# Chemical equilibrium processes in Nature, environment transformation and studies of Le Chatelier principle for Life HOMEOSTASIS and technologies

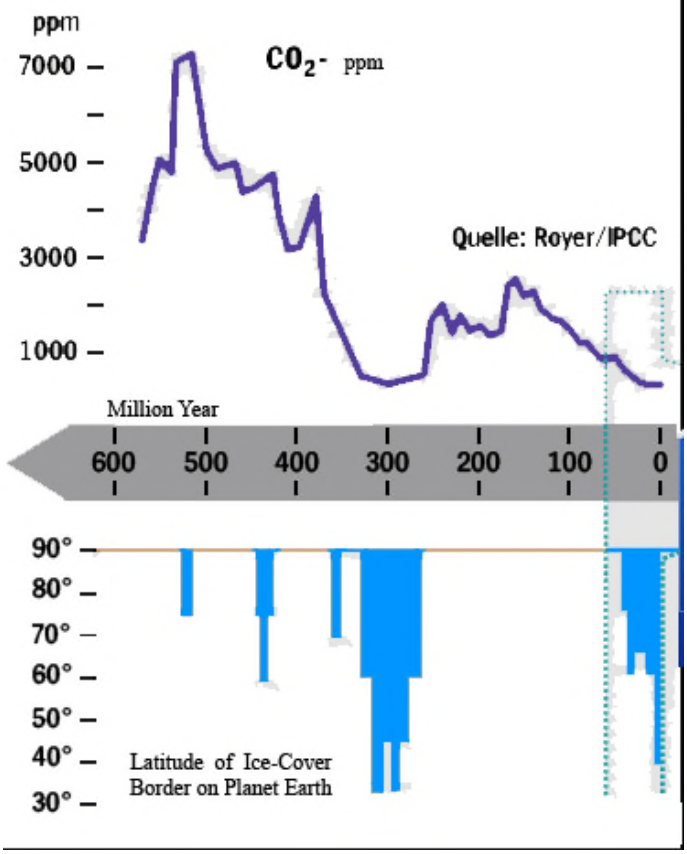
Global observations last hundred years confirm warming of planet or increase surface temperature per 0.5° degrees of planet Earth, what accompanies environmental changes. For example, storms or storming cyclones intensity and frequency, increases carbonic dioxide or carbonic(IV) oxide concentration in air from 0,029 % volume fractions in 1900 year to 0,039% (Ilgonis Vilks Terra 2009) volume fractions in 2012 year .

Draining from reaction medium heat (cooling, what usually describe with decreasing of temperature) has shifts the equilibrium to direction of exothermic reaction or reverse way adding heat shifts the equilibrium to direction of **exothermic** reaction, et cetera in air is evolving the $CO_2\uparrow$.

In many discussions about chemical equilibrium nature is known example, that exist equilibrium between carbon(IV) oxide and in water dissociated bicarbonate anion with hydrogen ions. $CO_2$ gas dissolution reaction is **exothermic** therefore warming the planet shifts equilibrium towards $CO_2$ gas evolving direction. As well as planet Earth and oceans warming increase $CO_2$ in air.

$$H_2O+CO_2\uparrow_{gas} \underset{\text{evaporation}}{\overset{\text{from air}}{\rightleftharpoons}} H^+ + HCO_3^- + Q;\ \Delta H = -10.5\ {}^{kJ}/_{mol}\ \textbf{exothermic}$$

Reconstruction climate of Earth shows temperature and $CO_2$ 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 60%, what corresponds 600000 ppm. As is seen climate changes are occurring with corresponding chemical equilibrium disarranging and new equilibrium establishing, what we can observe as $CO_2$ concentration changes in air.




Before 600 million years $CO_2$ concentration in atmosphere approximately like present-day 0.03% volume fractions, what agree 300 ppm. Atmospheric oxygen $O_2$ concentration approximately 1% from today's 20.95% volume fraction was unconformable for bulk of present-day animal species. Approximately 600 million years back Earth was ice covered reminding Snowball Earth. Glacier fast melting provokes $CO_2$ concentration growth up to 60% - 600000 ppm. Due to greenhouse effect temperature increases from -50° up to 45° degrees, what because of photosynthetic reaction brought oxygen $O_2$ concentration fast increase above present-day 20.95% up to 30% volume fractions, and in 10000 years period established oxygen $O_2$ content level in atmosphere 20.95% volume fraction for next 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 13558 years ago and ended about 11500 years ago and preceding warmer interglacial period end at 13558 years 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 13558 years. What causes ice ages is not completely understood. The composition of the **atmosphere**, changes in the position of our **planet around the Sun**, changes in **ocean currents** and **the Sun radiation** as **spot activity** irregular as well as regular (11 year periods) changes are some of the important factors that control the climate. Exist else unknown factors influence on climate? **Sun** and Earth increase! Earth circumference in 3000 years increases per 60 km (40 074 km -60 km), Mayan astronomers and to days since measure difference. **Solar** wind $4H^+ + 4e^-$ react with oxygen produces water:

$$4H^+ + 4e^- + O_2 \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} 2\,H_2O + Q$$ in **exothermic** reaction.

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

**PreCembrian Ediacaran period 635 – 545** million years ago


Ediacara Hills in Australia, where famous fossils

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.

**Cambrian period 545 – 495** million years ago


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

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.

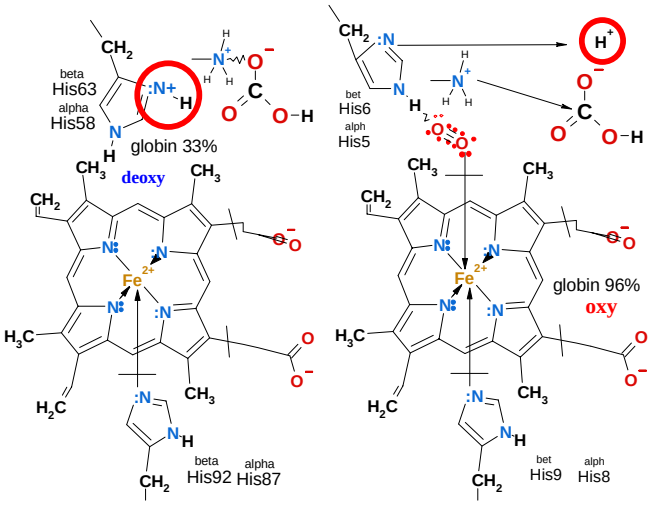
Carbon dioxide concentration increase on air change global equilibrium for green plants photosynthetic PRC red and blue light photon energy absorption assimilated ΔG free $C_6H_{12}O_6$+6$O_2$ for life processes sustaining $\Delta G+Q+6CO_2\uparrow_{gas}+6H_2O \underset{\text{combustion}}{\overset{\text{photo synthesis}}{\rightleftharpoons}} C_6H_{12}O_6+6O_2$; endoergic ΔG=2970 kJ/mol, endothermic ΔH=2805 kJ/mol

In global equilibrium of life nature organisms are imagine expressed as glucose ($C_6H_{12}O_6$) and oxygen ($O_2$) „combusted" transforming reverse way to water and carbon dioxide. So cells and our organisms use in photosynthetic reaction accumulated energy of red and blue light photons. In life nature occurring is reverse reaction of photosynthesis „combustion", of which evolved energy is used for our organism warming and maintenance the life processes in body that is **homeostasis** of oxygen consuming life body.

550 and 200 millions year ago in 10 million year period was observing increased oxygen concentration on air 35% volume fractions comparing with present-day 20,95% volume fractions. Higher temperature and greater oxygen concentration accelerate evolution of animals on Earth and scientists think, that it promote multi cellular organisms and humans birth on planet Earth.

Scientists in investigations have clear up, that ordinary plant species existence is possible if carbon dioxide $CO_2$ concentration in air do not drops below 0,005% volume fraction 50 ppm, other way green plants on Earth perish due to insufficient material $CO_2$ resources, which dramatically would lead to oxygen $O_2$ extinction on planet Earth atmosphere and for us not to be what to breath and after all also what to eat, because no more glucose $C_6H_{12}O_6$ created, however on Earth such risk of evolution never have been exist.

Oxygens $O_2$ from AIR 20.95% $O_2\uparrow$gas assimilation reaction through membrane aquaporins to form $O_{2aqua\text{-}Blood}$ in $O_{2AIR}+H_2O \overset{\text{aquaporin}}{\rightleftharpoons} H_2O+O_{2aqua\text{-}Blood}$ , Four oxygen molecules $O_{2aqua\text{-}Blood}$ have adsorbed on **shuttle** deoxy hemoglobin $4O_{2aqua}+(H^+His63,58)_4Hb_T$ ·salt bridges$(HCO_3^-)_4 \Leftrightarrow Hb_R(O_2)_4+4H^++4HCO_3^-$ s release releases four protons $4H^+$, $4HCO_3^-$, change the venous blood concentration $[O_{2aqua\text{-}Blood}]=1{,}85\cdot10^{-5}$ M to stabilize arterial blood concentration $[O_{2aqua\text{-}Blood}]=6\cdot10^{-5}$ M and shift to right oxygen concentration sensitive **shuttle Hb** equilibrium. To right deviation regulates erythrocytes glycolysis metabolite $BPG^{5-}$ as acid salt of glycerate $G^-$ **2,3** dihydroxy **phosphate** esters $H_2COPO_3^{2-}$-$HCOPO_3^{2-}$-$COO^-$ with homeostasis concentration $[BPG^{5-}]$= 5 mM. Krebs-Citric cycle exothermic and exoergic reactions consume oxygen and $BPG^{5-}$ squeeze in to **cavity** to stabilize arterial concentration $[O_{2aqua}]=6\cdot10^{-5}$M from stored reserves 459 times referring to arterial blood initial solution concentration $[O_{2aqua}]=6\cdot10^{-5}$M. Each $H^+$ and $HCO_3^-$ ion shifts respiration equilibrium to right $H^+ + HCO_3^- + Q \Leftrightarrow H_2O + CO_2\uparrow_{gas}$ via membrane channels. As $Hb_T$ capture $H^+$ after $O_2$ desorbtion due to Krebs-Citric cycle consumption in oxidative phosphorylation forming product $CO_{2aqua}$. Carbonic anhydrase converts $CO_{2aqua}$ to $HCO_3^-$ and $H_3O^+$ ions maintaining stabile blood pH=7.36±0.01 due to capture in **shuttle** hemoglobin bicarbonate linked with $HCO_3^-\ldots H_3^+N$—amino acid salt bridge and equal produced protons $[CO_{2Krebs}]=0{,}0275=[HCO_3^-]=[H^+]$ deoxy $(H^+His63,58)_4Hb_T$ what venous blood brings to ***lungs***.




$$Q_{aqua}+CO_{2aqua}+2H_2O \leftarrow \overset{CA}{\rightarrow} H_3O^+ + HCO_3^- \leftarrow \overset{\text{Membrane}}{\rightarrow} H_2O+H_2CO_3+Q_{gas} \leftrightarrow H_2O+CO_2\uparrow_{gas}+H_2O\uparrow_{gas}.$$

Endothermic evaporation reactions gradual sequences: **1)** $CO_{2aqua}+2H_2O+Q \leftarrow \overset{CA}{\rightarrow} H_3O^+ + HCO_3^-$ endothermic $\Delta H_r$= +9.75 $^{kJ}/_{mol}$; **2)** $H_3O^+ + HCO_3^- \leftarrow \overset{\text{Membrane}}{\rightarrow} H_2O+H_2CO_3+Q$ exothermic$\Delta H_r$=-9.76 $^{kJ}/_{mol}$ and hydrogen ions acidity shift $H_2CO_3$ **endothermic** $\Delta H_r$= +20.3 $^{kJ}/_{mol}$ decomposition **3)** $H_2CO_3+Q \rightarrow H_2O+CO_2\uparrow_{gas}$ breath out by concentration gradient, heat supply and proton channeling in lungs after $O_2 + H^+Hb_T \leftrightarrow Hb_RO_2+H^+$.

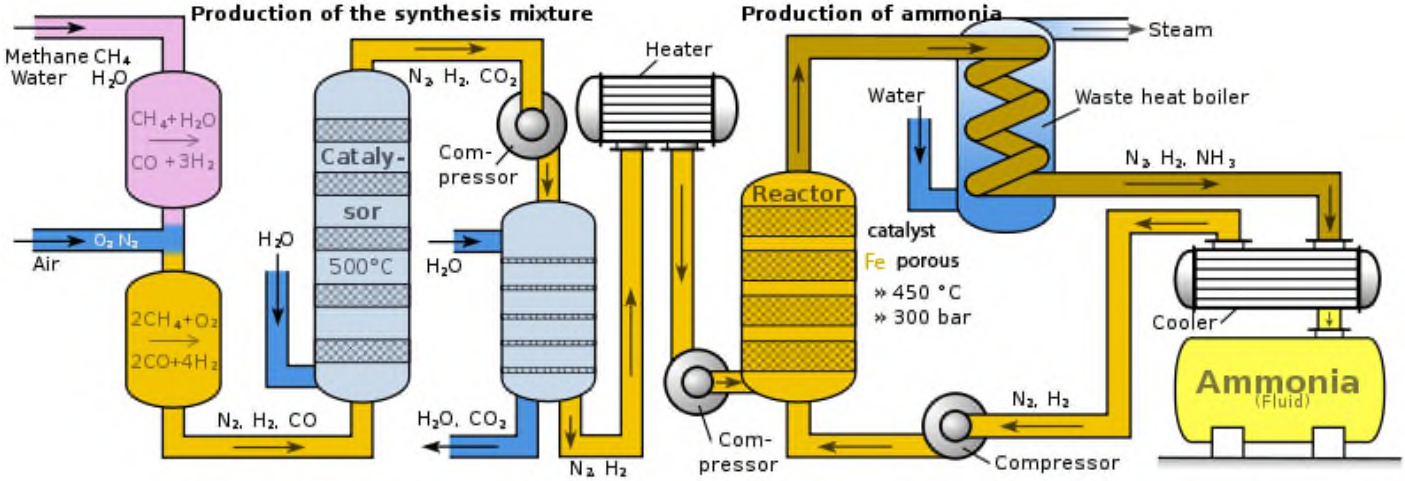
1) hydrogen $H^+$ ion concentration (acidity) increase shifts equilibrium right side => $Hb_T$ adsorbed $O_2$ yield $H^+$;

2) bicarbonate $HCO_3^-$ concentration increase breaking linked $HCO_3^-\ldots H_3^+N$- shifts equilibrium right side =>;

3) heating + **Q** shifts equilibrium right side → (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 $CO_2\uparrow_{gas}$ breathing out).

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 ignite. In oil, gas and coal refining industry arises huge amount of hydrogen $H_2$, as well hydrogen atoms containing organic compounds was heated. Up to1920 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 Chatlier 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° C temperature, but at modern equipment optimal established 450° 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 $\mathbf{pNH_3}\downarrow$ 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 nit`rogen and hydrogen mixture. Heated 450° 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:

$$N^0{}_2 + 3H^0{}_2 \underset{450°C,\ 30MPa}{\overset{\mathbf{Fe\ porous}}{\rightleftharpoons}} 2N^{-3}H^{+1}{}_3 + Q\ (92\ kJ)\ ;\ \mathbf{NH_3}\uparrow + \mathbf{H_2O} \underset{\text{reverse reaction}}{\overset{\text{direct reaction}}{\rightleftharpoons}} NH_4^+ + OH^- + \mathbf{Q}\ .$$

1. Gas product $\mathbf{NH_3}\uparrow$ concentration is diminished dissolving in water or condensing liquid, equilibrium shifts to product $\mathbf{NH_3}$ right and $\mathbf{NH_3}$ outcome increases;
2. Increasing pressure above 30 MPa equilibrium shifts to left and product $\mathbf{NH_3}$ outcome decreases;
3. Decreasing pressure below 30 MPa decreases velocity of reaction on catalyst porous iron **Fe** surface and product $\mathbf{NH_3}$ gain decreases;
4. Increasing temperature above 450° C degrees, equilibrium shifts to direction of endothermic reaction to left, towards initial compounds $N_2$ + $3H_2$ and product $\mathbf{NH_3}$ yield decreases;
5. Decreasing temperature below 450° C degrees, equilibrium shifts to direction of exothermic reaction to right, towards product $\mathbf{NH_3}$ and yield increases, but decreases reaction velocity on catalyst porous iron **Fe** surface and product $\mathbf{NH_3}$ 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 $\mathbf{HNO_3}$ 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 $\mathbf{NaNO_3}$ and from India purchased salpeter of India $\mathbf{KNO_3}$. 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 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 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.

**Chemical equilibrium disruption processes in Nature, environment transformation and importance of Le Chatlier theorem discovery for Life HOMEOSTASIS and technologies**

1. Warming of planet Earth increases carbonic dioxide gas $CO_2$ concentration in air.
2. Carbonic dioxide gas concentration growth shifts equilibrium for green plant photosynthetic reaction to product formation and increases in reaction produced glucose $C_6H_{12}O_6$ and oxygen $O_2$ amount.
3. Le Chatelier's principles in **Homeostasis** does work as two equilibria shifts of inspirated oxygen $O_2$ adsorbtion on hemoglobine or myoglobine and following shifts ones more breeze out $CO_2$ in lungs on epithelial cells surface as evidence biological oxidation with oxygene in live cells.
4. Catalysts do not change reaction equilibrium state: concentration, pressure and temperature influence on equilibrium, but increases velocity for establishing of equilibrium.
5. Haber for ammoniac synthesis cycle found optimal circumstances, applying Le Chatlier theorem and determined catalyst , which increases velocity for establishing of equilibrium.
6. Ozone equilibrium on upper atmospheric layers depends on compounds, which react out with ozone and so decreasing ozone concentration 10 to 15 kilometer high.

From AIR in water dissoluted oxygen through aquaporins entrance in arterial blood :

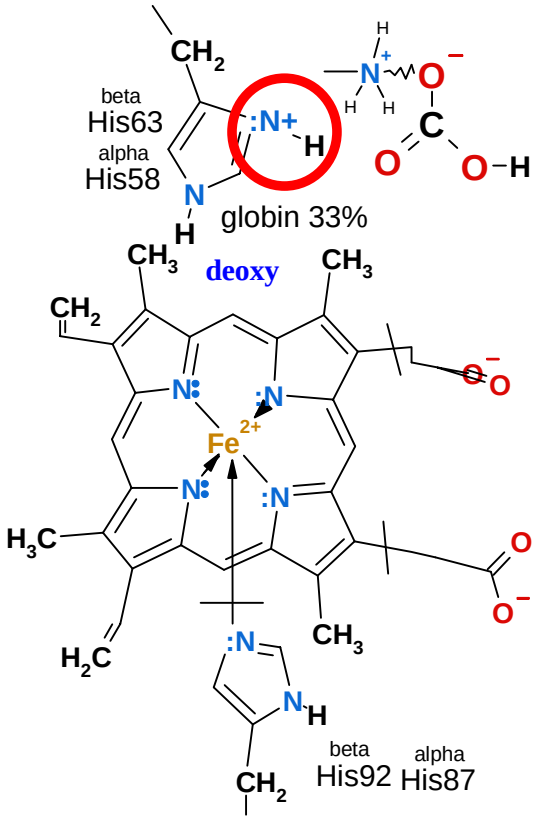
$$O_{2AIR}+H_2O \overset{aquaporin}{\rightleftharpoons} H_2O+O_{2aqua\text{-}Blood}$$ . 4 Oxygen molecules $O_{2aqua\text{-}Blood}$ of blood plasma-water medium adsorb on **shuttle** deoxy hemoglobin $Hb_T$:

$(H^+His63,58)_4Hb_T+4O_{2aqua\text{-}Blood} \Leftrightarrow Hb_R(O_2)_4+4H^+$ , release four protons 4 $H^+$ and salt bridge linked bicarbonate $4HCO_3^-$ . It stabilize venous blood concentration $[O_{2aqua\text{-}Blood}]=1{,}85\cdot10^{-5}$ M to arterial $[O_{2aqua\text{-}Blood}]=6\cdot10^{-5}$ M and shift to right oxygen concentration sensitive equilibrium :

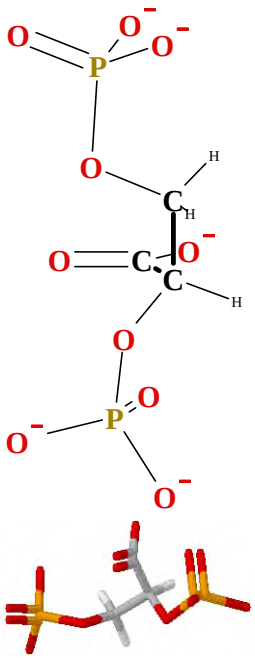
$$4O_{2aqua\text{-}Blood}+(H^+His63,58)_4Hb_T \cdots salt \cdots bridges(HCO_3^-)_4 \Leftrightarrow Hb_R(O_2)_4+4H^+ +4\,HCO_3^-$$ .

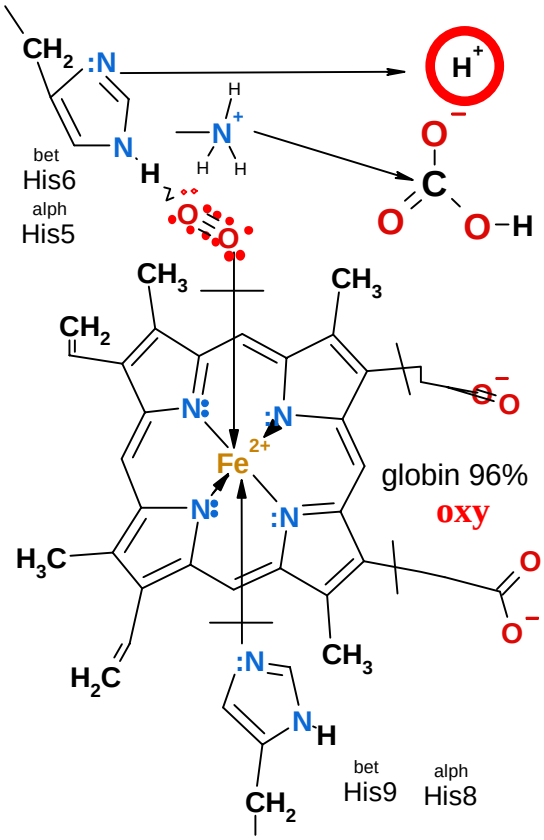
Shift to right regulates erythrocytes glycolysis metabolite as $H_2COPO_3^{2-}$-$HCOPO_3^{2-}$-$COO^-$ **2,3**-dihydroxy acid salt $G^-$ **bisphospho** glycerate esters $BPG^{5-}$ with homeostasis concentration $[BPG^{5-}]$= 5 mM. $BPG^{5-}$ squeezed out from **cavity** has stored reserves 459 times of the stabilized blood concentration $[O_{2aqua}]=6\cdot10^{-5}$M.

Krebs-Citric cycle exothermic and exoergic reactions consume oxygen and $BPG^{5-}$ squeezed in **cavity** desorbs oxygen stabilizing concentration in water from stored reserves 459 times referring to arterial concentration amount $[O_{2aqua}]=6\cdot10^{-5}$M. From water and $CO_{2aqua}$ enzyme carbonic anhydrase produce $HCO_3^-$ and $H_3O^+$ ions as equal count $H^+$ and $HCO_3^-$ particles in exchange between equal desorbed oxygen $O_2$ molecule account: $Hb_R(O_2)_4+4H^+ \Leftrightarrow 4O_{2aqua\text{-}Blood}+(H^+His63,58)_4Hb_T$, kept physiologic pH=7.36±0.01 value. Bicarbonate captured by salt bridge $HCO_3^-\ldots H_3^+N$- in the same amount $[CO_{2Krebsa}]=0{,}0275$ M=$[HCO_3^-]=[H^+]$ of protons count in deoxy $(H^+His63,58)_4Hb_T$ **shuttle** of venous blood circulation reach the **lungs**.




bis**phosphate**
glyceride
**2,3-ester** salt
$[BPG^{5-}]$=5 mM






Via membrane channels on epithelial surface reaching $H^+$ , $HCO_3^-$ ions shift respiration equilibrium to right:

$H^+ +HCO_3^- + Q \Leftrightarrow H_2O + CO_2\uparrow_{gas}$, with heat supply in the centre of body to **lungs** epithelial surface.

Endothermic $\Delta H_r$= +20.281 $^{kJ}/_{mol}$ evaporation processes in three gradual reactions on the sequence:

**1)** $CO_{2aqua}+2H_2O+Q \leftarrow \overset{CA}{\rightarrow} H_3O^+ +HCO_3^-$ endothermic $\Delta H_{HCO3-}$= +9.75 $^{kJ}/_{mol}$;

**2)** $H_3O^+ +HCO_3^- \leftarrow \overset{Membrane}{\rightarrow} H_2O+H_2CO_3+Q$ $\Delta H_{H2CO3}$= -9.76 $^{kJ}/_{mol}$ exothermic and

**3)** hydrogen ions made acidity pH=5 shifts $H_2CO_3$ endothermic $\Delta H_{CO2}$= +20.291 $^{kJ}/_{mol}$ decomposition $H_2CO_3+Q \rightarrow H_2O+CO_2\uparrow_{gas}$ respiration to AIR. Over all process drive concentration gradients, heat supply and movement protons, bicarbonates through **lungs** channels as oxygen adsorbed. **Lungs** breath out $CO_2\uparrow_{gas}$ in endothermic process $\Delta H_r=\Delta H_{HCO3-}+\Delta H_{H2CO3}+\Delta H_{CO2}$=+9.75 -9.76+20.291=+20.281 $^{kJ}/_{mol}$

$$Q_{aqua}+ CO_{2aqua}+2H_2O \leftarrow \overset{CA}{\rightarrow} H_3O^+ +HCO_3^- \leftarrow \overset{Membrānas}{\rightarrow} H_2O+H_2CO_3+Q_{gas} \leftrightarrow H_2O+CO_2\uparrow_{gas}+H_2O\uparrow_{gas}.$$

from Krebs-Citric cycle product $CO_{2aqua}$ to lungs alveolar epithelial surface with pH=5 $CO_2\uparrow_{gas}$.

**COMPLEX and ENZYME governed EQUILIRIA in human organism**

Complex reactions are all 3000 in human body maintaining **HOMEOSTASIS** governed by ENZYMES.

Human body complex reactions are four 4 of five 5 except 2. parallel non Enzymatic reactions:

1. gradual-sequential reactions,
3. joint-tandem reactions,
4. competitive-regulatory reactions and
5. radical Enzymatic reactions.

Enzymatic reactions — 5 complex reactions — Non Enzymatic reactions the HAZARD for organism LIFE

Page 7th : http://aris.gusc.lv/BioThermodynamics/Kinetics.pdf

**1. GRADUAL-CONSECUTIVE**
organized as sequence of **ENZYMES** in
Glycolysis, Krebs cycle, Replication,
Polymerisation (Polycondensation)

**1. Chaotic**

Page 7th : http://aris.gusc.lv/BioThermodynamics/74LidzsvarsDabaEngl.pdf

**ENZYMES** are **SPECIFIC** and **SELECTIVE**
single product **Impossible=>**

**2. PARALLEL products formation**
multiple products

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

Thermodynamics forbiddens
$\Delta G=\Delta H-\Delta S\cdot T>0$ is positive no reaction possible

**4. COMPETITIVE** regulation as **inhibition** and **allostery**
sensitive to concentration $O_{2aqua}$, $HCO_3^-$, $H^+$
His63,58 as for hemoglobin, His64 for myoglobin
as regulated back response prevent over production
pH=7.36, arterial $[O_{2aqua}]=6\cdot10^{-5}$ M, venouse $[O_{2aqua}]=1.8\cdot10^{-5}$ M.

**4. Chaotic**

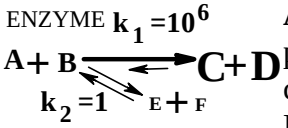
**5. ENZYMATIC RADICAL REACTIONS**
in isolated active site single product
prevent radical-chain initiation

non-ENZYMATIC radical-chain reaction
multiple chain products formation

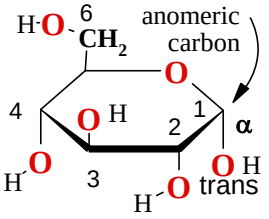
**1. PARALLEL Products** avoid **ENZYMES** governed **REACTIONS**

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. As ENZYME governed reaction drive reactions in needed direction for **HOMEOSTASIS** PATHWAY.

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




**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.



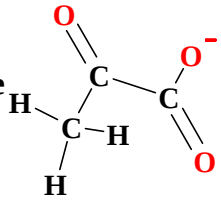

## 2.GRADUAL (CONSECUTIVE) ENZYME supported EQUILIBRIA SEQUENCE

Glycolysis is most popular gradual equilibria sequence in human organism **HOMEOSTASIS** PATHWAYS.

**Glc** $\overset{\text{Glc transporter}}{\underset{1}{\rightleftharpoons}}$ **Glc** $\overset{\text{Hexokinase}}{\underset{2}{\rightleftharpoons}}$ **Glc6P** $\overset{\text{Isomerase}}{\underset{3}{\rightleftharpoons}}$ **Fruc6P** $\overset{\text{Kinase1}}{\underset{4}{\rightleftharpoons}}$ **Fruc6P1P** $\overset{\text{Aldolase}}{\underset{5}{\rightleftharpoons}}$ **GlycAld**

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

**GlycAld** $\overset{\text{DHkinase}}{\underset{6}{\rightleftharpoons}}$ **13BPG** $\overset{\text{Kinase}}{\underset{7}{\rightleftharpoons}}$ **3PG** $\overset{\text{Mutase}}{\underset{8}{\rightleftharpoons}}$ **2PG** $\overset{\text{PyruvateKinase}}{\underset{9}{\rightleftharpoons}}$ **2 pyruvate**



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 $O_2$ asimilation in organism and $CO_2$ respiration out.

**I)** $O_{2AIR}+H_2O \overset{\text{aquaporin}}{\rightleftharpoons} H_2O+O_{2aqua}$; **deoxy**$(H^+\text{His63,58})_4Hb_T$ $+4O_{2aqua} \leftarrow [O_2]=6\cdot10^{-5}$ M$\rightarrow$ **oxy**$Hb_R(O_2)_4+4H^+$,

**II)** $Q_{aqua}+CO_{2aqua}+2H_2O \overset{CA}{\longleftrightarrow} H_3O^+ + HCO_3^- \overset{\text{membrane}}{\rightleftharpoons} H_2O+H_2CO_3+Q(gas) \rightleftharpoons H_2O + CO_2\uparrow_{gas} + H_2O$.

## 3. ENZYMATIC JOINT TANDEM EQUILIBRIA drive forbidden REACTIONS

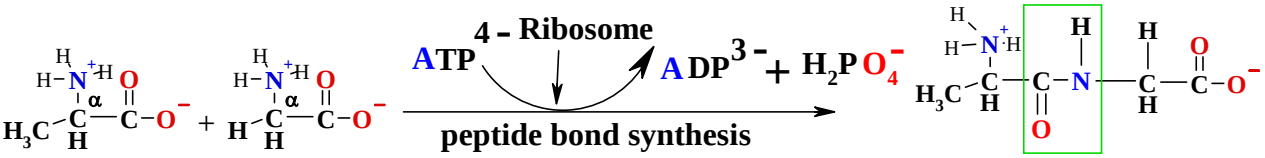
http://aris.gusc.lv/BioThermodynamics/BioChemicalPprocesE.pdf

**Green** plants **Photosynthesis** reaction is thermodynamically forbidden as endoergic $\Delta G_r$= +2970,441 $^{kJ}/_{mol}$: $6CO_2 + 6H_2O + Q$ —x no → $C_6H_{12}O_6 + 6O_2$ and as endothermic reaction $\Delta H_{reac}>0$ $\Delta H_{reac}$= +2805,27 $^{kJ}/_{mol}$. 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** $C_6H_{12}O_6$, **oxygen** **6** $O_2$ 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 $C_6H_{12}O_6 + 6O_2$ wich becomes compensate for the overall process thermodynamically possible. Global **P**hotosynthesis oxygen equilibrium concentration is 20.95%=$[O_2\uparrow_{gaiss}]$. To decrease concentration, for example, 2%=$[O_2\uparrow_{gaiss}]$ **Plant Enzymes** **P**hotosynthesis quick restore Global concentration in air 20,95%. Global **P**hotosynthesis equilibrium further shift supplying the heat **Q** and $CO_2$ . Therefore Global warming promote increase of **Q** and $CO_2$ and so furthere **P**hotosynthesis, but in Ace Age **P**hotosynthesis stop down:

$$6CO_2 + 6H_2O + Q \overset{\text{light: red, blue; E=hν; PRC; photo synthesis}}{\underset{\text{combustion}}{\rightleftharpoons}} C_6H_{12}O_6 + 6O_2$$

The ENZYME complex Ribosomes are for Peptide Bond synthesis: ala + gly→ala-gly+ $H_2O$ with free energy $\Delta G_{reac}$=**+17.2** $^{kJ}/_{mol}$ transfer shift **ATP** hydrolyze exoergic free energy $\Delta G_{hydrolize}$= **-30.5** $^{kJ}/_{mol}$ which part is used free energy store $\Delta G_{reac}$ =**+17.2** $^{kJ}/_{mol}$ in one mole of peptide bond.

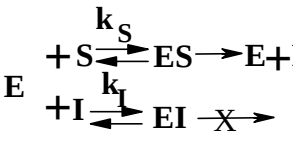
Ala [A] Alanine + Gly [G] Glycine $\overset{\text{4 – Ribosome; ATP; ADP}^{3-} + H_2PO_4^-}{\underset{\text{peptide bond synthesis}}{\longrightarrow}}$ Ala-Gly AG AlaninoGlycine



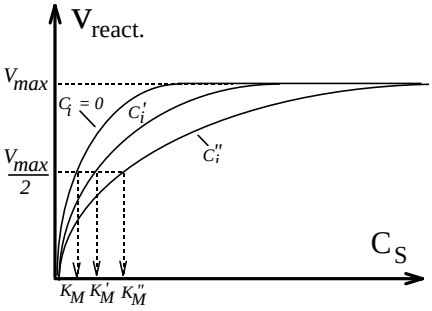
## 4. COMPETITIVE regulated ENZYME EQUILIBRIA allostery and inhibition

with $O_{2aqua}$, $HCO_3^-$, $H^+$ concentrations sensitive His63,58 hemoglobin and His64 myoglobin shuttle through back response regulated shift of equilibrium according Le Chatelier's Principle-Theorem stabilise pH=7.36, arterial concentration $[O_{2aqua}]=6\cdot10^{-5}$ M and venous concentration $[O_{2aqua}]=1.8\cdot10^{-5}$ M.

*In competitive equilibria two different initial compounds compete on one ENZYME through distinguish equilibria regulate* according Le Chatelier's principle-theorem *products* amount in constant expression $K_{eq}=\frac{[\text{products}]}{[\text{initial\_compounds}]}$ ratio.




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 $\mathbf{C_E}$ involved into competitive inhibition equilibrium. Physiologic ENZYME regulation is an equilibrium which shifting to right side promoted by inhibitor concentration $\mathbf{C_I}$ increase, for example, using medicine aspirin, warfarin e.c..




$\vec{\mathbf{v}}_{react.} = \frac{\mathbf{v_{max}} \mathbf{C_S}}{\mathbf{K_m} + \mathbf{C_S}}$ *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* $\mathbf{v_{max}}$**..**

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

## 5. ENZYMATIC restricted RADICAL REACTIONS EQUILIBRIA and non ENZYMATIC radical-chain multiple reactions products

**ENZYMATIC reactions** avoid open radical – chain reactions n one manner. Human organism ENZYMES realized radical reactions occur in proteins closed active site pocket on prosthetic group heme iron $\mathbf{Fe^{3+}}$. Cell ENZYMES driven radical reactions as **oxidation**, **peroxidation** form the stabilr products and Catalase toxic peroxide $\mathbf{2H{:}{-}{\bullet\bullet}{:}O{-}{:}{-}O{:}{\bullet\bullet}{-}{:}H}$ converted to biological goods oxygen $\mathbf{O_2}$, water $\mathbf{2H_2O}$, heat **Q** .

**Activated** oxygen **Singlet** molecule $\mathbf{\bullet{:}{:}O{-}{:}{-}O{:}{:}\bullet}$ having one covalent bond found on ENZYME heme pockets iron $\mathbf{Fe^{3+}}$ by donor acceptor bond (in **peroxidases**, **dismutases**, **CATALASES**). ENZYMES active site pockets are isolated by hydrophobic pocket from surrounded water medium $\mathbf{H_2O}$ + $\mathbf{O_2}$ with oxygen concentration (from $[O_2]=1{,}85\cdot10^{-5}$ M in venozām blood up to $[\mathbf{O_2}]=6\cdot10^{-5}$ M in arterial blood). 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** risk increases five times. Peroxide accumulation risk decreases $30\bullet10^6$ thirty million times with CATALASE.

$$\vec{\mathbf{v}} \sim [\mathbf{O_2}] \text{ or } \vec{\mathbf{v}} \sim [\mathbf{H_2O_2}]$$

Non ENZYMATIC radical-chain reactions hazards as multiple damages generation.
Non-ENZYMATIC radical-chain reaction produce many different products, that forbidden in life strategy, which damages life molecular structures and ENZYMATIC complexes natural processes Oxidative stress and technology hazards was the reason for Apollo cosmos project closing in 70th of 20 century.

That not acceptable in ENZYME governed radical reactions, where necessary form one specific product.
Radical formation from $\mathbf{H_2}$ and $\mathbf{Br_2}$ begins by light radiation ***initiation*.**
***Initiation*** is first stage of radical formation as activated particles with low activation energy $\mathbf{E_a}$=>0 kJ/mol. The radical here is photochemical: $\mathbf{Br_2}$ molecules absorb light photons, forming from bromine molecule $\mathbf{Br_2}$ uncoupled bromine atom radicals **Br•** + **Br•** with unpaired electron **•**: **Br-:-Br** $\xrightarrow{\sim h\nu}$ **Br• + Br•**
***Propagation*** is second stage of radical-chain reaction. Where active particles **Br•** radicals are short-living active particles, that react in the ***propagation***: **Br•+ H-:-H → H• + H-:-Br** .

In this reaction a stable molecule of product **HBr** is formed and a new radical active particle - **H•** atom is formed. **H•** reacts further and continue the radical-chain ***propagation***: **H• + Br-:-Br → Br• + H-:-Br** .
Here again a product (**HBr**) molecule is formed and an **Br•** atom is created again, **Br•** radical atom can react with next $\mathbf{H_2}$ 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 $\mathbf{H_2}$ and $\mathbf{Br_2}$ reaction one can imagine **3** different reactions, in which radical-active particles die:

**Br• + H• → HBr; Br• + Br• → $\mathbf{Br_2}$; H• + H• → $\mathbf{H_2}$**

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.