Aris Kaksis 2023. Riga Stradin's University

Medical Chemistry show functional active molecules formation conditions as attractors.

Attractors Thermodynamics is the quantitative study of the energy **G** transductions that occur in living cells for the functions in nature of the **chemical** processes underlying these transductions which are drivers and destiny declared by Ilya Prigogine Nobel Prize 1977.

Organisms are membranes compartmented complex reactions clusters with compounds mixture, in which dissipative structure molecules having generate functional activity and what irreversible drive with certain Attractors Brownian molecular engines free energy change to minimum, develop evolution and surviving as non-equilibrium homeostasis instruments.

Atmospheric oxygen attractor **O_2** 20,95 % of Photosynthesis

Green plants **CO_2** assimilation and **O_2 OSMOSIS** photosynthesis production attractors.

Experimental research of ability photosynthesis reach oxygen concentration 20,95 %. Preparation 2% oxygen air show retention during 24 hours the normal level , stopping the rate of photosynthesis at homeostasis concentration 20,95% of volume.

Attractor 20,95 % oxygen in atmosphere works locally for photosynthetic organisms and mesurments proov this attractor global influence to maintain oxygen concentration 20,95%.

Nernst's potential O_{2aqua}/ H_2O red-ox system physiologic mechanism of acidosis and oxidative stress.

Destructive hazard for life! Oxidative stress causes chaos, contamination with **non enzymatic** oxidation

in multiple chain reactions and parallel products so degrading and destroying the organism!

Water medium, blood plasma oxygen is strong reagent **1,229** V referring to half reaction:

$$\underset{\text{oxidized form}}{O_{2aqua} + 4H_3O^+} \quad + \quad \underset{\text{free electrons}}{4e^-} \quad \Leftrightarrow \quad \underset{\text{reduced form}}{6\,H_2O}$$

Concentration arterial $[O_{2aqua}] = 6*10^{-5}$ M and pH=7,36 concentration $[H_3O^+]=10^{-7,36}$ M.

$$E = \mathbf{1,228}\text{ V} + 0,01478 \bullet \lg([O_{2aqua}] \bullet [H^+]^4) = 1,229 + 0,01478*\log(6*10^{-5}*10^{-7,36\bullet 4}) = \mathbf{0,7305}\text{V}$$

Water concentration value $E_o = E° + 0,0591/4*\log(1/[H_2O]^6)$; $[H_2O] = {}^{996,23}/_{18} = 55,346$ M.

Oxidative stress risk decrease about $\Delta \mathbf{E}_{O2aqua\ pH} = E - E_o = 0,7305 - \mathbf{1,228} = -\underline{\mathbf{0.4975}}$ V and minimised free energy content for oxygen about $\Delta \mathbf{G}_{\mathbf{min}} = \Delta \mathbf{E}_{O2aqua\ pH} * \mathbf{F} * \mathbf{n} = -0,\mathbf{4975}*96485*4/1000 = -\mathbf{192}\ {}^{kJ}/_{mol}$;

1) Water 55,346 M decreases potential from **1,383 V** to standard **1,228 V** about $-\underline{\mathbf{0,155}}$ V= ΔE_{H2O}.

$$E_o = E° + {}^{0,0591}/_4 * \log({}^1/_{[H2O]}{}^6) = \mathbf{1,383} + 0,01478*\log({}^1/_{55,346}{}^{\wedge 6}) = \mathbf{1,228}\text{ V} ;$$

Oxidative stress risk decrease about $\Delta E_{H2O} = E° - E_o = \mathbf{1,228} - \mathbf{1,383} = -\underline{\mathbf{0.155}}$ V and minimised free energy content for oxygen about $\Delta \mathbf{G}_{\mathbf{min}} = \Delta E_{H2O} * \mathbf{F} * \mathbf{n} = -0,\mathbf{155}*96485*4/1000 = -\mathbf{59,82}\ {}^{kJ}/_{mol}$;

Total oxidative stress risk decrease $\Delta \mathbf{G}_{\mathbf{min}} = \Delta \mathbf{E}_{O2aqua\ pH} + \Delta \mathbf{G}_{H2O} = -\mathbf{192}\ -\mathbf{59,82} = -\mathbf{251,82}\ {}^{kJ}/_{mol}$;

2) Acid H_3O^+ increases 10 times the potential increases about $\Delta E_{H3O+} = \mathbf{0,05912}$ V .

$\Delta E_{H3O} = 0,01478 \bullet \lg([H^+]^4) = 0,01478*\log(10^{\wedge(4)}) = \mathbf{0,05912}$ V; Free energy content for oxygen increases about $\Delta \mathbf{G}_{\mathbf{max}} = \Delta E_{H3O} * \mathbf{F} * \mathbf{n} = 0,05912*96485*4/1000 = \mathbf{22,817}\ {}^{kJ}/_{mol}$;

3) Air 20.95% replaced with 100% oxygen $[O_{2aqua}]$ concentration 5 times increase potential about $\Delta E_{O2100\%} = 0,01478 \bullet \lg(100\%\ [O_{2aqua}]) = 0,01478*\log(5) = +\underline{\mathbf{0,0103}}$ V . Free energy content for oxygen increases about $\Delta \mathbf{G}_{\mathbf{max}} = \Delta E_{H3O} * \mathbf{F} * \mathbf{n} = 0,01033*96485*4/1000 = \mathbf{3,987}\ {}^{kJ}/_{mol}$;

NASA Apollo Moon project closes 1972 because of oxidative stress and technical hazards risk.

Attractors two approaches for equilibrium

Thousands of Biochemical reactions have been studied as active mass law trend to equilibrium.

Attractor reaching time $t_{attractor}$ establish free energy change minimum in mixture of compounds. Active mass law of reactions velocity are equal for direct and reverse reaction. Factorial of products $\mathbf{[C]^c \bullet [D]^d}$ and reactants $\mathbf{[A]^a \bullet [B]^b}$ concentration ratio becomes constant in expression: aA + bB <=> cC + dD ; $K_{equilibrium} = \frac{\mathbf{k_{\rightarrow}}}{\mathbf{k_{\leftarrow}}} = \frac{\mathbf{[C]^c \bullet [D]^d}}{\mathbf{[A]^a \bullet [B]^b}}$

Prigogine thermodynamic relates to non equilibrium complex reaction Biochemistry, but equilibrium state attractor is Prigogine dissipative structures containing complex reactions destiny of irreversible processes to which tended system , that works as instruments of Brownian molecular engines for evolution and surviving, homeostasis.

Homeostasis biochemical active mass law Le Chatelier's principle for Prigogine attractor free energy change minimum reaching drive ratio of products over reactants concentration factorial $\mathbf{[A_H]^a}$, $\mathbf{[B_H]^b}$, $\mathbf{[C_H]^c}$, $\mathbf{[D_H]^d}$ with trend to erase $\mathbf{\Delta G_{Homeostasis}}$ value up to zero:

$$\mathbf{\Delta G_{Homeostasis}} = \mathbf{\Delta G_{eq}} + \mathbf{R \bullet T \bullet ln}\left(\frac{\mathbf{[C_H]^c \bullet [D_H]^d}}{\mathbf{[A_H]^a \bullet [B_H]^b}}\right) \neq 0 \, .$$

Established equilibrium free energy change for homeostasis finish $\mathbf{\Delta G_{Homeostasis}}$ is zero and Calculate one standard free energy change at equilibrium state using constant $\mathbf{K_{eq}}$ value:

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

Versus **Hess Law** for five complex reactions (**r**) calculation order of products minus reactants : Standard enthalpy change for reaction: $\mathbf{\Delta H_{Hess}} = \Sigma \mathbf{\Delta H^{\circ}}_{products} - \Sigma \mathbf{\Delta H^{\circ}}_{reactants}$;

Standard entropy change for reaction: $\mathbf{\Delta S_{Hess}} = \Sigma \mathbf{\Delta S^{\circ}}_{products} - \Sigma \mathbf{\Delta S^{\circ}}_{reactants}$;

Standard free energy change for reaction: $\mathbf{\Delta G_{Hess}} = \Sigma \mathbf{\Delta G^{\circ}}_{products} - \Sigma \mathbf{\Delta G^{\circ}}_{reactants}$ or

$$\mathbf{\Delta G_{Hess}} = \Delta H_{\mathbf{Hess}} - T \cdot \Delta S_{\mathbf{Hess}}\ .$$

Favored and unfavored Hess constant calculate with exponent

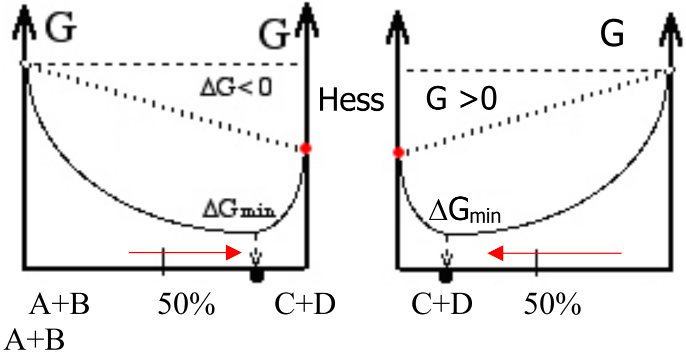
$$\mathbf{K_{Hess} = exp(-\Delta G_{\text{Hess}}/R/T) = e^{-\Delta G_{Hess}/RT}}.$$

Favored equilibrium 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 $\mathbf{K_{eq}}$ established energy change minimum. For isolate mixture of compounds at equilibrium free energy change :

$$\mathbf{\Delta G_{eq} = -R \bullet T \bullet ln(K_{eq}) = \Delta G_{min}}\ ; \text{ so } |\ \mathbf{\Delta G_{eq}}\ | = |\ \mathbf{\Delta G_{min}}\ | < |\ \mathbf{\Delta G_{Hess}}\ |$$

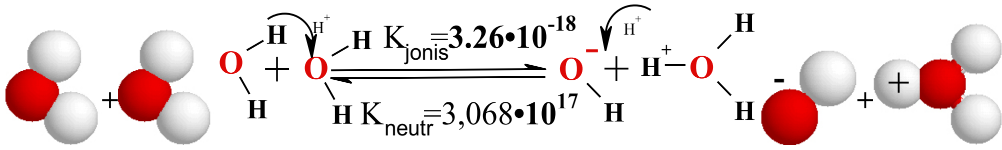
minimised as Prigogine attractor versus complete conversion with Hess law according Le Chatelier's principle tend to reach Prigogine attractor at equilibrium mixture. Free energy change minimum $\mathbf{\Delta G_{min}}$ is Ilya Prigogine declared attractor to which trend reaction inverse nor favored Direct forwards nor reverse unfavored backwards direction or opposite, which determine inverse constants for: direct $K_{eq1} = 1\ /\ K_{eq2}$ and reverse reaction.

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



Water protolysis and neutralization inverse $\mathbf{H_2O+H_2O+Q}+\Delta G \Leftarrow\Rightarrow \mathbf{H_3O^+ + OH^-}$

Free energy standard change from Hess law is positive so than unfavored, endoergic reaction:



$$\mathbf{K_{eq1}}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=\mathbf{3{,}26\bullet10^{-18}}$$

$$\Delta \mathbf{G_{eq}=-R\bullet T\bullet ln}\left(\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}\right)=8{,}3144\bullet298{,}15\bullet\mathbf{ln}(10^{-17{,}48678})=99{,}8\ {}^{kJ}/_{mol},$$

Endothermic and endoergic water protolysis reaction Hess free energy change $\Delta \mathbf{G_{Hess}}=\Delta \mathbf{G_{protolyse}}=101{,}9\ {}^{kJ}/_{mol}$ positive, but minimized in mixture reached equilibrium

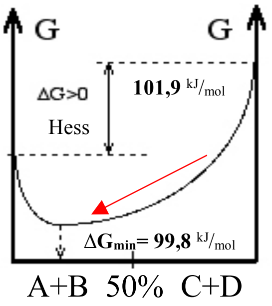
$$\mathbf{K_{eq1}}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=\mathbf{3.26\bullet10^{-18}}\ ;\ \text{up to } \Delta \mathbf{G_{min}}=\Delta \mathbf{G_{eq}}=99{,}8\ {}^{kJ}/_{mol}$$

Free energy change ΔG_{Hess} for pure compounds by absolute value in Hess law is greater. Reaching equilibrium mixture of compounds free energy change minimizes: $\mathbf{99{,}8\ {}^{kJ}/_{mol}=|\Delta G_{eq}|<|\Delta G_{Hess}|=101{,}9\ {}^{kJ}/_{mol}}$

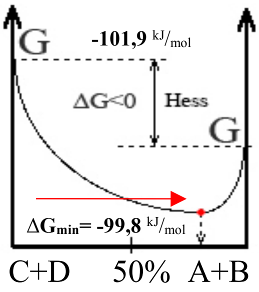
All reactions trend to Prigogine attractor minimum of free energy change $\Delta \mathbf{G_{min}}=\Delta \mathbf{G_{eq}}$ at equilibrium mixture with active mass law inverse reactions constants:

$$3.26\bullet10^{-18}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=K_{eq1}=\frac{1}{K_{eq2}}=\frac{1}{\frac{[H_2O]\cdot[H_2O]}{[OH^-]\cdot[H_3O^+]}}=\frac{1}{3{,}068*10^{17}}\ .$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.



$\mathbf{H_2O+H_2O}$ reactants products $\mathbf{H_3O^+ + OH^-}$



$\mathbf{H_3O^+ + OH^-}$ reactants products $\mathbf{H_2O+H_2O}$

The small products amount $[\mathbf{H_3O^+}]=[\mathbf{OH^-}]=10^{-7}$ M and water concentration in power 2 two exponent for one liter : $[\mathbf{H_2O}]^2=({}^{997}\text{g/L} / 18\ \text{g}/_{mol})^2=3065.96\ \text{M}^2$.

page 15th .

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

Free energy standard change from Hess law is positive so than unfavored, endoergic reaction:

$$\Delta G_{protolysis}=\Delta H_{protolysis}-T\Delta S_{protolysis}=42{,}36\ {}^{kJ}/_{mol}\ .$$

Equilibrium reaches free energy minimum in mixture of compounds ratio for constant expression:

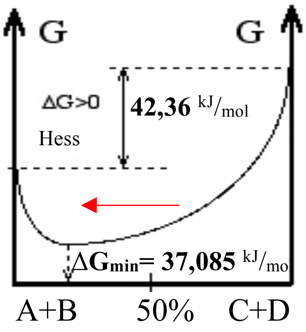
$$\mathbf{K_{eq}}=\frac{[H^+]\cdot[CH_3COO^-]}{[H_2O]\cdot[CH_3COOH]_{nedis}}=K_a/[\mathbf{H_2O}]=1{,}76*10^{-5}/55{,}3=10^{-6{,}497}$$

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

Endothermic and endoergic acetic acid protolysis Hess free energy change is $\Delta \mathbf{G_{protolysis}}$ positive $42{,}36\ {}^{kJ}/_{mol}$ as unfavored reaction, but minimised $\Delta \mathbf{G_{min}}=\Delta \mathbf{G_{eq}}=37{,}085\ {}^{kJ}/_{mol}$

$$\mathbf{K_{eq}}=\frac{[H^+]\cdot[CH_3COO^-]}{[H_2O]\cdot[CH_3COOH]_{nedis}}=\mathbf{10^{-6{,}497}}$$

in mixture reaching equilibrium Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching in mixture reactant compounds sum with sum of products $\mathbf{H_3O^+ + CH_3COO^-}$. Free energy change minimum reaching establishes equilibrium.



$\mathbf{CH_3COOH+H_2O}$

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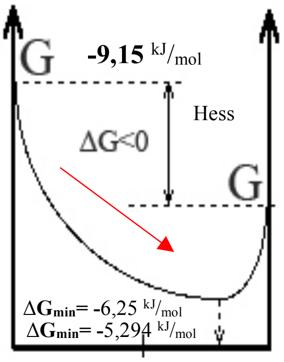
Ions from crystalic Na^+Cl^-=>Na^++Cl^- solubility product dissociation process as electrolyte solution

$\Delta G_{dissociation} = \Delta H_{dissociation} - T\Delta S_{dissociation} = -9{,}15\ ^{kJ}/_{mol}$ favored reaction.

At equilibrium reached free energy change minimum on solubility product and physiologic 0,9% solution expression according compounds concentration factorial in mixture:

$$K_{sp}=K_{eq}=[Na^+_{aq}]*[Cl^-_{aq}]/[NaCl]= =4{,}0952*4{,}0952/1{,}3482=12{,}4393$$

$$K_{0,9\%}=[Na^+_{aq}]*[Cl^-_{aq}]/[NaCl]=0{,}15115*0{,}15115/0{,}0027=8{,}4616;$$



$\Delta G_{sp}= -R\bullet T\bullet \ln(K_{sp})=-8{,}3144\bullet 298{,}15\bullet \ln(12{,}4393)= -6{,}25\ ^{kJ}/_{mol}$,

$\Delta G_{0,9\%}= -R\bullet T\bullet \ln(K_{0,9\%})=-8{,}3144\bullet 298{,}15\bullet \ln(8{,}4616)=-5{,}294\ ^{kJ}/_{mol}$,

Endothermic and exoergic solubility Hess free energy change $\Delta G_{Hess}= -9{,}15\ ^{kJ}/_{mol}$ is negative, but minimised $\Delta G_{min} =\Delta G_{0,9\%}= -5{,}294^{kJ}/_{mol}$ in physiologic 0,9 % mixture reached equilibrium $K_{0,9\%}=[Na^+_{aq}]*[Cl^-_{aq}]/[NaCl_{aq}]= 8{,}4616$ or solubility $\Delta G_{sp}= -6{,}25^{kJ}/_{mol}$ reached $K_{sp}=K_{eq}=12{,}4393$. Prigogine attractor free energy change minimum ΔG_{min} for crystalline sodium chloride Na^+Cl^- **solubility** product. At free energy minimum ΔG_{min} reaching establishes equilibrium.

$$K_{sp}=\frac{[Na^+]_{aqua}\cdot[Cl^-]_{aqua}}{[Na^+Cl^-]_{aqua}}=12{,}44.$$

Dissociation degree α=4,0952/5,4434=75,2 % Crystaline Na^+Cl^- reactant compound is A 50% B+C__ and in mixture $Na^+_{aqua} + Cl^-_{aqua}$ are products.

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching mixture at equilibrium. Free energy change minimum reaching establishes equilibrium.

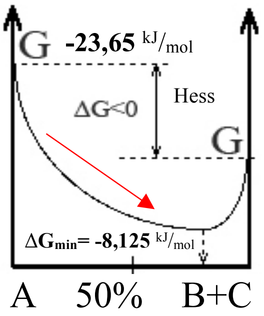
9th page .

Sodium acetate solubility products equilibrium $CH_3COONa_s \rightleftarrows Na^+_{aqua}+CH_3COO^-_{aq}$ electrolyte dissociations thermodynamics

$\Delta G_{dissociation} = \Delta H_{dissociation} - T\Delta S_{dissociation} = 23{,}6\ ^{kJ}/_{mol}$ favored reaction.

At equilibrium reached frees energy minimum according compound concentration $C_{CH3COONa}= 5{,}1493\ ^{mol}/_{L}$ in expression for mixture components factorial:

$$K_{sp}= K_{eq} =[Na^+]*[CH_3COO^-]=5{,}1493*5{,}1493= 26{,}515 .$$



$\Delta G_{eq}=-R\bullet T\bullet \ln(K_{eq})=-8{,}3144\bullet 298{,}15\bullet \ln(26{,}515)= -8{,}125\ ^{kJ}/_{mol}$,

Exothermic and exoergic CH_3COONa_s solubility dissociations Hess free energy change $\Delta G_{dissociation}$ negative $-23{,}65\ ^{kJ}/_{mol}$ as favored reaction, but minimises up to $\Delta G_{min}= \Delta G_{eq}= -8{,}125\ ^{kJ}/_{mol}$

in mixture reaching equilibrium $K_{eq}=\frac{[Na^+]\cdot[CH_3COO^-]}{[CH_3COONa]_{solid}}=26{,}515.$

In mixture reactant compound is A crystalline CH_3COONa_s mol fraction one $[CH_3COONa_s]_{solid}=1$ and $Na^+_{aqua} + CH_3COO^-_{aqua}$ B+C are products.

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

Free energy change minimum reaching establishes equilibrium mixture.

12th page .

Ammonium 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.

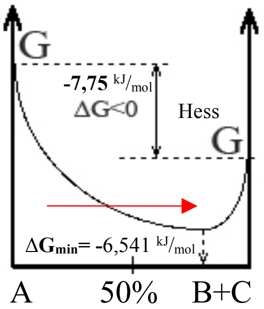
At equilibrium reached frees energy minimum according compound mixture in expression:

$$K_{eq} = \frac{[NH_4^+]_{aqua} \cdot [Cl^-]_{aqua}}{[NH_4Cl]_{aqua}} = 3{,}97651*3{,}97651/1{,}13 = 13{,}9935$$

$\mathbf{\Delta G_{eq} = -R \bullet T \bullet ln(K_{eq})} = -8{,}3144 \bullet 298{,}15 \bullet \mathbf{ln}(13{,}9935) = -6{,}541\ {}^{kJ}/_{mol}$,,

Endothermic and exoergic $NH_4Cl_{(s)}$ dissociations reaction free energy $\mathbf{\Delta G_{dissociation}}$ negative $-7{,}75\ {}^{kJ}/_{mol}$ as favored reaction,
but minimises up to $\Delta G_{min} = \Delta G_{eq} = -6{,}541\ {}^{kJ}/_{mol}$

in mixture reaching equilibrium $K_{eq} = \frac{[NH_4^+]_{aqua} \cdot [Cl^-]_{aqua}}{[NH_4Cl]_{aqua}} = 13{,}9935$.



Mixture reactant compound is crystalline ammonium chloride NH_4Cl_{aqua} (A) and $NH_4^+{}_{aq} + Cl^-{}_{aqua}$ (B+C) are products.

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

Free energy change minimum reaching establishes equilibrium mixture.

13th page .

Ammonium water $NH_4^+{}_{aq} + H_2O + \Delta G + Q \Rightarrow NH_{3aq} + H_3O^+$

protolysis -dissociations thermodynamics

$\Delta G_{protolysis} = \Delta H_{protolysis} - T\Delta S_{protolysis} = 121{,}2\ {}^{kJ}/_{mol}$ unfavored reaction.

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

$$\frac{[NH_3]_{aqua} \cdot [H_3O^+]}{[NH_4^+]_{aqua} \cdot [H_2O]} = K_a = [H_2O] \frac{3.26*10^{-18}}{1{,}78*10^{-5}} = 55{,}3*1{,}831*10^{-13} = 1{,}013*10^{-11}$$

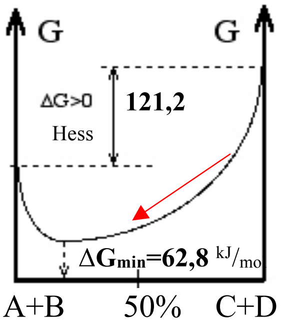
$\mathbf{\Delta G_{eq} = -R \bullet T \bullet ln(K_a)} = -8{,}3144 \bullet 298{,}15 \bullet \mathbf{ln}(1{,}013*10^{-11}) = 62{,}76\ {}^{kJ}/_{mol}$,

Endothermic and endoergic $NH_4^+{}_{(aq)}$ protolysis reaction free energy

$\mathbf{\Delta G_{protolysis}}$ positive $121{,}2\ {}^{kJ}/_{mol}$ as unfavored reaction,

but minimises 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 $NH_{3(aq)} + H_3O^+$ (C+D) are products.

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

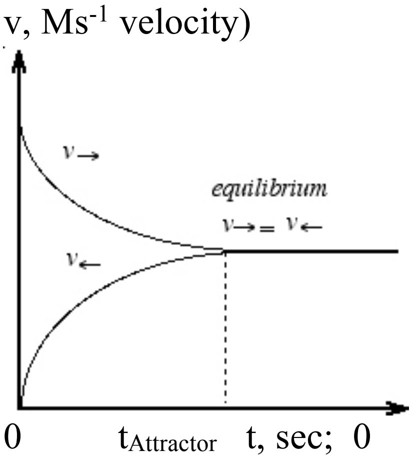
Free energy change minimum reaching establishes equilibrium mixture.

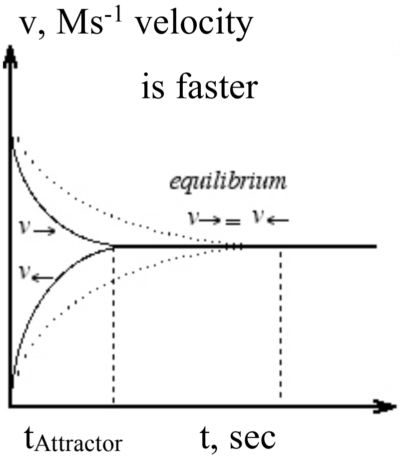
16th page .

ACTIVE MAS velocity for reaching of Prigogine attractor

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

Mass action Law for Direct $\overset{\rightarrow}{\mathbf{v}} = \overset{\rightarrow}{\mathbf{k}} \cdot \mathbf{C}_{\mathbf{A}}^{\mathbf{a}} \cdot \mathbf{C}_{\mathbf{B}}^{\mathbf{b}} \Leftarrow \underset{\text{revers}}{\overset{\text{direct}}{\longleftrightarrow}} \Rightarrow \overset{\leftarrow}{\mathbf{v}} = \overset{\leftarrow}{\mathbf{k}} \cdot \mathbf{C}_{\mathbf{C}}^{\mathbf{c}} \cdot \mathbf{C}_{\mathbf{D}}^{\mathbf{d}}$ for Reverse reaction .





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

Living organisms thousands of Biochemical reactions have been studied as at equilibria. Reaction is irreversible if reverse constant is zero $\overset{\leftarrow}{\mathbf{k}} = 0$ or close to zero and attractor reaching time $t_{\text{Attractor}}$ is slow or trends to infinit long time $t_{\text{Attractor}} \Rightarrow \infty$.

If reverse velocity constant is positive $\overset{\leftarrow}{\mathbf{k}} > 0$, than attractor ($t_{\text{Attractor}}$) constant velocity $\overset{\rightarrow}{\mathbf{v}} = \overset{\leftarrow}{\mathbf{v}}$ reaching limit just direct reaction velocity constant $\overset{\rightarrow}{\mathbf{k}}$ because direct reaction of Initial compounds becomes equal to reverse reaction of products $\overset{\rightarrow}{\mathbf{v}} = \overset{\leftarrow}{\mathbf{v}}$.

Attractor free energy change minimum at equilibrium state reaching time $t_{\text{Attractor}}$ depends on Direct reaction velocity. For example, Hydrogen peroxide conversion to life resources $\mathbf{O_{2aqua}+H_2O+Q}$ is slow $\mathbf{k}_{\rightarrow}=1.191\bullet10^{-8}$ $\mathrm{Ms^{-1}}$. CATALASE peroxide consume thirty million times $30\bullet10^6$ faster. Irreversible CATALASE reactivity for peroxide consuming is Prigogine attractor, that indispensible for Life driving to product 100% efficiency erasing $\mathbf{H_2O_{2aqua}}$ molecules and convert to $\mathbf{O_{2aqua}+H_2O+Q}$:

Carbon dioxide 0,04% of air do not act with water : $CO_2\uparrow_{gas}+\Delta G_{aqua}\Leftrightarrow Q+CO_{2aqua}$; just solute in water with solubility $[CO_{2aqua}]=K_{eqH2O}*[CO_2\uparrow_{air}]=1{,}882*0{,}0004=0{,}00075125$ M. Enzyme carbonic anhydrase **CA** drive irreversible water solute carbonic dioxide reaction with two water molecules:

$CO_{2aqua}+2H_2O+Q \overset{}{=}\underline{\mathbf{CA}}\rightarrow H_3O^++HCO_3^-$, so $[CO_{2aqua}+HCO_3^-]/[CO_2\uparrow_{air}]=30{,}6$ times: from 0,00075 M increased ratio to 0,0023 M. Limestone, dolomite, chalk and marble rocks formation possible if air $[CO_2\uparrow_{air}]=0{,}04\%$ react with water. Distinction of Carbonic Anhydrase on Earth the assimilation of $\mathbf{CO_2}$ in aqua sphere decreases 30,6 times :

4th, 46rd page .

Irreversible enzyme reactivity for products reaching in living organism are Ilya Prigogine declared attractors for organism 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.

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:

$$C_6H_{12}O_6 + 6O_{2aqua} + 6H_2O \Rightarrow 6HCO_3^- + 6H_3O^+ + \Delta G + Q;\ \Delta G_{Hess} = -2570{,}4\ ^{kJ}/_{mol};\ \Delta H_{Hess} = -2805.27\ ^{kJ}/_{mol}$$

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

$$Gly\text{-}Gly_{aqua} + H_2O \xRightarrow{peptidase} Gly_{aqua} + Gly_{aqua} + Q + \Delta G\ ;\ \Delta G_{Lehninger} = -9{,}2\ ^{kJ}/_{mol}\ ;\ \Delta H_{Hess} = -32{,}8\ ^{kJ}/_{mol}$$

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

$$AB \Rightarrow A + B,\ \Delta G = \Delta H - T\cdot\Delta S < 0,\quad \Delta S > 0 \quad \text{and} \quad \Delta H < 0\ ;$$

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:

$$A + B \Rightarrow AB,\qquad \Delta H < 0 \text{ and } \Delta S < 0\ ;\ \Delta G = \Delta H - T\cdot\Delta S$$

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**):

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

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:

$$AB \Rightarrow A + B \qquad \Delta H > 0 \text{ and } \Delta S > 0\ ;\ \Delta G = \Delta H - T\cdot\Delta S$$

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: $|T\cdot\Delta S| > |\Delta H|$

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

4. ENDOTHERMIC, ENDOERGIC REACTION OF SYNTHESIS.

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

$$6HCO_3^- + 6H_3O^+ + \Delta G + Q \Rightarrow C_6H_{12}O_6 + 6O_{2aqua} + 6H_2O;\ \Delta G_{Hess} = 2570{,}4\ ^{kJ}/_{mol};\ \Delta H_{Hess} = 2805.3\ ^{kJ}/_{mol}$$

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

$$Gly_{aqua} + Gly_{aqua} + Q + \Delta G \xRightarrow{ribosome} Gly\text{-}Gly_{aqua} + H_2O\ ;\ \Delta G_{Lehninger} = 9{,}2\ ^{kJ}/_{mol}\ ;\ \Delta H_{Hess} = 32{,}8\ ^{kJ}/_{mol}$$

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 **conclusions**: *1) If the direct reaction is always spontaneous, the reverse one is forbidden.(cases 1 and 4). 2) If 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 .

Energy change **minimum** and **reactivity drive reaction complexes irreversibly** in **homeostasis**

Medical Chemistry show functional active molecules formation conditions as attractors.

Organism biochemical environment forming fast equilibria 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 [H_3O^+]=$10^{-7,36}$ M, temperature 310,15 K degree.

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

7th page .

5 complex Enzyme reactions

Enzyme governed complexe reactions drive the LIFE in 5 ways

Versus non Enzymatic reactions

chaos and contamination

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 $\Delta G=\Delta H-\Delta S \cdot T>0$

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

4. Chaotic

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 life maintenance. With enzyme specification as selectivity attractors organise: gradual-consecutive, joint-tandem, competitive regulation allostery and inhibition, enzyme driven radical reactions.

Organisms are compartmented complex reactions clusters of compounds mixture, 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.

Certain aspects of **Attractor** pH=7,36 hydrogen ions concentration $[H^+]=10^{-7,36}$ M

Brønsted CA $\mathbf{CO_{2aqua}}$ + $\mathbf{H_2O}$, hemoglobin **shuttle** of $\mathbf{O_2}$ and $\mathbf{HCO_3^-}$ + $\mathbf{H^+}$ enzymes complexes

8. ÷ 10. Pages:

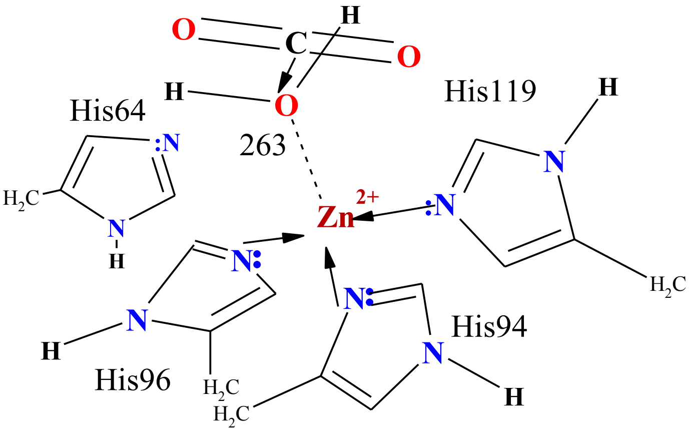
Enzyme **Carbonic anhydrase** made acid/base equilibrium $\mathbf{H_2O^{-CA-}CO_2/HCO_3^-+H_3O^+}$

There are **shuttle** buffer systems, that act in the human organism and allow **pH** of the organism to be stabilized constant in narrow interval to prevent changes ($\mathbf{pH = 7.36^{+0,02}_{-0,01}}$) despite the fact, that organism produces great amount of metabolic $[\mathbf{CO_{2aqua}}]+[\mathbf{HCO_3^-}]=0,0275$ M in homeostasis.

The **CA** made amount of acidic products is $[\mathbf{H_3O^+}]=[\mathbf{HCO_3^-}]=0,0275$ M compensated by **shuttle** hemoglobin, myoglobin and buffer solution of **CA**. **CA** buffer of blood are connected to **shuttle** hemoglobin captured proton $\mathbf{H^+}$ and $\mathbf{HCO_3^-}$ by oxygen $\mathbf{O_{2aqua}}$ desorbtion, due to consumed oxygen, are formed metabolic oxidation products in target cells of ***tissues***:

Hydrogen carbonate buffer system carbonic anhydrase equilibrium keeps weak acid CO_{2aqua} and bicarbonate ions at normal levels $[HCO_3^-]=0.0154$ M, $[CO_{2aqua}]=0.0076$ M, referring to 56,23 released volume CO_2 from 100 mL blood as *alkaline reserve* 2,036 / 1 in clinic evaluation. Carbon dioxide forms by oxidation of carbohydrates, of fats and of proteins.

Bicarbonate is created as hydration product by CA enzyme active coordination center of ion $\mathbf{Zn^{2+}}$. It's location in enzyme carbonic anhydrase coordination pocket drive the hydration process: $CO_{2aqua}+2H_2O \rightleftarrows CA(\mathbf{Zn^{2+}}) \rightleftarrows H_3O^++HCO_3^-$ and more details : $(CA\mathbf{Zn^{2+}})H_2O(263)+H_2O+CO_{2aqua} <= (CA\mathbf{Zn^{2+}} \leftarrow OH^-+H^++H_2O) => HCO_3^-+H_3O^+$



Shuttle of O_2 , $(HCO_3^- + H^+)$ enzymes Hemoglobin, Myoglobin

$\mathbf{Hb_R(O_2)_4+4H^+} + 4HCO_3^- \Leftrightarrow \mathbf{4O_{2aqua}} + (\mathbf{H^+}His63,58)_4\mathbf{Hb_T}$...salt bridges...$4HCO_3^-$ stabilizing blood arterial concentration $[\mathbf{O_2}\ _{aqua}]=6\cdot10^{-5}$ M and minimum venous $[\mathbf{O_2}\ _{aqua}]=1.85\cdot10^{-5}$ M. Deoxy hemoglobin $(\mathbf{H^+}His63,58)_4\mathbf{Hb_T}$ capture four protons 4 $\mathbf{H^+}$ at histidine residues and 4 HCO_3^- in venous hemoglobin form of erythrocytes deoxy $(\mathbf{H^+}His63,58)_4\mathbf{Hb_T}$ (Tense state). In **lungs shuttle** absorbs oxygen make arterial oxy hemoglobin $(\mathbf{O_2}His63,58)_4\mathbf{Hb_R}$ (**Relax** state) releasing 4 $\mathbf{H^+}$ and 4 $\mathbf{HCO_3^-}$.

1) One of two dominate buffer systems is enzyme **CA** made Brønsted Acid/Base endothermic process: $Q+CO_{2aqua}+2H_2O \xleftrightarrow{CA} H_3O^++HCO_3^-$ which consume heat **Q** of exothermic oxidation reactions. Its shift to right support low stabilized pH=7,36±0,01 of hydrogen ions H_3O^+ concentration $[H_3O^+]=10^{-7,36}$ M in products and drive high water $2H_2O$ concentration in square exponent $[H_2O]^2=(993,36/18,0153)^2=55,139^2=3040,4$. Oxidation product CO_{2aqua} as bicarbonate salt bridge linked $HCO_3^-\ldots H_3^+N-$ and equal produced protons $[H^+]=[CO_{2aqua}]=0,0275=[HCO_3^-]$ captures deoxy $(H^+His63,58)_4Hb_T$...salt bridges...$4HCO_3^-$ **shuttle** and brings to ***lungs***.

Lungs evaporates $CO_2\uparrow_{gas}+H_2O\uparrow_{gas}$ endothermic $\Delta H_r=+54,5$ $^{kJ}/_{mol}$, but exoergic $\Delta G_r=-82,1$ $^{kJ}/_{mol}$:

$$H_3O^++HCO_3^- +Q \xleftrightarrow{\text{Membrane transport } H^++HCO3^- \text{ channeling}} H_2O+CO_2\uparrow_{gas}+H_2O\uparrow_{gas} + \Delta G_r \,.$$

Symbol $(H^+His63,58)_4Hb_T$ to a **Shuttle** molecule of hemoglobin is convenient to write instead the complicated structure of hemoglobin. Deoxy hemoglobin is capturing $4O_{2aqua}$ and oxy hemoglobin completely deprotonated 4 H^+ and desorbed 4 HCO_3^-. Fast equilibrium make oxygen concentration $[O_{2aqua}]=6\cdot10^{-5}$ M and is sensitive to decrease of concentration $[O_{2aqua}]$ in **tissues**:

$$4O_{2aqua} + (H^+His63,58)_4Hb_T\text{...salt bridges...}4HCO_3^- \Leftrightarrow (O_2His63,58)_4Hb_R +4H^++ 4HCO_3^-.$$

Lungs venous blood hemoglobin saturation with oxygen 459 times restore circulated arterial blood $[O_{2aqua}]=6\cdot10^{-5}$ M amount in one liter O2Solutions.doc . Adsorbed four $4O_{2aqua}$ $(O_2His63,58)_4Hb_R+4H^++4HCO_3^-$ in products release four protons 4 H^+ and bicarbonate ions 4 HCO_3^-, promoting evaporation $CO_2\uparrow_{gas}+H_2O\uparrow_{gas}$ on ***lungs*** epithelia surface, and removing out of organism $[H^+]=459*6*10^{-5}=0,0275$ M amount $H^++H_2O \Rightarrow H_3O^+$, that is equal to total by respiration evaporated $[CO_2\uparrow_{gas}]=0,0275$ M amount on one liter of blood volume.

Shift to the left $(O_2His63,58)_4Hb_R+4H^++4HCO_3^-$ from deoxy captured **shuttle** $(H^+His63,58)_4Hb_T$...salt bridges...$4HCO_3^-$ oxygen depending concentration $[O_{2aqua}]=6\cdot10^{-5}$ M adsorbtion-desorbtion equilibrium explain pH stabilization at 7.36.

That explain, why pH is not changed, despite acid $CO_{2\,aqua}$ product which involved in **CA** equilibrium. Henderson-Haselbalh homeostasis pH value expression leave the ratio $[HCO_3^-]/[CO_{2aqua}]=2,0263$ practicaly unchanged as intact both concentrations bicarbonate $[HCO_3^-]$ and carbon dioxide $[CO_{2aqua}]$:

$7.36 = pH = pK+\log([HCO_3^-]/[CO_{2aqua}])=7.0512+\log([HCO_3^-]/[CO_2])$ anti logarithm is being alkaline reserve $[HCO_3^-]/[CO_{2aqua}]=10^{(pH-pK)}=10^{(7.36-7.0512)}=10^{0.3088}=2,0361/1$. ***Lungs*** when in venous blood erythrocytes deoxy $(H^+His63,58)_4Hb_T$...salt bridges...$4HCO_3^-$ **Shuttle** enzymes by oxygen O_{2aqua} adsorbtion release of protons H^+ and HCO_3^- so in ***Lungs*** evaporates carbon dioxide $CO_2\uparrow_{gas}$ as breathed out in AIR. In such a way two equilibria stabilize arterial oxygen concentration $[O_{2aqua}]=6\cdot10^{-5}$ M with **shuttle** enzymes by oxygen adsorbtion-desorbtion and **CA** buffer system made value pH=7,36 with oxidation driven the exchange metabolism of O_2 and CO_2 respiration to interface human body / environment.

2) Broad band silencing buffer is the protein friendly to pH=7,36 as average pK_a=7,36. This one has to be explained as 47 parallel multiple equilibria of protolytic acid groups of amino acids (shown in Table) with silencing interval from pH=6 to pH=7,36. That create protonate amines $\mathbf{R\text{-}NH_3^+}$ and deprotonate carboxylates $\mathbf{R\text{-}COO^-}$ for functional activity of enzymes in proteins, amino acids, carbonic acids and amines with broadband silencing interval from pH=6 to pH=7,36. For example, glutamic acid pK_a reference to physiologic pH value smaller as $pK_{aR\text{-}COO^-}=4.25<7.36$. So for all **R-COO⁻** groups negative charge at pH=7.36. For protonated amines pK_a are greater for pH 7.36. For example glutamic acid protonated amine have greater $pK_{a\text{-}NH3+}= 8.8 > 7.36$. So for all $\mathbf{R\text{-}NH_3^+}$ groups positive charge at pH=7.36.

Table show 47 constants pK_a for 20 amino acids of four type protolytic equilibria:

acid = base $+H^+$;
1. $\mathbf{R\text{-}COOH} = \mathbf{R\text{-}COO^-} + H^+$;
2. $\mathbf{R\text{-}NH_3^+} = \mathbf{R\text{-}NH_2} + H^+$;
3. $\mathbf{Tyr}\text{-phenol-}\mathbf{OH} = \mathbf{Tyr}\text{-phenol-}\mathbf{O^-} + H^+$,
4. $\text{Cys-SH} = \text{Cys-S}^- + H^+$

Average constant $\mathbf{pK_{a\_mean}}$ value for parallel protolytic equilibria sum is divided by number NpK_a of equilibria:

$$\mathbf{pK_{a\_mean}} = (\Sigma\, pK_{a\,R\,group} + pK_{a\text{-}NH3+} + pK_{a\text{-}COOH})/NpK_a$$

In *Ostwald's dilution law* Attractor pH=7.36 of solution relates to physiologic concentration **C** logarithm:

$$\text{Attractor pH}=\frac{\mathbf{pK_{a\_mean}} - \log \mathbf{C}}{2} = 7.36 \text{ physiologic condition in living organisms}$$

Amino acid and protein at isoelectric point value pH**=IEP** sum of total overall **ion** charge is zero

0——— acidic charge (+)—————zero „**0**" charge **IEP**———in basic medium charge minus (**-**)———→pH scale

$\mathbf{-COOH}$ & $\mathbf{-NH_3^+}$ positive charge ……………………$\mathbf{-COO^-}$ & $\mathbf{-NH_3^+}$…………………… charge is negative $\mathbf{-COO^-}$ & $\mathbf{-NH_2}$

IgG1.pdb. ; 1MBO.pdb;

Amino Acid	pK_{aCOOH}	pK_{aNH3+}	$pK_{aRgroup}$
Isoleucine	2.36	9.68	
Valine	2.32	9.62	
Leucine	2.36	9.60	
Phenylalanine	1.83	9.13	
Cysteine	1.96	10.28	8.18
Methionine	2.28	9.21	
Alanine	2.34	9.69	
Proline	1.99	10.96	
Glycine	2.34	9.60	
Threonine	2.11	9.62	
Serine	2.21	9.15	
Tryptophan	2.38	9.39	
Tyrosine	2.20	9.11	10.07
Histidine	1.82	9.17	6.00
Aspartate	1.88	9.60	3.65
Glutamate	2.19	9.67	4.25
Asparagine	2.02	8.80	
Glutamine	2.17	9.13	
Lysine	2.18	8.95	10.53
Arginine	2.17	9.04	12.48

Attractor pH=7,36 ±0.01 at physiologic conditions

Table given maximal $pK_{a\text{-}COOH^-}$ value smaller about 7,36:

$pK_{a\text{-}COOH^-}=4.25<7{,}36$ and given

smallest $pK_{a\text{-}NH3+}$ value grater about $7{,}36<8{,}80=pK_{a\text{-}NH3+}$

Table5.3 Reginald H. Garrett, Charles M. Grishman, **Biochemistry**, University of Virginia 1995

Myoglobin $\mathbf{pK_{a\_mean}}$ =7,3641 attractor concentration **C** =$10^{-7,3559}$ M

Albumin molecule E7G.pdb 7,32=IEP 7 fatty acids small (–) charge and 7,40=IEP absent faaty acids small (+) positive at physiologic pH=7.36, but gamma *Globulin* IgG1.pdb molecule has positive (+) charge, as is greater $\mathbf{pK_{a\_mean}}$ =IEP=7.91 at physiologic pH=7.36.

Attractor pH=7.36 physiologic concentration is **C**=$10^{-6,80838}$ M

Human genome encoded 31078 are identified 23371 and unknown 7707 proteins. Attractor 7,36 pH concentration ranges from $10^{-6,2}$ M to $10^{-7,4002}$ M and average mean 10^{-7} M. Refer to 20000 proteins in summary concentration is $2*10^{-3}$ = 0,002 M. For bicarbonates summary $[CO_{2aqua}]+[HCO_3^-]$=0,023 M determins pH=7,36 as well 20 alpha L-amino acids providing Attractor pH=7,36 concentration for all proteins in organisms. For example 18 proteins:

$$pH=\frac{pK_a - \log C}{2} = \frac{7{,}3198 - \log 10^{-7{,}4002}}{2} = \mathbf{14{,}720}/2 = 7{,}36$$ albumin Attractor concentration is C=$10^{-7,4002}$ M .

pH=$\frac{pK_a - \log C}{2} = \frac{7{,}3641 - \log 10^{-7{,}3559}}{2}$=**14,720**/2=7,36 mioglobin Attractor concentration is C=$10^{-7{,}3559}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7{,}91162 - \log 10^{-6{,}80838}}{2}$ =**14,720**/2=7,36 γ-globulin Attractor concentration C=$10^{-6{,}80838}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{8{,}5228261 - \log 10^{-6{,}2}}{2}$=**14,720**/2=7,36 AQP-0 Attractor concentration C=$10^{-6{,}2}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7{,}637963 - \log 10^{-7{,}082}}{2}$=**14,720**/2=7,36 AQP-1 Attractor concentration C=$10^{-7{,}082}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7{,}36988 - \log 10^{-7{,}3502}}{2}$=**14,720**/2=7,36 CA-2 Attractor concentration C=$10^{-7{,}3502}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7{,}48983 - \log 10^{-7{,}23017}}{2}$ =**14,720**/2=7,36 CATALASE Attractor conc. C=$10^{-7{,}23017}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7{,}9782 - \log 10^{-6{,}7418}}{2}$=**14,720**/2=7,36 PCTP Attractor conc. C=$10^{-6{,}7418}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7{,}3515556 - \log 10^{-7{,}3684444}}{2}$=**14,720**/2=7,36 CERT Attractor conc. C=$10^{-7{,}3684}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7{,}8124638 - \log 10^{-6{,}9075362}}{2}$ =**14,720**/2=7,36 CPTP Attractor conc. C=$10^{-6{,}9075}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7{,}6758065 - \log 10^{-7{,}0441935}}{2}$=**14,720**/2=7,36 ACD11 Attractor conc. C=$10^{-7{,}04419}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7{,}5906111 - \log 10^{-7{,}1293889}}{2}$ =**14,720**/2=7,36 GAP ASAP1 Attractor conc. C=$10^{-7{,}1293889}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7{,}6496 - \log 10^{-7{,}0704}}{2}$ =**14,720**/2=7,36 mouse STARD4 Attractor conc. C=$10^{-7{,}0704}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{8{,}0456818 - \log 10^{-6{,}6743182}}{2}$ =**14,720**/2=7,36 human STARD1 Attractor conc. C=$10^{-6{,}6753}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7{,}4338926 - \log 10^{-7{,}2861074}}{2}$ =**14,720**/2=7,36 KES1_YEAST Attractor conc. C=$10^{-7{,}286}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{8{,}1354167 - \log 10^{-6{,}5845833}}{2}$ =**14,720**/2=7,36 NLTP1_WHEAT Attractor conc. C=$10^{-6{,}58458}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7.8727 - \log 10^{-6{,}8473}}{2}$ =**14,720**/2=7,36 COX-2 human 1DIY.pdb Attractor conc. C=$10^{-6{,}8473}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7.6666087 - \log 10^{-7{,}0533913}}{2}$=**14,720**/2=7,36 ADH IV human Attractor conc. C=$10^{-7{,}0533913}$ M

pH=$\frac{pK_a - \log C}{2} = \frac{7{,}7505286 - \log 10^{-6{,}96947}}{2}$=**14,720**/2=7,36 human AR TES Attractor conc. C=$10^{-6{,}96947}$ M

3) pH=7,36 second is dominate phosphate buffer system. Henderson Haselbalh studies on **system** middle point [$\mathbf{Na_2HPO_4}$]=[$\mathbf{NaH_2PO_4}$] pH has equal to constant value pH=**p**$\mathbf{K_a}$=7,199 .

$$7.199 = \mathbf{pK_a+log}\ \frac{[HPO_4^{2-}]}{[H_2PO_4^{-}]}\ ;\ \text{as}\ \mathbf{log}\ \frac{[HPO_4^{2-}]}{[H_2PO_4^{-}]} = \mathbf{log\ 1}=0$$

Calculate the ratio [$\mathbf{HPO_4^{2-}}$] / [$\mathbf{H_2PO_4^-}$] of solution having **Attractor pH** =7,36 value !

$$\text{Attractor } 7.36 = \mathbf{pK_a+log}\ \frac{[HPO_4^{2-}]}{[H_2PO_4^{-}]}\ ;\ \text{ratio}\ \frac{[HPO_4^{2-}]}{[H_2PO_4^{-}]} = 10^{7.36-7.199} = 10^{0.161} = 1.45\ \text{the ratio}$$

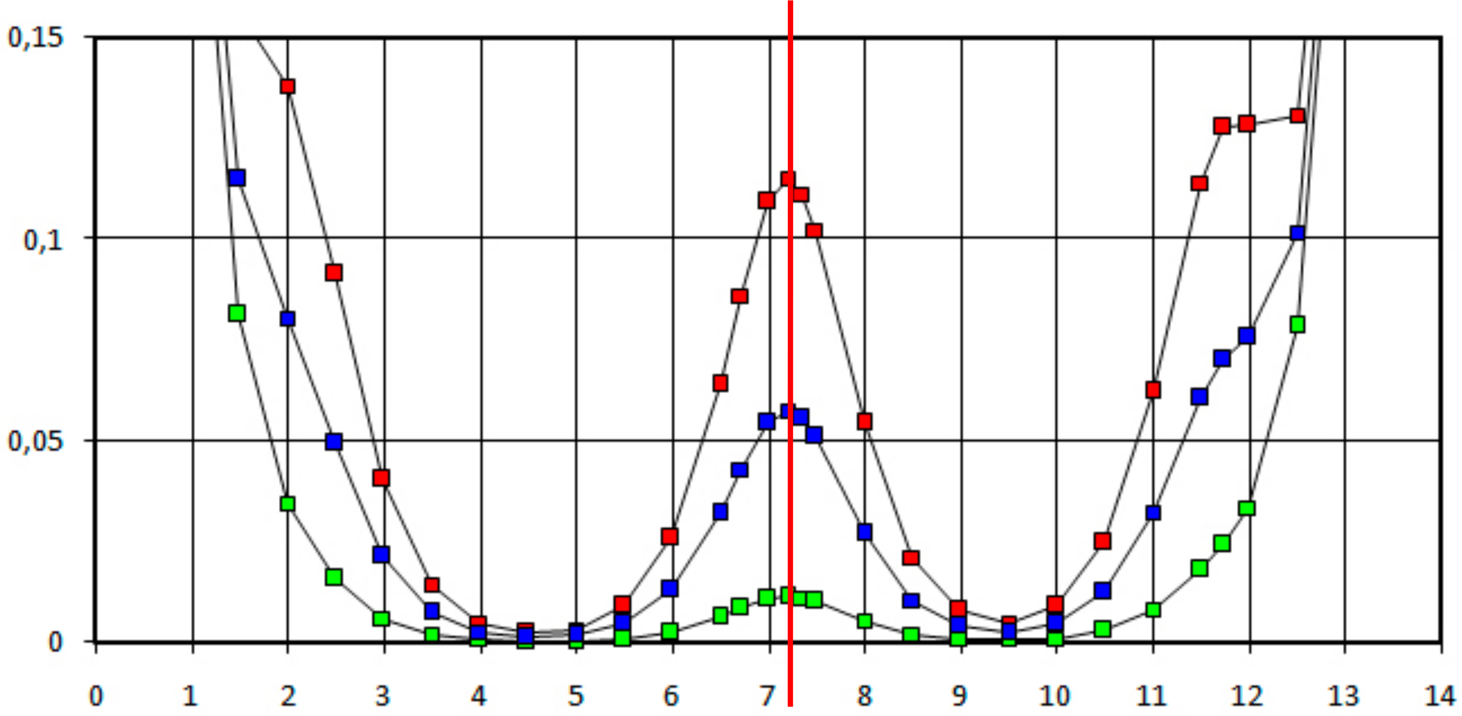
Salt [$\mathbf{HPO_4^{2-}}$] prevails over weak acid form [$\mathbf{H_2PO_4^-}$] times 1.45 as ratio .

Buffer capacity **β** on buffer system middle point is friendly to Attractor 7.36.

1 Buffer solution dilution dose no change value pH is constant as $\mathbf{n_{salt}/n_{acid}}$= constant.
the same for ten times diluted buffer $\mathbf{n_{salt}/n_{acid}}$=const. amount ratio logarithm is log(1)=0!
1.a Water drinking in human organism pH=7,36 value do not change and not intact!
2. Buffer capacity is proportional to concentration **β~C** !
3. Buffer solution **Middle point pH=p**$\mathbf{K_a}$ **.** Buffer capacity has the maximal value $\mathbf{\beta_{max}}$!

Mark on graph maximum !

β , eq.mol/L **$H_3PO_4/H_2PO_4^-$** **p**$\mathbf{K_a}$**=7.199, $H_2PO_4^-/HPO_4^{2-}$** **HPO_4^{2-}/PO_4^{3-}**



Concentration of Buffer solution C_{buffer}=0.2 M 🟥 red

pH→

Concentration of Buffer solution C_{buffer}=0.1 M 🟦 blue

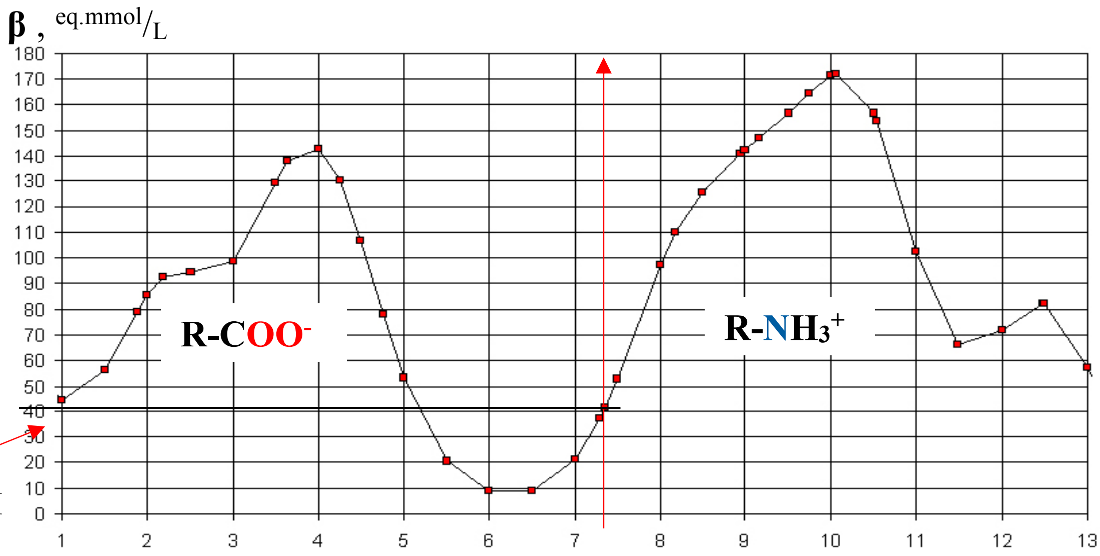
Concentration of Buffer solution C_{buffer}=0.02 M 🟩 green

4. Buffer capacity at **middle point** is $\mathbf{\beta_{max}}$ = 0.55•C as **β=0.55•0.2** = **0.11** eq.mol/L and **β'=0.55•0.02=0.011** eq.mol/L !

5. Buffer solution **middle point** Buffer capacity against the acid and the base is symmetrically equal $\mathbf{\beta_{ac}=0.11}$ eq.mol/L=$\mathbf{\beta_b}$, $\mathbf{\beta'_{ac}=0.011}$ eq.mol/L=$\mathbf{\beta'_b}$!

Proteins buffer have silence region from **pH=6** to 7.36 . 23 thousand protein total buffer solution concentration is C_{buffer}=3 mM. Muscle cytosol proteins the Buffer capacity at physiologic pH=7.36 is

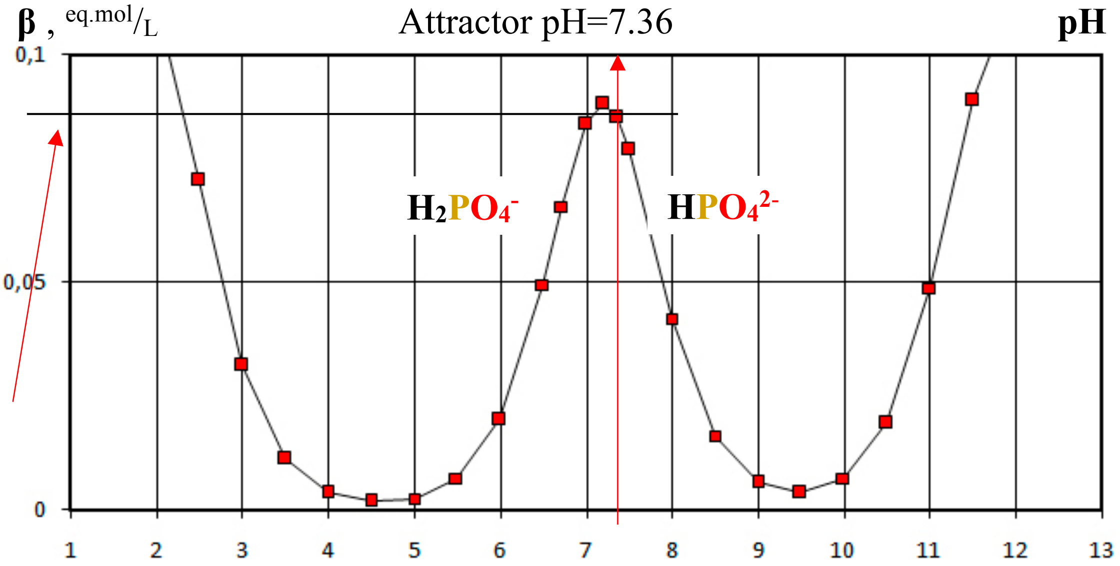
β =40 mM
30.3 %=40/132*100%



Total phosphate buffer systems concentration [$H_2PO_4^-$]+[HPO_4^{2-}] in muscle cells cytosol is C_{buffer}=0.155 M

The Buffer capacity at physiologic pH=7.36 is

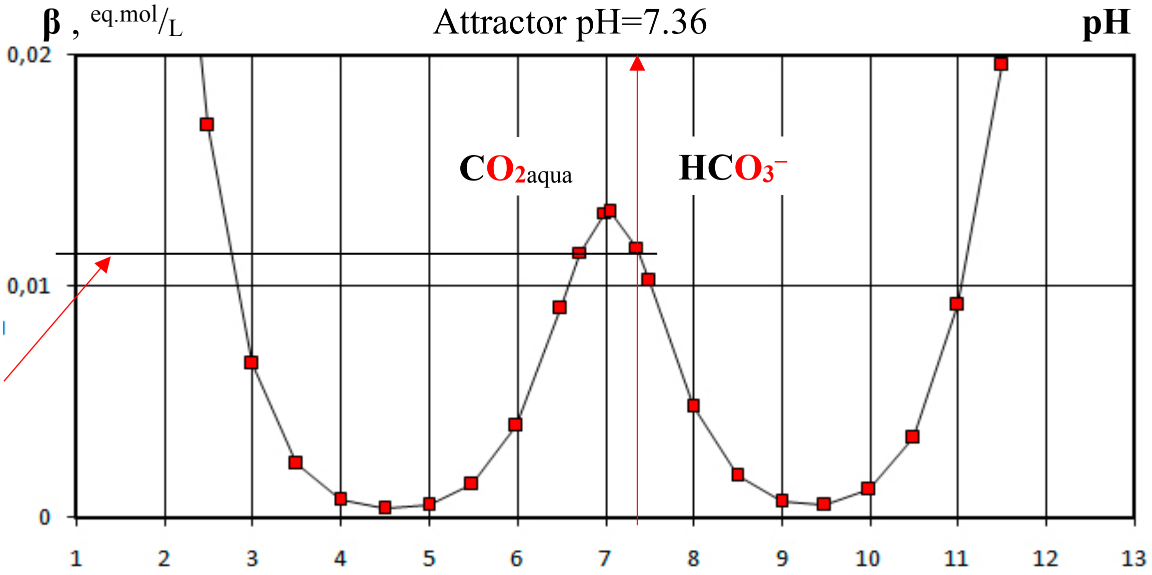
β =80 mM
66.6 %=80/132*100%



Total bicarbonate buffer system concentration [CO_{2aqua}]+[HCO_3^-] is

C_{buffer}=0.023 M.
The Buffer capacity at physiologic pH=7.36 is

β =12 mM
9.1 %=12/132*100%



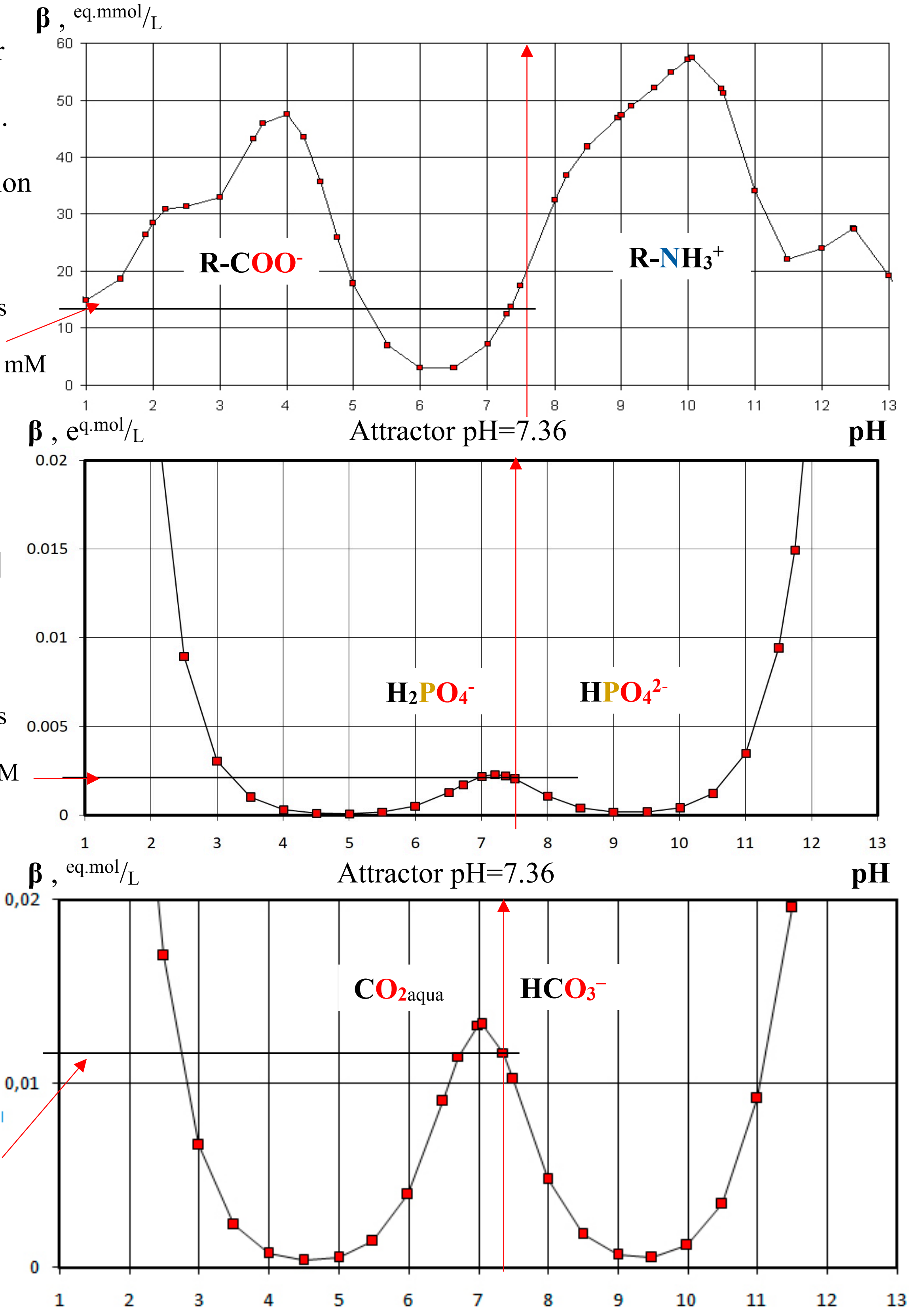
Total Buffer capacity β_{sum}=40+80+12=132 eq.mmol/L ; Attractor pH=36 **pH**

Figure 3. Cytosol muscle cells. Buffer capacities versus pH values from 1 to 13. Actual buffer capacity at Attractor pH=7.36 for two dominate phosphates , bicarbonate and total protein made buffer capacity sum.

proteins + phosphates + bicarbonate ,
at pH=7.36: proteins +([$H_2PO_4^-$]+[HPO_4^{2-}])+([CO_{2aqua}]+[HCO_3^-]),
total buffer capacity: 100% = **30.3 %** + **66.6 %** + **9.1** %;

Buffer capacity is acid Δn_{ac} or base Δn_b equivalent_mols / in one Liter changing pH per one unit **ΔpH=**±1.

Three buffer systems in human organism by total sum as stabile attractor pH=7.36 create in Cytosol muscle cells functional activity as charged groups. **R-COO⁻**, **R-NH3⁺**, **HPO_4^{2-}**, **R-PO_4^{2-}**, **HCO_3^-**.



Proteins buffer have silence region from **pH=6** to 7.36 . Protein total buffer solution concentration C_{buffer}=1 mM for albumin.

The Buffer capacity at physiologic pH=7.36 is

β =12 mM

46.15%=12/26*100%

Total phosphate buffer systems concentration [$H_2PO_4^-$]+[HPO_4^{2-}] in blood plasma C_{buffer}=0.004 M.

The Buffer capacity at physiologic pH=7.36 is

β =2 mM

7.7 %==2/26*100%

Total bicarbonate buffer system concentration [CO_{2aqua}]+[HCO_3^-] in blood plasma is

C_{buffer}=0.023 M.

The Buffer capacity at physiologic pH=7.36 is

β =12 mM

46.15%=12/26*100%

Total Buffer capacity β_{sum}=12+2+12=26 $^{eq.mmol}/_L$ Attractor pH=7.36 **pH**

Figure 4. Extra Cellular space Blood plasma. Buffer capacities versus pH values from 1 to 13. Actual buffer capacity at Attractor pH=7.36 for two dominate phosphates , bicarbonate and total protein made buffer capacity sum. proteins + phosphates + bicarbonate ,
at pH=7.36: proteins +([$H_2PO_4^-$]+[HPO_4^{2-}])+([CO_{2aqua}]+[HCO_3^-]),
total buffer capacity: 100% = **46.15%** + **7.7%** + **46.15%**;

Buffer capacity is acid Δn_{ac} or base Δn_b equivalent_mols / in one Liter changing pH per one unit **ΔpH**=±1.

Three buffer systems in human organism by total sum as stabile multipurpose Attractor pH=7.36 create in Extra Cellular, Blood plasma functional activity with charged groups **R-COO**$^-$, **R-NH**$_3^+$, **HPO**$_4^{2-}$, **R-PO**$_4^{2-}$, **HCO**$_3^-$ as free and linked in amino acids, proteins, nucleic acids, carbohydrates, coenzymes **R** molecules.