

CATALASE indispensable **Krebs cycle** engine unfavored equilibrium to favored efficiency • 100%

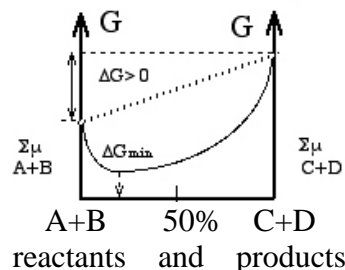
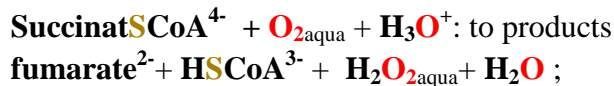


$$= \Delta G^\circ_{\text{H}_2\text{O}} + \Delta G^\circ_{\text{H}_2\text{O}_2} + \Delta G^\circ_{\text{fumarat}} + \Delta G^\circ_{\text{HSCoA}} - \Delta G^\circ_{\text{O}_2} - \Delta G^\circ_{\text{SuccinatSCoA}} - \Delta G^\circ_{\text{H}_3\text{O}^+} = 320,773 \text{ kJ/mol}$$

$$\text{pK}_{\text{eq}} = -\log(\text{K}_{\text{eq}}) = \log(e) * (-320,773 * 1000 / 8,3144 / 298,15) = -56,2;$$

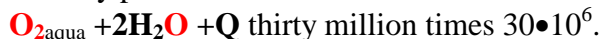
$$\text{K}_{\text{eq}} = \text{EXP}(-\Delta G_r / R/T) = 10^{-\text{pK}_{\text{eq}}} = 10^{-56,2}, 298,15 \text{ K (25 C}^\circ)$$

Endoergic dehydrogenation unfavored reactants conversion:



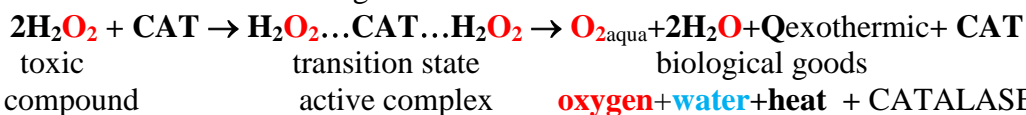
In mitochondria and peroxisomes

enzyme catalase increase favored velocity peroxide **2H-O-O-H** conversion in to biological goods



Enzyme CAT is 1. involved into **reaction** 2. decreasing activation energy **Ea** and

3. improve geometric factor **A** from worse value zero **A** => **0** to maximally optimized one **A** => **1**, that each collision is geometrically active and effective **100%** with geometric factor **A** = **1** favorable conversion to products.



Biocatalyst enzyme-CATALASE according Cambridge University professor Alana Fersht shows great catalytic

activity:
$$\vec{v}_{\text{enz}} = k_{\text{cat}} / K_M \cdot [\text{E}] \cdot [\text{H}_2\text{O}_2] = 3,6 \cdot 10^7 \cdot [\text{E}] \cdot [\text{H}_2\text{O}_2],$$

Usual catalase concentration is small $[\text{E}] = 10^{-8} \text{ M}$ and $\vec{v}_{\text{enz}} = 0,36 \cdot [\text{H}_2\text{O}_2] \text{ s}^{-1}$. Activation energy of catalase

Ea = 29 J/mol and geometric factor **A** = 0.1311 active collision fraction is 0.988 and velocity constant value is 0.1296 M⁻¹s⁻¹, 98.8% of total collisions are active and converting to products **O**_{2aqua} + **2H**_{2O} + **Q**:

$$\vec{k} = A \cdot e^{-\frac{E_a}{RT}} = A \cdot e^{-\frac{29}{8,314 \cdot 298}} = A \cdot 0,988 = 0,1296 \text{ M}^{-1}\text{s}^{-1}, \vec{v} = \vec{k} \cdot [\text{H}_2\text{O}_2]^2 = A \cdot 0,988 \cdot [\text{H}_2\text{O}_2]^2$$

$$\sqrt{\vec{v}} = \sqrt{\vec{k}} \cdot [\text{H}_2\text{O}_2] = 0,36 \cdot [\text{H}_2\text{O}_2]; \frac{\vec{v}_{\text{CAT}}}{\vec{v}} = \frac{0,36}{1,19 \cdot 10^{-8}} = (4.) 30 \cdot 10^6 \text{ times greater velocity constant increase}$$

$$\Delta H_r = 2\Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{O}_2} - 2\Delta H^\circ_{\text{H}_2\text{O}_2} = -11,715 - 2 * 285,85 - (2 * -191,17) = -201,08 \text{ kJ/mol exothermic}$$

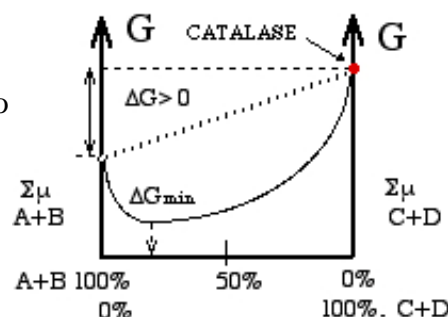
$$\Delta S_r = 2\Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{O}_2} - 2\Delta S^\circ_{\text{H}_2\text{O}_2} = 110,876 + 2 * 69,9565 - (2 * 143,9) = 250,789 - 287,8 = -37,011 \text{ J/mol/K}$$

$$\Delta G_r = \Delta H_r - T * \Delta S_r = -201,08 - 310,15 * -0,037011 = -201,08 + 11,478962 = -189,601 \text{ kJ/mol exoergic favored}$$

$$\text{pK}_{\text{eq}} = -\log(\text{K}_{\text{eq}}) = -\log(\text{exp}(1)) * (-189,601 * 1000 / 8,3144 / 298,15) = 33,217 ;$$

$$\text{K}_{\text{eq}} = \text{EXP}(-\Delta G_r / R/T) = 10^{-\text{pK}_{\text{eq}}} = 10^{33,217}, 298,15 \text{ K (25 C}^\circ)$$

Exoergic dismutation reaction favored reactants: **2H**_{2O}₂ + **CAT** converting to biologic goods products: **O**_{2aqua} + **2H**_{2O} + **Q** heat ; After unfavored fumarate production from succinate Catalase followed in complex reaction sequence and favored stabile fumarate efficiency • 100% because erasing **H**_{2O}₂



$$: \text{K}_{\text{eq}} = 10^{-56,2} = \frac{[\text{fumarate}^{2-}] \cdot [\text{HSCoA}^{2-}] \cdot [\text{H}_2\text{O}] \cdot [\text{H}_2\text{O}_2]}{[\text{Succinate}^{2-}] \cdot [\text{O}_2] \cdot [\text{H}_3\text{O}^+]} \text{ CATALASE, as peroxide}$$

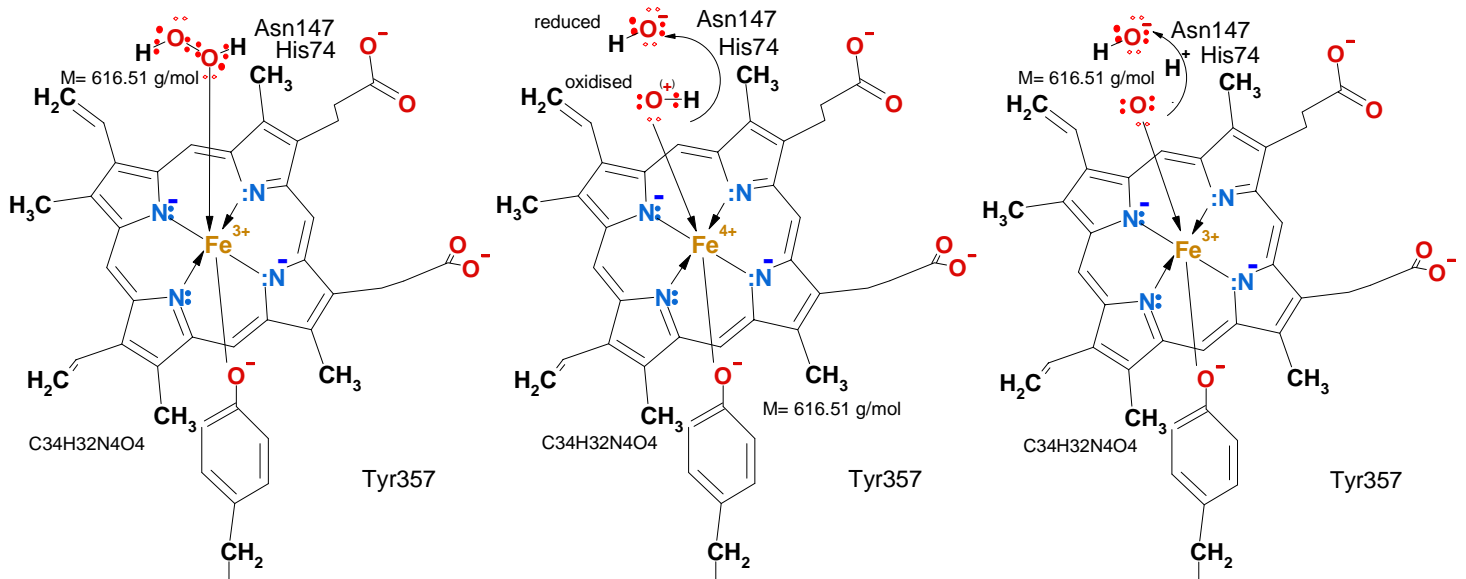
consumed to zero $[\text{H}_2\text{O}_2]^2 = 0 \text{ mol/liter}$ and process velocity limits only succinate dehydrogenase enzyme.

Irreversible Catalase reactivity is Prigogine attractor indispensable Brownian molecular engine which drive Krebs cycle for evolution, survival and homeostasis.

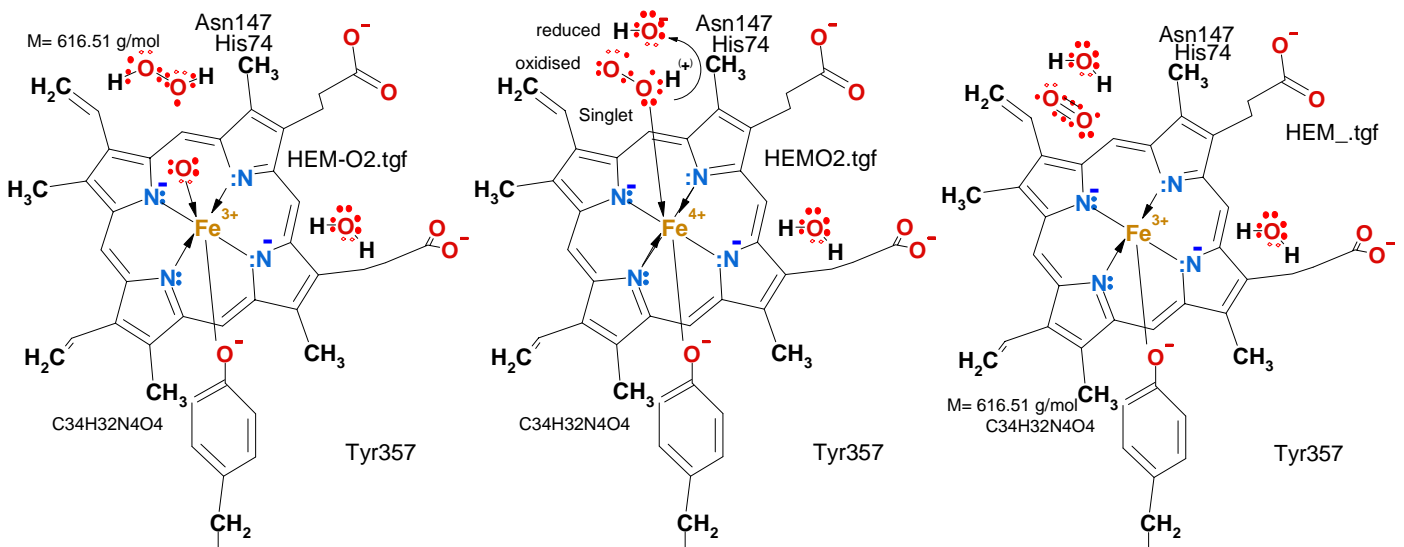
Catalase consume each peroxide molecule $30 \cdot 10^6$ times faster to produce **O**_{2aqua} + **2H**_{2O} + **Q** heat.

Advanced Studies of Chromo Protein CATALASE Heme pocket active site

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



Reaction mechanism six steps CATALASE driven peroxide dismutation collision with Fe(III)-O-Tyr357-E.

1. **H-O-O-H + Fe(III)-O-Tyr357-E --> HO⁻Red + Ox H-O-Fe(IV)-O-Tyr357-E-->.....**
2. **-->HO⁻Red + OxH-O-Fe(IV)-O-Tyr357-E-->HO⁻Red + H⁺-His74,Asn147+Ox O-Fe(III)-O-Tyr357-E->...**
3. **-->HO⁻Red + H⁺-Asn147+O-Fe(III)-O-Tyr357-E-->H₂O + Ox O-Fe(III)-O-Tyr357-E (1)**
4. **H-O-O-H + O->Fe(III)-O-Tyr357-E-->HO⁻Red + H-O-O-Fe(IV)-O-Tyr357-E-->.....**
5. **->HO⁻Red + OxH-O-O-Fe(IV)-O-Tyr357-E-->HO⁻Red+H⁺-His74,Asn147+OxO-O->Fe(III)-O-Tyr357-E...**
6. **--> HO⁻Red + H⁺-Asn147+OxO-O->Fe(III)-O-Tyr357-E--> H₂O+O₂+Fe(III)-E(2).....**

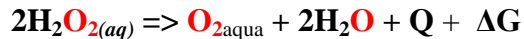
Iron collided oxygen atom oxidised Ox **O-Fe(III)** second left oxygen atom reduced **HO⁻Red**

Peroxide $\text{H}_2\text{O}_{2(aq)} + \text{H}_2\text{O}_{2(aq)}$ oxygen atoms dismutation to $\Rightarrow \text{O}_{2\text{aqua}} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{Q}$

Calculate ΔH_r , ΔS_r , ΔG_r at standard conditions 298.15 K. Reaction is **exothermic**, **athermic**, **endothermic**? Peroxide $2\text{H}:\ddot{\text{O}}:\ddot{\text{O}}:-\ddot{\text{O}}:\ddot{\text{O}}:\text{H}$ conversion to $\text{O}_{2\text{aqua}} + 2\text{H}_2\text{O} + \text{Q}$ at human temperature (37 C) 310.15 K, using the data table! Mention whether the reaction will be **exoergic** or **endoergic**!

Initial compounds peroxide \Rightarrow products oxygen + water

Substance	ΔH_r° , kJ/mol	ΔS_r° , J/mol/K
$\text{H}_2\text{O}_2(aq)$	-191,17	143,9
$\text{O}_{2\text{aqua}}$	-11,715	110,876
H_2O	-285,85	69,9565



$$1. \Delta H_{\text{reaction}} = \Sigma \Delta H^\circ_{\text{products}} - \Sigma \Delta H^\circ_{\text{initial compounds}}$$

$$2. \Delta S_{\text{reaction}} = \Sigma \Delta S^\circ_{\text{products}} - \Sigma \Delta S^\circ_{\text{initial compounds}}$$

$$3. \Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T \cdot \Delta S_{\text{reaction}}$$

$$1. \Delta H_r = 2\Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{O}_2} - 2\Delta H^\circ_{\text{H}_2\text{O}_2} = \dots \text{kJ/mol}$$

$$\dots = -11,715 - 2 \cdot 285,85 - (2 \cdot -191,17) = -133407583,4 + 383,415 = -201,08 \text{ exothermic} \dots \text{kJ/mol}$$

$$2. \Delta S_{\text{dispersed}} = -\Delta H_r / T = -(-201,08) / 310,15 = 648,33 \dots \text{J/mol/K}$$

$$\Delta S_r = 2\Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{O}_2} - 2\Delta S^\circ_{\text{H}_2\text{O}_2} = \dots \text{J/mol/K}$$

$$\dots = 110,876 + 2 \cdot 69,9565 - (2 \cdot 143,9) = 250,789 - 287,8 = -37,011 \dots \text{J/mol/K}$$

$$\Delta S_{\text{total}} = \Delta S_r + \Delta S_{\text{dispersed}} = -37,011 + 648,33 = +611,319 \dots \text{J/mol/K}$$

$$3. \Delta G_r = \Delta H_r - T \cdot \Delta S_r = -201,08 - 310,15 \cdot (-0,037011) = \dots \text{kJ/mol}$$

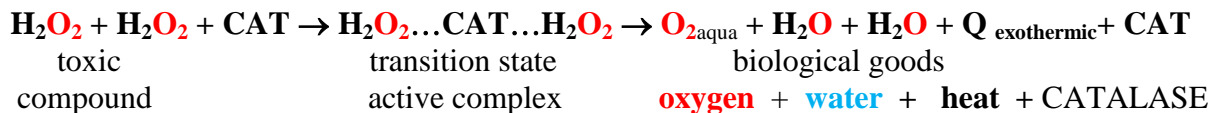
$$\dots = -201,08 + 11,478962 = -189,601 \text{ exoergic} \dots \text{kJ/mol}$$

$$T \cdot \Delta S_{\text{total}} = 0,611319 \cdot 310,15 = +189,6 \dots \text{kJ/mol}$$

$$\text{bound } T\Delta S_n \leftarrow \text{dispersed-lost energy} \leftarrow \Delta G_{\text{reversereaction}} = +189,6 \dots \text{kJ/mol}$$

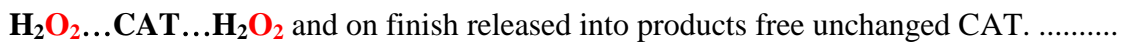
$$\dots \text{spontaneous exoergic reaction } \Delta G_{\text{reaction}} = -189,6 \dots \text{kJ/mol}$$

$$Q = 201,08 \dots \text{kJ/mol} \text{ evolved heat in products - exothermic reaction} \dots$$



CATALASE reactivity producing life resources $\text{O}_{2\text{aqua}} + 2\text{H}_2\text{O} + \text{Q}$

1. **Catalyst** CATALASE (CAT) is involved to reaction active transition state complex formation



2. **Catalyst** (CAT) decrease activation energy E_a from 79000 J/mol to 29 J/mol times 2724 less.

3. **Catalyst** (CAT) improve geometric factor $A=0.01$ to $A=0.13$ times 13 beter.

4. **Catalyst** CATALASE increase reaction velocity constant k from $1.9 \cdot 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$ to $0.36 \text{ M}^{-1} \text{ s}^{-1}$

\rightarrow
times $30 \cdot 10^6$ thirty million more.

5. Prigogine attractor CATALASE reactivity is indispensable Krebs cycle engine for succinate in dehydrogenase conversion to fumarate efficiency • 100% producing: **oxygen + water + heat** ($\text{O}_{2\text{aqua}} + 2\text{H}_2\text{O} + \text{Q}$)

6. CATALASE consume peroxide $30 \cdot 10^6$ thirty million times faster