free energy change ΔG_{eq} equilibrium and Hess Law	ΔG_{Hess} kJ/mol	
ADP^{2-}+H$_2$O=>AMP$^-$+H$_2$PO$_4^-$;**ΔG_{bd}**=-22.85 kJ/mol;**K_{bd}=$K_{bdLeninger}$/[H$_2$O]**=10075; without pH	**-108.8**	pH=?
ADP^{3-}+2H$_2$O=>AMP^{2-}+HPO$_4^{2-}$+**H$_3$O$^+$**; **$K_{bdLeninger}$**=557649; **$\Delta G_{Lehninger}$**=-32.8 kJ/mol;	**-97.49**	pH=7.36
AMP^{2-}+H$_2$O=>adenosine+HPO$_4^{2-}$; **ΔG_{AmL}**=-14.2 kJ/mol;**K_{AmL}**=307.4;	**-93.5**	pH=7.36
Fruc6P^2 +H$_2$O =>Fruc+HPO$_4^{2-}$;**$\Delta G_{Lehninger}$**=-15.9 kJ/mol; **K_{eq}**=11.0305, **ΔG_{eq}**=-5.951 kJ/mol;	**-14.154**	I=0.2 M
Glyc1P^{2-}+H$_2$O=>Glycerol+HPO$_4^{2-}$;**$\Delta G_{Lehninger}$**=-9.2 kJ/mol; **K_a**=40,9055659488465,	**-14.294**	pH=7.36
PalmitCoA^{4-}+H$_2$O=>CH$_3$(CH$_2$)$_{14}$COOH+HSCoA^{4-}; **ΔG_{aL}**=-22,35 kJ/mol; **K_{aL}**=8235.15	**-136,4**	pH<4.5
PalmitCoA^{4-}+2H$_2$O=>CH$_3$(CH$_2$)$_{14}$COO$^-$+H$_3$O$^+$+HSCoA^{4-}; **K_a**=455783; **$\Delta G_{Lehninger}$**=-32.5 kJ/mol;	**-198**	pH=7.36
AcetylCoA^{4-}+H$_2$O=>CH$_3$COOH+HSCoA^{4-}; **K_{aL}**=5728; **ΔG_{aL}** = -21.45 kJ/mol	-333,96	pH<4.5
AcetylCoA^{4-}+2H$_2$O=>CH$_3$COO$^-$+HSCoA^{4-}+H$_3$O$^+$; **$\Delta G_{Leninger}$**=-31.4 kJ/mol; **K_a=$K_{Leninge}$**=317018	**-105,6**	pH=7.36
PyruvEnolP^{3-}+H$_2$O=> H$_3$CC=OCOO$^-$+HPO$_4^{2-}$;**$\Delta G_{Leninger}$**=-61.9 kJ/mol**; K_a**= 69902464988	**-190.3**	pH=7.36
PyruvEnolP^{3-}+ADP^{3-}+H$_3$O$^+$=>H$_3$CC=OCOO$^-$+ATP^{4-}+H$_2$O; **ΔG_{abb}**= -31,.4 kJ/mol;; **K_{abb}**=317017,6	**-90.72**	I=0.2 M
Glycat31P^{4-}+H$_2$O=>**Glycat3P^{3-}**+H$_2$PO$_4^-$; **K_{aL}=$K_{aLehninger}$/[H$_2$O]**=7833705; **ΔG_{aL}**=-39.4 kJ/mol;	-81.3	pH<7.199
Glycat31P^{4-}+2H$_2$O=>**Glycat3P^{3-}**+HPO$_4^{2-}$+H$_3$O$^+$;**K_a**==433562158.5; **$\Delta G_{Lehninger}$**=-49.3 kJ/mol.	**-107.75**	pH=7.36
Pcreatine^{2-}+H$_2$O→creatine+**HPO$_4^{2-}$**; **$\Delta G_{Lehninger}$**=-43 kJ/mol; **$K_{Leninge}$**=34145290.295;	-55.3	I=0.2 M
PCr^{2-}+ADP^{3-}+H$_3$O$^+$=>Cr+ATP^{4-}+H$_2$O; **K_{abb}**=154.854; **ΔG_{abb}**=-12.5 kJ/mol;	-94.946	pH=7.36
H$_2$P$_2$O$_7^{2-}$+H$_2$O=**H$_3$O$^+$+HP$_2$O$_7^{3-}$**; **ΔG_{eq}**=48,31 kJ/mol; **K_{eq}=$K_{H2P2O72}$/[H$_2$O]**=$10^{-6.72}$/55.3=$10^{-8,463}$	**25.73**	pH=6.72
H$_3$PO$_4$+H$_2$O=>H$_2$PO$_4^-$+H$_3$O$^+$;**$\Delta G_{Lehninger}$**=12.66 kJ/mol; **K_{eq1}= 7.113•10^{-3}**;**ΔG_{eq}**=22.21 kJ/mol;**ΔG_{Hess}**=	58.28	pK=
H$_2$PO$_4^-$+H$_2$O=>HPO$_4^{2-}$+H$_3$O$^+$;**$\Delta G_{Lehninger}$**=64.96 kJ/mol; **K_{eq2}= 1.1428•10^{-9}**;**ΔG_{eq2}**=51.04	70	pK=7.199
kJ/mol;**ΔG_{Hess}**=		
HPO$_4^{2-}$+H$_2$O=>PO$_4^{3-}$+H$_3$O$^+$; **$\Delta G_{Lehninger}$**=94.48 kJ/mol; **K_{eq3}= 8.07•10^{-15}**; **ΔG_{eq}**=80.44 kJ/mol; **ΔG_{Hess}**=	94.5	-
Glc1P^{2-}+H$_2$O=>Glc+HPO$_4^{2-}$;**$\Delta G_{Lehninger2}$**=-20.9-kJ/mol;K_{a2}=48.07;	**-68.25**	pH=7.36
Glc6P^{2-}+H$_2$O=>Glc+HPO$_4^{2-}$;ΔG_L=-13.8 kJ/mol; **K_{aL}**=261.62;	-38.55	I=0.25 M

Hydrolysis reactions rule attractors of the high rate water protolysis **H$_2$O** =>**H$^+$**+**OH$^-$** , which instantly protonate the electrophilic atoms of oxygen, nitrogen or sulfur in **ATP^{4-}**, ADP^{2-}, AMP^{2-}, **HP$_2$O$_7^{3-}$**, AcetylCoA^{4-}, **PyruvEnolP^{3-}**, Pcreatine^{2-}, **Glycat31P^{4-}**, Glc1P^{2-}, Glc6P^{2-} ect. compounds. Kinases and coenzyme A dependant transferases irreversibly open nucleophilic groups :phosphoryl **$^+$PO$_3^{2-}$**, pyro-phosphoryl **$^+$P$_2$O$_6^{3-}$**, acyl groups for nucleophilic attack of high rate protolysis create electrophilic negatively charged groups : **OH$^-$**, **HO-PO$_3^{2-}$**, **HP$_2$O$_7^{3-}$**. Thus **ATP^{4-}**, ADP^{2-}, AMP^{2-}, **HP$_2$O$_7^{3-}$**, AcetylCoA^{4-}, **PyruvEnolP^{3-}**, Pcreatine^{2-}, **Glycat31P^{4-}**, Glc1P^{2-}, Glc6P^{2-} ect. compounds participates **covalently** in the **enzyme**- catalyzed hydrolysis to which its contributes **free** energy **ΔG** and almost invariably represent two-**2**-step processes. Protolysis attractors : **[H$_2$O]**=55.3 M water, pH=7.36 **[H$_3$O$^+$]**=$10^{-7.36}$ M concentrations stay at equilibria while homeostasis of hydrolysis continues.

The high rate water protolysis **H$_2$O** =>**H$^+$**+**OH$^-$** rules the direct **hydrolysis** pathway of **ATP^{4-}** (or **GTP^{4-}**). For example, **non covalent** binding of **ATP^{4-}** (or of **GTP^{4-}**), followed by its **hydrolysis** to ADP^{3-} (or **GDP^{3-}**) and **P$_i$**=HPO$_4^{2-}$ provide the energy to **cycle** some proteins between two **2** conformations, **producing** mechanical motion. This occurs in muscle contraction and in the movement of **enzymes** along **DNA** or of **ribosomes** along **messenger mRNA**. The **energy**-dependent reactions **catalyzed** by **helicases**, **RecA** protein, and some **topoisomerases** (**DNA** Metabolism) also involve direct **hydrolysis** of **phospho anhydride** bonds. **GTP^{4-}**-binding proteins that act in **signaling pathways** directly **hydrolyze GTP^{4-}** to drive **conformational** changes that terminate **signals** triggered by **hormones** or by other **extracellular factors** Signaling.

The living organisms **phosphate** reactions are driven with attractors **pH** and [H$_2$O]. **Free** energies minimization in **hydrolysis** (Fig. 1-9) are exoergic "High-energy'' **hydrolysis** more negative about **-20** kJ/mol and "low-energy'' compounds have a less negative **ΔG**. Based on this criterion, **ATP^{4-}**, with a **ΔG_{eqL}**=-30.5 kJ/mol of h**ydrolysis**, is a high-energy compound; **glucose 6-phosphate^{2-}** and Glc1P^{2-} with hydrolysis **ΔG_{eqL}**=-13.8 kJ/mol and -20.9 kcal/mol, are a low energy phosphate transfer compounds.

a $PCr^{2-}+H_2O=>Cr^{-}+HPO_4^{2-}$; ΔG_a= -43 $^{kJ}/_{mol}$ **;** K_a=34145290.295 .

bb $ADP^{3-}+HPO_4^{2-}+H_3O^{+}=>ATP^{4-}+2H_2O$; ΔG_{bb} =-30.5 $^{kJ}/_{mol}$; K_{bb}=0.000004535142; at pH=7.36.

$PCr^{2-}+ADP^{3-}+H_3O^{+}=>Cr+ATP^{4-}+H_2O$; $K_{abbLehninger}$=34145290.295*0.000004535142=154.854; pie pH=7.36;

Sum: $\Delta G_{abb}=\Delta G_a+\Delta G_{bb}$=-43+30.5= -12.5 $^{kJ}/_{mol}$; 310.15 K ΔG_{310_K}= -13 $^{kJ}/_{mol}$

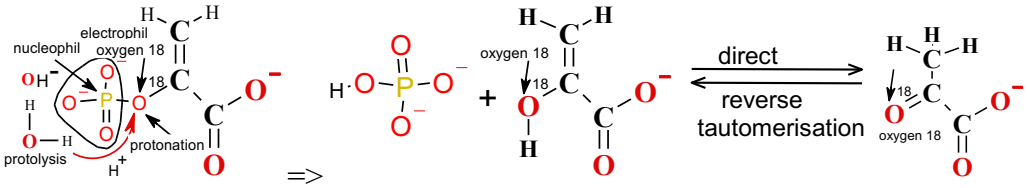
Creatine kinase mb fraction appears in blood after damage of myocyte or neuron cell wall.

Table 1-4. ATP coupling reactions for group **transfer** by Hess, Lehninger, equilibrium Free Energy changes.

Hydroxonium ions H_3O^+ un H_2O present free energy change in ΔG_{eq} equilibrium , Hess	ΔG_{Hess} $^{kJ}/_{mol}$	
mppa)$CH_3(CH_2)_{14}COO^-+HSCoA^{4-}+ATP^{4-}=>HP_2O_7^{3-}+AMP^{2-}+PalmitateCoA^{4-}$;$K_{mppa}$=213.8;$\Delta G_{mppai}$=-13.3 $^{kJ}/_{mol}$	**-195.6**	pH=7.36
HPO_4^{2-}+ADP^{3-}+$PalmitCoA^{4-}$=>$CH_3(CH_2)_{14}COO^-$+$HSCoA^{4-}$+**ATP^{4-}**;K_{bba}=2.067;$\Delta G_{bbaLehni}$=-1.8 $^{kJ}/_{mol}$;	**-88.5**	pH=7.36
$AcetylCoA^{4-}+2H_2O=>CH_3COO^-+HSCoA^{4-}+H_3O^+$;$\Delta G_{Lehninger}$=-31.4 $^{kJ}/_{mol}$; $K_{Leninge}$=317017.64;	**-105.6**	pH=7.36
$AcetylCoA^{4-}+ADP^{3-}+HPO_4^{2-}=>CH_3COO^-+CoA^{4-}+ATP^{4-}$;$K_{ab}$=1.4381; ΔG_{ab}=**-0.9007** $^{kJ}/_{mol}$;	**-6.025**	pH=7.36
$PyruvEnolP^{3-}$+H_2O=> $H_3CC(=O)COO^-$+HPO_4^{2-};$\Delta G_{Leninger}$=-61.9 $^{kJ}/_{mol}$**;** K_a= 69902464988	**-190.3**	pH=7.36
$PyruvEnolP^{3-}$+$ADP^{3-}+H_3O^+$=>$H_3CC(=O)COO^-$+$ATP^{4-}+H_2O$; ΔG_{abb}= -31..4 $^{kJ}/_{mol}$;; K_{abb}=317017.6	**-90.72**	I=0.2 M
PCr^{2-}+**$ADP^{3-}+H_3O^+$**=>**Cr+$ATP^{4-}+H_2O$**; K_{abb}=154.85; **ΔG_{abb}**=-12.5 $^{kJ}/_{mol}$; **ΔG_{310_K}**=-13 $^{kJ}/_{mol}$	-94.95	pH=7.36
$Pcreatine^{2-}+H_2O\rightarrow creatine+$**$HPO_4^{2-}$**; $K_{Ellington}$=3.46*10^7; 308 K; $\Delta G_{Ellington}$=-44.45 $^{kJ}/_{mol}$;	-55.3	25°C
Glc+$ATP^{4-}+H_2O$=>$Glc6P^{2-}+ADP^{3-}+H_3O^+$;$K_{eq}$=5.83•$10^2$; ΔG_{eq}=**-R•T•ln(K_{eq})**=-15.78 $^{kJ}/_{mol}$	-50.285	pH=7.36
$HOPO_2OPO_2OH^{2-}+H_2O=>H_2PO_4^-+H_2PO_4^-$; **$\Delta G_{pp}$=-9.25** $^{kJ}/_{mol}$; **K_{pp}=$K_{Lehningerpp}$/[H_2O]**=41.748	**-70.94**	pH=?+
$HP_2O_7^{3-}$+$2H_2O$=>HPO_4^{2-}+HPO_4^{2-}+**H_3O^+**; **K_{app}**=2310.57; $\Delta G_{LeningeH}$=-19.2 $^{kJ}/_{mol}$;	**-85.6**	pH=7.36
$H_2P_2O_7^{2-}$+ADP^{2-}=>$H_2PO_4^-$+ATP^{3-}; $\Delta G_{abbpppPH}$=21.25 $^{kJ}/_{mol}$; **$K_{abbpppPH}$**=0.0001893	**27.39**	pH=?_
$HP_2O_7^{3-}$+ADP^{3-}=>HPO_4^{2-}+ATP^{4-}; **K_{abbpp}**=0.01047878; **ΔG_{abbpp}**=11.3 $^{kJ}/_{mol}$;	**13.967**	pH=7.36
polyPhosphate**$HP_2O_7^{3-}$**+ADP^{3-}=> polyPhosphateHPO_4^{2-} +ATP^{4-}; $\Delta G_{Lehninger}$ = -20 $^{kJ}/_{mol}$;	-43.03	pH=7.36
$Glc1P^{2-}+ADP^{3-}+H_3O^+$=>Glc+$ATP^{4-}+H_2O$; $\Delta G_{Lehninger}$ = 9.6 $^{kJ}/_{mol}$;	-47.035	pH=7.36
Glc+$ATP^{4-}+H_2O$=>$Glc1P^{2-}+ADP^{3-}+H_3O^+$;$\Delta G_{a22b}$=42.36 $^{kJ}/_{mol}$; **K_{a2b}**=0.000260614;	**47.035**	pH=7.36
$Fruc6P^-+ADP^{2-}$=>Fruc+ATP^{3-};$\Delta G_{Lehninger}$=4.65 $^{kJ}/_{mol}$; $K_{Leninge}$=0.1532	**23.7**	pH<7.199
$Fruc6P^{2-}+ADP^{3-}+H_3O^+$ =>Fruc+ $ATP^{4-}+H_2O$; $\Delta G_{abb}=\Delta G_a+\Delta G_{bb}$=14.6 $^{kJ}/_{mol}$; K_{abb}=0.002768	**85.426**	pH=7.36
Gln+ H_2O =>$Glu^-+NH_4^+$; $\Delta G_{aLeninger}$=-14.2 $^{kJ}/_{mol}$; **K_{a}**$_{Leninger}$=307.43;	**-183.65**	7.36=pH
$Glu^-+NH_4^++ATP^{4-}+H_2O$=>Gln+$ADP^{3-}+HPO_4^{2-}+H_3O^+$; **$\Delta G_{ab}$=35.66** $^{kJ}/_{mol}$; K_{ab}=0.0000005657	**254.9**	pH=7.36
Glycerol1P$^-$+ ADP^{2-}=>Glycerol+ ATP^{3-}; **$\Delta G_{Leninger}$**=11.35 $^{kJ}/_{mol}$**;** **K=K_{abbL}*[H_2O]**=0.010267	**40**	pH<7.199
Glycerol1$P^{2-}+ADP^{3-}+H_3O^+$=>Glycerol+$ATP^{4-}+H_2O$; ΔG_{abb}=21.3 $^{kJ}/_{mol}$; K_{abb}=0.00018550674	**101.7**	pH=7.36

Phosphates P-O bond dissociation **enthalpy ΔH_{P-O}= 370** $^{kJ}/_{mol}$ is positive. For all chemical bonds disruption require positive energy **$\Delta H>0$**. **Phosphate** compounds hydrolysis free energy change negative $\Delta G<0$ have reaching Prigogine attractor minimized content G of compound in mixture. "High-energy **phosphate**" ATP^{4-} or other **phosphate** compounds hydrolysis trends to Prigogine attractor $\Delta G_{min}=\Delta G_{eq}$ at equilibrium mixture.

Hess **$\Delta G_{Hess}=G°_{prod}-G°_{react}$** and Prigogine **$\Delta G_{eq}=-R•T•\ln(K_{eq})$** additive free energy change are sequential **$\Delta G_{totalHess}=\Delta G_{aHess}+\Delta G_{bHess}$** or **$\Delta G_{totalEq}=\Delta G_{aEq}+\Delta G_{bEq}$** reactions **a** and sequential **bb** tandem **synthesis** the breakdown **P-O** bond for exchange to another with a more negative (-) free energy content. For **P_i**=HPO_4^{2-} disconnection from **phospho-enol pyruvate** (**PEP**) releases more energy **ΔG_{aEq}**=-61.9 $^{kJ}/_{mol}$ than is released **ΔG_{bbEq}**=30.5 $^{kJ}/_{mol}$ in condensation of **P_i**=HPO_4^{2-} with ADP^{3-}, the direct donation of a **phosphoryl** group from **PEP** to **ADP** is tandem of **a**, **bb favored** reaction**:** **$\Delta G_{total}=\Delta G_a+\Delta G_{bb}=\Delta G_{abb}$**=30,5-61.9= -31,4 $^{kJ}/_{mol}$**;**



=> pyruvate

a Phosphoenol-$pyruvate^{3-}+H_2O$=>$pyruvate^-+HPO_4^{2-}$; **$\Delta G_{aLeninger}$**=-61,9 $^{kJ}/_{mol}$**;** **ΔG_{aHess}= -190,3** $^{kJ}/_{mol}$**;**

bb $ADP^{3-}+HPO_4^{2-}+H_3O^+$ => $ATP^{4-}+2\ H_2O$; **$\Delta G_{bbLehninger}$**= 30,5 $^{kJ}/_{mol}$ **;** **ΔG_{bbHess}=99,58** $^{kJ}/_{mol}$; pH=7,36

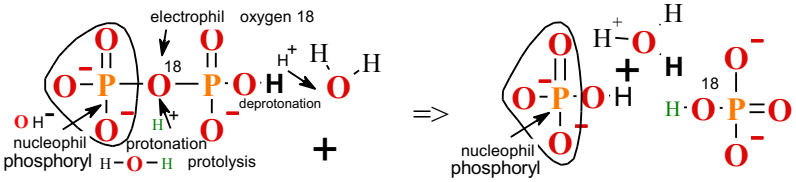
Sum **abb**: **$PyruvEnolP^{3-}$**+$ADP^{3-}+H_3O^+$=>$pyruvate^-+ATP^{4-}+H_2O$;

$\Delta G_{totalEq}=\Delta G_{a}$$_{Lehninger}+\Delta G_{bb}$$_{Lehninger}=\Delta G_{abb}$=-61,9+30,5= -31,4 $^{kJ}/_{mol}$**;** **$\Delta G_{abbHess}$=-190,3+99,58= -90,72** $^{kJ}/_{mol}$**;**

Phosphorylated compounds classification have a high or low **phosphoryl** group negative transfer **potential**. Prigogine minimization equilibrium ΔG_{Eq} give smaller by absolute value about Hess law ΔG_{Hess} in sequence $|\Delta G_{Eq}| < |\Delta G_{Hess}|$. The homeostasis absolute value $|\Delta G|$ rule attractors pH=7.36 and $[H_2O]$=55.3 M. **Phosphoenol-pyruvate** is very high, than of ATP^{4-} and less for **glucose 6-phosphate** lower.

pH=7.36; between pK_{a3}=6.72 un pK_{a4}=**9.46**

pH=7.36;Pyrophosphate	pKa	ΔH°	C
$H_4P_2O_7 = H^+ + H_3P_2O_7^-$	0.83	-9.2	-90
$H_3P_2O_7^- = H^+ + H_2P_2O_7^{2-}$	2.26	-5.0	-130
$H_2P_2O_7^{2-} = H^+ + \mathbf{HP_2O_7^{3-}}$	6.72	0.5	-136
$\mathbf{HP_2O_7^{3-}} = H^+ + P_2O_7^{4-}$	**9.46**	1.4	-141

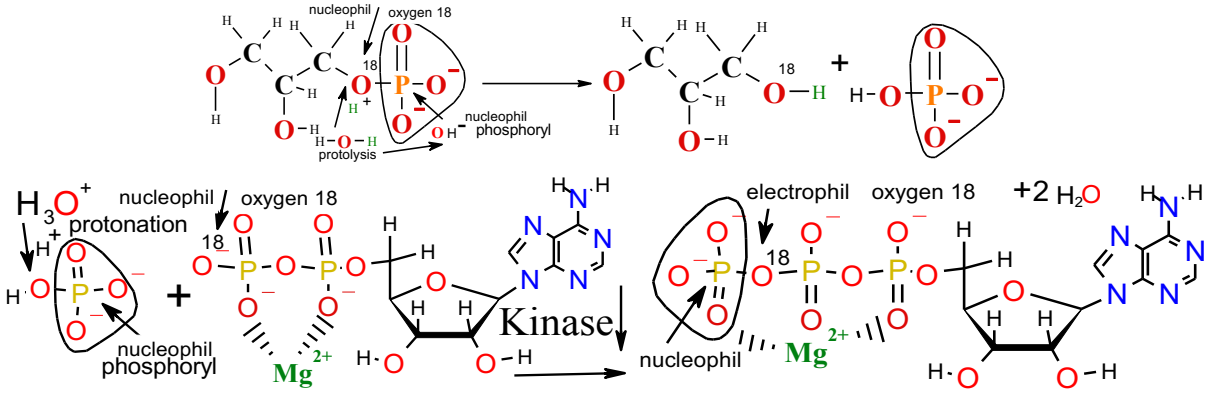


a $\mathbf{HP_2O_7^{3-}}$ +HOH+HOH =>HPO_4^{2-}+HPO_4^{2-}+$\mathbf{H_2OH^+}$; $\Delta G_a = \Delta G_{Lehninger}$=-19.2 $^{kJ}/_{mol}$; ΔG_{aHess}=**-85.6** $^{kJ}/_{mol}$;

bb ADP^{3-}+HPO_4^{2-}+H_3O^+=>ATP^{4-}+2H_2O ; ΔG_{bb} =30.5 $^{kJ}/_{mol}$; ΔG_{bbHess}=**99.58** $^{kJ}/_{mol}$;

abb: $\mathbf{HP_2O_7^{3-}}$+ADP^{3-} =>HPO_4^{2-} +ATP^{4-}; $\Delta G_{abb} = \Delta G_a + \Delta G_{bb}$=-19.2+30.5=11.3 $^{kJ}/_{mol}$; pH=7.36

$\Delta G_{aHess} + \Delta G_{bbHess}$=**-85.6+99.58=13.98** $^{kJ}/_{mol}$; Hess calculation from data in tables;

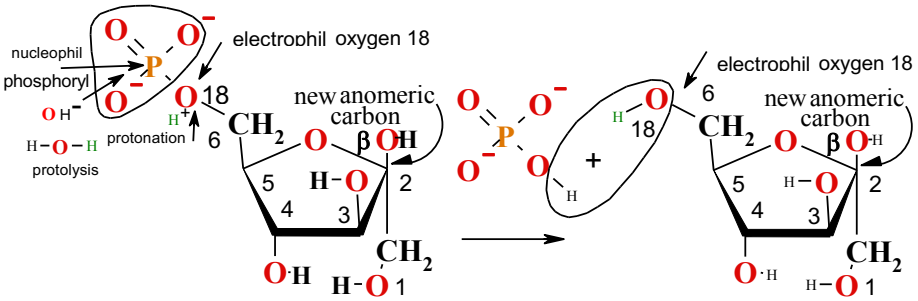


a Glycerol-1-$phosphate^{2-}$+H_2O=>Glycerol+HPO_4^{2-}; $\Delta G_a = \Delta G_{Leninger}$=-9.2 $^{kJ}/_{mol}$**;** ΔG_{aHess}=**-46.43** $^{kJ}/_{mol}$;

bb ADP^{3-}+HPO_4^{2-}+H_3O^+=>ATP^{4-}+2H_2O ; ΔG_{bb} =30.5 $^{kJ}/_{mol}$; ΔG_{bbHess}=**101.724** $^{kJ}/_{mol}$;

abb: Glycero-l-1$phosphate^{2-}$+ADP^{3-}+H_3O^+=>Glycerol+ATP^{4--}+H_2O; ΔG_{ab}=17.87-31.41=-13.537 $^{kJ}/_{mol}$;

$\Delta G_{aHess} + \Delta G_{bbHess}$=**-46.43+101.724= 55.3** $^{kJ}/_{mol}$; ΔG_{Hess} Hess calculation from data in tables;

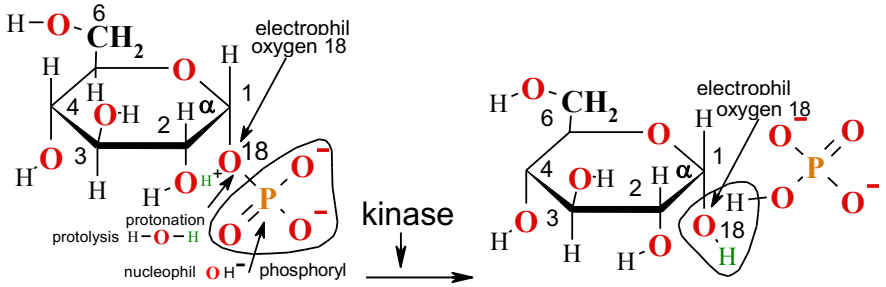


a Fructose-6-$phosphate^{2}$ +H_2O => Fructose + HPO_4^{2-} ; $\Delta G_a = \Delta G_{Lehninger}$=-15.9 $^{kJ}/_{mol}$; ΔG_{aHess}=**-70.951** $^{kJ}/_{mol}$;

bb ADP^{3-}+HPO_4^{2-}+H_3O^+=>ATP^{4-}+2H_2O ; ΔG_{bb} =30.5 $^{kJ}/_{mol}$; ΔG_{bbHess}=**99.58** $^{kJ}/_{mol}$;

abb: Fruc6P^{2-}+ADP^{3-}+$\mathbf{H_3O^+}$=>Fruc+ATP^{4-}+$\mathbf{H_2O}$; $\Delta G_{abb} = \Delta G_a + \Delta G_{bb}$=-15.9+30.5=14.6 $^{kJ}/_{mol}$;;

$\Delta G_{aHess} + \Delta G_{bbHess}$=**-70.951+99.58=28.6** $^{kJ}/_{mol}$; ΔG_{Hess} Hess calculation from data in tables;



a $\Delta G_{Lehninger}$=-20.9 $^{kJ}/_{mol}$; **Glc1P^{2-}+H_2O=>Glc+HPO_4^{2-}+ΔG+Q**; pH=7.36; ΔG_{Hess}= **-36.1** $^{kJ}/_{mol}$;

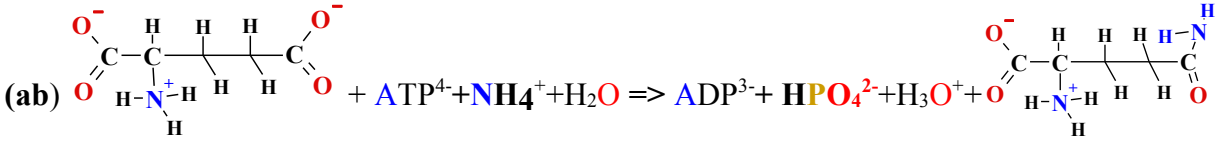
bb ADP^{3-}+HPO_4^{2-}+H_3O^+=>ATP^{4-}+2H_2O ; ΔG_{bb} =30.5 $^{kJ}/_{mol}$; ΔG_{bbHess}=**99.58** $^{kJ}/_{mol}$;

abb: **Glc1P^{2-}+ADP^{3-}+H_3O^+ => Glc+ATP^{4-}+H_2O**; $\Delta G_{a2b} = \Delta G_{a2} + \Delta G_b$=-20.9+30.5= 9.6 $^{kJ}/_{mol}$;

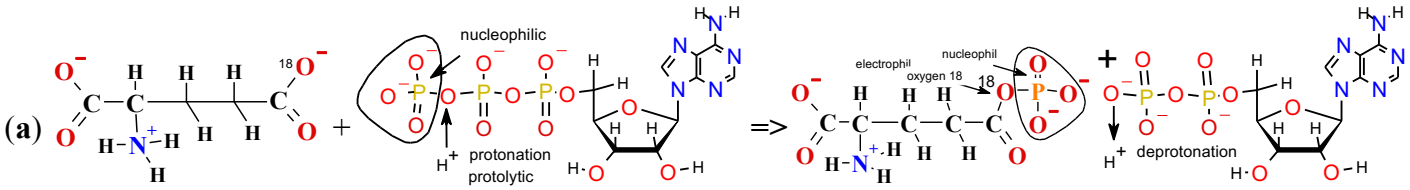
$\Delta G_{aHess} + \Delta G_{bbHess}$=**-36.1+99.58=63.48** $^{kJ}/_{mol}$; ΔG_{Hess} Hess calculation from data in tables;

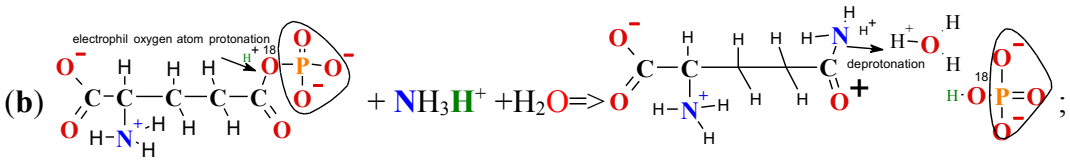
Catabolism synthesis “high-energy” phosphates are intermediate. High rate protolysis with protonation and reverse deprotonation of electrophilic oxygen, nitrogen atom maintains charged groups **R-COO$^-$**, **R-NH$_3^+$**, **HPO$_4^{2-}$**, **R-PO$_4^{2-}$**, **HCO$_3^-$** nor free nor bound to **R** molecules (amino acids, proteins, phosphates, nucleic acids, carbohydrates, coenzymes). Functional activation of molecules for **homeostasis** order drive reactions in enzyme complex reaction five types. Inactive compounds convert to following favored irreversible process. The **phosphoryl** groups transfer under rules of attractors **pH=7,36** and [H$_2$O]=55,3 M effectively puts **free** energy **ΔG** to target compounds, that it has more **free** energy **ΔG** to give up during subsequent metabolic conversions. Above the **synthesis** of **glucose 6-phosphate** is accomplished by **phosphoryl** group transfer from ATP^{4-}.

Phosphorylation equation in one-step reaction for Glutamine synthase we see how this



Glutamate Glutamine synthase Glutamine





Actual two-2-step reaction in sum:

a Glu$^-$ + NH$_4^+$ => Gln +H$_2$O; **ΔG$_{a\text{Lehninger}}$=14,2** $^{kJ}/_{mol}$; **ΔG$_{a\text{Hess}}$=183.65** $^{kJ}/_{mol}$;

b ATP^{4-}+2 H$_2$O =>ADP^{3-}+ HPO$_4^{2-}$ +H$_3$O$^+$ **; ΔG$_b$=-30,5** $^{kJ}/_{mol}$; **ΔG$_{b\text{Hess}}$=-99,58** $^{kJ}/_{mol}$;

ab: Glu$^-$+NH$_4^+$+ATP^{4-}+H$_2$O=>Gln +ADP^{3-}+HPO$_4^{2-}$+H$_3$O$^+$;35,66 $^{kJ}/_{mol}$;**ΔG$_{eqab}$**=14,2-30,5 **=-16.3** $^{kJ}/_{mol}$;

Work paper 29th page: Tables **ΔG$_{abHess}$= 84,07** $^{kJ}/_{mol}$;

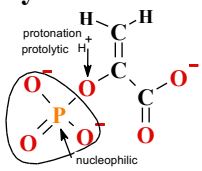
Figure 1-8. Nucleophilic displacement reactions of $^+PO_3^{2-}$ under rule high rate protolysis of oxygen protonate and unbound as OH$^-$ from phosphate atom **P** nucleus (H$^+$+-O-PO$_3^{2-}$=> OH$^-$+$^+$PO$_3^{2-}$) so open for **nucleophilic attack** to $^+PO_3^{2-}$. Any of the three **3 P** atoms (α, β, or γ) may serve as the **electrophilic target** for **nucleophilic attack** by the labeled **nucleophilic C-^{18}O:** in this case. The **nucleophilic** may be an **alcohol** (**C-^{18}OH**), a **carboxyl** group (**RCO^{18}O$^-$**), or a **phospho anhydride** (a **nucleoside mono-** or **diphosphate**, for example).

(**α**) When the oxygen **O** of the **nucleophilic attacks** the position, the **bridge oxygen -O-** of the **product** is labeled, indicating that the group transferred from ATP^{4-} is a **phosphoryl** ($^+PO_3^{2-}$), not a **phosphate** (-OPO$_3^{2-}$).

(**β**) **Attack** on the beta position displaces **AMP**$^{2-}$ and leads to the transfer of a **pyro-phosphoryl** $^+PO_2^-$-O-PO$_3^{2-}$ not **pyro-phosphate** group (-OPO$_2^-$-O-PO$_3^{2-}$) to the **nucleophilic**.

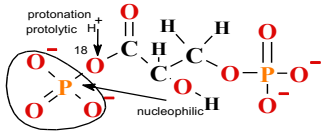
(**2β**) **Attack** on the ADP^{3-} **beta** position displaces **PP$_i$** =$^+PO_2^-$-O-PO$_3^{2-}$ and transfers the **adenylyl** group (A) to the **nucleophilic**.

-61,9↑ **PyruvEnolP**$^{3-}$+H_2O=>H_3CC=$OCOO^-$+HPO_4^{2-};

1. 

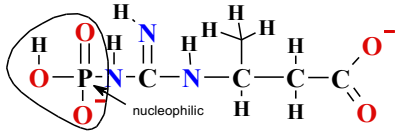
$\Delta G_{Lehninger}$= -61.9 $^{kJ}/_{mol}$;

Glycerat31P^{4-}+2H_2O=>Glycerat3P^{3-}+HPO_4^{2-}+H_3O^+

2. 

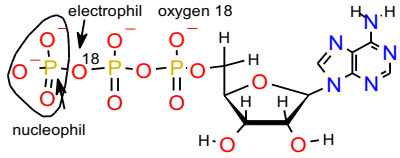
$\Delta G_{aLehninger}$=-49,3 $^{kJ}/_{mol}$

Pcreatine^{2-}+H_2O→creatine+**HPO$_4^{2-}$**;

3. 

ΔG_{Lehnin}=-43 $^{kJ}/_{mol}$;

ATP^{4-}+2H_2O=>ADP^{3-}+HPO_4^{2-}+H_3O^+;

4. 

ΔG_{bLe}=-30,5 $^{kJ}/_{mol}$;

5. Glc6P $^{2-}$+H_2O=>Glc+HPO_4^{2-}; ΔG_{aL}=-13.8 $^{kJ}/_{mol}$;
6. **GlyGly**$_{aq}$+**H_2O**=>**Gly**$_{aq}$+**Gly**$_{aq}$; ΔG_{aL}=-9.2 $^{kJ}/_{mol}$;
7. Glyc1P^{2-}+H_2O=>Glycerol+HPO_4^{2-}; ΔG_L=-9,2 $^{kJ}/_{mol}$
8. $H_2PO_4^-$+H_2O=>HPO_4^{2-}+H_3O^+;ΔG_{eq}=51,04 $^{kJ}/_{mol}$;

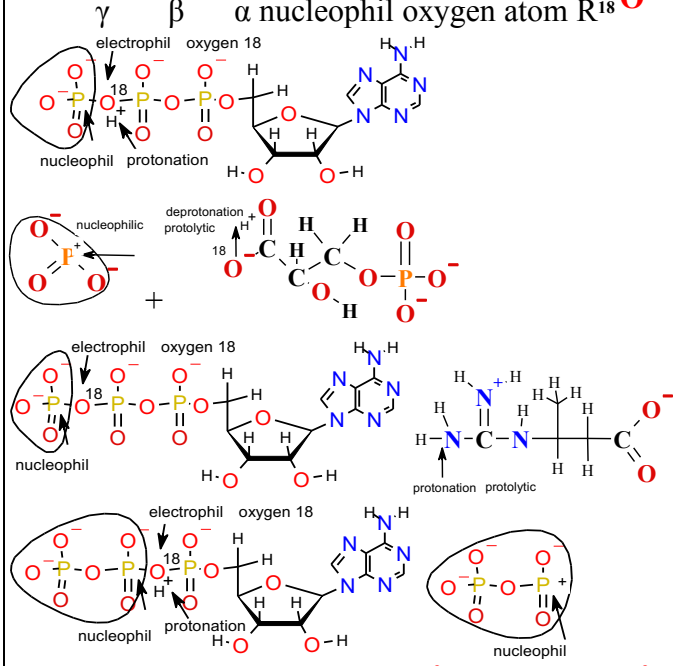


Figure 1-10. Nucleophilic $^+PO_3^{2-}$, $^+PO_2^-$-O-PO_3^{2-} **phosphoryl** and **pyro-phosphoryl** group transfer reaction from ATP^4 to molecules for homeostasis activation are with high rate protolysis attractors [H_2O]=55,3 $^{mol}/_L$, pH=7,36 [**H_3O^+**]=$10^{-7,36\ mol/L}$ rules driven by protonation and deprotonation.

Figure 1-9. High rate protolysis attractors [H_2O]=55,3 $^{mol}/_L$, pH=7,36 [**H_3O^+**]=$10^{-7,36\ mol/L}$ rule the perfect order processes of homeostasis for enzyme complex reactions in five ways. **Phosphoryl** group protolytic generation with electrophilic oxygen atom protonation in ATP^{4-} anhydride bonds is high energy nucleophilic **phosphoryl** groups $^+PO_3^{2-}$ donors. The **phosphoryl** groups flow catalyze **enzymes** called **kinases**, driven to Prigogine attractors with **free** energy change minimization in homeostasis $\Delta G_{Homeostasis}$**<0**. **Cellular attractors** [H_2O]=55,3 $^{mol}/_L$ and [**H_3O^+**]=$10^{-7,36\ mol/L}$ rule HPO_4^{2-} release in **phosphate hydrolysis** which has an even lower **phosphoryl** group transfer potential.

Glucose activation with phosphate is relevant catabolic reactions that occur in every living cell. Because of its intermediate position on the scale of group transfer potential, ATP^{4-} can carry energy ΔG_{Hess} from high-energy **phosphate** compounds produced by catabolism to compounds such as **glucose**, converting them into more **reactive** species. ATP^{4-} thus serves as the energy ΔG_{Hess} investor in all living cells.

Enzymes perform **phosphoryl** group transfer with ***kinetic*** certainty behalf of high rate protolysis attractors [H_2O]=55,3 $^{mol}/_L$, pH=7,36 [**H_3O^+**]=$10^{-7,36\ mol/L}$ rule. The activation energy **E_a** (**200** to **400** $^{kJ}/_{mol}$) required for breake of **phospho anhydride** bonds. Absence of enzymes does not process spontaneously .

Phosphoryl group opens nucleophilic after high rate protolysis attractors protonate phospho-anhydride bond oxygen atom to electrophilic acceptor **OH**$^-$, which formed after water deprotonation. Specific **enzymes** activity decreased energy **E_a** drive **phosphoryl** group transfer from ATP^{4-} to acceptor. The cell is able to **regulate** the energy $\Delta G_{Homeostasis}$ transfer governed with ATP^{4-} **enzymes**.

Any of the three **3 P** atoms (α, β, or ,γ) may serve as the **electrophilic target** for **nucleophilic attack** by the labeled **nucleophilic R—^{18}O:** in this case. The **nucleophilic** may be an **alcohol** (**R-OH**), a **carboxyl** group (**RCOO**$^-$), or a **phospho anhydride** (a **nucleoside mono-** or **diphosphate**, for example).

(**a**) When the oxygen atom of the **nucleophilic attacks** the position, the **bridge oxygen -^{18}O-** of the **product** is labeled, indicating that the group transferred from ATP^{4-} is a **phosphoryl** $^+PO_3^{2-}$, not a **phosphate** -$^{18}OPO_3^{2-}$.

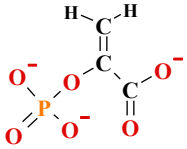
(**b**) **Attack** on the beta position displaces **AMP** and leads to the transfer of a **pyro-phosphoryl** (not **pyro-phosphate**) group to the **nucleophilic**.

(**c**) On the gamma position displaces **PP_i=$^+PO_2^-$-O-PO_3^{2-}** and transfers the **adenylyl** group to the **nucleophilic**.

At homeostasis calculations Biochemistry constants for water [$\mathbf{H_2O}$]=55,3 M , physiologic pH=7,36 for hydronium ion concentration [$\mathbf{H_3O^+}$]=$10^{-7,36}$ M and standard thermodynamic temperature T-298,15 K are included in Lehninger equilibrium constants $\mathbf{K}_{\text{Lehninger}}$ of principles Biochemistry published issues.

Table 1-5.Lehninger homeostasis constants $\mathbf{K}_{\text{Leninger}}$ included [$\mathbf{H_2O}$] [$\mathbf{H_3O^+}$],T in equilibrium contants $\mathbf{K_{eq}}$.

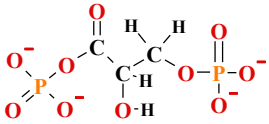
1. **PyruvEnolP^{3-}**+H_2O=>$H_3CC{=}OCOO^-$+HPO_4^{2-};



$\Delta\mathbf{G}_{\text{Leninger}}$=-**R•T•ln**($\mathbf{K}_{\text{Leninger}}$)=-8,3144•298,15•**ln**(69902464988)= -61,9 $^{kJ}/_{mol}$;

$\mathbf{K}_{\text{Leninger}}$= 69902464988= $\dfrac{[CH_3C{=}OCOO^-]\cdot[HPO_4^{2-}]}{[H_2O]\cdot[\text{PyruvEnolP}^{3-}]}$

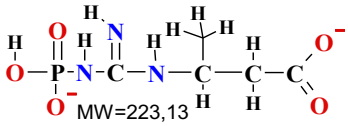
2. **Glycerat31P^{4-}**+2H_2O=>**Glycerat3P^{3-}**+HPO_4^{2-}+H_3O^+;



$\Delta\mathbf{G}_{\text{Leninger}}$=-**R•T•ln**($\mathbf{K}_{\text{Leninger}}$)=-8,3144•298,15•**ln**(433562158,5) = -49,3 $^{kJ}/_{mol}$;

$\mathbf{K}_{\text{Leninger}}$= 433562158,5= $\dfrac{[HPO_4^{2-}]\cdot[H_3O^+]\cdot[\text{Glycerat3P}^{3-}]}{[H_2O]^2\cdot[\text{Glycerat13P}^{4-}]}$

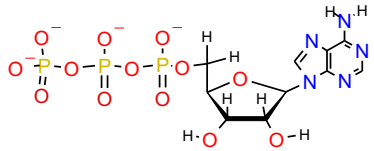
3. Pcreatine^{2-}+H_2O→creatine+**HPO_4^{2-}**;



$\Delta\mathbf{G}_{\text{Leninger}}$=-**R•T•ln**($\mathbf{K}_{\text{Leninger}}$)=-8,3144•298,15•**ln**(34145290,2951607)=-43 $^{kJ}/_{mol}$;

$\mathbf{K}_{\text{Leninger}}$= 34145290,2951607= $\dfrac{[\text{creatine}]\cdot[HPO_4^{2-}]}{[\text{Pcreatine}^{2-}]\cdot[H_2O]}$

4. ATP^{4-}+2H_2O=>ADP^{3-}+HPO_4^{2-}+H_3O^+;



$\Delta\mathbf{G}_{\text{Leninger}}$=-**R•T•ln**($\mathbf{K}_{\text{Leninger}}$)=-8,3144•298,15•**ln**(220500,2) = -30,5 $^{kJ}/_{mol}$;

$\mathbf{K}_{\text{Leninger}}$= 220500,2= $\dfrac{[HPO_4^{2-}]\cdot[\text{ADP}^{3-}]\cdot[H_3O^+]}{[H_2O]^2[\text{ATP}^{4-}]}$

5. Acetyl-CoA^{4-}+2H_2O=>CH_3COO^-+CoA^{4-}+H_3O^+;-;$\Delta G_{\text{Lehninger}}$=-31,4 $^{kJ}/_{mol}$;

CoA

$\Delta\mathbf{G}_{\text{Leninger}}$=-**R•T•ln**($\mathbf{K}_{\text{Leninger}}$)=-8,3144•298,15•**ln**(317017,6) = -31,4 $^{kJ}/_{mol}$;

$\mathbf{K}_{\text{Leninger}}$=317017,6= $\dfrac{[CH_3COO^-]\cdot[HSCoA^{3-}]\cdot[H_3O^+]}{[H_2O]^2\cdot[\text{Acetyl-CoA}^{3-}]}$

6. Glc6P^{2-}+H_2O=>Glc+HPO_4^{2-}; $\Delta\mathbf{G}_{\text{Leninger}}$=-**R•T•ln**($\mathbf{K}_{\text{Leninger}}$)=-8,3144•298,15•**ln**(261,62) = -13,8 $^{kJ}/_{mol}$;

$\mathbf{K}_{\text{Lehninger}}$=[Glc]*[$HPO_4^{2-}$]/[Glc6P^{2-}]/[$H_2O$]=261,62= $\dfrac{[Glc]\cdot[HPO_4^{2-}]}{[\text{Glc6P}^{2-}]\cdot[H_2O]}$

7. **Gly**$_{aq}$+**H_2O**=>**Gly**$_{aq}$+**Gly**$_{aq}$; $\Delta\mathbf{G}_{\text{Leninger}}$=-**R•T•ln**($\mathbf{K}_{\text{Leninger}}$)=-8,3144•298,15•**ln**(40,906)=-9,2 $^{kJ}/_{mol}$;

$\mathbf{K}_{\text{Leninger}}$=40,906= $\dfrac{[H_3N^+CH_2COO^-]\text{Gly}_2}{[H_2O]\cdot[H_3N^+\text{GlyGlyCOO}^-]\text{Gly}}$

$\Delta\mathbf{G_{min}}$= $\Delta\mathbf{G_{0,2M}}$=-6,54 $^{kJ}/_{mol}$; $K_{0,2M}$=13,994; I=0,2 M ionic strength.

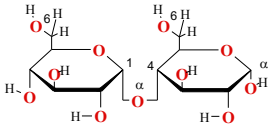
8. Glyc1P^{2-}+H_2O=>Glycerol+HPO_4^{2-}; $\Delta\mathbf{G}_{\text{Leninger}}$=-**R•T•ln**($\mathbf{K}_{\text{Leninger}}$)=-8,3144•298,15•**ln**(40,906) = -9,2 $^{kJ}/_{mol}$;

$\mathbf{K}_{\text{Leninger}}$= 40,906= $\dfrac{[HPO_4^{2-}]\cdot[\text{Glycerol}]}{[H_2O]\cdot[\text{Glycerol1P}^{2-}]}$

9. $H_2PO_4^-$+H_2O=>HPO_4^{2-}+H_3O^+; $\Delta\mathbf{G}_{\text{Leninger}}$=-**R•T•ln**($\mathbf{K}_{\text{Leninger}}$)=-8,3144•298,15•**ln**($10^{-7,199}$)=6,844 $^{kJ}/_{mol}$;

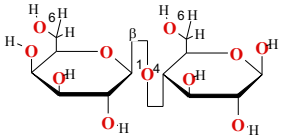
$\dfrac{[HPO_4^{2-}]\cdot[H_3O^+]}{[H_2PO_4^-]\cdot[H_2O]}$ =$\mathbf{K_{eq}}$==1,144*10^{-9}; $10^{-7,199}$= $\dfrac{[HPO_4^{2-}]_{aqua}\cdot[H_3O^+]}{[H_2PO_4^-]_{aqua}}$ =$\mathbf{K_a}$

10. Maltose+H_2O<=>Glc+Glc; $\Delta G_{Leninger}$=-R•T•ln($K_{Leninger}$)=-8,3144•298,15•ln(519,4)= -15,5 $^{kJ}/_{mol}$;



$$K_{Leninger}=519,4=\frac{[Glc]\cdot[Glc]}{[Maltose]\cdot[H_2O]}$$

11. Lactose + H_2O <=> Glc + Gal; $\Delta G_{Leninger}$=-R•T•ln($K_{Leninger}$)=-8,3144•298,15•ln(610,35)= -15,9 $^{kJ}/_{mol}$;



$$K_{Leninger}=610,35=\frac{[Glc]\cdot[Gal]}{[Lactose]\cdot[H_2O]}$$

Attractors, H_2O and H_3O^+ drive ATP^{4-} to transfer **Phosphoryl, Pyro-phosphoryl** and **Adenylyl Groups**

ATP^{4-} are generally **SN2** (substitution **nucleophilic** bimolecular) **nucleophilic** displacements, in which the **nucleophil** may be, for example, the oxygen **O** of an **alcohol** or **carboxylate** or a **nitrogen** of **creatine** or of the side chain of **arginine** or **histidine**. Each of the three **3 phosphates** of ATP^{4-} is susceptible to **nucleophilic attack** (Fig. 1-10) different products.

Nucleophilic attack by an **alcohol** on the gamma **phosphate** (Fig. 1- 10a) displaces ADP^{3-} and produces a new **phosphate ester**. Studies with ^{18}O-labeled **reactants** have shown that the bridge oxygen **O** in the new compound is derived from the **alcohol**, not from ATP^{4-}; the group transferred from **ATP** is a **phosphoryl** ($^+PO_3^{2-}$), not a **phosphate** ($-^{18}OPO_3^{2-}$). **Phosphoryl** group transfer from ATP^{4-} to **glutamate** (Fig. 1-8) or to glucose (**hexokinase**) involves **attack** at the γ position of the ATP^{4-} molecule.

Attack at the beta **phosphate** of ATP^{4-} displaces AMP^{2-} and transfers a **pyro-phosphoryl** (not **pyrophosphate**) group to the **attacking nucleophil** (Fig. 1-10b). For example, the formation of **5'-phosphoRiboze 1-pyro-phosphate**, a key intermediate in **nucleotide synthesis**, occurs as an **-OH** of the **Riboze attacks** the beta **phosphate**.

Nucleophilic attack at the alpha position of ATP^{4-} displaces $PP_i=^+PO_2^-\text{-}O\text{-}PO_3^{2-}$ and transfers **adenylate** (**5'-**AMP^{2-}) as an **adenylyl** group (Fig. 1-10c); the reaction is an **adenylylation** (a-den'-i-li-la'-shun, probably the most ungainly word in the biochemical language). Notice that **hydrolysis** of the α-β **phospho anhydride** bond releases considerably more energy in water $\Delta G_{bLehninger}$= -30.5 $^{kJ}/_{mol}$ than **hydrolysis** of the β-γ bond $\Delta G_{Lehninger}$=-45,6 $^{kJ}/_{mol}$; Table 3. $HP_2O_7^{3-}=PP_i$ formed as a byproduct of the **adenylylation** is **hydrolyzed** to two **2** P_i by the ubiquitous enzyme **inorganic pyro-phosphatase,** $\Delta G_{Lehninge}$**=-19.2** $^{kJ}/_{mol}$ releasing and "push" for the **adenylylation** reaction. In thereby providing a further energy effect, both **2 phospho anhydride** bonds of ATP^{4-} are split in the overall reaction. **Adenylylation** reactions are in Work calculations 24th, 30rd, 31st page:

pp) $HP_2O_7^{3-}$**+2** H_2O=>HPO_4^{2-}+HPO_4^{2-}+H_3O^+; $\Delta G_{ppLehninger}$**= -19.2** $^{kJ}/_{mol}$; ΔG_{ppHess}**=-85.6** $^{kJ}/_{mol}$;

b) ATP^{4-}+$2H_2O$=>AMP^{2-}+ $HP_2O_7^{3-}$+H_3O^+; $\Delta G_{bLehninger}$**=-45.6** $^{kJ}/_{mol}$; ΔG_{bHess}**=-111,45** $^{kJ}/_{mol}$;

Hess law energy change is more $\Delta G_{ppbHess}=\Delta G_{ppHess}+\Delta G_{bHess}$**=-85.6 -111,45=-197** $^{kJ}/_{mol}$ negative as Prigogine minimum at equilibrium: $\Delta G_{ppbLehninger}=\Delta G_{ppLehninger}+\Delta G_{bLehninger}$**=-45.6** $^{kJ}/_{mol}$**-19.2=-64.6** $^{kJ}/_{mol}$.

ppb) ATP^{4-}+$4H_2O$=>AMP^{2-}+ HPO_4^{2-}+HPO_4^{2-}+2H_3O^+; $\Delta G_{ppbLehninger}$**=-64.6** $^{kJ}/_{mol}$; $\Delta G_{ppbHess}$**=-197** $^{kJ}/_{mol}$:

$$K_{ppb}=EXP(-\Delta G_{ab}/R/T)=EXP(64600/8,3144/298,15)=207737828686=\frac{[HPO_4^{2-}]^2\cdot[H_3O^+]^2\cdot[AMP^{2-}]}{[H_2O]^4\cdot[ATP^{4-}]}$$ at equilibrium.

Primary attractors concentrations $[H_2O]$=55,3 M and $[H_3O^+]=10^{-7,36}$ M and in human erythrocyte assuming high rate protolysis homeostasis concentrations are $[AMP^{2-}]=0,02*10^{-3}$ M , $[ATP^{4-}]=2,25*10^{-3}$ M and $[HPO_4^{2-}]=1,65*10^{-3}$ M : $K_{homeostasis}=K_{ppb}*[H_3O^+]^2/[H_2O]^4=4,22*10^{-11}\frac{[HPO_4^{2-}]^2\cdot[AMP^{2-}]}{[ATP^{4-}]}$.

Human erythrocyte : $K_{homeostasis}=4,22*10^{-11}*1,65^2*10^{-3*2}*0,02*10^{-3}/2,25/10^{-3}=1.02*10^{-18}$ is far favored from Prigogine equilibrium minimum K_{ppb} to which trends reaction $K_{homeostasis}<<K_{ppb}$ for conversion the reactants to products as $1.02*10^{-18}=K_{homeostasis}<<K_{ppb}=207737828686$ and never reach high rate protolysis equilibrium as homeostasis is non equilibrium state and equilibrium state is attractor for non equilibrium state homeostasis:

ATP^{4-}+$4H_2O$=>AMP^{2-}+ HPO_4^{2-}+HPO_4^{2-}+2H_3O^+.

Note: Primary attractors $[H_2O]$=55,3 M and $[H_3O^+]=10^{-7,36}$ M with enzymes irreversible reactivity create of self-organization homeostasis perfect order, which with high rate protolysis drive Brownian molecular engines for evolution and surviving.

Attractors, [**H_2O**]=55,3 M and [**H_3O^+**]=$10^{-7,36}$ M with **energy-coupling** perform **Fatty acid** activation. The first step in the activation of a **fatty acid**-either for **energy-yielding oxidation** (see **fatty acid** conversion to => **acyl-CoA**) or for use in the **synthesis** of more complex **lipids** (Lipid Biosynthesis)-is its attachment to the **carrier coenzyme A** (Fig. 1-11). The direct condensation of a **fatty acid** with **coenzyme A** is **endoergic**, but the formation of **fatty acyl-CoA** is made **exoergic** by stepwise removal of two **2 phosphoryl** groups from ATP^{4-} First **1st**, **adenylylate** (AMP^{2-}) is transferred from ATP^{4-} to the **carboxyl** group of the **fatty acid**, forming a mixed **anhydride** (**acyl adenylate**) and liberating **PP_i.** The **thiol** group of **coenzyme A** then displaces the **adenylate** group and forms a **thio-ester** with the **fatty acid**. Two **2** reactions homeostasis sum attractors water [**H_2O**]=55,3 M, hydroxonium ion concentration [**H_3O^+**]=$10^{-7,36}$ M at temperature T=298,15 K energetically equivalent to the **exoergic hydrolysis** of ATP^{4-} to AMP^{2-} and **PP_i** $\Delta G_{bLehninger}$= **-45.6** $^{kJ}/_{mol}$ and the **endoergic**: formation of **acyl-CoA** $\Delta G_{cLehninger}$=**31.4** $^{kJ}/_{mol}$. **Acyl-CoA** is made energetically favorable by **hydrolysis** of the **PP_i** by **pyro-phosphatase**. **Fatty acid** activate both the **phospho anhydride** bonds of ATP^{4-} and broken **PP_i hydrolysis**. The sum of the free energy change for the **hydrolysis** is Work calculations 23th, 28th, 33rd page:

c) $CH_3COO^-+HSCoA^{4-}+H_3O^+ => Acetyl\text{-}CoA^{4-}+2H_2O$; $\Delta G_{cLehninger}$=**31.4** $^{kJ}/_{mol}$; ΔG_{Hess}=**105,6** $^{kJ}/_{mol}$;

pp) $\mathbf{HP_2O_7^{3-}+2\ H_2O => HPO_4^{2-}+HPO_4^{2-}+H_3O^+}$; $\Delta G_{ppLehninger}$= **-19.2** $^{kJ}/_{mol}$; ΔG_{ppHess}=**-85.6** $^{kJ}/_{mol}$;

b) $ATP^{4-}+2H_2O => AMP^{2-}+ \mathbf{HP_2O_7^{3-}}+H_3O^+$; $\Delta G_{bLehninger}$=**-45.6** $^{kJ}/_{mol}$; ΔG_{bHess}=**-111,45** $^{kJ}/_{mol}$;

ppb) $ATP^{4-}+4H_2O => AMP^{2-}+ \mathbf{HPO_4^{2-}+HPO_4^{2-}+2H_3O^+}$; $\Delta G_{ppbLehninger}$=**-64.6** $^{kJ}/_{mol}$; $\Delta G_{ppbHess}$=**-197** $^{kJ}/_{mol}$;

Hess law energy change is more $\Delta G_{ppbcHess}=\Delta G_{ppHess}+\Delta G_{bHess}+\Delta G_{cHess}$ **=-85.6 -111,45+105,6=-91.45** $^{kJ}/_{mol}$ negative as Prigogine : $\Delta G_{ppbcLehninger}=\Delta G_{ppLehninger}+\Delta G_{bLehninger}+\Delta G_{cLehninger}$=**-45.6-19.2+31.4=-33.**4 $^{kJ}/_{mol}$.

ppbc) $CH_3COO^-+HSCoA^{4-}+ATP^{4-}+2H_2O => Acetyl\text{-}CoA^{4-}+AMP^{2-}+\mathbf{HPO_4^{2-}+HPO_4^{2-}+H_3O^+}$; ΔG_L=**-33.**4 $^{kJ}/_{mol}$:

$$\mathbf{K}_{ppbc}=EXP(-\Delta G_{ppbc}/R/T)=EXP(33400/8,3144/298,15)=710347,58=\frac{[HPO_4^{2-}]^2\cdot[AMP^{3-}]\cdot[Acetyl\text{-}CoA^{4-}]\,[H_3O^+]}{[ATP^{4-}]\cdot[CH_3COO^-]\,[HSCoA^{4-}]\,[H_2O]^2}.$$

Primary attractors concentrations [**H_2O**]=55,3 M and [**H_3O^+**]=$10^{-7,36}$ M and in human erythrocyte assuming high rate protolysis homeostasis concentrations are $[HSCoA^{4-}]=[Acetyl\text{-}CoA^{4-}]$ and $[CH_3COO^-]=10^{-4}$ M :

$$\mathbf{K}_{Homeostasis}=\mathbf{K}_{ppbc}[H_3O^+]/[H_2O]^2=710347,6*10^{-7,36}/55,3^2=0,0000101229=\frac{[HPO_4^{2-}]^2\cdot[AMP^{3-}]\cdot[Acetyl\text{-}CoA^{4-}]}{[ATP^{4-}]\cdot[CH_3COO^-]\,[HSCoA^{4-}]}.$$

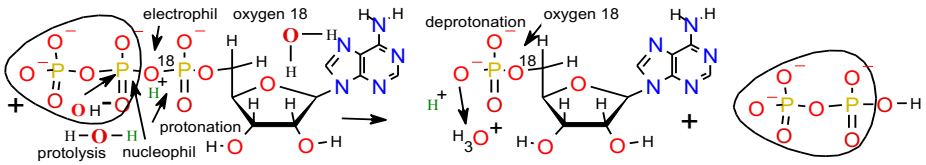
$\mathbf{K}_{homeostasis}$=0,0000101229*1,65^2*10^(-3*2)*0,02*10^(-3)/2,25/10^(-3)/10^(-4)=$2.45*10^{-9}$ is far favored from Prigogine equilibrium minimum $\mathbf{K}_{ppbc}$ to which trends reaction $\mathbf{K}_{homeostasis}$<<$\mathbf{K}_{ppbc}$ for conversion the reactants to products as $2.45*10^{-9}$ =$\mathbf{K}_{homeostasis}$ << $\mathbf{K}_{ppbc}$=710347,58 and never reach high rate protolysis equilibrium as homeostasis is non equilibrium state and equilibrium state is attractor for non equilibrium state homeostasis:

$$CH_3COO^-+HSCoA^{4-}+ATP^{4-}+2H_2O => Acetyl\text{-}CoA^{4-}+AMP^{2-}+\mathbf{HPO_4^{2-}+HPO_4^{2-}+H_3O^+}.$$

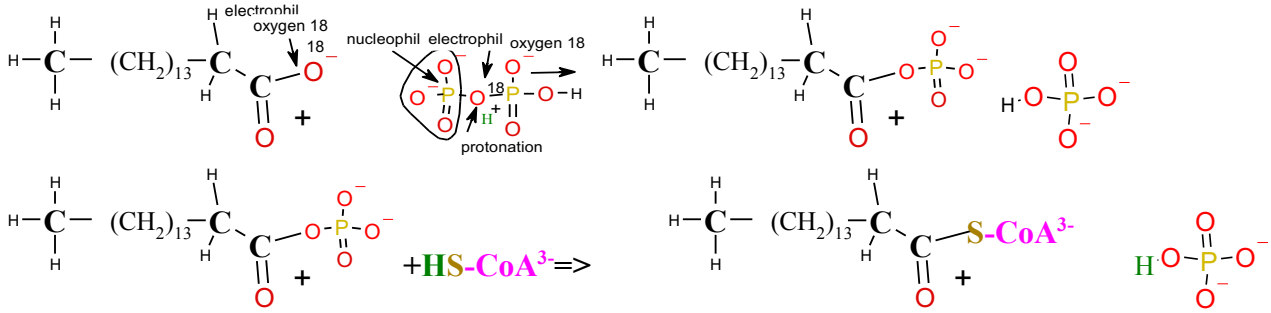
Note: Primary attractors [**H_2O**]=55,3 M and [**H_3O^+**]=$10^{-7,36}$ M with enzymes irreversible reactivity create of self-organization homeostasis perfect order, which with high rate protolysis drive Brownian molecular engines for evolution and surviving.

Attractors, [H_2O]=55.3 M and [H_3O^+]=$10^{-7.36}$ M create **amino acids AAc** funktional activity **AAc**CoA^{4-}.

The activation of **amino acids** before their **polymerization** into proteins (see **Amino-acylation** of **tRNA)** is accomplished by an analogous set of reactions in which a **transfer RNA** molecule takes the place of **coenzyme A**. Unfavored reaction K_{abcEq}<1 of the cleavage of ATP^{4-} to AMP^{2-} and **PP$_i$** ($HP_2O_7^{3-}$) attractors converts to favored $K_{abcLeninger}$>1 constant , which work with ATP^{4-} as an energy source to produce light flashes.



Palmitate => **PP_i^{2-}—inorganic pyro-phosphatase=> 2 HPO_4^{2-}**;



Thio-ester bond conserves of the energy "**invested**" from ATP^{4-}.

Figure 1-11. Adenylylation reaction in **activation** of a **fatty acid.** Both **phospho anhydride** bonds of ATP^{4-} hydrolise in the formation of **palmitoyl-coenzyme A**. First **1st**, ATP^{4-} **donates adenylate** (AMP^{2-}), forming the **fatty acyl-adenylate** and releasing **PP$_i$**, which is **hydrolyzed** by **inorganic pyro-phosphatase**. The "**energized**" **fatty acyl** group is then transferred to **coenzyme A** ($HS\text{-}CoA^{3-}$), with in **c, b, pp**.

Attractors, [H_2O]=55.3 M and [H_3O^+]=$10^{-7.36}$ M create **palmitate** funktional activity $PalmitCoA^{4-}$.

Water [H_2O]=55.3 M and physiologic pH=7.36 for hydroxonium ion concentration [H_3O^+]=$10^{-7.36}$ M at temperature T-298.15 K form favored Lehninger constant $K_{Lehninger}$ value with 100% product efficiency. Attractors converts unfavored reaction K_c=0.000002194 to favored equilibrium $K_{ppbcLehninger}$ = 459474.77 with negative frees energy change $\Delta G_{ppbcLehninger}$ = **-32.32** $^{kJ}/_{mol}$.

c) $CH_3(CH_2)_{14}COO^- + H_3O^+ + HSCoA^{4-} => PalmitCoA^{4-} + 2H_2O$; $\Delta G_{aLehninger}$=**32.5** $^{kJ}/_{mol}$; ΔG_{aHess}=**112.5** $^{kJ}/_{mol}$;

b) $ATP^{4-} + 2H_2O => AMP^{2-} + HP_2O_7^{3-} + H_3O^+$; $\Delta G_{bLehninger}$=**-45.6** $^{kJ}/_{mol}$; ΔG_{bHess}=**-111.45** $^{kJ}/_{mol}$;

pp) $HP_2O_7^{3-}$ **+2** $H_2O => HPO_4^{2-} + HPO_4^{2-} + H_3O^+$; $\Delta G_{ppLehninger}$= **-19.2** $^{kJ}/_{mol}$; ΔG_{ppHess}=**-85.6** $^{kJ}/_{mol}$;

Hess law energy change is more $\Delta G_{ppbcHess} = \Delta G_{ppHess} + \Delta G_{bHess} + \Delta G_{cHess}$=**-85.6-111.45+112.5=-84.55** $^{kJ}/_{mol}$ negative as Prigogine : $\Delta G_{ppbcLehninger} = \Delta G_{ppLehninger} + \Delta G_{bLehninger} + \Delta G_{cLehninger}$=**32.5-45.6-19.22=-32.32** $^{kJ}/_{mol}$.

ppbc sum: $CH_3(CH_2)_{14}COO^- + HSCoA^{4-} + ATP^{4-} + 2H_2O = PalmitCoA^{4-} + HPO_4^{2-} + HPO_4^{2-} + H_3O^+$;

$$K_{ppbc} = \exp(-\Delta G_{ppbc}/R/T) = \exp(32320/8.3144/298.15) = 459474.77 = \frac{[HPO_4^{2-}]^2[AMP^{2-}]\cdot[Palmitate\text{-}CoA^{4-}]\cdot[H_3O^+]}{[CH_3(CH_2)_{14}COO^-]\cdot[HSCoA^{4-}]\cdot[ATP^{4-}]\cdot[H_2O]^2}$$

Primary attractors concentrations [H_2O]=55.3 M and [H_3O^+]=$10^{-7.36}$ M and in human erythrocyte assuming high rate protolysis homeostasis concentrations are [$HSCoA^{4-}$]=[$Palmitat\text{-}CoA^{4-}$] and [Palmitat]=10^{-4} M :

$$K_{Homeostasis} = K_{ppbc}[H_3O^+]/[H_2O]^2 = 459474.77*10\text{^}(^{-7.36})/55.3\text{^}2 = 0.0000065586 = \frac{[HPO_4^{2-}]^2[AMP^{2-}]\cdot[Palmitate\text{-}CoA^{4-}]}{[CH_3(CH_2)_{14}COO^-]\cdot[HSCoA^{4-}]\cdot[ATP^{4-}]}$$

$K_{homeostasis}$=0.0000065586*1.65^2*10^(-3*2)*0.02*10^(-3)/2.25/10^(-3)/10^(-4)=$1.59*10^{-9}$ is far favored from Prigogine equilibrium minimum K_{ppbc} to which trends reaction $K_{homeostasis} << K_{ppbc}$ for conversions the reactants to products as $1.59*10^{-9}$ =$K_{homeostasis}$ << K_{ppbc}=459474.77 and never reach high rate protolysis equilibrium as homeostasis is non equilibrium state and equilibrium state is attractor for non equilibrium state homeostasis:

$CH_3(CH_2)_{14}COO^- + HSCoA^{4-} + ATP^{4-} + 2H_2O = PalmitCoA^{4-} + HPO_4^{2-} + HPO_4^{2-} + H_3O^+$.

Note: Primary attractors [H_2O]=55.3 M and [H_3O^+]=$10^{-7.36}$ M with enzymes irreversible reactivity create of self-organization homeostasis perfect order, which with high rate protolysis drive Brownian molecular engines for evolution and surviving.

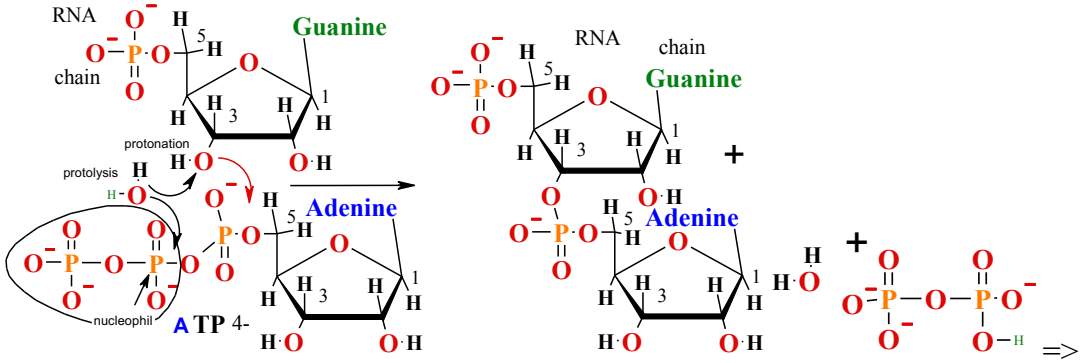
Assembly of Informational Macromolecules drive attractors, $[H_2O]$=55,3 M and $[H_3O^+]=10^{-7,36}$ M

Attractors convert unfavored reaction to favored homeostasis $K_{Homeostasis}<1$ with trend to $K_{equilibriumr}>1$.

When **simple precursors** are assembled into **high molecular weight compounds** (**HMC**) **polymers** with **defined sequences** (**DNA**, **RNA**, proteins), as described in detail in Information Pathways of this studies, **free** energy ΔG_{Hess} is required both for the **condensation** of **monomer units** and for the creation of **ordered sequences** and its replication. The **precursors** for **DNA** and **RNA synthesis** are **nucleoside triphosphates**, and **polymerization** is accompanied by hydrolysis of the **phospho anhydride** linkage between the α and β **phosphates**, with the release of **PP$_i$** (Fig. 1-12). The moieties transferred to the growing **polymer** in these reactions are **adenylate** **AMP^{2-}**, **guanylate** **GMP^{2-}**, **cytidylate** **CMP^{2-}**, or **uridylate** **UMP^{2-}** for **RNA synthesis**, and their **deoxy** analogs with **TMP^{2-}** in place of **UMP^{2-}** for **DNA synthesis**. As noted above, the activation of **amino acids** for protein **synthesis** involves the donation of **adenylate** groups from ATP^{4-}, and we shall see in Protein Metabolism that several **steps** of protein **synthesis** on the **ribosome** are also accompanied by GTP^{4-} **hydrolysis**. In all of these cases, the **exoergic** breakdown of a **nucleoside triphosphate** is coupled to the **endoergic** process of **synthesizing** a **polymer** of a **specific sequence RNA** chain lengthened by one **-pG+pA**:

a) $GMP^{2-}+AMP^{2-}+H_3O^+ \Rightarrow GMP^{2-}\text{-}AMP^{-}+2H_2O$; $\Delta G_{aeq}=20$ kJ/mol; $\Delta G_{aHess}=70$ kJ/mol;

b) $ATP^{4-}+2H_2O \Rightarrow AMP^{2-}+HP_2O_7^{3-}+H_3O^+$; $\Delta G_{bLehninger}=\mathbf{-45.6}$ kJ/mol; $\Delta G_{bHess}=\mathbf{-111,45}$ kJ/mol;



pp) $HP_2O_7^{3-}+2H_2O \Rightarrow HPO_4^{2-}+HPO_4^{2-}+H_3O^+$; $\Delta G_{ppLehninger}=\mathbf{-19.2}$ kJ/mol; $\Delta G_{ppHess}=\mathbf{-85.6}$ kJ/mol;

Figure 1-12. Nucleoside triphosphates ATP^{4-} in RNA synthesis. With each **nucleoside mono-phosphate** added to the growing chain, one **PP$_i^{2-}$** is released and **hydrolyzed** to two **2 HPO_4^{2-}** of two **2 phospho anhydride** bonds for each **nucleotide** added the free energy **ΔG** for forming the bonds in the **RNA polymer** and for assembling a **specific sequence nucleotides**.

GMP^{2-}Ribose3-OH+$ATP^{4-}+2H_2O \Rightarrow GMP^{2-}\text{-}AMP^{-}+2HPO_4^{2-}+H_3O^+$; $\Delta G=\mathbf{-X?}$ kJ/mol; negative as Prigogine free energy change minimum: $\Delta G_{abpp}=\Delta G_a+\Delta G_{bLehninger}+\Delta G_{ppLehninger}=20\mathbf{-45,6-19,22=-44.8}$ kJ/mol.

$$K_{abpp}=\exp(-\Delta G_{abpp}/R/T)=\exp(44820/8{,}3144/298{,}15)=71151394=\frac{[HPO_4^{2-}]^2\cdot[GMP^{2-}\text{-}Phospho\,Adenine^{-}]\cdot[H_3O^+]}{[ATP^{4-}]\cdot[GMP^{2-}\text{-}Ribose\text{-}3\text{-}OH]\cdot[H_2O]^2}$$

Primary attractors concentrations $[H_2O]$=55.3 M, $[H_3O^+]=10^{-7.36}$ M and in human erythrocytes high rate protolysis assuming homeostasis concentrations are $[GMP^{2-}]=[GMP^{2-}\text{-}AMP^{-}]$, $[HPO_4^{2-}]=1.65*10^{-3}$ M that create functionally activate nucleotides like as **Adenine** designated as ATP^{4-} :

$$K_{Homeostasis}=K_{abpp}\,[H_3O^+]/[H_2O]^2=71151394*10\text{^}(^{-7{,}36})/55{,}3\text{^}2=0{,}0010156245=\frac{[HPO_4^{2-}]^2\cdot[GMP^{2-}\text{-}Phospho\,Adenine^{-}]}{[ATP^{4-}]\cdot[GMP^{2-}\text{-}Ribose\text{-}3\text{-}OH]}.$$

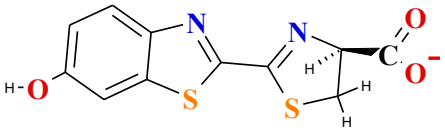
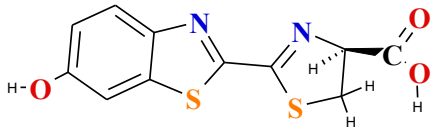
$K_{homeostasis}$=0,0010156245*1,65^2*10^(-3*2)/2,25/10^(-3)= 0,000001228905645 is far favored from Prigogine equilibrium minimum K_{pppbc} to which trends reaction $K_{homeostasis}<<K_{pppbc}$ for conversions the reactants to products as 0,000001229=$K_{homeostasis}$ << K_{pppbc}=71151394 and never reach high rate protolysis equilibrium as homeostasis is non equilibrium state and equilibrium state is attractor for non equilibrium state homeostasis:

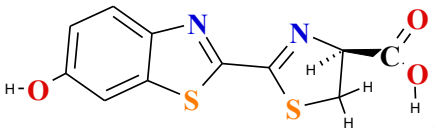
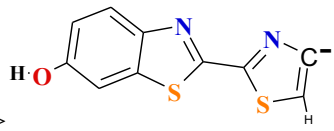
GMP^{2-}Ribose3-OH+$ATP^{4-}+2H_2O \Rightarrow GMP^{2-}\text{-}AMP^{-}+2HPO_4^{2-}+H_3O^+$.

Note: Primary attractors $[H_2O]$=55.3 M and $[H_3O^+]=10^{-7.36}$ M with enzymes irreversible reactivity create of self-organization homeostasis perfect order, which with high rate protolysis drive Brownian molecular engines for evolution and surviving.

Firefly Flashes: Glowing light photons reports of ATP^{4-}

Bioluminescence requires considerable amounts of energy ΔG. In the firefly, ATP^{4-} is used in a four set of reactions that converts chemical energy ΔG into light photon energy E_{photon}= ~hν. Attractors of high rate protolysis require activate molecules for generation of a light flash ~hν . The reaction involve protolytic hydrolyse of ATP^{4-} , **pyro-phosphate** , CO_{2aqua} . In the presence of molecular oxygen O_{2aqua} and **luciferase**, the **luciferin** undergoes a multi-step **oxidative decarboxylation** to **oxy-luciferin** by emission of light ~hν. **Luciferin** is regenerated from **oxy-luciferin** in a subsequent series of reactions. As few **pico-moles** (**10^{-12} mol**) of ATP^{4-} are measured in minute quantities by the intensity $I=k\bullet[ATP^{4-}]$ of the light flash Ψ produced ~hν. Firefly dehydrogenation: **Ox O_{2aqua}+4 H_3O^++4 e^- = 6 H_2O; $E^{\circ 1}$=1,383 V;**

Carboxylate protonation  + H_2O =>  +OH^-;

 +OH^-=>  +$CO_{2\ aqua}$+OH^-+3H+ e^-; dehydrogenation

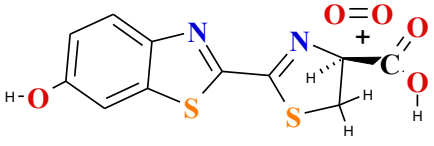
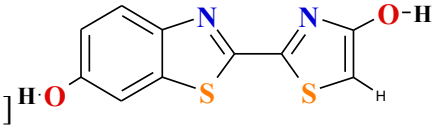
Red Luciferin+OH^-=?luciferin+$CO_{2\ aqua}$+OH^-+3H($3H^+$+3e^-)+e^-; $E^{\circ 2}$=-0,22 V ÷ 0.24 V; average $E^{\circ 2}$=-0 V

$E^{\circ 2}{}_{H2O}$ =-0+0,0591/4*log([H_2O]^2)=-0+0,0591/4*log(55,3333^2)=-0+0.0515=**-0,0515 V**

$\Delta E^\circ=E^{\circ 2}{}_{H2O}-E^{\circ 1}$=0,0515-1,383=**1.3315 V**, **n** is **2**;

$\Delta G_{eqAerobic}=\Delta E^\circ\bullet F\bullet n$=-1,3315*4*96485/1000= $-R\bullet T\bullet\ln(K_{eq})$= **-514** $^{kJ}/_{mol}$

a) Luciferin+OH^-+4H_3O^++O_{2aqua}=>Oxy-luciferin+$CO_{2\ aqua}$+OH^-+6H_2O ; $\Delta G_{aLehninger}$=**-514** $^{kJ}/_{mol}$;

 [ ] 

b) ATP^{4-}+2H_2O=>AMP^{2-}+**$HP_2O_7^{3-}$**+H_3O^+; $\Delta G_{bLehninger}$=**-45.6** $^{kJ}/_{mol}$; ΔG_{bHess}=**-111,45** $^{kJ}/_{mol}$;

ab) **Luciferin**+ 3**H_3O^+**+O_{2aqua}+ATP^{4-}=>**Oxy-luciferin**+$CO_{2\ aqua}$+4H_2O+ AMP^{2-}+**$HP_2O_7^{3-}$**;

CA) CO_{2aqua}+2H_2O+ΔG+Q=v1$\overset{CA}{>}$**H_3O^++HCO_3^-** ; ΔG_{CA}=60.14 $^{kJ}/_{mol}$; ΔG_{CAHess}=102 $^{kJ}/_{mol}$;

abCA) **Luciferin**+3**H_3O^+**+O_{2aqua}+ATP^{4-}=> **Oxy-luciferin**+2H_2O+ AMP^{2-}+**$HP_2O_7^{3-}$+ H_3O^++HCO_3^-** ;

abCA) Luciferin+2H_3O^++O_{2aqua}+ATP^{4-}=>Oxy-luciferin+HCO_3^-+2H_2O+AMP^{2-}+$HP_2O_7^{3-}$+

pp) $HP_2O_7^{3-}$+2H_2O=>HPO_4^{2-}+HPO_4^{2-}+H_3O^+; $\Delta G_{ppLehninger}$= **-19.2** $^{kJ}/_{mol}$; ΔG_{ppHess}=**-85.6** $^{kJ}/_{mol}$;

abCApp) Luciferin+H_3O^++O_{2aqua}+ATP^{4-}=> Oxy-luciferin+AMP^{2-}+HCO_3^-+2HPO_4^{2-};

Energy : ΔG_{abCApp}= ΔG_a+$\Delta G_{bLehninger}$+ΔG_{CA} $\Delta G_{ppLehninger}$=-513,879-45,6+60,14-19,22=**-518.56** $^{kJ}/_{mol}$.

K_{abCApp}=**exp(-ΔG_{abpp}/R/T)**=exp(518560/8,3144/298,15)=$7.06*10^{90}$= $\frac{[HPO_4^{2-}]^2[AMP^{2-}]\cdot[HCO_3^-]\cdot[\text{Oxy Luciferin}]}{[ATP^{4-}]\cdot[\text{Luciferin}]\cdot[O_2]\cdot[H_3O^+]}$.

Primary attractors concentrations [H_2O]=55.3 M, [H_3O^+]=$10^{-7.36}$ M and in human erythrocytes high rate protolysis assuming homeostasis concentrations [AMP^{2-}]=$0,02*10^{-3}$ M , [ATP^{4-}]=$2,25*10^{-3}$ M, arterial blood [O_{2aqua}]=$6*10^{-5}$ M, [HPO_4^{2-}]=$1.65*10^{-3}$ M, []=0,0154 M that create functionally activate molecules:

$K_{Homeostasis}=K_{abCApp}/[H_3O^+]$=7,06*10^90/10^(-7,36)=$1,617*10^{98}$= $\frac{[HPO_4^{2-}]^2[AMP^{2-}]\cdot[HCO_3^-]\cdot[\text{Oxy Luciferin}]}{[ATP^{4-}]\cdot[\text{Luciferin}]\cdot[O_2]}$.

$K_{homeostasis}$=1,617*10^98*1,65^2*10^(-3*2)*0,02*10^(-3)* 0,0154/2,25/10^(-3)=$1,617*10^{88}$ is favored from Prigogine equilibrium minimum K_{abCApp} to which trends reaction $K_{homeostasis}<<K_{abCApp}$ for conversions the reactants to products as $1,617*10^{88}=K_{homeostasis} << K_{abCApp}=7.06*10^{90}$ and never reach high rate protolysis equilibrium as homeostasis is non equilibrium state and equilibrium state is attractor for non equilibrium state homeostasis:

Luciferin+H_3O^++O_{2aqua}+ATP^{4-}=> Oxy-luciferin+AMP^{2-}+HCO_3^-+2HPO_4^{2-};

Note: Primary attractors [H_2O]=55.3 M and [H_3O^+]=$10^{-7.36}$ M with enzymes irreversible reactivity create of self-organization homeostasis perfect order, which with high rate protolysis drive Brownian molecular engines for evolution and surviving.

Attractors generate functional activity of ATP^{4-} for **Transport** and **Muscle Contraction**

ATP^{4-} can supply the energy ΔG for transporting the **ion** or a **molecule** across a membrane into another **aqueous** compartment. For osmosis against and for transport along the gradient is down. Transport processes are two-thirds **2/3** of the energy consumed at **rest** . Na^+ and K^+ across **plasma** membranes pump via the Na^+K^+**ATPase**. The **transport** of Na^+ and K^+ **cycle** process results in the conversion of ATP^{4-} to ADP^{3-} and P_i, but it is the free-energy change ΔG of ATP^{4-} **hydrolysis** that drives the **cyclic** changes in protein **conformation** that result in the **electro-genic** anti parallel **pumping** of Na^+ and K^+ through membrane.

In the **contractile system** of skeletal muscle cells, **myosin** and **actin** are specialized to transduce the chemical energy ΔG of ATP^{4-} into **motion.** ATP^{4-} hydrolytic cycle of **myosin** subsequent reactions as **contractile** motion engines. ATP^{4-} binds tightly to **myosin**, holding the protein in that **conformation**. The **hydrolysis** of bound ATP^{4-}, dissociate from the protein the ADP^{3-} and P_i, allowing to relax into a second **conformation** until another molecule of ATP^{4-} binds. The binding and subsequent **hydrolysis** of ATP^{4-} (by **myosin** **ATPase**) provide the energy ΔG that **forces cyclic** changes in the **conformation** of the **myosin head**. The change in **conformation** of many individual **myosin** molecules sums in the sliding of **myosin fibrils** along **actin filaments**, which translates into macroscopic **contraction** of the **muscle fiber**.

Note: This production of mechanical motion at the expense of ATP^{4-} is functionally activated with primary protolysis attractors $[H_2O]$=55.3 M , $[H_3O^+]=10^{-7.36}$ M and with enzymes irreversible reactivity create perfect order of self-organization homeostasis, which with high rate protolysis drive Brownian molecular engines for evolution and surviving.

Concentration gradients $[ATP^{4-}]/[ADP^{3-}]$ **generation for Nucleotides in All Cells**

Nucleoside triphosphates GTP^{4-}, UTP^{4-}, and CTP^{4-} and **de-oxy-nucleoside tri-phosphates** $dATP^{4-}$, $dGTP^{4-}$, $dTTP^{4-}$, and $dCTP^{4-}$ are generated and maintained as the **nucleoside tri-phosphate** NTP^{4-} forms by **phosphoryl** group transfer to the corresponding **nucleoside diphosphates NDPs** and **mono-phosphates NMPs**. ATP^{4-} is the primary high energy **phosphate** compound produced by catabolism, in the processes of **Glycolysis**, **oxidative phosphorylation**, and, in **photo-synthetic** cells, **photo-phosphorylation**. Specific enzymes **kinases** carry **phosphoryl** groups from ATP^{4-} to the other **nucleotides**. **Nucleoside diphosphate kinase,** found in all cells, under Mg^{2+} coordination protolytic activate transfer of **phosphoryl** group ($^+PO_3^{2-}$): ATP^{4-} + NDP^{3-} (or $dNDP^{3-}$) ⟶ ADP^{3-} + NTP^{4-} (or $dNTP^{4-}$) what drive negative **ΔG= -X?** $^{kJ}/_{mol}$;

Irreversibility of homeostasis order create relatively high $[ATP^{4-}]/[ADP^{3-}]$ ratio with protolysis activated attractors water $[H_2O]$=55,3 M , physiologic pH=7,36 hydroxonium ions concentration $[H_3O^+]=10^{-7,36}$ M drive to favored homeostasis constant as negative energy $\Delta G_{Homeostasis}$= -X < 0 value:

$$K_{Homeostasis}=exp(-\Delta G_{Homeostasis}/R/T)=exp(X/8,3144/298,15)= KX>1 \text{ greater as one ,}$$

with the net formation of **NTPs** and **dNTPs**. The enzyme catalyzes a two-**2**-step **phosphoryl transfer**.
1. phosphoryl group transfer from ATP^{4-} to **active-site** Histidine residue the **enzyme** intermediate.
Second: Then the **phosphoryl** group is transferred from the **P-His** residue to an **NDP acceptor**. Enzymes are **non specific** for the **bases** (**A**, **G**, **U**, **C**, **T**) in the **NDP** and works equally well on **dNDPs** and **NDPs**. The **synthesized NTPs** and **dNTPs** give the corresponding **NDPs** and a supply of ATP^{4-}.

When ADP^{3-} accumulates as a result of **phosphoryl** group transfers from ATP^{4-}, such as when **muscle** is **contracting** vigorously, the **ADP** interferes with ATP^{4-}-dependent **contraction**. **Adenylate kinase** coordinated with Mg^{2+} catalyzes and removes **ADP** by the reaction to create higher concentration gradient $[ATP^{4-}]/[ADP^{3-}]$:

$$2\ ADP^{3-} \longrightarrow ATP^{4-} + AMP^{2-}\ ;$$

Generation the concentration $[ATP^{4-}]/[ADP^{3-}]$ gradients increase ATP^{4-} molecules functional activity and as protolysis activate attractor drive the life processes in homeostasis. This reaction is fully reversible, so the enzyme can also convert AMP^2 (produced **pyro-phosphoryl** or **adenylyl** group transfer from ATP^{4-}) into ADP^{3-}, which can then be **phosphorylated** to ATP^{4-} through one of the catabolic **pathways**. A similar enzyme, **guanylate kinase** converts GMP^{2-} to GDP^{3-} at the expense of ATP^{4-}. By **pathways** such as these, energy ΔG accumulates in the catabolic product to generate concentration gradients $[ATP^{4-}]/[ADP^{3-}]$ which is used to supply the cell with all required **NTPs** and **dNTPs** according its concentrations .

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