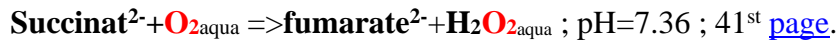


CATALASE indispensable **Life** molecular engine for reaction favored, hundred percents • 100% efficiency



$$\Delta G_{Hess} = \Delta G^{\circ}_{H_2O_2} + \Delta G^{\circ}_{fumarate} - \Delta G^{\circ}_{O_2} - \Delta G^{\circ}_{Succinat} = -151,549 - 519,4688 - (-522,414 + 16,4) = -165 \text{ kJ/mol};$$

$$\Delta G_{Hess} = \Delta H_{Hess} - T \cdot \Delta S_{Hess} = -48.16 - 298.15 \cdot 0.0458 = -61.815 \dots \text{ kJ/mol exoergic}$$

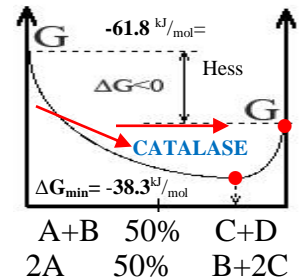
$$\Delta G_{min} = \Delta G_{eq} = (E^{\circ}_{Red} - E^{\circ}_{Ox}) \cdot F \cdot n = (0,2512 - 0,4495) \cdot 96485 \cdot 2 = (-0.1983) \cdot 96485 \cdot 2 = -38,3 \text{ kJ/mol};$$

$$K_{eq} = \exp(-\Delta G_{eq}/R/T) = \exp(382565,95/8,3144/298,15) = 5057721 \text{ favored equilibrium}$$

Essential unsaturated fatty acid elongation C20:4 and ethyl group -CH₂-CH₂- conversion to cis double bond H>C=C<H in peroxisomes is negative ΔG_{Hess}=-61.8 kJ/mol free energy change, but minimized reaching equilibrium mixture ΔG_{min}=ΔG_{eq}=-38.3 kJ/mol .

CATALASE in complex reaction sequence favors stable unsaturated fatty acid product

efficiency • 100%: $K_{eq} = 5057721 = \frac{[Fumarate^{2-}] \cdot [H_2O_2]}{[Succinate^{2-}] \cdot [O_2]}$ **CATALASE** because erasing



peroxide to zero [H₂O₂]=0 mol/liter and process velocity limits only dehydrogenase enzyme. Attractors, enzymes reactivity are indispensable Brownian molecular engines for homeostasis, evolution and survival.

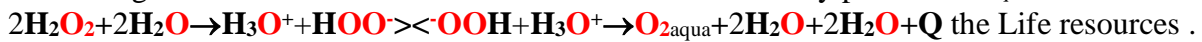
High rate protolysis activate $G_{H_2O} + G_{HOOH} = 0 + 274,5 = 274,5 \text{ kJ/mol}$ to $G_{H_3O^+} + G_{HO_2^-} = 22,4 + 328 = 350,4 \text{ kJ/mol};$

1), 2), 3): $2H_2O_2 + 2H_2O$ protolysis $\rightarrow H_3O^+ + HOO^- >< OOH + H_3O^+$ collision $\rightarrow O_{2aqua} + 2H_2O + 2H_2O + Q;$

1) Protolysis $HOOH + H_2O \rightleftharpoons H_3O^+ + HOO^-$ pK_a=11.75 create collisions disproportionation $HOO^- >< ^-OOH$.

2) High activation energy $E_a = 79000 \text{ J/mol}$ colliding $HOO^- >< ^-OOH$ with slow velocity $\vec{k} = 1.416 \cdot 10^{-16} \text{ M}^{-2}\text{s}^{-1}$ constant disproportionate ^-OOH oxidize atoms to O_{2aqua} and second atoms ^-OOH reduce about 2 OH^- ions,

3) which neutralizing to water: $2OH^- + 2H_3O^+ \rightarrow 2H_2O + 2H_2O$. In summary produce $O_{2aqua} + 2H_2O + 2H_2O + Q;$



Collision negative to positive $HOO^- > Fe^{3+}$ have $E_a = 29 \text{ J/mol}$ indispensable law activation energy and with protonation the His74 and Asn 147 velocity constant increases over absent **CATALASE** 30 million times as geometric factor **A** improve to $A \Rightarrow 0.131$:



Protolysis activate transition state complex **oxygen + water + heat + CATALASE,**

Negative anions collisions with positive iron Fe^{3+} ion produce life resources 30 million times faster.

reactivity: $\vec{v}_{enz} = k_{cat}/K_M \cdot [E] \cdot [H_2O_2] = 3.6 \cdot 10^7 \cdot [E] \cdot [H_2O_2]$, because collision $HOO^- \Rightarrow Fe^{3+}$ activation energy

$E_a = 29 \text{ J/mol}$ of Catalase is low. Usual Catalase concentration is small $[E] = 10^{-8} \text{ M}$ and $\vec{v}_{enz} = 0.36 \cdot [H_2O_2] \text{ s}^{-1}$. The geometric factor $A = 0.131$ active collision fraction is 0.988 and 98.8% of total collisions are active and converting to products $O_{2aqua} + 2H_2O + Q$ with velocity constant value is:

$$\vec{k} = A \cdot e^{-\frac{E_a}{RT}} = 0.131 \cdot e^{-\frac{29}{8,314 \cdot 298}} = 0.131 \cdot 0.988 = 0.1296 \text{ M}^{-1}\text{s}^{-1}, \vec{v} = \vec{k} \cdot [H_2O_2]^2 = 0.1296 \cdot [H_2O_2]^2 \text{ Ms}^{-1}.$$

At absence catalyst activation energy of ions collisions $HOO^- >< ^-OOH$ is very high $E_a = 79000 \text{ J/mol}$ and low geometric factor $A = 0.01$ make the Arrhenius velocity constant expression negligible small:

$$\vec{k} = A \cdot e^{-\frac{E_a}{RT}} = 0.01 \cdot e^{-\frac{79000}{8,314 \cdot 298}} = 0.01 \cdot 1.419 \cdot 10^{-14} = 1.419 \cdot 10^{-16} \text{ M}^{-1}\text{s}^{-1}.$$

$$\vec{v} = \vec{k} \cdot [H_2O_2]^2 = 1.419 \cdot 10^{-16} \cdot [H_2O_2]^2 \text{ Ms}^{-1}; \text{ if } [H_2O_2] = 1 \text{ M}; \sqrt{\vec{v}} = \sqrt{\vec{k}} \cdot [H_2O_2] = 1.191 \cdot 10^{-8}.$$

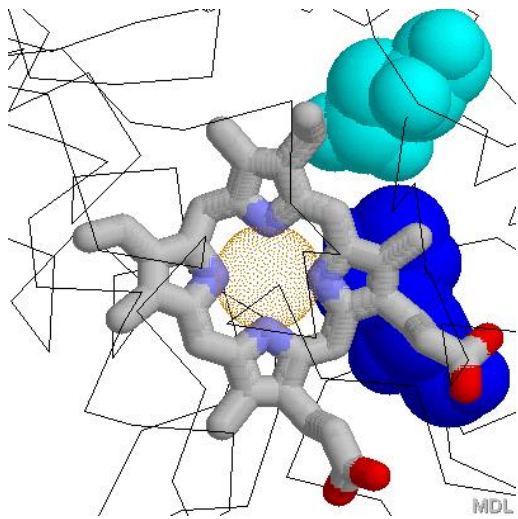
As $\sqrt{\vec{v}} = \frac{CAT \sqrt{\vec{k}}}{\sqrt{k}} \cdot [H_2O_2] = 0.36 \cdot [H_2O_2]$; $\frac{CAT \sqrt{\vec{k}}}{\sqrt{k}} = \frac{0,36}{1,19 \cdot 10^{-8}} = (4.) 30 \cdot 10^6$ times greater velocity constant increase

$$\Delta G_{eqStandard} = (E^{\circ}_{H_2O_2} - E^{\circ}_{H_2O_2Ox}) \cdot F \cdot n = (0,4495 - 1,6855) \cdot 96485 \cdot 2 = (-1,1845) \cdot 96485 \cdot 2 = -238,5 \dots \text{ kJ/mol};$$

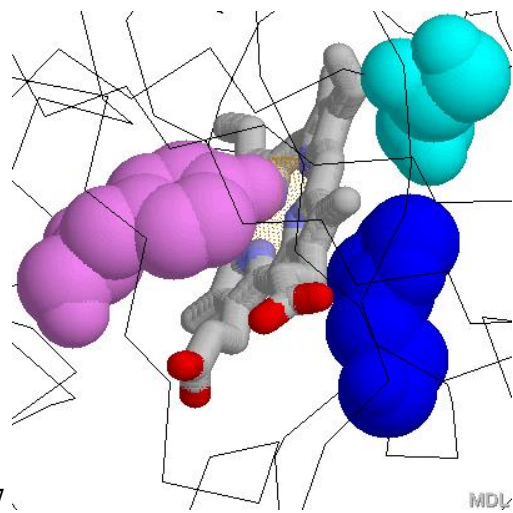
$$\Delta G_{HessAlberty} = G_{O_2} + 2G_{H_2O} - 2G_{H_2O_2} = 330 + 2 \cdot (0) - (2 \cdot 284) = -238 \dots \text{ kJ/mol}; \text{ Alberty}$$

Absolute potential scale is coinciding with Alberty absolute free energy scale.

$$\frac{[O_2]_{aqua} \cdot [H_2O]^2}{[H_2O_2]_{aqua}^2} = K_{eqStandard} = K_{H_2O_2} = \exp(-\Delta G_{eqStandard}/R/T) = \exp(238500/8,3144/298,15) = 10^{41,8} \dots$$

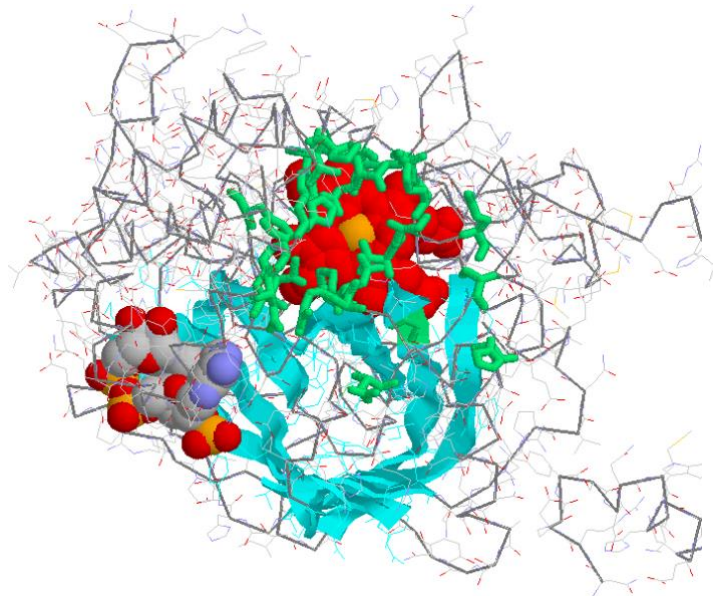


MDL Asn147, His74,

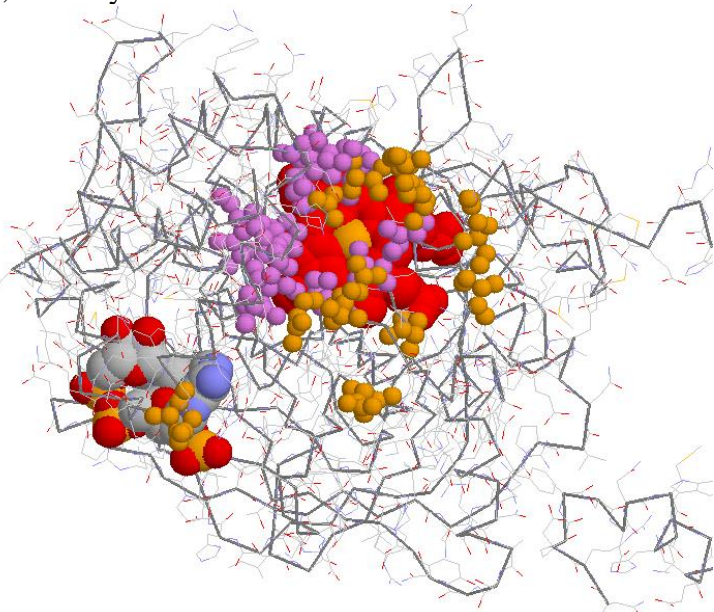


Tyr357,

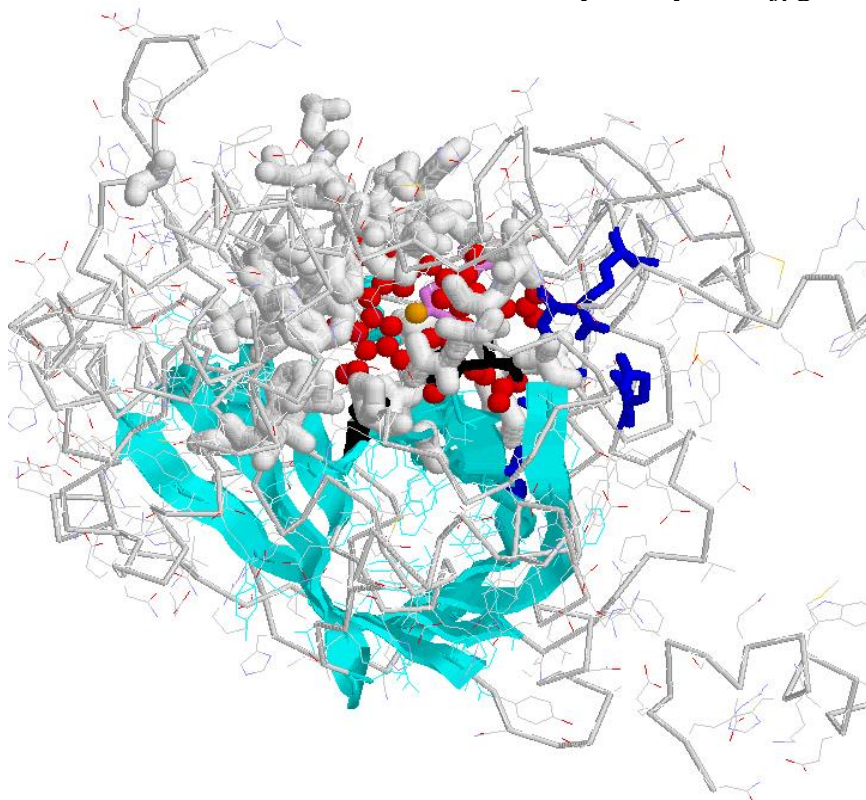
MDL



Piltuve1.jpg



PiltuveHydroPhylPhob.jpg

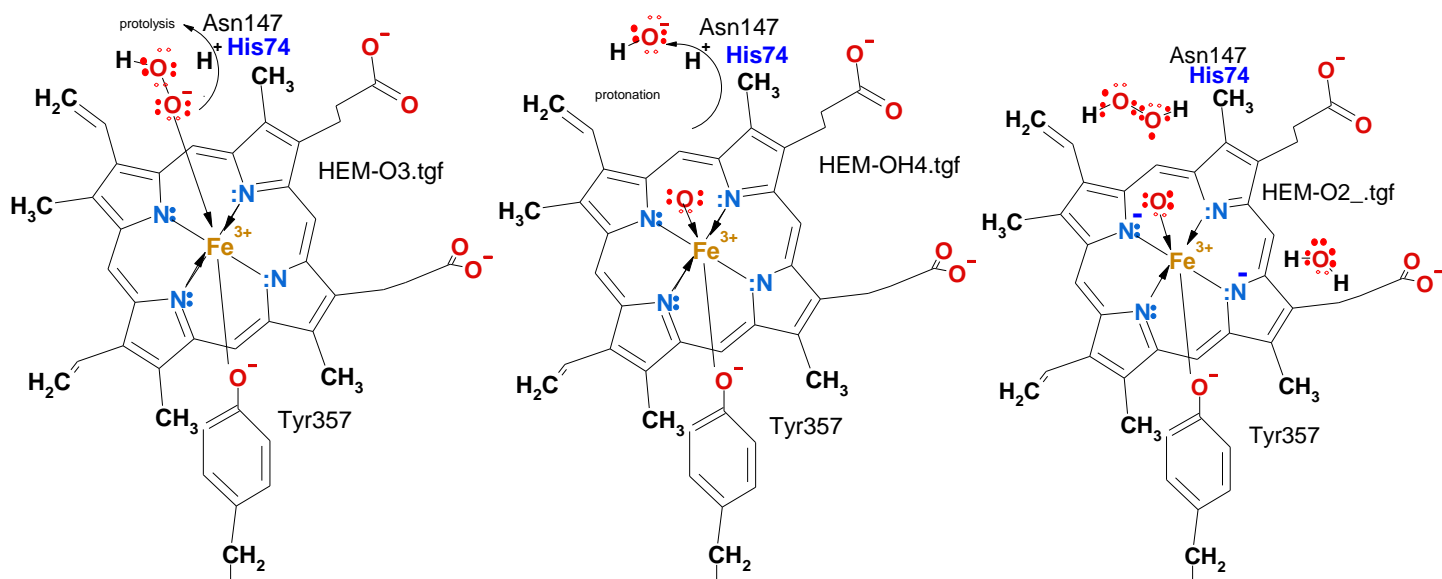


PiltuveHydroPhylPhob.jpg

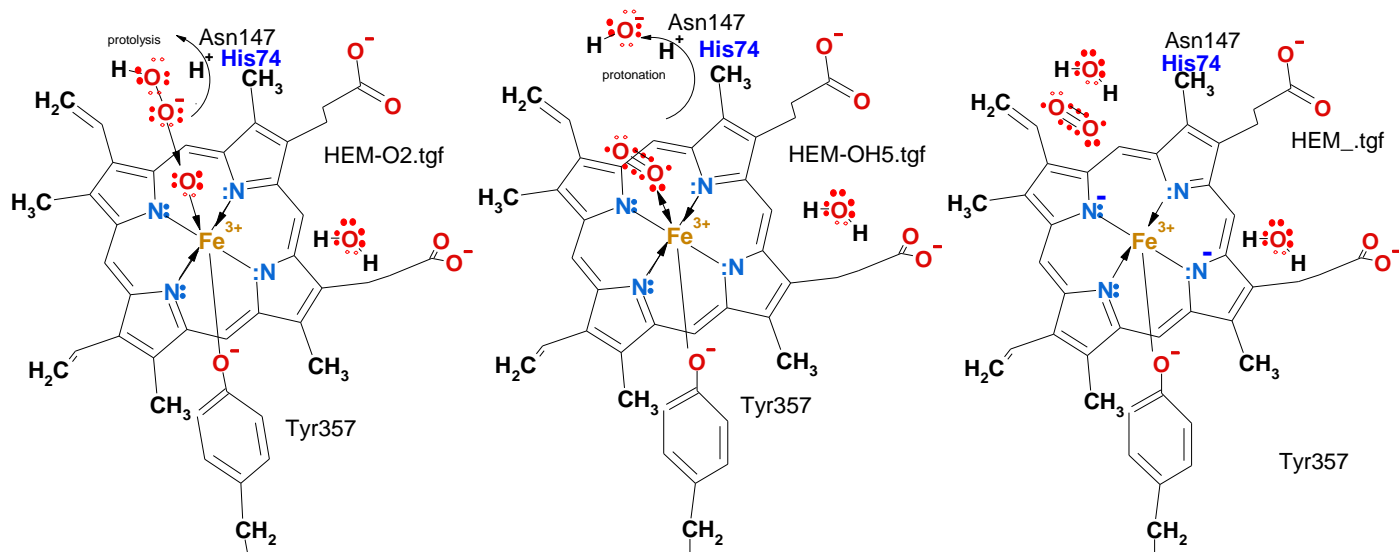
CATALASE funnel with iron(III) **Fe(III)** in coordination center

Experimental research:

Oxidised oxygen atom colliding iron Ox **H-O-Fe(IV)** left reduced second oxygen atom **HO⁻**



Heme pocket with 28 hydrophobic amino acids – in waterless medium oxidation-reduction reaction absent:
 Val72,Val73,Ala75,Val115,Ala116,Pro128,Gly130,Val145,Gly146,Phe153,Ile154,Ala157,Leu159,Phe160,
 Pro161,Phe163,Ile164,Leu198,Leu298,Ala332,Phe333,Pro335,Met349,Leu350,Gly352,Ala356,Pro358,Ala434



Dismutation reaction mechanism in steps with protonation **His74**, **Asn174** of peroxide deprotonation in negative charged anion oxygen atom collisions to active site positive atom iron charge **Fe(III)-O-Tyr357-E**:

1. **H-O-O-H** protolysis + **His74** + **Fe(III)-O-Tyr357-E** => **H⁺-His74** protonate + **HOO⁻** -> + **Fe(III)-O-Tyr357-E**
2. **H⁺His74** protonation + **HOO⁻** -> + **Fe(III)-O-Tyr357-E** => **HO⁻Red** + **H⁺His74** protonate + **Ox O-Fe(IV)-O-Tyr357-E**
3. **HO⁻Red** + **H⁺-His74** protonate + **Ox O-Fe(IV)-O-Tyr357-E** => **Red H2O** + **His74** + **Ox O-Fe(IV)-O-Tyr357-E**
4. => **H-O-O-H** protolysis + **Asn147** + **O-Fe(IV)-O-Tyr357-E** => **H⁺Asn147** + **HOO⁻** -> + **O-Fe(IV)-O-Tyr357-E**
5. **H⁺Asn147** + **HOO⁻** -> + **O-Fe(IV)-O-Tyr357-E** => **HO⁻Red** + **H⁺Asn147** + **Ox O-O-Fe(IV)-O-Tyr357-E**
6. => **HO⁻Red** + **H⁺Asn147** + **Ox O-O-Fe(IV)-O-Tyr357-E** => **Red H2O** + **Asn147** + **Ox O-O-Fe(IV)-O-Tyr357-E**
7. **Red H2O** + **Ox O-O-Fe(IV)-O-Tyr357-E** => **Red H2O** + **Ox O=O** + **-Fe(III)-O-Tyr357-E**

Summary: **2H₂O₂ + CAT -> H₃O⁺ + HOO⁻ > Fe(III) < OO⁻H + H₃O⁺ -> O_{2(aqua)} + 2H₂O + Q_{exothermic} + CAT**

Protolysis activate transition state complex **oxygen + water + heat + CATALASE**:

1. Colliding oxygen atom oxidized and deprotonate: Ox **O-Fe(III)** and **H⁺His74**, **Asn174** ;
2. second oxygen atom reduced **HO⁻Red** and protonate.

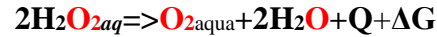
High rate protolysis peroxide reduction and oxidation = disproportionation.

Calculate ΔH_{Hess} , ΔS_{Hess} , ΔG_{Hess} . Reaction is **exothermic, athermic, endothermic**? Peroxide **2H₂O₂ → O₂ + 2H₂O**

conversion to **O₂ + 2H₂O + Q**, using table data! Mention will be reaction **exoergic** or **endoergic**!

$$\Delta G_{Hess} = \Delta G^{\circ}_{O_2} + 2\Delta G^{\circ}_{H_2O} - 2\Delta G^{\circ}_{H_2O_2} = 16,40 + 2*(-151,549) - (2*(-48,39)) = -189,9 \text{ kJ/mol exoergic}$$

Substance	ΔH°_H / kJ/mol	ΔS°_H / J/mol/K	ΔG°_H / kJ/mol
H ₃ O ⁺	-285,81	-3,854	-213,275
H ₂ O ₂ (aq)	-191,99	-481,688	-48,39
H ₂ O ₂ (aq)	-191,17	143,9	-134,03
O ₂ aqua	-11,70	-94,2	16,40
O ₂ aqua	-11,715	110,876	16,4
H ₂ O	-286,65	-453,188	-151,549
H ₂ O	-285,85	69,9565	-237,191



Biochem Thermodynamic 2006 Massachusetts Technology Institute University Alberta 1997.

$$\begin{aligned} \Delta H_{Hess} &= \Delta H^{\circ}_{O_2} + 2\Delta H^{\circ}_{H_2O} - 2\Delta H^{\circ}_{H_2O_2} = -201,02 \text{ kJ/mol} = -201,06 \text{ kJ/mol} \\ &= -11,7 - 2*286,65 - (2*(-191,99)) = -201,02 \text{ kJ/mol}; \\ &= -11,7 - 2*285,85 - (2*(-191,17)) = -201,06 \text{ kJ/mol}; \end{aligned}$$

$$\Delta S_{dispersed} = -\Delta H_H / T = -(-201,02) / 298,15 = 674,2 \text{ J/mol/K}; \Delta S_{dispersed} = -\Delta H_H / T = -(201,06) / 298,15 = 674,36 \text{ J/mol/K};$$

$$\Delta S_{Hess} = \Delta S^{\circ}_{O_2} + 2\Delta S^{\circ}_{H_2O} - 2\Delta S^{\circ}_{H_2O_2} = -94,2 + 2*(-453,188) - (2*(-481,688)) = -37,2 \text{ J/mol/K};$$

$$\Delta S_{Hess} = \Delta S^{\circ}_{O_2} + 2\Delta S^{\circ}_{H_2O} - 2\Delta S^{\circ}_{H_2O_2} = 110,876 + 2*69,9565 - (2*143,9) = -37 \text{ J/mol/K};$$

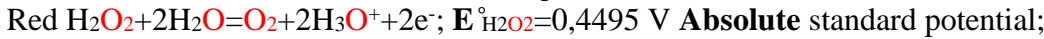
$$\Delta S_{kopēja} = \Delta S_H + \Delta S_{dispersed} = -37,2 + 674,2 = 637 \text{ J/mol/K}; \Delta S_{kopēja} = -37,011 + 674,36 = 637,35 \text{ J/mol/K};$$

$$\Delta G_{Hess} = \Delta H_H - T \Delta S_H = -201,02 - 298,15 * -0,0372 = -189,9 \text{ kJ/mol eksoergiska patvalģa.}$$

$$\Delta G_{Hess} = \Delta H_H - T \Delta S_H = -201,06 - 298,15 * -0,037 = -190 \text{ kJ/mol};$$

$$T \Delta S_{kopēja} = 0,637 * 298,15 = 189,9 \text{ kJ/mol}; T \Delta S_{kopēja} = 0,63735 * 298,15 = 190 \text{ kJ/mol};$$

Half reactions RedOx Nernst's equations for reduced and for oxidised form balance of electrons:



$$\Delta G_{eqStandard} = (E^{\circ}_{H_2O_2} - E^{\circ}_{H_2O_2Ox}) * F * n = (0,4495 - 1,6855) * 96485 * 2 = (-1,185) * 96485 * 2 = -238,5 \text{ kJ/mol};$$

$$\Delta G_{HessAlberty} = G_{O_2} + 2G_{H_2O} - 2G_{H_2O_2} = 330 + 2*(0) - (2*284) = -238 \text{ kJ/mol}; \text{ Alberty}$$

Absolute potential scale is coinciding with Alberty absolute free energy scale.

$$G_{H_2O_2} = G_{O_2aqua} + 2G_{H_2O} + \Delta G_{AlbertyStandard} = 330 + 2*0 + 218,9 = 2*274,5 = 548,9 \text{ kJ/mol};$$

$H_2O_2 = 1 \text{ M Biochemistry concentrations } [O_{2aqua}] = 6*10^{-5} \text{ M}, [H_3O^+] = 10^{-7,36} \text{ M}, [H_2O] = 55,3 \text{ M}.$

$$\frac{[O_2]_{aqua} \cdot [H_2O]^2}{[H_2O_2]_{aqua}^2} = K_{eqStandard} = K_{H_2O_2} = \exp(-\Delta G_{eqStandard} / R / T) = \exp(238500 / 8,3144 / 298,15) = 10^{41,8} \text{}$$

$$E_{Red} = E^{\circ}_{H_2O_2} + 0,0591 / 2 \cdot \lg([O_{2aqua}] * [H_3O^+]^2 / [H_2O_2] / [H_2O]^2) = 0,4495 + 0,0591 / 2 \cdot \lg(6*10^{-5} * 10^{(-7,36*2)} / 1 / 55,3^2) = -0,2132 \text{ V}$$

$$-E_{Ox} = -E^{\circ}_{H_2O_2Ox} + 0,0591 / 2 \cdot \lg([H_2O_2] * [H_3O^+]^2 / [H_2O]^4) = -1,6855 + 0,0591 / 2 \cdot \lg(1 * 10^{(-7,36*2)} / 55,3^4) = -2,3265 \text{ V}$$

$$[H_2O_2] = 1 \text{ M}; \Delta G_{eqBioChem} = (E^{\circ}_{Red} - E^{\circ}_{Ox}) * F * n = (-0,2132 - 2,3265) * 96485 * 2 = (-2,5397) * 96485 * 2 = -490,1 \text{ kJ/mol};$$

$$\Delta G_{Alberty} = G_{O_2Biochem} + 2G_{H_2OBioChemistry} - 2G_{H_2O_2} = 78,08 + 2*85,64 - 2*364,79 = -480,22 \text{ kJ/mol};$$

Exothermic and exoergic **H₂O₂** dismutation reaction Hess law

Homeostasis free energy change $\Delta G_{Alberty} = -480,22 \text{ kJ/mol}$ is negative,

Hess **Alberty** free energy change $\Delta G_{HessAlberty} = -238 \text{ kJ/mol}$ is negative,

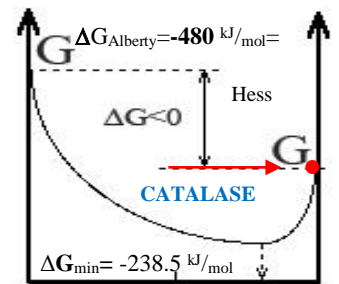
Absolute potential scale $\Delta G_{eqStandard} = -238,5 \text{ kJ/mol}$ coinciding with Absolute free energy scaling. reaching equilibrium mixture constant

$$K_{eqBioChem} = 10^{41,8} \text{}$$

Le Chatelier principle mean Prigogine attractor the free energy change minim ΔG_{min}

reaching. High rate protolysis attractors pH=7,36, air oxygen 20,95% stay at equilibrium state, while homeostasis irreversibly continues, as is non equilibrium state.

Prigogine attractors of Nobel Prize in Chemistry since 1977th. CATALASE erase peroxide molecules H₂O₂ in 100% efficiency for $\omega=6$, $\omega=3$ essential fatty acids elongation synthesis in peroxisomes. CATALASE reactivity is indispensable Brownian molecular engine for the irreversible homeostasis evolution and survival.



A+A 50% B+2C.
reactants **2H₂O₂(aq)**
products **O₂aqua + 2H₂O**

High rate protolysis $\text{HOOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HOO}^-$ $pK_a = 11,75$ make possible peroxide anions collisions $\text{HOO}^- \rightarrow \text{OOH}$ as disproportionation reactants in active complex transition state, what create indispensable activation energy $E_a = 79000 \text{ J/mol}$ with slow velocity constant $\vec{k} = 1.416 \cdot 10^{-16} \text{ M}^{-1}\text{s}^{-1}$ of product formation :



Referring to water and $\text{CO}_{2\text{gas}}$ zero $G_{\text{H}_2\text{O}} = G_{\text{CO}_{2\text{gas}}} = 0 \text{ kJ/mol}$ level activate homeostasis products free energy are peroxide, hydroxonium and peroxide ions: $G_{\text{H}_2\text{O}_2} = 274.5 \text{ kJ/mol}$; $G_{\text{H}_3\text{O}^+} + G_{\text{HOO}^-} = 22.44 + 418.32 = 440.76 \text{ kJ/mol}$; At present **Catalase** for colliding negative and positive ions $\text{HOO}^- \rightarrow \text{Fe}^{3+}$ have $E_a = 29 \text{ J/mol}$ indispensable activation energy : $\text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 + \text{Fe}^{3+} \rightarrow \text{His74-H}^+ + \text{HOO}^- \rightarrow \text{Fe}^{3+} + \text{OOH} + \text{Asn147-H}^+ \rightarrow \text{O}_{2\text{aqua}} + \text{H}_2\text{O} + \text{H}_2\text{O} + Q_{\text{exothermic}} + \text{Fe}^{3+}$.

Protonate **His74** and than **Asn147 Catalase** velocity is $\frac{\text{CAT} \sqrt{\vec{k}}}{\sqrt{\vec{k}}} = \frac{0,36}{1,19 \cdot 10^{-8}} = 30 \cdot 10^6$ million times faster.

Free energy of activate homeostasis products referring to water and $\text{CO}_{2\text{gas}}$ zero $G_{\text{H}_2\text{O}} = G_{\text{CO}_{2\text{gas}}} = 0 \text{ kJ/mol}$ are peroxide, hydroxonium and anion of peroxide: $G_{\text{H}_2\text{O}_2} = 364.8 \text{ kJ/mol}$; $G_{\text{H}_3\text{O}^+} + G_{\text{HOO}^-} = 22.44 + 418.32 = 440.76 \text{ kJ/mol}$;

High rate protolysis **Attractors Catalase** reactivity is indispensable molecular engine producing the life resources : **oxygen + water + heat** ($\text{O}_{2\text{aqua}} + 2\text{H}_2\text{O} + Q$). **Catalases** erase peroxide molecules thirty million times faster. So activate perfect order of homeostasis reactions with hundred percents • 100% efficiency.

High rate protolysis $\text{HOOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HOO}^-$ being at equilibrium state, while irreversible homeostasis including peroxide disproportionation continues as non-equilibrium state. Protolysis high rate equilibrium state of deprotonation promote the water concentration $[\text{H}_2\text{O}] = 55.3 \text{ M}$ as reactant $\text{HOOH} + \text{H}_2\text{O} \rightleftharpoons$ and homeostasis established attractor value $\text{pH} = 7,36$ as $\rightleftharpoons \text{H}_3\text{O}^+ + \text{HOO}^-$ hydroxonium ion $[\text{H}_3\text{O}^+] = 10^{-7,36} \text{ M}$ concentration. Both support in square protolysis disproportionation reactants in active complex transition state $[\text{H}_2\text{O}]^2 \rightleftharpoons [\text{H}_3\text{O}^+]^2$ of peroxide anions collisions, what generate indispensable activation energy $E_a = 79000 \text{ J/mol}$:



toxic	transition state	biological goods
compound	active complex	oxygen + water + heat .

Peroxide disproportionation velocity depends on colliding peroxide anions $\text{HOO}^- \rightarrow \text{OOH}$ activation energy $E_a = 79000 \text{ J/mol}$ and geometric factor $A = 0.01$ value.

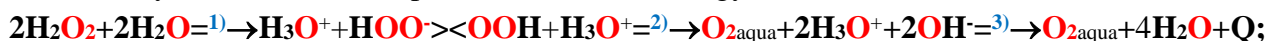
Peroxide disproportionation velocity increases on decrease activation energy $E_a = 29 \text{ J/mol}$ of colliding peroxide anions HOO^- and iron cation Fe^{3+} in CATALASE active site pocket which geometric factor increases 13^{theen} times reaching value $A = 0.13$.



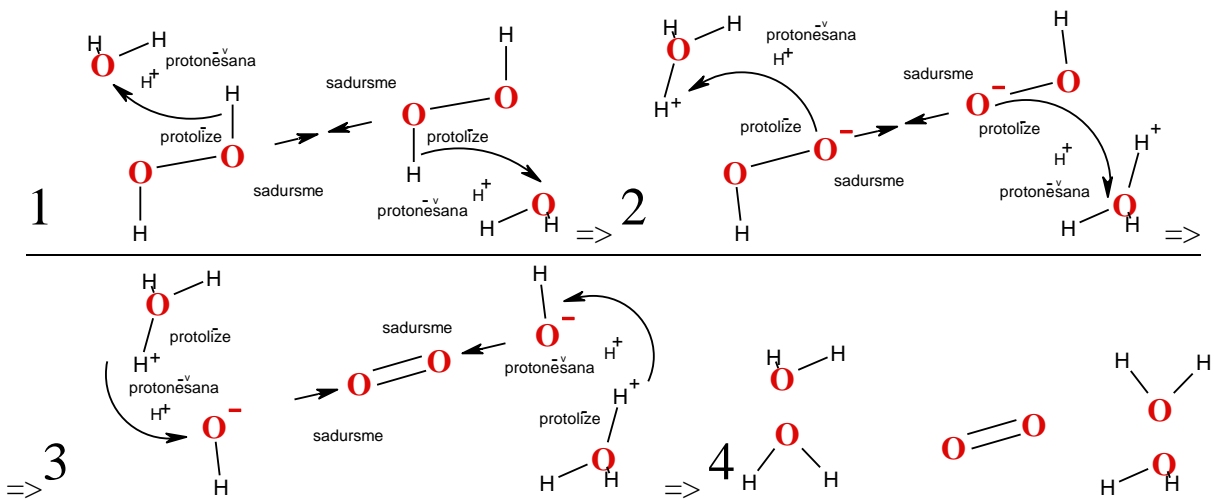
CATALASE reactivity as molecular engine factory producing resources $\text{O}_{2\text{aqua}} + 2\text{H}_2\text{O} + Q$ for life.

Results and Conclusions Summary

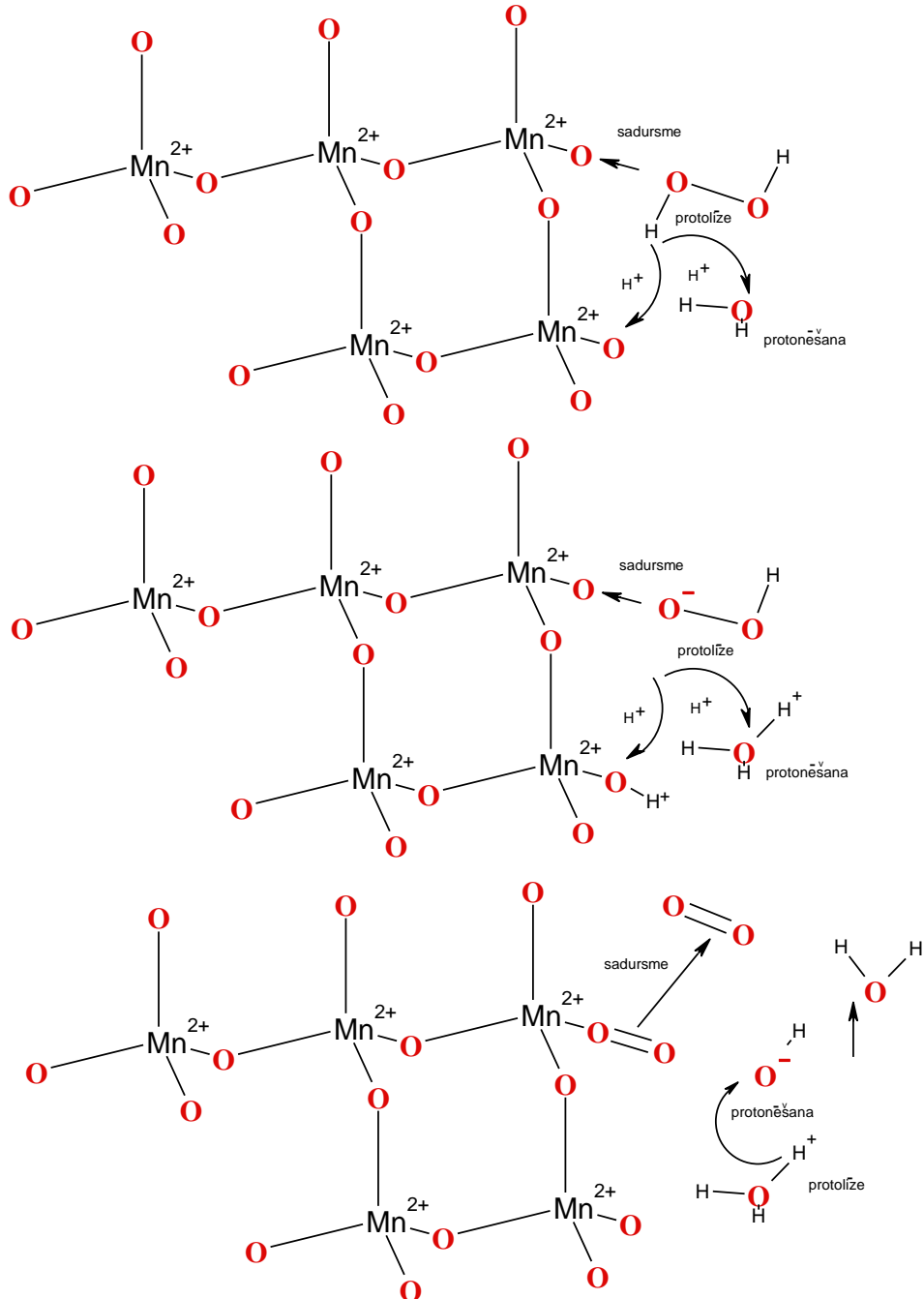
- Catalyst** CATALASE (CAT) is involved to reaction active transition state complex formation.
 $\text{H}_3\text{O}^+ + \text{HOO}^- \rightarrow \text{CAT} + \text{OOH} + \text{H}_3\text{O}^+$ and on finish released into products free unchanged CAT.
- Catalyst** (CAT) decrease activation energy E_a from 79000 J/mol to 29 J/mol times 2724 less.
- Catalyst** (CAT) improve geometric factor $A = 0.01$ to $A = 0.13$ and is 13^{theen} times better.
- Catalyst** CATALASE increase reaction velocity constant \vec{k} from $1.9 \cdot 10^{-8} \text{ M}^{-1}\text{s}^{-1}$ to $0.36 \text{ M}^{-1}\text{s}^{-1}$
times $30 \cdot 10^6$ thirty million more.
- High rate protolysis attractors for Catalase reactivity is indispensable life molecular engine converting to • 100% efficiency the life resources production: **oxygen + water + heat** ($\text{O}_{2\text{aqua}} + 2\text{H}_2\text{O} + Q$).....
- CATALASE erase peroxide molecules $30 \cdot 10^6$ thirty million times faster.....
- Absence of catalyst at collision indispensable activation energy $E_a = 79000 \text{ J/mol}$ for three reactions:



- 1) Protolysis reaction , than 2) oxidation of colliding O atoms and reduction second O atom to hydroxide OH-
- 3) finally neutralization.



Catalyst by manganese(II) oxide MnO .



Catalyst by iron(III) oxide Fe_2O_3 .

