## Aris Kaksis, dep. Human Physiology and Biochemistry, <u>aris.kaksis@rsu.lv</u>, Riga Stradin's University, Functionally activate oxygen and carbon dioxide molecules with high rate protolysis equilibria as Biosphere Self-Organization Attractors create perfect order homeostasis reactions to link bioenergetic.

**Abstract.** The quantitative studies for oxygen and carbon dioxide functional activity reveal multiply generated Self-Organization Attractors: pH=7.36, enzyme Carbonic Anhydrase reactivity, water concentration  $[H_2O]=55.3 \text{ mol/}_{Liter}$ , air oxygen level 20.95 %, osmolar concentration 0.305 M, ionic strength 0.25 M, temperature 310.15 K degree etc.. <sup>[1]</sup> High rate protolysis with water make oxygen fire safe and **CO**<sub>2aqua</sub> functional active for Life Biochemistry. In 2023 are hundred Years of Brønsted - Lowry protolysis with water, which high rate protonation stay at equilibria while homeostasis continues. Dissolute oxygen forms <u>arterial</u> concentration [O<sub>2aqua</sub>]=6\*10<sup>-5</sup> M as safe Bioenergetic sustaining isooxia with Attractors of Self-Organization. <sup>[3]</sup>

Thermodynamic indicate Biosphere indispensability to reach Self-Organization Attractor values. Destiny is trend to minimum of free energy change in homeostasis. Attractors made functionally active molecules Self-Organize the perfect reactions order in homeostasis. <sup>[2,3,4]</sup> Deviation from Attractor values disorder the homeostasis. The Chaos stops the homeostasis which disappears as extinct from Biosphere.

Keywords: Biosphere, Thermodynamics, Self-Organization, Attractors, Bioenergetics.

**Introduction**. Ilya Prigogine in 1954 demonstrates the isolate mixture of compounds in reactions trend reach Free energy change minimum at equilibrium state. <sup>[2]</sup> Prigogine in 1977 declares: equilibrium state is Attractor for non-equilibrium state in reactions mixture of compounds. <sup>[3,4]</sup> Prigogine explains perfect order formation as Self-Organization Attractors for Universe and Sciences.

About Universe creation in perfect order Maria Kuman:,,The nonlinear no equilibrium theory of Prigogine is also called The Chaos Theory because it claims that our Universe was created in perfect order out of the chaos.". <sup>[5]</sup> Chaos is just apparent disorder. The Biosphere belongs to our human civilization as part of perfect Universe.

Attractors create perfect order with functionally active molecules. Self-Organization with Attractors in dissipative structures makes the homeostasis order. Biochemistry Thermodynamic studies indicate Attractor vales of two types: the primary Attractors are common for Life Biosphere (air oxygen level 20.95 % O<sub>2</sub>, Carbonic Anhydrase CA reactivity), the secondary Attractors are for individual organisms (generate concentration gradients, isooxia-homeostasis Norma) and multipurpose Attractor values (pH=7.36, water, concentration).

Free energy content for protolysis products  $H_3O^++OH^-$  increases to 99.8 kJ/mol from  $H_2O+H_2O$  zero 0: to  $H_2O+H_2O <=>H_3O^++OH^-$ ;  $K_{H3O+OH}=[H_3O^+]*[OH^-]/[H_2O]^2=3.26 \cdot 10^{-18}$ ;  $\Delta G_{H3O+OH}=-R \cdot T \cdot ln(K_{H3O+OH})=99.8$  kJ/mol.

#### **Thermodynamic methods**

Four Attractors and decreased Oxygen power for functional activity isooxia. Water triplet state of oxygen, its concentration  $[H_2O]=55.3 \text{ mol/}_{\text{Liter}}$ , air oxygen level 20.95 % for five hundred million Years, pH=7.36 for the concentration  $[H_3O^+]=10^{-7.36}$  M.

Water solution oxygen keeps triplet state for temperatures from  $0^{\circ}$  C to  $100^{\circ}$  C. Oxygen no reaction with water, prevent singlet formation and is inactive. **Triplet** oxygen atoms in molecule bound with three covalent bonds •:O=O:•, however degenerate electron pair loosen another covalent orbital as radical, therefore in total **triplet** exhibit <u>double bond</u> :O=O: .

Air oxygen 20.95 % concentration as Attractor forms functional active solutions in arterial and venous blood. Blood plasma contact interface with air dissolute  $[O_{2aqua}]=9.77 \cdot 10^{-5}$  M concentration, if osmolarity is Cosm=0.305 M, ionic strength I=0.25 M, air oxygen is 20.95 %. <sup>[6,1]</sup> Blood solubility constant Ko2\_blood is:  $1 0.7 0 \times 10.5 0.005 10.222 M 10 pV02 blood$ 1/10

$$\mathbf{K}_{O2blood} = [\mathbf{O}_{2aqua}] / [\mathbf{O}_{2gas}] = 9.768 \times 10^{-5} / 0.2095 = 10^{-5.55} \text{ M} = 10^{-p} \mathbf{K}_{O2blood}.$$

Oxygen water solutions through membrane aquaporins in osmosis against concentration gradients form arterial  $[O_{2aqua}] = 6*10^{-5}$  M and venous  $[O_{2aqua}] = 0.426 \cdot 10^{-5}$  M <u>concentrations</u> <sup>[6]</sup>, what corresponds to isooxia (homeostasis Norma).  $O_{2gas_AIR}+H_2O+\Delta G < \underline{Aquaporins} = > O_{2aqua-Blood}+Q$ .

Hyperoxia, oxygen excess as oxidative stress with acidosis mechanism accumulate increasing Free energy content. The oxygen becomes fire-insecure for Biochemistry as oxidative stress hazard for Life.

Note: Oxidative stress causes **non enzymatic** oxidation in multiple radical chain and reactions of parallel products formation to contaminate and destroy the organism! Destructive hazard for Life!

Rotating Electrode Method and Oxygen Reduction Electro catalysts: detect oxygen solubility.

Solubility at 25° C 298.15 K divide gas mol fraction one  $[O_{2gas}]=1: [O_{2aqua}]=K_{O2}=1.22*10^{-3} \text{ M/1}= \frac{[O_{2aqua}]}{[O_{2aqua}]} .$ <sup>[7]</sup>

Atmosphere oxygen 20.95 % mol fraction is 0.2095. Solubility from air 20.95 % proportional to mol fraction

 $[O_{2agua}] = 1.22 \times 10^{-3} \times 0.2095 = 2.556 \times 10^{-4} \text{ M}$ . Mol fraction of water solution is ratio:  $[O_{2agua}]/[H_2O]$ .

Thermodynamic solubility product is calculates in ratio:

 $\mathbf{K}_{sp} = \frac{[\mathbf{O}_{2 \text{ aqua}}]}{[\mathbf{O}_{2 \text{ gas}}] \cdot [\mathbf{H}_{2}\mathbf{O}]} = \mathbf{K}_{\mathbf{O}2} / [\mathbf{H}_{2}\mathbf{O}] = 1.22 \times 10^{-3} / 55.3 = 2.205 \times 10^{-5} \text{ and Free energy change minimum in expression:}$  $G_{02aqua} = \Delta G_{sp} = -R \bullet T \bullet ln(K_{sp}) = -8.3144 * 298.15 * ln(2.205 * 10^{-5}) = 26.58 \text{ kJ/mol}. \text{ Water solution oxygen free energy}$ content increases about 26.58 kJ/mol, but inactive triplet oxygen is most negative benefit Attractor for homeostasis.

Table 1. Standard  $\Delta H^{\circ}_{Hess}$ ,  $\Delta S^{\circ}_{Hess}$  and  $\Delta G^{\circ}_{Hess}$  values of formation from elements, at ionic strength 0.25 M, at 298.15 K degree.<sup>[1]</sup>Biochemistry thermodynamic 2006<sup>[8]</sup>in bold are data for pH=7.36.

Substance	$\Delta H^{\circ}_{Hess}$ , $kJ/mol$	$\Delta S^{\circ}_{Hess}$ , $J/_{mol/K}$	$\Delta G^{\circ}_{Hess}$ , $kJ/mol$	Free energy content accumulation <sup>kJ</sup> / <sub>mol</sub>
O2aqua	-11,70	-94,2	16,40	
O2aqua	-11,715	110,876	16,4	
O <sub>2gas</sub>	0	205,152	-61,166	
H <sub>3</sub> O <sup>+</sup>	-285,81	-3,854	-213,275	Protolysis accumulates in ions H <sub>3</sub> O <sup>+</sup> +OH <sup>-</sup> :
OH-	-230,015	-10,9	-157,2	G <sub>H30++0H</sub> .=99.8
H <sub>2</sub> O	-285,85	69,9565	-237,191	$G_{02}=303.1 \text{ kJ/mol}; G^{\circ}_{H2gas}=\frac{85,64}{8} \text{ kJ/mol}; \text{ Alberty} [8]$
$H_2O$	-286,65	-453,188	-151,549	
CO <sub>2</sub> aqua	-413,798	117,5704	-385,98	Solubility accumulate energy $\Delta G_{spCO2aqua} = 8.3845 \text{ kJ/mol};$
CO <sub>2</sub> gas	-393,509	213,74	-394,359	· · · · ·
HCO <sub>3</sub> -	-692,495	-494,768	-544,969	Hess for: Enthalpy $\Delta H_{\text{Hess}}$ , for Entropy $\Delta S_{\text{Hess}}$ , and
HCO <sub>3</sub> -	-689,93	98,324	-586,94	for Free energy $\Delta G_{\text{Hess}}$ .

 $O_{2\text{gas AIR}}+H_2O+\Delta G \xrightarrow{\text{Aquaporins}} = >O_{2\text{aqua-Blood}}+Q.$ 

Exothermic:  $\Delta H_{\text{Hess}}$ =-11.7 kJ/mol, Endoergic:  $\Delta G_{\text{Hess}}$ =77.6 kJ/mol,  $\Delta S_{\text{dispersed}}$ =- $\Delta H_{\text{Hess}}$ /T=39.2 J/mol/K. Solubility Hess Entropy  $\Delta S_{\text{Hess}} = \Delta S^{\circ}_{\text{O2}aqua-Blood} - \Delta S^{\circ}_{\text{O2}gas-AIR} = -299 \text{ J}_{\text{mol/K}};$ Solubility collect Hess Free energy in oxygen one mol O<sub>2aqua-Blood</sub> is positive value:

 $\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} = -11.7 - 298.15 * -0.299352 = 77.55 \text{ kJ/mol} endoergic.$ 



products O<sub>2aqua-Blood</sub>.

Figure 1. Exothermic and endoergic Hess oxygen solubility having Free energy change positive  $\Delta G_{Hess}=77.55 \text{ kJ/mol}$ , but minimized Free energy change  $\Delta G_{min}=\Delta G_{sp}=G_{02aqua}=26.58 \text{ kJ/mol}$  reaching solubility product equilibrium mixture:

 $K_{sp} = \frac{[O_{2 \text{ aqua}}]}{[O_{2 \text{ gas}}] \cdot [H_2 O]} = 2.205 * 10^{-5}.$ 

Le Chatelier principle is reaching Prigogine declared Attractor for non-equilibrium state Free energy change minimum  $\Delta G_{min}$ . Non- equilibrium mixture of compounds trends reaching equilibrium state - minimum  $\Delta G_{min}$ , but

never do as homeostasis is non-equilibrium state.

Blood plasma oxygen is strong oxidant according half reaction classic standard potential Eo=1.229 Volts <sup>[2]</sup>:  $O_{2aqua}+4H_3O^+ + 4e^- <=> 6H_2O$ ; E°=1.383 V thermodynamic standard potential; oxidized form free electrons reduced form.

1) Two **Attractors**: air oxygen **O**<sub>2</sub> 20.95 % and pH=7.36 minimize Free energy content in one mol of **O**<sub>2aqua</sub>, with arterial blood concentration  $[O_{2aqua}]=6*10^{-5}$  M and pH=7.36 concentration  $[H_3O^+]=10^{-7.36}$  M.

 $E = E_o + 0.01478 \bullet lg([\text{O}_{2aqua}] \bullet [\text{H}_3\text{O}^+]^4) = 1.229 + 0.01478 * log(6*10^{-5}*10^{-7.36*4}) = 0.731 \text{ Volts} \ .$ 

Oxidative stress potential decreases about  $\Delta E_{02aqua pH} = E - E_0 = 0.73 - 1.229 = -0.497$  Volts and minimizes Free energy content for oxygen about:  $\Delta G_{min} = \Delta E_{02aqua pH} * F * n = -0.497 * 96485 * 4/1000 = -192 kJ/mol$ .

2) Attractor water concentration decreases thermodynamic standard potential from

1.383 Volts to classic standard potential 1.229 Volts <sup>[1]</sup> about -0.154 Volts = $\Delta E_{H20}$ .

Water concentration  $[H_2O]=^{996.23}/_{18}=55.3$  M value forms thermodynamic standard potential E°=1.383 Volts which classically included in E<sub>o</sub> classic standard potential:

 $E_0 = E^{\circ} + \frac{0.0591}{4} \log(\frac{1}{[H20]^6}) = 1.383 + 0.01478 \log(\frac{1}{55.346^6}) = 1.229$  Volts;

Attractor [H2O] concentration oxidative stress potential decreases about: ΔE<sub>H2O</sub>=E<sup>°</sup>-E<sub>o</sub>=1.229-1.383=-0.154
Volts and minimizes Free energy content decreasing about ΔG<sub>arterial</sub>=ΔE<sub>H2O</sub>\*F\*n=-0.154\*96485\*4/1000=-59.82
<sup>kJ</sup>/<sub>mol</sub>. Total oxidative stress potential decreases about ΔE=ΔE<sub>O2aqua\_pH</sub>+ΔE<sub>H2O</sub>=-0.497-0.155=-0.652 Volts. With Attractors of air O<sub>2</sub> 20.95 %, pH=7.36 and [H2O]=55.3 M total water solution Free energy decreases about: G<sub>O2Biochem\_arterial</sub>=G<sub>O2aqua</sub>+ΔG<sub>arterial</sub>+G<sub>O2sp</sub>=303.1-251.6+26.58=78.08 <sup>kJ</sup>/<sub>mol</sub>. Poetic one says to smother the flame. Oxygen becomes fire safe–functional active Norma for Life. Strong oxidant free energy content G<sub>O2=303.1</sub> <sup>kJ</sup>/<sub>mol</sub> becomes G<sub>O2Bio</sub>=237,2-151.55=78.08 <sup>kJ</sup>/<sub>mol</sub> times 3.88 less active therefore fire safe for Biochemistry with free energy G<sub>O2Bio</sub>=78.08 <sup>kJ</sup>/<sub>mol</sub>. Free energy content with potential decrease prevents oxidative stress. Extra Free energy accumulation increases oxygen power and create hyperoxia, which disorder homeostasis with chaotic oxidation. That destroy organism with abnormal activate O<sub>2aqua</sub> molecules.

NASA Apollo project closed 1972 due to hyperoxia, because astronauts had to work in pure 100 % oxygen atmosphere, which is five times greater about global Attractor value 20.95 % oxygen. Hyperoxia is hazard nor for astronauts nor for NASA technologic Apollo equipment devices.

Hypoxia is specific order of homeostasis for decreased oxygen concentration. Hypoxia switch on the Hypoxia Induced Factors cell proteins HIF, which work on nuclear receptors induce in cells processes with decreased oxygen concentration - deficiency. The Nobel Prize 2019 in Medicine.

#### Synthesis of Carbonic Anhydrase CA indispensable Attractor.

Carbonic Anhydrase reactivity and generate Physiologic buffer solutions total equilibrium value pH=7.36 as Self-Organization Attractors. In reaction CO<sub>2</sub>+2H<sub>2</sub>O products (CO<sub>2aqua</sub>) H<sub>3</sub>O<sup>+</sup>+HCO<sub>3</sub><sup>-</sup> accumulate free energy content GH3O++HCO3-=8.38 kJ/mol+60 kJ/mol is indispensable for functional activity of bicarbonate buffer system on the planet Earth for perfect reactions order in homeostasis complex processes.

 $CO_2$  no reaction with water  $H_2O$  at absence of CA.  $CO_2$  is small soluble and slow react with  $OH^-$ . Solubility  $CO_{2gas} + H_2O + \Delta G \le CO_{2aqua} + Q$  product constant:  $K_{spCO_{2aqua}} = [CO_{2aqua}]/[CO_{2gas}]/[H_2O] = 0.034$  is unfavored but exothermic  $\Delta H_{\text{Hess}} = \Delta H^{\circ} C_{2ag} - \Delta H^{\circ} C_{2as} = -20.3 \text{ kJ/mol}$ .

 $\Delta G_{spCO2aqua} = -R \cdot T \cdot ln(K_{spCO2aqua}) = -8.3144 \cdot 298.15 \cdot ln(0.034045)/1000 = 8.379 \cdot kJ_{mol}$  minimum. Air 0.04 % mol fraction [CO<sub>2gas</sub>]=0.0004 dissolute concentration is:

 $[\mathbf{CO}_{2aqua}] = \mathbf{K}_{spCO2aqua} * [\mathbf{H}_{2}\mathbf{O}] * [\mathbf{CO}_{2gas}] = 0.034045 * 55.3457 * 0.0004 = 0.000753 \text{ M}.$ Carbon dioxide  $CO_{2aqua}$  react with  $OH^{-}$  times 10<sup>6</sup> slower about neutralization reaction:

 $H_3O^+ + HCO_3 = >CO_{2aqua} + 2H_2O + \Delta G + Q$ , because neutralization velocity constant is  $k_2 = 5.16885 \times 10^{18} \text{ M}^{-2} \text{s}^{-1}$ . but OH<sup>-</sup> ions: CO<sub>2aqua</sub>+OH<sup>-</sup>=>HCO<sub>3</sub><sup>-</sup> velocity constant  $k_{10H}$  is from  $1.5 \times 10^2$  M<sup>-2</sup>s<sup>-1</sup> to 1.5 M<sup>-2</sup>s<sup>-1</sup>. Reaction is

favored  $\Delta G_{\text{Hess}HC03}$ -=G<sub>HC03</sub>--(G<sub>C02aqua</sub>+G<sub>OH</sub>-)=46,08-(8,379+77,36)=-**39,66** kJ/mol with equilibrium constant:  $[HCO_{3}]/[CO_{2aqua}]/[OH^{-}]=K_{eq_HCO_{3}}=EXP(-\Delta G_{eq_HCO_{3}}/R/T)=EXP(39659/8,3144/298,15)=8871734=10^{6,948},$ with exothermic heat production Q:  $\Delta H_{\text{Hess}} = \Delta H^{\circ}_{\text{HCO3}} - \Delta H^{\circ}_{\text{CO2}} - \Delta H^{\circ}_{\text{OH}} = -48.68 \text{ kJ/mol}$ . HCO3<sup>-</sup> => CO<sub>2aqua</sub>+OH<sup>-</sup>:  $k_{10H-}/k_{2HCO3} = K_{eq_HCO3} = 1.5 \times 10^2 / k_{2HCO3} = 8871734; k_{2HCO3} = k_{10H-}/K_{eq_HCO3} = 1.5 \times 10^2 / 8871734 = 1.6908 \times 10^{-5}.$ Decomposition  $HCO_3 = CO_{2aqua} + OH^{-1}$  velocity constant  $k_{2HCO3}$  is from 1.6908\*10<sup>-5</sup> to 1.6908\*10<sup>-7</sup>. Reaction with **OH** ions is hundred billions to ten trillion 10<sup>13</sup> times slower about CA Carbonic Anhydrase velocity

constant.

CA Carbonic Anhydrase protolytic reactivity create functional active bicarbonate buffer Self-Organization Attractor pH=7.36 with generate concentration gradients for transport  $H_3O^+$ ,  $HCO_3^-$ ,  $CO_{2aqua}$  and osmosis.<sup>[9]</sup> CA Carbonic Anhydrase high rate protolysis reaction of CO<sub>2aqua</sub> with two water molecules:

 $CO_{2aqua}+2H_2O+\Delta G+Q=v1CA>H_3O++HCO_3$  and velocity constant is:  $k_{1CO2aqua}=1.5\times10^8 M^{-1}s^{-1}$ . [9] Neutralization  $H_3O^+$ + $HCO_3^-$ <=CA> $CO_{2aqua}$ + $2H_2O$  velocity constant is times  $10^{10.54}$  higher about Carbonic Anhydrase velocity constant:  $k_2/k_1c_{02aqua}=5.16885*10^{18}/1.5/10^8=10^{10.54}$ .

CA protolysis equilibrium constant have calculated in the velocity constants ratio expression:

 $\mathbf{K_{eqCAHCO3aqua}=k_{1CO2aqua}/k_{2}=\frac{[\text{HCO}_{3}^{*}]_{aqua}.[\text{H}_{3}\text{O}^{+}]}{[\text{CO}_{2}]_{aqua}\cdot[\text{H}_{2}\text{O}]^{2}}=\mathbf{K}_{a\_CO2aqua}/[\text{H}_{2}\text{O}]^{2}=10^{\wedge(-7.0512)}/55.3^{2}=2.906*10^{-11}=10^{-10.54}.$ 

Bicarbonate buffer system acid protolysis constant  $pK_{a}$  co2<sub>aqua</sub>=7.0512 is friendly to pH=7.36:

 $K_{a}CO2aqua = K_{eq}CAHCO3aqua * [H_2O]^2 = [HCO_3^-]aqua \cdot [H_3O^+] = 10^{-7.0512} = 10^{-p}Ka_CO2aqua$  $[CO_2]_{aqua}$ 

Original pK<sub>a</sub> co<sub>2aqua</sub>=7.0512 obtained and calculate for BUFFER solution.<sup>[1]</sup>

Neutralization:  $H_{3}O^{+}+HCO_{3} <=>CO_{2aqua}+2H_{2}O$  constant is inverse to protolysis and favored:

$$K_{eqNeutralization} = 1/K_{eqCAHCO3aqua} = [HCO_3] * [H_3O^+] / [CO_{2aqua}] / [H_2O]^2 = 1/2.906 / 10^{-11} = 34412000000 = 10^{10.54}.$$

Hess Free energy change is exoergic:  $\Delta G_{\text{Hess}} = 2\Delta G^{\circ}_{\text{H20}} + \Delta G^{\circ}_{\text{C02}} - \Delta G^{\circ}_{\text{H30}} - \Delta G^{\circ}_{\text{HC03}} = -102 \text{ kJ/mol};$ 

```
\Delta G_{\text{Hess}} = 2G_{\text{H20}} + G_{\text{C02qua}} - G_{\text{H30}} - G_{\text{HC03}} = 2*0 + 8.379 - 22,44 - 46,08 = -60.14 \text{ kJ/mol} and
```

Enthalpy Hess change exothermic:  $\Delta H_{\text{Hess}} = 2\Delta H^{\circ}_{H20} + \Delta H^{\circ}_{C02} - \Delta H^{\circ}_{H30} - \Delta H^{\circ}_{HC03} = -7.19 \text{ kJ}_{mol}$ . Neutralization is favored reaction. Free energy change minimum expression is negative:

 $\Delta \mathbf{G}_{eqNeutralization} = -\mathbf{R} \cdot \mathbf{T} \cdot \mathbf{ln} (\mathbf{K}_{eqNeutralization}) = -8.3144 \cdot 298.15 \cdot \mathbf{ln} (34412000000) = -60.14 \text{ kJ/mol.}$ **CO<sub>2aqua</sub>** protolysis minimum is positive:

 $\Delta \mathbf{G}_{eqCAHCO3aqua} = -\mathbf{R} \cdot \mathbf{T} \cdot \mathbf{ln} (\mathbf{K}_{eqCA\_HCO3aqua}) = -8.3144 \cdot 298.15 \cdot \mathbf{ln} (1/34412000000) = \mathbf{60.14}^{kJ/mol}.$ 



Figure 2. Exothermic and exoergic neutralization Hess Free energy change  $\Delta G_{eqNeutralization}$  negative -102 kJ/mol, but minimizes  $\Delta G_{min} = \Delta G_{eqNeutralization} = -60.14 kJ/mol$ reaching equilibrium mixture: KeqNeutralization=34412000000 at presence of CA Carbonic Anhydrase. Carbon dioxide reaction with hydroxide anions is slow

because of small factorials velocity  $k_{1\text{OH}}$  from  $1.5*10^2$  M<sup>-2</sup>s<sup>-1</sup> to 1.5 M<sup>-2</sup>s<sup>-1</sup> and concentrations [CO<sub>2aqua</sub>]=0.0007512 M, [OH<sup>-</sup>]=10<sup>-6.64</sup> M. Carbonic Anhydrase synthesis solved for bioenergetic perfect order homeostasis as Self-Organization Attractor. [3,4]

Reactants  $H_3O^+$ + $HCO_3^-$  products  $CO_{2aqua}$ + $2H_2O_{2aqua}$ 

# pH=7.36 multipurpose Self-Organization Attractor creates positive and negative charged groups R-COO<sup>-</sup>, R-NH<sub>3</sub><sup>+</sup>, HPO<sub>4</sub><sup>2-</sup>, R-PO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> as free and linked in **R** molecules: amino acids, proteins, nucleic acids, carbohydrates, coenzymes.

Buffer systems in the Life organism trend to Self-Organization Attractor **pH** value **7.36**. Each of dominate buffer system have 7.36 friendly maximum (Figure 3. and 4.) of the buffer capacity: dihydrogen phosphate  $pK_{a\_H2PO4}=7.199$ <sup>[1]</sup> and Carbonic Anhydrase create protolysis calculate constant:  $pK_{a\_CO2aqua}=7.0512$ .<sup>[1]</sup>

Table 2. <sup>[6]</sup> Proteins as long chain polypeptides and free amino acids with four type acid groups constitute 47 values for classic acid constants. In three forms pK<sub>a-COOH</sub>, pK<sub>a-NH3+</sub>, pK<sub>aRgroup</sub>:

for deprotonate carboxylate negative anion **R-COO**<sup>-</sup>,

for protonate positive	charged a	ummonium c	cation <b>R-NH</b> 3	+,
neutral phenolic acid Tyr-	H and C	vs <b>-SH</b> neutr	al sulfhydryl	groups.

		1		
Amino Acid	рК <sub>аС</sub> оон	pK <sub>aNH3+</sub>	pKaRgroup	20 amino acids four type protolysis groups
Isoleucine	2.36	9.68		classic 47 acids constant pKa values:
Valine	2.32	9.62		1. <b>R-COOH</b> <=> <b>R-COO</b> <sup>-</sup> + <b>H</b> <sup>+</sup> , 22 values of groups 47;
Leucine	2.36	9.60		2. <b>R-NH</b> <sub>3</sub> +<=> <b>R-NH</b> <sub>2</sub> + <b>H</b> <sup>+</sup> 22+1=23 values of groups 47;
Phenylalanine	1.83	9.13		3. Tyr-phenol-OH<=>Tyr-phenolate-O <sup>-</sup> +H <sup>+</sup> ;
Cysteine	1.96	10.28	8.18	4. Cvsteine-SH<=>Cvsteine-S <sup>-</sup> +H <sup>+</sup> one group.
Methionine	2.28	9.21		Biochemical environment Self-Organization Attractor
Alanine	2.34	9.69		nH-7 36 creates molecules functional activity as charged groups:
Proline	1.99	10.96		pri-7.50 creates inforcedies functional activity as charged groups.
Glycine	2.34	9.60		carboxylate $\mathbf{R}$ - $\mathbf{C}\mathbf{O}\mathbf{O}^{-}$ and ammonium $\mathbf{R}$ - $\mathbf{N}\mathbf{H}_{3}^{+}$ .
Threonine	2.11	9.62		Maximal carboxylate pK <sub>a-CooH</sub> -value smaller about 7.36=pH:
Serine	2.21	9.15		pK <sub>a-COOH</sub> =4.25< including fatty acids too 4.9<7.36 and
Tryptophan	2.38	9.39		smallest ammonium pKa-NH3+ value grater about 7.36<9.04=pKa-NH3+
Tyrosine	2.20	9.11	10.07	NnK <sub>2</sub> number of parallel protolytic equilibria
Histidine	1.82	9.17	6.00	average mean $nK_{a}$ mean value is calculated as:
Aspartate	1.88	9.60	3.65	$nK_{a} = \frac{(\sum nK_{a} - n - \sum nK_{a})}{(\sum nK_{a} - n - \sum nK_{a})} = \frac{(\sum nK_{a} - n - \sum nK_{a})}{(\sum nK_{a} - n - \sum nK_{a})}$
Glutamate	2.19	9.67	4.25	Ostwald's dilution law calculates the pH of solution
Asparagine	2.02	8.80		at concentration C logarithm.
Glutamine	2.17	9.13		nK = log C
Lysine	2.18	8.95	10.53	$nH = \frac{pra_{a}mean}{mean}$
Arginine	2.17	9.04	12.48	2

#### Shuttle hemoglobin stabilized multipurpose Self-Organization Attractor pH=7.36.

Hemoglobin in tissue desorbs oxygen  $O_{2aqua}$  for exchange to  $HCO_3^-$  and  $H^+$  but in lungs releases  $HCO_3^-$  and  $H^+$  due to adsorption of oxygen  $O_{2aqua}$ . <sup>[6]</sup> Exchange equilibrium established oxygen concentration in arterial  $6 \cdot 10^{-5}$  M and venous  $0.426 \cdot 10^{-5}$  M according actual hemoglobin sensitive <u>oxygen concentration in blood</u>:

 $\label{eq:rection} fraction~[(H^+)Hb_T...salt~bridges...(HCO_3^-)]=0.04~,~fraction~[Hb_R(O_2)]=0.96,~^{[6]}~venous~concentration~[O_{2aqua}]=0.426\cdot10^{-5}~M~,$ 

fraction [(H<sup>+</sup>)Hb<sub>T</sub>...salt bridges...(HCO<sub>3</sub><sup>-</sup>)]=0.37, fraction [Hb<sub>R</sub>(O<sub>2</sub>)]=0.63. <sup>[6]</sup> In one blood circulation organism consume 0.96-0.63=0.33 fraction of oxygen from arterial saturated fraction 0.96=[Hb<sub>R</sub>(O<sub>2</sub>)]. <sup>[6]</sup> Stabilized Norma concentrations [HCO<sub>3</sub><sup>-</sup>]=0.0154 M, [CO<sub>2aqua</sub>]=0.0076 M sustain Self-Organization Attractor pH=7.36.

Henderson Haselbalh expression for Brensted protolysis calculates Attractor value 7.36:

 $pH=pK_a+\log \left[\frac{[HCO_3^-]}{[CO_2]_{aqua}}\right] = 7.0512 + \log(0.0154 \text{ M/}0.0076 \text{ M}) = 7.36.$ 

Self-Organization Attractor 7.36 creates functional activity of molecules with charged groups negative, positive: HPO4<sup>2-</sup>, HCO3<sup>-</sup>, R-COO<sup>-</sup>, R-NH3<sup>+</sup>, R-PO4<sup>2-</sup> as free and linked in molecules R: amino acids, proteins, nucleic acids, carbohydrates, coenzymes. 11<sup>th</sup> and 12<sup>th</sup> pages: <u>BUFFER solution</u>. <sup>[1]</sup>



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 phosphate , bicarbonate and total protein made buffer capacity sum. proteins + phosphate + 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  $\Delta n_{ac}$  or base  $\Delta n_b$  equivalent\_mols/ in one Liter changing pH per one unit  $\Delta pH=\pm 1$ .

Three type buffer systems create multipurpose Self-Organized Attractor pH=7.36 for perfect homeostasis order with charged groups as free and linked in molecules R.



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  $\Delta n_{ac}$  or base  $\Delta n_b$  equivalent\_mols/ in one Liter changing pH per one unit  $\Delta pH=\pm 1$ . Three type buffer systems create multipurpose Self-Organized Attractor pH=7.36 for perfect homeostasis order with charged groups as free and linked in molecules R.

11<sup>th</sup> and 12<sup>th</sup> pages: **BUFFER** solution. <sup>[1]</sup>



The primary Self-Organization Attractor air oxygen O<sub>2</sub> 20.95 %.

Figure 5. Dynamic growth of CO<sub>2</sub> in atmosphere last thirty Years. CO<sub>2</sub> and O<sub>2</sub> cycle combined data from: 1991<sup>st</sup> Kotz JC, Purcell KF 700 Gt of CO<sub>2</sub> in atmosphere <sup>[10]</sup>, 2003<sup>rd</sup> White VM 725 Gt of CO<sub>2</sub> <sup>[11]</sup> and 2020<sup>th</sup> Carbon cycle University Calgary 800 Gt of CO<sub>2</sub> in atmosphere. <sup>[12]</sup>

Civilization with regular pollutions add about 1.2 % to atmosphere annual 4.55 Gt to reach **800** Gt  $CO_2\uparrow_{gas}$  in 2020<sup>th</sup> as well bulk 98.8 % irregular changed of totally global and cosmic processes oscillation see on Figure 6. for 600 million Years. Ocean and in all Earth waters dissolute 47 times greater  $CO_{2aqua}$  amount 38500 as in atmosphere 800 Gt, but carbonate (Ca,Mg)CO<sub>3\_solid</sub> sediments in Earth crust contains 70 times more CO<sub>2</sub> as in atmosphere .

The Carbonic Anhydrase and photosynthesis each Year assimilates  $CO_2$  amount 15.4 % from atmosphere 800+4.55 Gt producing glucose 307.5 Gt with carbon mass 120+3 Gt. Photosynthesis evolved oxygen amount in atmosphere 300-147=153 Gt restore and maintain primary Self-Organization Attractor oxygen  $O_2$  level 20.95 % during 500 million Years.

Combustion products  $CO_2$  as carbon amount 2Gt of fossil fuel dissolute warm up the oceans in reaction with OH<sup>-</sup> ions 0.167\*10<sup>15</sup>\*69=11.5\*10<sup>15</sup> kJ. Warming heat in ocean 11.5\*10<sup>15</sup> kJ of  $CO_2$  is more as 100 times less the Photosynthesis and Carbonic Anhydrase cooling -2501\*10<sup>15</sup> kJ the Planet. <sup>[10,11,12]</sup>



Figure 6. Climate reconstruction history since 600 Million Years ago: Atmospheric **CO**<sub>2</sub> content in units' ppm, Earth ice Cover Border Latitude and temperature oscillation from -50° to 45° degrees. <sup>[13]</sup>

Reconstruction climate history of Earth shows temperature and atmospheric content **CO**<sub>2</sub> oscillation, which 600 million Years back in period 10000 Years is observing Earth warming from -50° C to 45° C degrees and carbon(IV) oxide gas concentration in air reaches 6 %, what corresponds 60000 ppm. Climate changes are occurring with primary Self-Organization Attractor Carbonic Anhydrase CA amount insufficiency in periods at 500 MY, 200 MY. Sufficient new primary Self-Organization Attractor CA amounts restoring in interglacial periods at 300 MY and to day 0-10 MY with decrease temperature and **CO**<sub>2</sub> atmospheric content below 1000 ppm. <sup>[13]</sup>

Before 600 million Years CO<sub>2</sub> concentration in atmosphere was 0.1 %, what agree 1000 units' ppm. Atmospheric oxygen O<sub>2</sub> concentration approximately 1 % below from today's 20.95 % volume fraction was unconformable for bulk of present-day animal species.

Approximately 600 million Years history Earth was ice covered reminding Snowball Earth. Glacier fast melting provokes atmospheric  $CO_2$  concentration growth up to 6 % 60000 ppm. Due to greenhouse effect temperature increased from -50° up to 45° degrees. That increase the photosynthetic reaction brought concentration of oxygen  $O_2$  fast above present-day 20.95 % up to 30 % for period in 10000 Years.

Biosphere primary Self-Organization Attractor in air oxygen O<sub>2</sub> 20.95 % is working global for 500 million Years. <u>Thermodynamic attractor with functionally active molecules O<sub>2aq</sub>, CO<sub>2aq</sub>. <sup>[1,6,13]</sup></u>

## 5 complex Enzyme reactions

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
- 2. ENZYMES specificity 100% efficiency of product singularity
- 3. JOINT-TANDEM SYNTHESIS Ribosomes for polypeptides, proteins Photosynthesis glucose and oxygen

2. PARALLEL reaction preseeding in chemistry as side products

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 O2aqua, CO2aqua

4. COMPETITIVE regulation as inhibition and allostery sensitive to concentration O<sub>2aqua</sub>, HCO<sub>3</sub><sup>-</sup>, H<sup>+</sup> (Le Chatelier principle) 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<sub>2aqua</sub>]=6·10<sup>-5</sup> M and venous [O<sub>2aqua</sub>]=0,426·10<sup>-5</sup> M.

Photosynthesis global stabilises oxygene concentration [O<sub>2AIR</sub>]= 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

Figure 7. Self-Organization Attractors claim order versus non-enzymatic reactions chaos and contamination. Five type complex reactions in enzyme clusters. Self-Organization Attractors sustain the functional activity perfect order for homeostasis. Deviation from Attractor values create homeostasis disorder as Chaos.

#### Summary Self-Organization Attractors create perfect order homeostasis link Bioenergetic.

**Self-Organization** Attractors create functional active molecules reactivity order for homeostasis and bioenergetic. The order of functionally active molecules drives homeostasis under rule Attractors. Reaching of Attractor values create homeostasis order out of disorder. Chaos disorders the homeostasis.

The molecules functional activation of oxygen  $O_{2aqua}$  decreases free energy content from  $G_{O2aqua}=303.1 \text{ kJ/mol}$  to  $G_{O2Bio}=78.08 \text{ kJ/mol}$ . Carbon dioxide reaction with water  $CO_2 + 2 \text{ H}_2O$  increases free energy content from zero  $G_{CO2+2H2O}=0 \text{ kJ/mol}$  to  $G_{H3O++HCO3}=68.38 \text{ kJ/mol}$ . Water in protolysis increases free energy content from zero  $G_{2H2O}=0 \text{ kJ/mol}$  to  $G_{H3O++HCO3}=68.38 \text{ kJ/mol}$ . Water in organism medium increases free energy content from zero  $G_{2H2O}=0 \text{ kJ/mol}$  to  $G_{H3O+OH}=99.8 \text{ kJ/mol}$ . Distilled water in organism medium increases free energy content from zero to  $G_{H2O}$ \_Biochemistry=85.65 kJ/mol. <sup>[1,8]</sup> Functional activation initiates Attractors. Attractors are two types and multipurpose. The primary Attractors common for Biosphere, the secondary Attractors for individual organisms and multipurpose pH=7.36, water, air oxygen.

**Oxygen** O<sub>2aqua</sub> 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  $[H_2O]=55.3 \text{ mol}/_{\text{Liter}}$ , air oxygen level 20.95 % for five hundred million Years, pH=7.36 for the concentration  $[H_3O^+]=10^{-7.36}$  M.

**CA Carbonic Anhydrase** work as primary Attractor for Biosphere which forms dominate bicarbonate buffer of  $CO_{2aqua}$  acid protolysis constant pK<sub>a</sub>=7.0512. Henderson Haselbalh expression Attractor value 7.36, which corresponds to concentration [H<sub>3</sub>O<sup>+</sup>]. Attractor 7.36 creates functional activity of molecules with charged groups negative and positive: HPO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, R-COO<sup>-</sup>, R-NH<sub>3</sub><sup>+</sup>, R-PO<sub>4</sub><sup>2-</sup> as free and linked in amino acids, proteins, nucleic acids, carbohydrates, coenzymes, **R** molecules. Carbonic Anhydrase synthesis solve perfect order of homeostasis and bioenergetic as Self-Organization Attractor. <sup>[3,4]</sup>

The Attractors values in organism compartments dissipative structures drive the perfect homeostasis order with enzymes clusters on five type complex reactions. Order is key for surviving of organism. Deviation from Attractor values cause loss the homeostasis order of functional activity. Chaotic reactions waste the resources and stop the homeostasis, the non-equilibrium complex processes. The homeostasis becomes extinct from Biosphere.

Water protolysis is **indispensable** for Attractors sustaining which stay at equilibrium while homeostasis and bioenergetic continue. Water protolysis accumulate free energy in products  $H_3O^++OH^-$  99,8 <sup>kJ</sup>/<sub>mol</sub>. Attractors destiny are irreversible free energy change  $\Delta G_{\text{Homeostasis}}$  transduction between functional active molecules.

1. Chaotic

4. Chaotic

Note: Homeostasis trend to equilibrium but never reaching because it is non-equilibrium state. Acknowledgements.

The author would like to acknowledge all the contributions of the field "Prigogine thermodynamic Attractors drive homeostasis with functionally activate  $O_{2aqua}$ ,  $CO_{2aqua}$ " which critically appreciate this study:

Thanks for critical discussions with MD Aivar Grinberg about Attractors in Biochemistry to see

indispensability for Life create functionally activate molecules to maintain the homeostasis of organisms.

Thanks for Riga Stradin's University Library about supporting literature studies.

Thanks for Riga Stradin's University department stuff of Human Physiology and Biochemistry who supporting may advanced studies in Biochemistry of Prigogine Thermodynamic Attractors.

## References.

- 1. David R. Lide. CRC Handbook of Chemistry and Physics .90th ed. Taylor and Francis Group LLC; 2010 .
- 2. Prigogine I, Defey R. Chemical Thermodynamics. Longmans Green & co ©; 1954.
- 3. Prigogine I, Nicolis G. Self-Organization in Non-Equilibrium Systems. Wiley, 1977.
- 4. Prigogine I. Time, Structure and Fluctuations. Lecture, The Nobel Praise in Chemistry; 1977.
- 5. <u>Kuman M. New light on the attractors creating order out of the chaos</u>. *Int J Complement Alt Med.* **11**(6), 337, (2018) ;
- Nelson DL, Cox MM. Lehninger Principles of Biochemistry. 5<sup>th</sup> ed. New York: W.H. Freman and company; 2008.
- 7. <u>Xing W, Yin G, Zhang J. Rotating Electrode Method and Oxygen Reduction Electrocatalysts</u>. *Elsevier*; 6 (2014).
- 8. <u>Alberty RA. Biochemical Thermodynamic's : Applications of Mathematics. John Wiley & Sons, Inc. 1-463,</u> (2006).
- 9. <u>Pinard MA, Mahon B, McKenna R. Probing the Surface of Human Carbonic Anhydrase for Clues towards the</u> Design of Isoform Specific Inhibitors. *BioMed Research International*; **2015**, 3 (2015).
- 10. Kotz JC, Purcell KF. Chemistry and chemical reactivity. Saunders College Publishing; 1991.
- 11. White VM. THE CARBON CYCLE, ISOTOPES, AND CLIMATE I and II. Lectures 37, 38; 2003 .
- 12. Hanania J, Pomerantz C, Stenhouse K, Toor J, Donev J. Carbon cycle. University of Calgary's 2020 .
- 13. Der wohltemperierte Planet. Der Spiegel. 2007 Nr.19:148-154. German .

### No Conflict of Interests.

The author declares that there is no conflict of interests regarding the publication of this paper.

## Authors' Contribution

Aris Kaksis with out financial contribution has alone study .