

Thermodynamic equilibrium state Attractor for non-equilibrium state with functionally active $O_{2\text{aqua}}$, $CO_{2\text{aqua}}$.

Oxygen functional activity limits air concentration 20.95% mol fraction 0.2095, which solubility in water is $[O_{2\text{aqua}}]=1.22 \cdot 10^{-3} \cdot 0.2095=2.556 \cdot 10^{-4}$ M called as isooxia Norma for Biosphere. Hyperoxia, oxidative stress and acidosis mechanism accumulate increasing Free energy content. The oxygen becomes fire-insecure for Biochemistry as oxidative stress with destructive hazards in life dissipative structures!

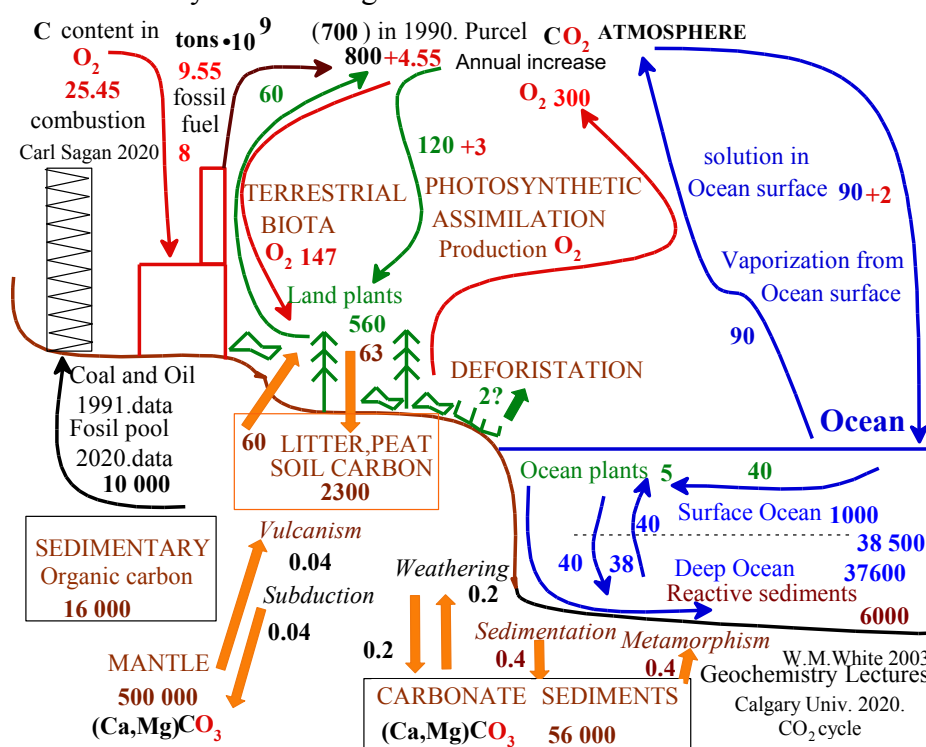
Enzyme Carbonic Anhydrase let $CO_{2\text{aqua}}$ react $CO_{2\text{aqua}}+2H_2O+9.8 \text{ kJ/mol} \xrightarrow{CA} H_3O^++HCO_3^-$ endothermic with two water molecules to increase $30.6=0.023/0.0007512=K_{eq}=[CO_{2\text{aqua}}+HCO_3^-]/[CO_{2\text{aqua_from_AIR}}]$ times content in water medium, if air 0.04 % mol fraction of $CO_{2\text{air}}$ is 0.0004. It stronger cool the Planet Earth.

Global observations last hundred Years confirm warming of planet or increase surface temperature per 0.5° degrees of planet Earth, what accompanies environmental changes. For example, storms or storming cyclones intensity and frequency, increases carbonic dioxide concentration in air from 0.029 % volume fractions in 1900 Year to 0.041% volume fractions in 2020 Year .

$CO_{2\text{gas}}-20.3 \text{ kJ/mol} \rightleftharpoons CO_{2\text{aqua}}+OH^- -48.68 \text{ kJ/mol} \rightleftharpoons HCO_3^- + \text{warming up} +69 \text{ kJ/mol}$ products exothermic. Adding heat shifts the equilibrium to **endothermic** reaction backwards $CO_{2\text{gas}} \rightleftharpoons CO_{2\text{aqua}}+Q_1=20.3 \text{ kJ/mol}$ and $CO_{2\text{aqua}}+OH^- \rightleftharpoons HCO_3^- + Q_2=48.68 \text{ kJ/mol}$ as $\Delta H_{Hess_sum}=-20.3-48.68=-69 \text{ kJ/mol}$ in air is evolving the $CO_{2\text{gas}}$.

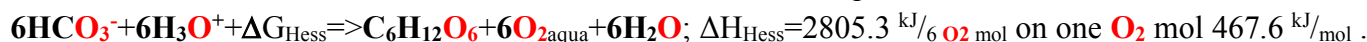
$CO_{2\text{gas}}$ with OH^- ions slow [velocity 46th page](#) velocity constant $k_{1OH}=1.5 \cdot 10^2 \text{ M}^{-2}\text{s}^{-1}$ is small.

Fossil combustions warm the oceans $0.167 \cdot 10^{15} \cdot 69=11.5 \cdot 10^{15} \text{ kJ}$ with CO_2 amount 2Gt dissolve and in reaction with OH^- ions. Warming heat in oceans $11.5 \cdot 10^{15} \text{ kJ}$ of CO_2 is 100 times less the Photosynthesis and Carbonic Anhydrase cooling $-2501 \cdot 10^{15} \text{ kJ}$ the Planet. ^[12,13,14] Civilization annual with combustion pollutions



add to 800 Gt atmospheric $CO_{2\text{gas}}$ content 4.55 Gt about plus 1.2% as well bulk 98.8 % irregular changed of totally global and cosmic processes on Earth. Ocean and in all Earth waters dissolve 47 times greater $CO_{2\text{aqua}}$ amount 38500 Gt as 800 Gt in atmosphere, but carbonate $(Ca,Mg)CO_{3\text{solid}}$ sediments in Earth crust contains 70 times more as in atmosphere 800 Gt. Green plant Photosynthesis each Year assimilates CO_2 amount 15.4% from atmosphere 800+4.55 and in water total producing glucose 307.5 Gt with 120 Gt carbon mass. Photosynthesis evolved oxygen amount in atmosphere $300-147=153$ Gt stabilizes global O_2 oxygen

Attractor concentration in atmosphere at 20.95% mol fraction of air 0.2095.



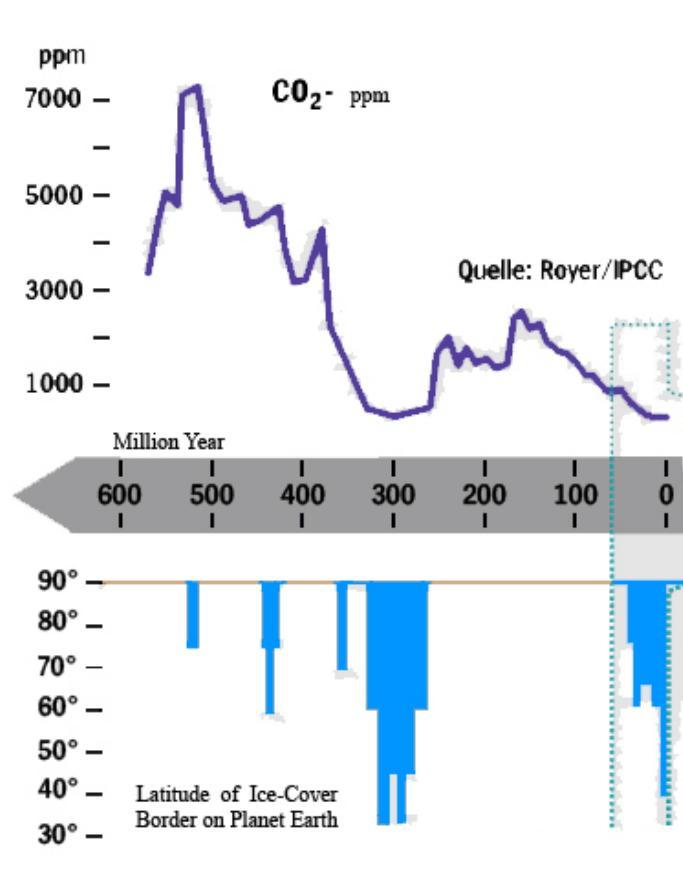
Carbonic Anhydrase and Photosynthesis $55.75+0+467.5=523.25 \text{ kJ/mol}$ cool planet on assimilate CO_2 , O_2 mol. Oxygen global balance $300 \text{ Gt} -147 \text{ Gt} =153 \cdot 10^9 \cdot 10^6 \text{ g} =153 \cdot 10^{15} \text{ g } O_2$ $32 \text{ g/mol } 4.78 \cdot 10^{15} \text{ mol}$ stabilize oxygen concentration 20.95%. Photosynthesis cool planet $2501 \cdot 10^{15} \text{ kJ}=4.78 \cdot 10^{15} \text{ mol} \cdot 523.25 \text{ kJ/mol}$;

The Carbonic Anhydrase and Photosynthesis to stabilize global air oxygen O_2 concentration 20.95%.

Conclusion: Warming planet surface and CO_2 atmospheric concentration regular increase cause fossil combustion. Nonlinear are cosmic dust mass , energy influx and Solar wind mass , energy influx and with volcanic intensive pollution in atmosphere on Earth are seen on climate reconstruction 600 million Years ago.

Solar ,cosmic, geological processes nonlinear, but relevant for life existence on planet Earth.

Reconstruction climate of Earth shows temperature and CO₂ oscillation, which 600 million Years back in historical 10000 Years period is observing Earth warming from -50° to 45° degrees and carbon(IV) oxide gas concentration in air reaches 6%, what corresponds 60000 ppm. Climate changes are occurring with CA and ocean freezing 500 MY, 200 MY. Restores melting ocean ice ecosystem at inter glacial ages 300 MY, 0-10 MY



decreasing temperature, CO₂ in ecosystem endothermic.

Before 600 million Years CO₂ concentration in atmosphere was 0.1% volume fractions, what agree 1000 ppm. Atmospheric oxygen O₂ concentration approximately 1% from today's 20.95% volume fraction was uncomformable for bulk of present-day animal species. Approximately 600 million Years back Earth was ice covered reminding Snowball Earth. Glacier fast melting provokes CO₂ concentration growth up to 6% - 60000 ppm. Due to greenhouse effect temperature increases from -50° up to 45° degrees, what because of photosynthetic reaction brought oxygen O₂ concentration fast increase above present-day 20.95% up to 30% .

Prigogine Attractor oxygen O₂ 20.95% concentration in air is working global for 500 million Years.

During the last 2.6 million Years or so in the **Quaternary** period, ice ages, also called glacial ages, were times of extreme cooling of the **Earth's climate** where ice sheets and other types of **glacier expanded** to cover large areas of land. Between ice ages there were warmer interglacial periods and we are now living during such a time. There have been many ice ages during the **last 2.6 million Years** but when people talk about the Ice

Age, they are often referring to the most recent glacial period, which start 13563 Years ago and ended about 11500 Years ago and preceding warmer interglacial period end 13563 Years ago because as written in Indians, Egyptians, Assyrians and Mayan calendar, the preceding proto civilization was go waste on data 11542 Year B.C. and refers to days civilization before 13563 Years. What causes ice ages is not completely understood. The composition of the **atmosphere**, changes in the position of **planets around the Sun**, changes in **ocean currents** and the **Sun radiation** as **spot activity** magnetic field regular 11 Years periods changes as yet unknown factors that change the climate. **Sun** and Earth increase as influence of cosmos! Earth circumference in 3000 Years increases per 60 km (40 074 km -60 km) from Mayan astronomers and to days since measure difference. **Solar** wind 4H⁺+4e⁻ react with oxygen produces water abundance on our planet Earth:

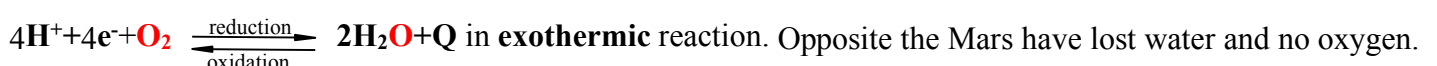




Image: A reconstruction of the England ice sheet in **Precambrian** North London (credit: The Natural History Museum, London)

Precambrian Ediacaran period 635 – 545 million Years ago



Known also as the Vendian, the Ediacaran was the final stage of Pre-Cambrian time. All life in the Ediacaran was soft-bodied - there were no bones, shells, teeth or other hard parts. As soft bodies don't fossilize very well, remains from this period are rare. The world's first ever burrowing animals evolved in the Ediacaran, though we don't know what they looked like. The only fossils that have been found are of the burrows themselves, not the creatures that made them. This period gets its name from the of this age were found.

Ediacara Hills in Australia, where famous fossils

Cambrian period 545 – 495 million Years ago



The Cambrian is famed for its explosion of abundant and diverse life forms. Life had diversified into many forms and many ways of living: animals now swam, crawled, burrowed, hunted, defended themselves and hid away. Some creatures had evolved hard parts such as shells, which readily fossilised and left a clear record behind. However, sometimes geologists get lucky and find beautiful fossils of soft and squishy creatures - as at the Burgess Shale site. In Cambrian times there was no much the centre of living activity.

life on land and little or none in freshwater - the sea was still very

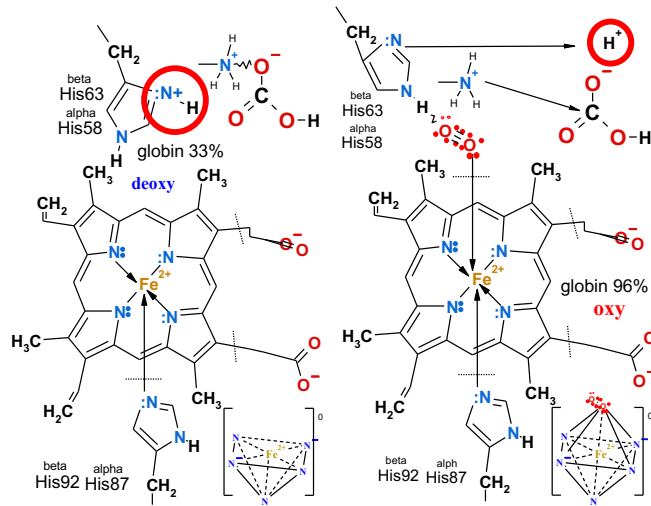
Enzyme reactivity is Prigogine dissipative structure molecular engine as instrument for Attractors reaching:

oxygen arterial concentration $[O_{2\text{aqua}}]=6\cdot 10^{-5}\text{M}$ [O2Solutions.pdf](#) ;

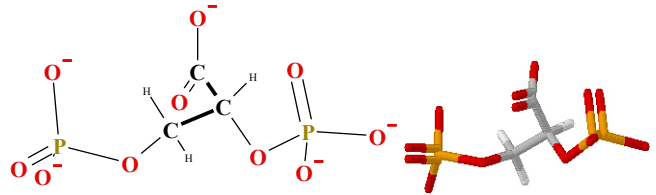
$\text{pH}=7.36=\text{pK}_a+\log([\text{HCO}_3^-]/[\text{CO}_{2\text{aqua}}])$ hydrogen ion $[\text{H}_3\text{O}^+]=10^{-7.36}\text{M}$ concentration; bicarbonate $[\text{HCO}_3^-]$ and $[\text{CO}_{2\text{aqua}}]$ generate concentration $0.023\text{M}=0.0154\text{M}+0.0076\text{M}$ gradient for of osmosis.

Oxygens from AIR 20.95% assimilation through membrane aquaporins to form $O_{2\text{aqua-Blood}}$

$O_{2\text{AIR}}+\text{H}_2\text{O} \xrightleftharpoons{\text{aquaporin}} \text{H}_2\text{O}+O_{2\text{aqua-Blood}}$, Four oxygen molecules $O_{2\text{aqua-Blood}}$ have adsorbed on **shuttle deoxy** hemoglobin $4O_{2\text{aqua}}+(\text{H}^+\text{His63,58})_4\text{Hb}_T$ · salt bridges $(\text{HCO}_3^-)_4 \leftrightarrow \text{Hb}_R(\text{O}_2)_4+4\text{H}^++4\text{HCO}_3^-$ release releases 4H^+ , 4HCO_3^- to stabilize arterial concentration shifting to right stored 33% of 96% ($0.02838\text{M}=473\cdot [O_{2\text{aqua}}]=6\cdot 10^{-5}\text{M}$) for tissues on shuttle heme $\text{Hb}_R(\text{O}_2)_4$. Venous blood concentration drops down to $[O_{2\text{aqua-Blood}}]=0.426\cdot 10^{-5}\text{M}$.



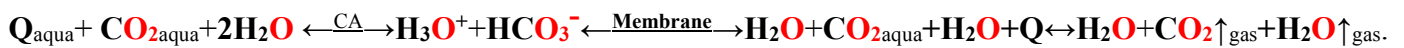
Shift to right regulates erythrocytes glycolysis metabolite



BPG⁵⁻ the salt of Glycerate- **G^{2,3}** dihydroxy diphosphate ester $\text{H}_2\text{COPO}_3^{2-}-\text{HCOPO}_3^{2-}-\text{COO}^-$ with homeostasis concentration $[\text{BPG}^{5-}]=5\text{mM}$. Oxidation exothermic and exoergic reactions consume oxygen and **BPG⁵⁻** squeeze in to **cavity** to stabilize concentration from stored reserve. Oxidation reactions produce H^+ , HCO_3^- ions which bind to histidin $\text{H}^+\text{His63,58})_4\text{Hb}_T$ and with salt bridges $(\text{HCO}_3^-)_4$.

After O_2 desorption from $\text{Hb}_R(\text{O}_2)_4$ **shuttle** in tissues due to oxidation forming water solute $\text{CO}_{2\text{aqua}}$. Hb_T capture four 4H^+ and four bicarbonate ions by salt bridge $\text{HCO}_3^- \dots \text{H}_3^+\text{N}-$ $0.02838\text{M}=[\text{HCO}_3^-]+[\text{CO}_{2\text{aqua}}]=[\text{H}^+]$ in equal amounts. Produced amount of $[\text{HCO}_3^-]=[\text{H}^+]$ joined on **deoxy** $(\text{H}^+\text{His63,58})_4\text{Hb}_T$ with venous blood circulation brings to **lungs**. Circulating enzyme complex: carbonic anhydrase, hemoglobin-myoglobin **shuttle** , channels of proton, bicarbonate and aquaporins stabilize arterial concentration $[O_{2\text{aqua}}]=6\cdot 10^{-5}\text{M}$ and $\text{pH}=7.36\pm 0.01$ hydrogen ions $[\text{H}_3\text{O}^+]=10^{-7.36}\text{M}$ physiologic concentration; bicarbonate and $\text{CO}_{2\text{aqua}}$ concentration sum $0.023\text{M}=0.0154\text{M}+0.0076\text{M}$ with ratio $2/1=[\text{HCO}_3^-]/[\text{CO}_{2\text{aqua}}]=0.0154\text{M}/0.0076\text{M}$.

Lungs alveolar through channels on membranes endothermic 14.05kJ/mol exhale $\text{H}_2\text{O}+\text{CO}_2\uparrow_{\text{gas}}+\text{H}_2\text{O}\uparrow_{\text{gas}}$



Endothermic gradual sequences: 1) $\text{CO}_{2\text{aqua}}+2\text{H}_2\text{O}+\text{Q} \xleftarrow{\text{CA}} \text{H}_3\text{O}^++\text{HCO}_3^-$; $\Delta\text{H}_{\text{Hess}}=+9.75\text{kJ/mol}$;

2) $\text{H}_3\text{O}^++\text{HCO}_3^- \xleftarrow{\text{Membrane}} 2\text{H}_2\text{O}+\text{CO}_{2\text{aqua}}+\text{Q}$ neutralization exothermic equilibrium $\Delta\text{H}_{\text{eq}}=-60\text{kJ/mol}$ and

3) $\text{H}_2\text{O}+\text{CO}_{2\text{aqua}}+\text{H}_2\text{O}+\text{Q}_{\text{gas}} \leftrightarrow \text{H}_2\text{O}+\text{CO}_2\uparrow_{\text{gas}}+\text{H}_2\text{O}\uparrow_{\text{gas}}$ endothermic $\Delta\text{H}_{\text{Hess}}=20.3+44=64.3\text{kJ/mol}$ exhale by

concentration gradient, heat supply and proton channeling in lungs after oxygen $\text{O}_2+\text{H}^+\text{Hb}_T \leftrightarrow \text{Hb}_R\text{O}_2+\text{H}^+$.

1) hydrogen H^+ ion concentration (acidity) increase shifts equilibrium right side $\Rightarrow \text{Hb}_T$ adsorbed O_2 yield H^+ ;

2) bicarbonate HCO_3^- concentration increase breaking linked $\text{HCO}_3^- \dots \text{H}_3^+\text{N}-$ shifts equilibrium right side \Rightarrow ;

3) heating + Q shifts equilibrium right side \rightarrow (Air breathing human as well as animals have the lungs located inside body and equipped with heat producing cells in alveolar area as heating support $\text{CO}_2\uparrow_{\text{gas}}$ breathing out).

Synthesis and Decomposition reactions four types

1. EXOTHERMIC, EXOERGIC DECOMPOSITION REACTION of hydrolysis and bio oxidation

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



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



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



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

2. EXOTHERMIC REACTIONS OF SYNTHESIS

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



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

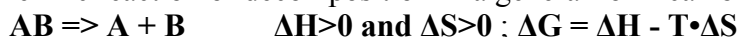
$$|\Delta\text{H}| > |\text{T} \cdot \Delta\text{S}|$$

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

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

3. ENDOTHERMIC , EXOERGIC REACTION OF DECOMPOSITION

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



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

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

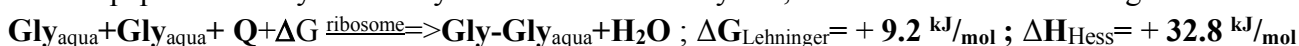
An endothermic reaction of decomposition occurs spontaneously at high enough temperatures.

4. ENDOTHERMIC, ENDOERGIC REACTION OF SYNTHESIS.

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



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



This kind of reactions can be generally expressed as: $\text{A} + \text{B} \Rightarrow \text{AB}; \quad \Delta\text{S} < 0 \quad \text{and} \quad \Delta\text{H} > 0$.

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, *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 .

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

Organism biochemical environment forming fast equilibria drive life processes with molecules functional activity Attractors: generate concentration gradients, air 20.95% [O₂], osmolar concentration 0.305 M, ionic strength 0.25 M, pH=7.36.

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

5 complex Enzyme reactions

Versus non Enzymatic reactions

Enzyme governed complex reactions drive the LIFE in 5 ways

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

1st 5th page:

[Thermodynamic attractor with functionally active O_{2\(aqua\)}, CO_{2\(aqua\)}](#)

4. COMPETITIVE regulation as inhibition and allostery

sensitive to concentration O_{2(aqua)}, HCO₃⁻, 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

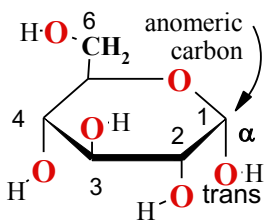
so stabilises Physiologic pH=7.36, arterial [O_{2(aqua)}]=6·10⁻⁵ M and venous [O_{2(aqua)}]=0,426·10⁻⁵ M.

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

4. Chaotic

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

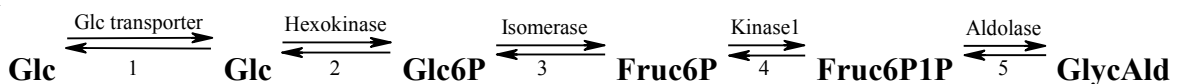
5. Contamination destructive chemistry with the chaotic radical chain reactions in multiple parallel products



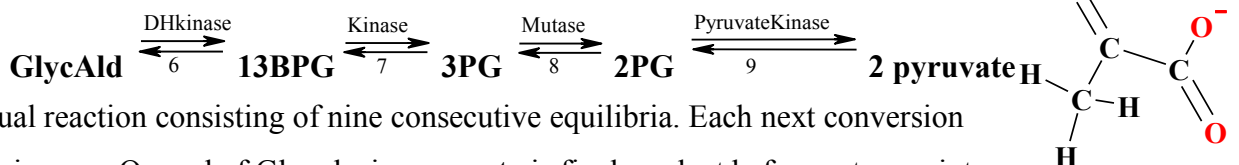
1. GRADUAL (CONSECUTIVE) ENZYME supported EQUILIBRIA SEQUENCE

Glycolysis is most popular gradual equilibria sequence in human organism

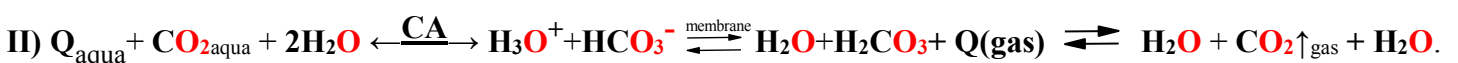
HOMEOSTASIS PATHWAYS.



Glycolysis PAYHWAY start with entrance **glucose (Glc)** from blood plasma into cytosole:



In fact is a gradual reaction consisting of nine consecutive equilibria. Each next conversion followed after prior one. On end of Glycolysis **pyruvate** is final product before entrance into mitochondria for Krebs cycle. Oxygen O₂ assimilation in organism and CO₂ respiration out.



2. Enzymes specificity 100% of product singularity; Chaos and pollutions by PARALLEL reactions In vitro organic compounds of human organism have been converted to many different reaction products, but in vivo ENZYMES perform just one product formation. Enzyme favors just one reaction with million times higher velocity as well per 10^6 produced bio molecules are possible just one 1 parallel side product or ever less formed. Reactivity of ENZYME drives reactions in needed direction for **HOMEOSTASIS** PATHWAY.

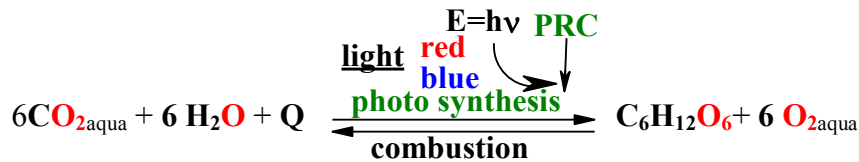
Parallel reactions in human body prevent ENZYMES. So single product forming of one initial compound.

ENZYMES $k_1=10^6$ A and B may react, forming two different kinds of products. The two possible kinds of products are formed in different amounts, because ENZYME governed reaction velocity constant k_1 is million times greater as parallel unfavorable reaction constant value k_2 . ENZYMES drive the favorite reaction with the efficiency 100% and with the velocity constant 1000000 times greater as other parallel reactions. Human organism biochemical reactions are governed by ENZYMES, which selectively faster forming perfect single product needed for life and never have made side products.

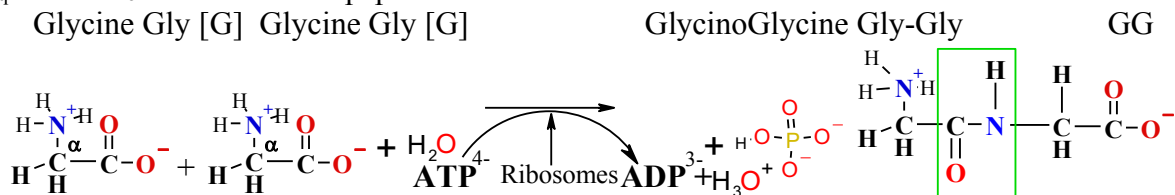
3. ENZYMATIC JOINT TANDEM EQUILIBRIA drive forbidden REACTIONS

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

Green plants **Photosynthesis** reaction is thermodynamically forbidden as endoergic $\Delta G_r = +2921.5 \text{ kJ/mol}$: $6\text{CO}_{2\text{aqua}} + 6\text{H}_2\text{O} + \text{Q} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_{2\text{aqua}}$ and as endothermic reaction $\Delta H_{\text{reac}} > 0$ $\Delta H_{\text{reac}} = +2812.6 \text{ kJ/mol}$. Tandem reactions are very common in biochemistry. Here the most common case is, that the equilibrium of building-up free energy rich compounds like protein, **glucose** $\text{C}_6\text{H}_{12}\text{O}_6$, **oxygen** 6O_2 in which entropy lowered and *Gibbs energy* is growing-accumulate. As the reaction alone is thermodynamically forbidden, the **red** and **blue** light photon absorption in Joint - Tandem reaction lowers *Gibbs's energy* in products $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ witch becomes compensate for the overall process thermodynamically possible. Global **Photosynthesis** oxygen equilibrium concentration is $20.95\% = [\text{O}_2 \uparrow_{\text{gaiss}}]$. To decrease concentration, for example, $2\% = [\text{O}_2 \uparrow_{\text{gaiss}}]$ **Plant Enzymes Photosynthesis** restore Prigogine Attractor concentration in air 20.95%. Attractor reaching velocity effects supplying the heat **Q** and **CO₂**. Therefore Global warming promote increase of **Q** and **CO₂** and so further **Photosynthesis**, but in Ace Age **Photosynthesis** stop down if Earth total covered by ice:



The ENZYME complex Ribosomes are for Peptide Bond synthesis: $\text{gly} + \text{gly} \rightarrow \text{gly-gly} + \text{H}_2\text{O}$ at Lehninger biochemical conditions $\text{pH} = 7.36$ un $[\text{H}_2\text{O}] = 55.3 \text{ M}$: with free energy $\Delta G_{\text{eq}} = 9.2$; $\Delta G_{\text{Hess}} = 57.3 \text{ kJ/mol}$ transfer shift ATP^+ hydrolyze exoergic free energy $\Delta G_{\text{LehningerEq}} = -30.5 \text{ kJ/mol}$ which part is used free energy store $\Delta G_{\text{eq}} = 9.2 \text{ kJ/mol}$ in one mole of peptide bond.



4. COMPETITIVE regulated ENZYME EQUILIBRIA allostery and inhibition

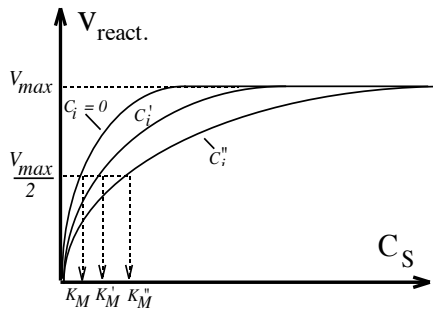
with $\text{O}_{2\text{aqua}}$, HCO_3^- , H^+ concentrations sensitive His63,58 hemoglobin and His64 myoglobin shuttle through back response regulated shift of equilibrium according Le Chatelier's Principle-Theorem stabilise $\text{pH} = 7.36$, arterial concentration $[\text{O}_{2\text{aqua}}] = 6 \cdot 10^{-5} \text{ M}$ and venous concentration $[\text{O}_{2\text{aqua}}] = 0.426 \cdot 10^{-5} \text{ M}$.

In competitive equilibria two different initial compounds substrate S and inhibitor I compete on one ENZYME regulate decrease the product amount [Product] and the velocity through distinguish equilibria K_{eq} , K_I according Le Chatelier's principle-theorem in expressions, increasing K_M in velocity v_{react} :

$$\begin{aligned} & \text{E} + \text{S} \xrightleftharpoons{k_S} \text{ES} \rightarrow \text{E} + \text{Prod} \\ & \text{E} + \text{I} \xrightleftharpoons{k_I} \text{EI} \rightarrow \text{X} \end{aligned}$$
 ENZYME governed reactions are regulated by inhibitors **I** concentration shift **E+S** product decrease. Inhibitor molecule **I** compete with substrate molecule **S** and shift substrate reaction to left according Le Chatelier theorem by decrease of ENZYME concentration C_E involved into competitive inhibition equilibrium. Physiologic ENZYME regulation is an equilibrium which shifting

$$K_{eq} = \frac{[\text{products}]}{[\text{initial_compounds}]} = \frac{[E] \bullet [\text{Product}]}{[E] \bullet [S]} = \frac{[\text{Product}]}{[S]}; K_I = \frac{[E]}{[E] \bullet [I]}; v_{react} = \frac{v_{max} C_S}{K_M + C_S}$$

to right side promoted by inhibitor concentration C_I increase, for example, using medicine aspirin, warfarin e.c..

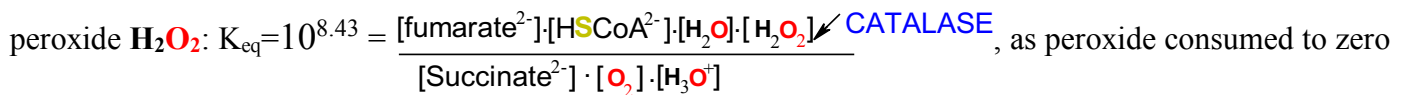


$\rightarrow v_{react} = \frac{v_{max} C_S}{K_m + C_S}$ *Competitive inhibition is as inhibition causes an increase of the Michaelis's constant K_M , value but doesn't affect the maximal velocity of reaction v_{max} .*

Note, that Michaelis's constant K_M has the meaning of a substrate concentration C_S at which the reaction velocity reaches 1/2 of maximal. $v_{react} = v_{max} / 2$.

5. Reaction complexes use peroxide radical enzymatic as molecular engines homeostasis support Exoergic dismutation Catalase reaction converts peroxide H_2O_2 to life resources: $O_{2(aqua)} + H_2O + Q$. Essential unsaturated fatty acid elongation C20:4 and ethyl group $-CH_2-CH_2-$ conversion to cis double bond $H>C=C<H$ in peroxisomes is exoergic, favored enzymatic conversion with negative free energy change like:

$\Delta G_{eq} = -48,127 \text{ kJ/mol}$. **CATALASE** as indispensable **Life** engine drive from minimum favored to end. Catalase in complex reaction sequence favors stable unsaturated fatty acid product efficiency • 100% because erasing



$[H_2O_2]^2 = 0 \text{ mol/liter}$ and process velocity limits only dehydrogenase enzyme.

Irreversible Catalase reactivity is Prigogine Attractor indispensable Brownian molecular engine which drive Life for evolution, survival of homeostasis.

Increased oxygen concentration is termed hyperoxia and medical symptom is called oxidative stress. Oxidative stress risk is proportional to oxygen or peroxide concentration. Five times higher oxygen

concentration **singlet** oxygen $:\cdot\cdot O : - : O : \cdot\cdot$ risk increases five times. $v \sim [O_2]$.

Non-ENZYMATIC radical-chain reaction produce many different products, that forbidden in life strategy, which damages life molecular structures and ENZYMATICAL complexes natural processes Oxidative stress and technology hazards was the reason for Apollo cosmos project closing in 72nd of 20 century.

That not acceptable in ENZYME governed radical reactions, where necessary form one specific product.

Radical formation from H_2 and Br_2 begins by light radiation **initiation**.

Initiation is first stage of radical formation as activated particles with low activation energy $E_a \rightarrow 0 \text{ kJ/mol}$. The radical here is photochemical: Br_2 molecules absorb light photons, forming from bromine molecule Br_2 uncoupled bromine atom radicals $Br\bullet + Br\bullet$ with unpaired electron \bullet : $Br\bullet + Br\bullet \xrightarrow{h\nu} Br\bullet + Br\bullet$

Propagation is second stage of radical-chain reaction. Where active particles $Br\bullet$ radicals are short-living active particles, that react in the **propagation**: $Br\bullet + H\text{-}H \rightarrow H\bullet + H\text{-}Br$.

In this reaction a stable molecule of product HBr is formed and a new radical active particle - $H\bullet$ atom is formed. $H\bullet$ reacts further and continue the radical-chain **propagation**: $H\bullet + Br\text{-}Br \rightarrow Br\bullet + H\text{-}Br$.

Here again a product (HBr) molecule is formed and an $Br\bullet$ atom is created again, $Br\bullet$ radical atom can react with next H_2 molecule and so the radical-chain reaction could **propagate** forever.

Termination is third stage radical-chain reaction. Radical-chain **termination** occurs, if two active particles meet to form non-radical molecule and no radical-chain **propagation** is possible after this. In case of H_2 and Br_2 reaction one can imagine 3 different reactions, in which radical-active particles die:



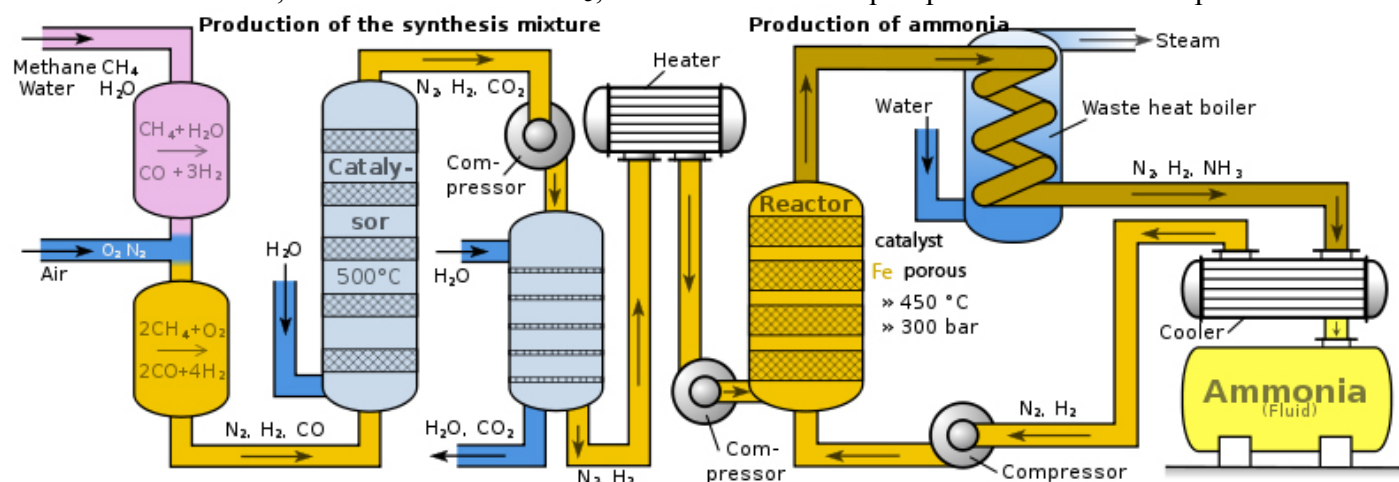
Reaction velocity in the case of a radical-chain reaction is determined by the velocity of radical-chain **initiation** and radical-chain **termination**: a) if **initiation** and **termination** occurs at the same velocity, chain will **propagate** with constant velocity (because the number of active radical particles is constant then),

b) if the velocity of **initiation** is greater, than the one of **termination**, the number of active radical particles is growing and the velocity of radical-chain **propagation** (of product formation) is growing, too,

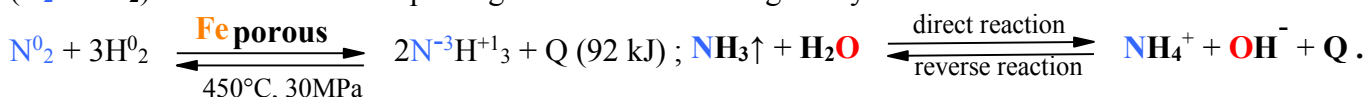
c) if the velocity of **termination** is higher, than the velocity of **initiation**, the number of the active radical particles is decreasing and the velocity of **propagation** product formation is decreasing, interrupt reaction.

Ammoniac can obtain in hydrogen reaction with nitrogen using catalyst porous iron **Fe**. At absence of catalyst reaction practically does not happen and has not established equilibrium. Therefore if hydrogen run out in air ammoniac not forms and only stand for dangerous explosion, because hydrogen reacts with oxygen if it ignites. In oil, gas and coal refining industry arises huge amount of hydrogen H_2 , as well hydrogen atoms containing organic compounds was heated. Up to 1920 Year in refinement factories hydrogen was combusted and hydrogen flame torches was factory landscape integral part, because accumulation of hydrogen mixture with oxygen is dangerous explosive.

Haber invents device for ammoniac obtaining and in 1920 Year on USA and UK oil refinement factories was mounted first equipments. Le Chatelier theorem has allowed up to optimal circumstances to develop ammoniac obtaining technology. Equilibrium influences temperature, pressure. Product pressure of ammoniac diminishes, condensation into liquid due to cooling or dissolution into water. In Haber process circulate two gases nitrogen N_2 and hydrogen $3H_2$. Initially equipment durability allowed 100 MPa pressure and $200^\circ C$ temperature, but at modern equipment optimal established $450^\circ C$ temperature and 30 MPa pressure. As catalyst uses porous iron **Fe**. Obtained equilibrium mixture contains 98% ammoniac. Condensed NH_3 in next box is made in water, in which dissolves NH_3 , or condensed and liquid product feels in transport tank.



Ammoniac gas pressure decreasing $p_{NH_3} \downarrow$ shifts equilibrium to right. Unused gases $N_2 + 3H_2$ returns in porous iron **Fe** reaction box and Haber cycle equilibrium established again during one second with 98% ammoniac volume fraction. To remove oxygen from air (N_2, O_2), mixture introduces in Bosh process together with methane and water (CH_4, H_2O) and obtains pure nitrogen and hydrogen mixture. Heated $450^\circ C$ nitrogen and hydrogen mixture ($N_2 + 3H_2$) compressed introduces in Haber cycle reactor, but Haber process rest of mixture ($N_2 + 3H_2$) returns in reactor repeating reaction in technological cycle:



1. Gas product $NH_3 \uparrow$ concentration is diminished dissolving in water or condensing liquid, equilibrium shifts to product NH_3 right and NH_3 outcome increases;
2. Increasing pressure above 30 MPa equilibrium shifts to left and product NH_3 outcome decreases;
3. Decreasing pressure below 30 MPa decreases velocity of reaction on catalyst porous iron **Fe** surface and product NH_3 gain decreases;
4. Increasing temperature above $450^\circ C$ degrees, equilibrium shifts to direction of endothermic reaction to left, towards initial compounds $N_2 + 3H_2$ and product NH_3 yield decreases;
5. Decreasing temperature below $450^\circ C$ degrees, equilibrium shifts to direction of exothermic reaction to right, towards product NH_3 and yield increases, but decreases reaction velocity on catalyst porous iron **Fe** surface and product NH_3 yield decreases

On Year 1990 in USA have produced 50 million tons ammoniac. Ammoniac is nitrogen source for fertilizers in agricultural industry, because ammoniac is resource for nitric acid HNO_3 manufacturing, but from nitric acid obtains nitric salts, which in agriculture industry designate with name salpeter. On first half 20th century Chile exports salpeter of Chile $NaNO_3$ and from India purchased salpeter of India KNO_3 . Those resources exhaust in former century, which replaces Haber cyclic process technology introducing on oil and gas refinement factories.

Ammoniac solution in water call about *ammoniac water*. Ammoniac very good dissolves in water. In medicine shops can to purchase liquid ammonia (smelling salts), what is ammoniac solution in water :

Life species on surface of Earth ozone layer cover from ultraviolet radiation of Sun. Ozone molecules O_3 forms on high layers of atmosphere 10 to 35 kilometers high. Ultraviolet radiation brakes double bond of oxygen molecule $O=O$, because collision energy is sufficient for overcome energy barrier in reaction, that crack covalent bonds: $O=O + Q \text{ energy (ultraviolet radiation)} \rightleftharpoons O + O$

Possibility, that split oxygen atoms met each other is negligible small, therefore reverse reaction velocity is very slow due to low oxygen atoms O concentration and possible is collision with other molecule of oxygen So forms ozone: $O_2 + O \rightarrow O_3$. Overall reaction of equilibrium is performing as formation of two ozone molecules $O=O + Q \text{ energy (ultraviolet radiation)} + 2 O_2 \rightleftharpoons O_3 + O_3$.

Equilibrium shifts towards ozone formation, if increases oxygen concentration and ultraviolet radiation supplied amount of energy Q .

Any compound, which react with ozone, dismantles ozone natural formation equilibrium in higher atmosphere layers and ozone concentration decreases, because ozone is depleted.

Ozone forms in devices, which are mounted with ultraviolet lamps (copyist, sanitary junctions of clinics, biological laboratories, agro cultural technologies and sterilization rooms). Ozone forms in electric discharges of sparkles. For example, oxygen ozonator of Riga water refinement and in time of thunder storm. If on air in electric discharge from nitrogen and oxygen forms nitric(II) oxide: $O_2 + N_2 \rightarrow 2 NO$, which react with oxygen: $O_2 + NO \rightarrow 2 NO_2 + O$ and atomic oxygen forms ozone: $O_2 + O \rightarrow O_3$.

Nitric(II) oxide also react with ozone : $O_3 + NO \rightarrow NO_2 + O_2$ and ozone reacting out to converts about oxygen and nitric(IV) oxide.

Thunder storm rain is fertile, because it makes richer soil with nitric oxides (NO_2 , NO) performing nitrates, which are valuable resource in plants life. If soil is richer with nitrates, then healthy and darker green look plants.

Thermodynamic equilibrium state is Attractor for non-equilibrium Homeostasis state

Attractors create functionally active $O_{2\text{aqua}}$, $CO_{2\text{aqua}}$ molecules which drive Homeostasis

1. Warming of planet Earth correlates with carbonic dioxide gas CO_2 concentration in air.
2. Carbonic dioxide gas concentration growth shifts to product formation and increases in reaction produced glucose $C_6H_{12}O_6$ but oxygen O_2 air Attractor amount 20.95% limits Photosynthesis production.
3. Prigogine non equilibrium **Homeostasis** does work as two processes of inhaled oxygen O_2 adsorption on hemoglobin and myoglobin and reverse breeze out CO_2 in lungs. Attractors driving **Homeostasis** with air O_2 concentration 20.95% and $pH=7.36=pK_a+\log([HCO_3^-]/[CO_{2\text{aqua}}])=7.0512+\log(0.0154 \text{ M}/0.0076 \text{ M})$.
4. Catalysts increase reaction velocity for Prigogine Attractor reactivity.
5. Haber for ammoniac synthesis cycle found non-equilibrium Attractor for its reaching time $t_{\text{Attractor}}$ decrease due to increase direct reaction velocity.
6. Ozone concentration on upper atmospheric layers depends on compounds, which react out with ozone and so decreasing ozone on 10 to 15 kilometer high.