

## Nernst's Ox-Red potential and membrane potential in volts Oxidation-reduction balancing with Nernst's half reactions .

Anniversary Nernst's Nobel Prize in Chemistry 1920:

**Metal** interface with solution, oxidant and reductant create **electrode** potential in volts.

**Electrochemical potential** both side membrane create ionic concentrations gradients  $C_{right\_side}/C_{left\_side}$ .

**Electrochemical** reactions across membrane drive E7class transport enzymes .

**Metal** free electron gas donate electrons to reduction and accept from oxidation half reactions .

**Metallic Electrode** is free electron source storage for RedOx half reactions.

Are classified such Type **electrodes**:

Type I: charged **ions** and free **electrons** transfer through **interface**;

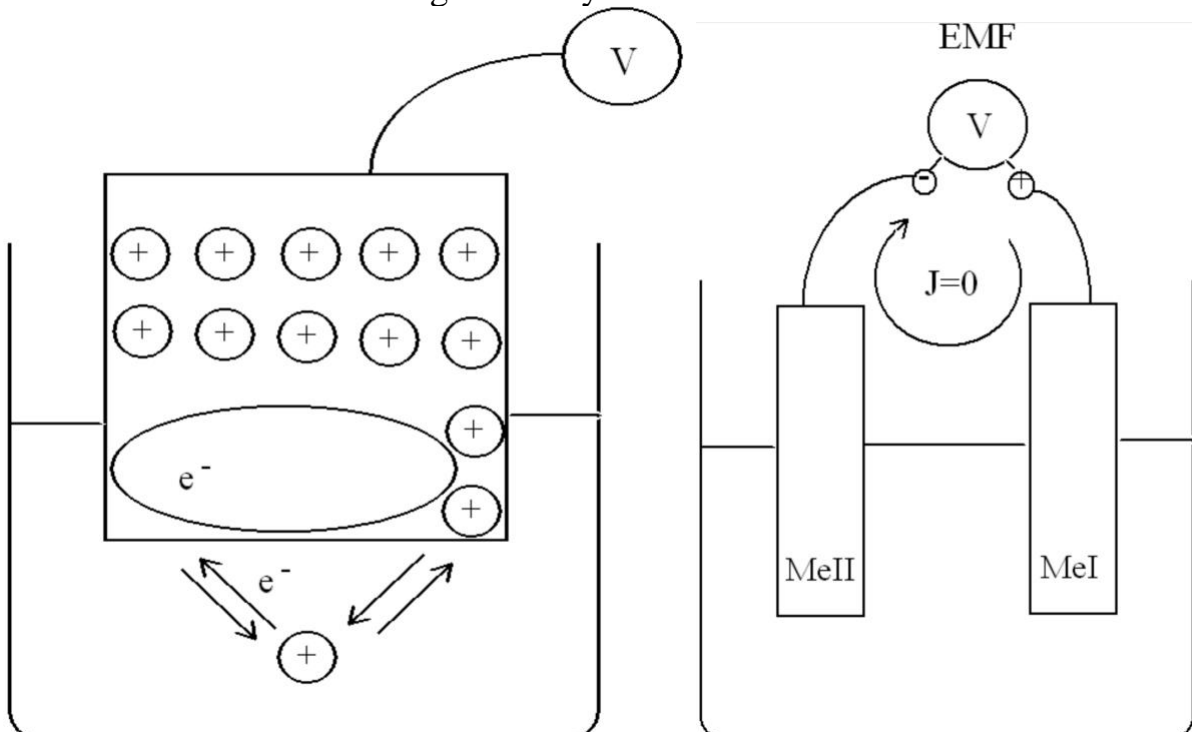
Type II: charged **ions** and free **electrons** transfer through **interface**;

**Red-Ox electrode**: charged **ions** and free **electrons** transfer through **interface**;

Membrane electrode: charged **ions** transfer through **interface** absent free **electrons**;

**Electrochemical** reactions driven charged **ions** gradient through **membrane** channels form **Membrane potential  $E_M$** .

Metal consist of electron  $e^-$  gas and crystalline metallic  $Me^+$  ions lattice frame.



Voltmeter with minus "-" and plus "+" clamps measures difference of potentials or **EMF** (Electric Motion Force)

between two **MeI (Indicator)** and **MeII (Standard)** on electric circuit linked electrodes :

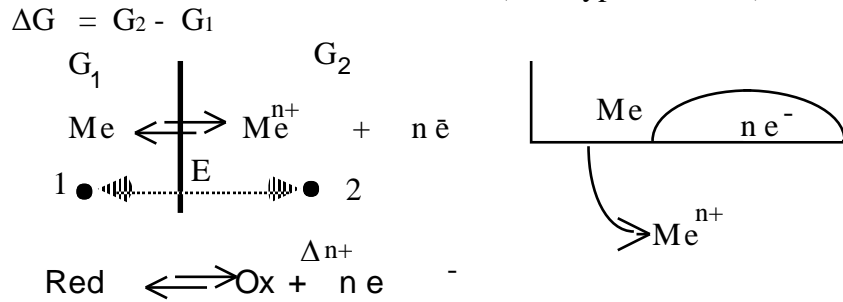
$$EMF = E_I - E_{II} \quad ; \quad E_I = EMF + E_{II}$$

**Indicator** electrode having  $E_I$  – has reactivity with solution - electrode of investigations,  
**Standard** electrode having  $E_{II}$  =constant– has no reactivity with environment into solution.

**Reference**

## The obtaining of Nernst's equation for the Reduction - Oxidation equilibrium.

(First type electrode)



One 1 mol of the reduced form **Red** transfer from left side to right side in reaction to oxidised form **Ox** is the Hess law calculated free energy change work  $W$  of one mol  $\text{Me}^{n+}$  transfer from point 1 into metal to point 2 into solution applied with negative value  $-\Delta G^\circ$  at electric potential value  $E$ . One mole  $\text{Me}^{n+}$  charge is  $q = nF$ , and work calculated as  $W = qE = nFE = W_{\text{work}} = nFE = -\Delta G^\circ = RT \ln K_{\text{eq}}$ .

Red-Ox equilibrium constant  $K_{\text{eq}} = \frac{[\text{Ox}] \cdot [e^{-}]^n}{[\text{Red}]}$  so

$$E = \frac{RT}{nF} \cdot \ln \left( \frac{[\text{Ox}] \cdot [e^{-}]^n}{[\text{Red}]} \right) = \frac{RT}{F} \cdot \ln([e^{-}]) + \frac{RT}{nF} \cdot \ln \left( \frac{[\text{Ox}]}{[\text{Red}]} \right) \quad \text{if } \frac{[\text{Ox}]}{[\text{Red}]} = 1 \text{ then}$$

$$E^\circ = \frac{RT}{F} \cdot \ln([e^{-}]) ; \ln([e^{-}]) = \frac{E^\circ F}{RT} = \text{const on metal surface unite and therefore } E^\circ = \text{const.}$$

Nernst's equation in natural (number  $e=2,7$ ) logarithm  $\ln$  and decimal (number 10) logarithm  $\lg$  form  $\ln(a) = \ln(10) \cdot \lg(a) = 2,3 \dots \cdot \lg(a)$  and temperature is  $T=298,15$  K degree:

$$E = E^\circ + \frac{RT}{nF} \cdot \ln \left( \frac{[\text{Ox}]}{[\text{Red}]} \right) ; \frac{\ln(10) \cdot R \cdot T}{F} = \frac{2,3 \cdot R \cdot T}{F} = 0,0591 \text{ V} ; E = E^\circ + \frac{0,0591}{n} \cdot \lg \left( \frac{[\text{Ox}]}{[\text{Red}]} \right)$$

### Second thermodynamic approach to obtaining Nernst's expression.

When equilibrium is established reactant and product chemical potential sum is equal  $\mu_{\text{Red}} + nF = \mu_{\text{Ox}} + n\mu_{e^{-}}$  but each chemical compound chemical potential is:  $\mu = \Delta G^\circ_A + RT \ln(N_A)$ , where  $N_A$  is substance A concentration (mol fraction).  $\Delta G^\circ$  is given compound A standard free energy of formation from elements. Free energy change Hess law of formation for pure compounds from elements  $\Delta G^\circ_{\text{Ox}}$ ,  $\Delta G^\circ_{e^{-}}$  and  $\Delta G^\circ_{\text{Red}}$ . In chemical equilibrium mixture  $\Delta G^\circ_{\text{Red}} + RT \ln(N_{\text{Red}}) + nF = \Delta G^\circ_{\text{Ox}} + RT \ln(N_{\text{Ox}}) + n\Delta G^\circ_{e^{-}} + RT \ln(N_{e^{-}}^n)$  Expressing  $E$  from equilibrium conditions of the chemical potentials  $\mu$ :

$$E = \frac{\Delta G^\circ_{\text{Ox}} + n\Delta G^\circ_{e^{-}} - \Delta G^\circ_{\text{Red}}}{nF} + \frac{RT}{nF} \cdot \ln \left( \frac{N_{\text{Ox}} \cdot N_{e^{-}}^n}{N_{\text{Red}}} \right) \quad \text{pure compound mol fraction is } N_A = 1.$$

Free electrons in separate phase (so called electron gas) of metal is just pure compound  $N_{e^{-}} = 1$  therefore

$$E = \frac{\Delta G^\circ_{\text{Ox}} + n\Delta G^\circ_{e^{-}} - \Delta G^\circ_{\text{Red}}}{nF} + \frac{RT}{nF} \cdot \ln N_{e^{-}}^n + \frac{RT}{nF} \cdot \ln \left( \frac{N_{\text{Ox}}}{N_{\text{Red}}} \right) . \quad \text{As pure compound } \ln(N_{e^{-}}^n) = 0.$$

So standard potential  $E^\circ = \frac{\Delta G^\circ_{\text{Ox}} + n\Delta G^\circ_{e^{-}} - \Delta G^\circ_{\text{Red}}}{nF}$  give Prigogine attractor the minimum of free energy change

$\Delta G_{\text{eq}}$  at equilibrium state smaller  $|E^\circ nF - \Delta G_{\text{eq}}| = |\Delta G^\circ_{\text{Ox}} + n\Delta G^\circ_{e^{-}} - \Delta G^\circ_{\text{Red}}| < |\Delta G_{\text{Hess}}|$  as pure Hess law.

**Conversion to decimal logarithm and thermodynamic standard  $T=298,15$  K degree we have Nernst's**

equation for reaction of reactants: **Reducing form**  $\rightleftharpoons$  **Ox** $^{\Delta n^{+}}$  + **ne** **Oxidising form**  $E = E^\circ + \frac{0,0591}{n} \cdot \lg \left( \frac{[\text{Ox}]}{[\text{Red}]} \right)$ .

In reaction **ne** electron lose (left at metal) exert towards solution transfer  $\Delta n^{+}$  positively charged ions **Ox** $^{\Delta n^{+}}$ . Electrons **ne** leaves at metal electron gas. Such  $\Delta n^{+}$  positive charge entrance into solution as oxidised form **Ox** $^{\Delta n^{+}}$  in products brings the chemical potential electrical part of negative electrons the energy  $n\Delta G^\circ_{e^{-}} = -nFE$ .

I type electrode hydrogen metal  $\underline{\text{H}}(\text{Pt})$  interface / to its cations  $\text{H}_3\text{O}^+$  solution application

Attractor  $\text{pH}=7.36$  staying at equilibrium have true  $\text{pOH}=6.64$  value as  $\text{pK}_w=14= \text{pH}+\text{pOH} =7.36 +6.64$ . Disaccount the water mass  $[\text{H}_2\text{O}]=963/18=53.5 \text{ M}$  over liter  $[\text{H}_2\text{SO}_4]=[\text{H}_3\text{O}^+]=1 \text{ M}$  solution with  $1.061 \text{ g/mL}$  density in Nernst equations for **hydrogen electrode** has classic standard potential  $E_{o\_classic}=0 \text{ V}$  reference zero:  $\underline{\text{H}}(\text{Pt})=\text{H}^++\text{e}^-$ ;  $E_{\text{classic}}=E_{o\_classic}+0.0591 \cdot \log K^{\circ}_{\text{classicH(Pt)}}=0+0.0591 \cdot \log[\text{H}^+]=0+0.0591 \cdot \log(1 \text{ M})=0 \text{ Volts}$ . [11]

Thermodynamic account Hydroxonium ions demand the water:  $\underline{\text{H}}(\text{Pt})+\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^++\text{e}^-$  and  $E^{\circ}_{\text{H}}=0.10166 \text{ V}$ . The ratio  $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]=1 \text{ M}/52.5 \text{ M}=X_{\text{H}_3\text{O}^+}/X_{\text{H}_2\text{O}}$  is mol fraction instead molarity  $[\text{H}^+]=1 \text{ M}$  at classic potential expression. The water account gave thermodynamic standard  $E^{\circ}_{\text{H}}=0.10166 \text{ V}$  on potential scale.

Nernst's expression with classic zero measurement demands thermodynamic standard potential  $E^{\circ}_{\text{H}}=0.10166 \text{ V}$  :

$$E = E^{\circ}_{\text{H}} + \frac{\ln(10) \cdot R \cdot T}{F \cdot 1} \cdot \log \frac{X_{\text{H}_3\text{O}^+}}{X_{\text{H}_2\text{O}}} = E_o + E^{\circ}_{\text{H}} + 0.0591 \cdot \log(1/52.5) = 0.10166 - 0.10166 = 0 \text{ V}$$

As ratio  $1=K_{\text{H(Pt)}}=X_{\text{H}_3\text{O}^+}/X_{\text{H}_2\text{O}}$  is one than  $E^{\circ}_{\text{H}}=0.10166 \text{ V}$  is thermodynamic standard potential:

$E = E^{\circ}_{\text{H}} + \frac{\ln(10) \cdot R \cdot T}{F \cdot 1} \cdot \log \frac{X_{\text{H}_3\text{O}^+}}{X_{\text{H}_2\text{O}}} = 0.10166 + 0.0591 \cdot \log(1) = 0.10166 \text{ V}$ . Metal oxidation free energy change minimum is different endoergic  $\Delta G_{\text{eq}} = E^{\circ}_{\text{H}} \cdot F \cdot 1 = 0.10166 \cdot 96485 \cdot 1 = 9.81 \text{ kJ/mol}$  instead Alberty is exoergic .

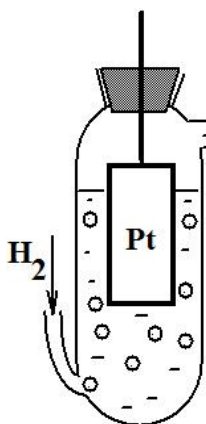
[Alberty](#) Hess value is exoergic;  $\Delta G_{\text{Hess\_eq}} = G_{\text{H}_3\text{O}^+} + G_{\text{e}^-} - (G_{\text{H(Pt)}} + G_{\text{H}_2\text{O}}) = 22,44 + 0 - (51,05 + 0) = -28,61 \text{ kJ/mol}$  .

Free energy changes are determined on water and carbon dioxide gas zero  $G_{\text{H}_2\text{O}} = G_{\text{CO}_2\text{gas}} = G_{\text{e}^-} = 0 \text{ kJ/mol}$  reference scale. Iterative found on absolute scale hydrogen standard potential is:  $E^{\circ}_{\text{H}} = -0,29654 \text{ V}$ . Equilibrium free energy minimum is exoergic:  $\Delta G_{\text{eq}} = E^{\circ}_{\text{H}} \cdot F \cdot 1 = -0,29654 \cdot 96485 \cdot 1 = -28,61 \text{ kJ/mol}$  coinciding with Alberty data. Absolute potential scale slips by  $\Delta E = -0,29654 - 0,10166 = -0,3982 \text{ Volts}$  down. Nernst's hydrogen equilibrium constant is grater as one:  $K_{\text{H(Pt)\_Red}} = [\text{H}_3\text{O}^+] \cdot [\text{e}^-] / [\text{H}_2\text{O}] / [\text{H(Pt)}] = \text{EXP}(-\Delta G_{\text{Alberty}}/R/T) = \text{EXP}(28612/8.3144/298.15) = 102954$  .

I type electrode Metal interface  $\underline{\text{H}}(\text{Pt})$  / on its cation  $\text{H}_3\text{O}^+$  solution application.

High rate protolysis attractors  $[\text{H}_3\text{O}^+]=10^{-7.36} \text{ M}$  ,  $\text{pH}=7.36$  and water mass  $[\text{H}_2\text{O}]=997/18=55.3 \text{ M}$  account in liter shows metal hydrogen strong reducing potential:  $E_{\text{pH}=7.36} = -0,29654 + 0,0591 \cdot \log(10^{-7.36}/55,3) = -0,8345 \text{ V}$  and free energy change minimum  $\Delta G_{\text{eqpH}_7.36} = E^{\circ}_{\text{H}} \cdot F \cdot 1 = -0,8345 \cdot 96485 \cdot 1/1000 = -80,5 \text{ kJ/mol}$  .

Nernst's half reaction metal reduction potential  $E^{\circ}_{\text{H}} = -0,29654 \text{ V}$  energy  $\Delta G_{\text{eq}} = -28,6 \text{ kJ/mol}$ .



Platinum sheet immersed in hydroxonium ions  $[\text{H}^+]=[\text{H}_3\text{O}^+]=[\text{H}_2\text{SO}_4]=1 \text{ M}$  sulfuric acid solutions  $\underline{\text{H}}(\text{Pt}) \rightleftharpoons \text{H}^++\text{e}^-$ :  $E = E^{\circ} + 0.0591 \cdot \log[\text{H}^+] = 0.0 + 0.0591 \cdot \log(1 \text{ M}) = 0 \text{ V}$  is classic.

Ratio  $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]=1/52.5=X_{\text{H}_3\text{O}^+}/X_{\text{H}_2\text{O}}$  give classic zero  $0$  insted thermodynamic standard potential:  $E^{\circ}_{\text{H}}=0.10166 \text{ V}$  and from Alberty data on absolute scale

absolute standard potential is  $E^{\circ}_{\text{H}} = -0,29654 \text{ Volts}$ .

$$\begin{array}{ccc} \text{absolute } E^{\circ}_{\text{H}} = -0.29654 \text{ V} & \text{classic zero } E^{\circ}_{\text{H}} = 0 \text{ V} & 0.10166 \text{ V } E, \text{V} \\ \hline E_{(\text{Pt})/\text{H}^+} = E^{\circ}_{\text{H}} + 0.0591 \cdot \log\left(\frac{X_{\text{H}_3\text{O}^+}}{X_{\text{H}_2\text{O}}}\right) & E_{\text{H\_classic}} = E^{\circ}_{\text{H}} + 0.0591 \cdot \log([\text{H}_3\text{O}^+]) & \text{thermodynamic } E^{\circ}_{\text{H}} \end{array}$$

Absolute standard potential  $E^{\circ}_{\text{H}} = -0,29654 \text{ V}$  based on Alberty hydrogen data  $G_{\text{H}_2\text{gas}} = 85,64 \text{ kJ/mol}$  and  $G_{\text{H}_2\text{aq}} = 103,24 \text{ kJ/mol}$  , which was detected on water and carbon dioxide gas zero scale  $G_{\text{H}_2\text{O}} = G_{\text{CO}_2\text{gas}} = G_{\text{e}^-} = 0 \text{ kJ/mol}$ . reducing agent at  $\text{pH}=7,36$  ,  $[\text{H}_3\text{O}^+]=10^{-7.36} \text{ M}$  with potential  $E = -0,2965 + 0,0591 \cdot \log(10^{-(7.36)}/55,3) = -0,8345 \text{ V}$ . is strong reductant. Free energy content in one mol metal hydrogen is:  $G_{\text{H(Pt)}} = 51.05 \text{ kJ/mol}$  .

**Table 1. Standard Electrodes Potentials**

**classic, Thermodynamic, absolute in Volts**

	Reduced form = Oxidized form	H <sub>2</sub> O disaccount classic zero E <sub>o</sub>	Thermodynamic. scale 0.10166 V	Absolute scale -0.3982 V
<b>H</b>	<b>H(Pt) + H<sub>2</sub>O = H<sub>3</sub>O<sup>+</sup> + (Pt) + e<sup>-</sup></b> <b>H(Pt) + OH<sup>-</sup> = H<sub>2</sub>O + (Pt) + e<sup>-</sup></b> <b>H<sub>2aq</sub> + 2H<sub>2</sub>O = 2H<sub>3</sub>O<sup>+</sup> + 2e<sup>-</sup> ; graphite Kaksis</b>	classic zero <b>0</b> -0.828	<b>0.10166</b> -0.8294	-0.2965 -1.2272 0.302
<b>O</b>	6H <sub>2</sub> O = O <sub>2</sub> <sup>(g)</sup> + 4 H <sub>3</sub> O <sup>+</sup> + 4e <sup>-</sup> H <sub>2</sub> O <sub>2</sub> + 2H <sub>2</sub> O = O <sub>2</sub> <sup>(aq)</sup> + 2H <sub>3</sub> O <sup>+</sup> + e <sup>-</sup> 4H <sub>2</sub> O = H <sub>2</sub> O <sub>2</sub> + 2 H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup> H <sub>2</sub> O <sub>2</sub> <sup>(aq)</sup> + 2H <sub>2</sub> O = O <sub>2</sub> <sup>(aq)</sup> + 2H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup> University Alberta	1.2288 1.2764 1.776 0.6945	- +1.48466 +1.58416 +2.08366 0.8477	1.0865 1.0829 1.6855 0.4495
	<b>HOO<sup>-</sup> + H<sub>2</sub>O = O<sub>2</sub><sup>(aq)</sup> + H<sub>3</sub>O<sup>+</sup> + 2e<sup>-</sup> ; Kaksis</b>	-	-	0.07587
<b>N</b>	<b>NO<sub>2</sub><sup>-</sup> + 2OH<sup>-</sup> = NO<sub>3</sub><sup>-</sup> + H<sub>2</sub>O + 2e<sup>-</sup> ;</b> Suchotina <b>HNO<sub>2</sub> + 4H<sub>2</sub>O = NO<sub>3</sub><sup>-</sup> + 3H<sub>3</sub>O<sup>+</sup> + 2e<sup>-</sup> ;</b> Kortly, Shucha <b>NO<sup>(g)</sup> + 6H<sub>2</sub>O = NO<sub>3</sub><sup>-</sup> + 4H<sub>3</sub>O<sup>+</sup> + 3e<sup>-</sup> ;</b> Kortly, Shucha <b>NH<sub>4</sub><sup>+</sup> + 13H<sub>2</sub>O = NO<sub>3</sub><sup>-</sup> + 10H<sub>3</sub>O<sup>+</sup> + 8e<sup>-</sup> ;</b> Suchotina	0.01 1.63 0.96 0.87	0.06016 1.93765 1.26765 1.13903	-0.3380 1.5395 0.8695 0.74083
<b>Br</b>	<b>2Br<sup>-</sup> = Br<sub>2</sub>(aq) + 2e<sup>-</sup> ;</b> CRC	1.0873	1.18896	0.79076
<b>Bi</b>	<b>BiO<sup>+</sup> + 6H<sub>2</sub>O = BiO<sub>3</sub><sup>-</sup> + 4H<sub>3</sub>O<sup>+</sup> + 2e<sup>-</sup> ;</b> Suchotina	1.80	2.210645	1.81245
<b>Mn H<sup>+</sup></b>	<b>Mn<sup>2+</sup> + 12H<sub>2</sub>O = MnO<sub>4</sub><sup>-</sup> + 8H<sub>3</sub>O<sup>+</sup> + 5e<sup>-</sup> ;</b> Kortly, Shucha	1.51	1.85885	1.46065
<b>H<sub>2</sub>O</b>	<b>MnO<sub>2</sub>↓ + 4OH<sup>-</sup> = MnO<sub>4</sub><sup>-</sup> + 2H<sub>2</sub>O + 3e<sup>-</sup> ;</b> Suchotina	0.603	0.63600	0.23780
<b>OH<sup>-</sup></b>	<b>MnO<sub>4</sub><sup>2-</sup> = MnO<sub>4</sub><sup>-</sup> + e<sup>-</sup> ;</b> Suchotina	0.558	0.65966	0.26146
<b>Pb</b>	<b>Pb<sup>2+</sup> + 6H<sub>2</sub>O = PbO<sub>2</sub>(s) + 4H<sub>3</sub>O<sup>+</sup> + 2e<sup>-</sup> ;</b> Kortly, Shucha	1.455	1.865645	1.46745
<b>S</b>	<b>H<sub>3</sub>SO<sub>3</sub> + 3H<sub>2</sub>O = SO<sub>4</sub><sup>2-</sup> + 2H<sub>3</sub>O<sup>+</sup> + 2e<sup>-</sup> ;</b> Suchotina <b>SO<sub>3</sub><sup>2-</sup> + 2OH<sup>-</sup> = SO<sub>4</sub><sup>2-</sup> + H<sub>2</sub>O + 2e<sup>-</sup> ;</b> Suchotina <b>S<sup>2-</sup> = S(s) + 2e<sup>-</sup> ;</b> Kortly, Shucha <b>H<sub>2</sub>S + 2H<sub>2</sub>O = S(s) + 2H<sub>3</sub>O<sup>+</sup> + 2e<sup>-</sup> ;</b> Kortly, Shucha <b>2S<sub>2</sub>O<sub>3</sub><sup>2-</sup> = S<sub>4</sub>O<sub>6</sub><sup>2-</sup> + 2e<sup>-</sup> ;</b> Suchotina	0.172 -0.93 -0.48 0.141 0.08	0.42815 -0.87984 -0.37834 0.34566 0.18166	0.029953 -1.27804 -0.77654 -0.05254 -0.2165
<b>Fe</b>	<b>Fe<sup>2+</sup> = Fe<sup>3+</sup> + e<sup>-</sup></b>	0.769	0.8707	0.4725
<b>Ag</b>	<b>Ag(s) = Ag<sup>+</sup> + e<sup>-</sup> ;</b> Kortly, Shucha	0.799	0.90066	0.5025
<b>I</b>	<b>2Ag(s) + 2OH<sup>-</sup> = Ag<sub>2</sub>O(s) + H<sub>2</sub>O + 2e<sup>-</sup> ;</b> Suchotina	0.345	0.39516	-0.00304
<b>Cu</b>	<b>3I<sup>-</sup> = I<sub>3</sub><sup>-</sup> + 2e<sup>-</sup> ;</b> Kortly, Shucha	0.6276	0.72926	0.33106
<b>F</b>	<b>Cu(Hg) = Cu<sup>2+</sup> + (Hg) + 2e<sup>-</sup> ;</b> Kortly, Shucha	0.3435	0.44516	0.04696
<b>Cl</b>	<b>2F<sup>-</sup> = F<sub>2</sub>(g) + 2e<sup>-</sup> ;</b> Kortly, Shucha <b>2Cl<sup>-</sup> = Cl<sub>2</sub>(g) + 2e<sup>-</sup> ;</b> Kortly, Shucha	2.87 1.358	2.97166 1.45966	2.5735 1.06146
<b>Cr</b>	<b>Cl<sub>2</sub>(g) + 4H<sub>2</sub>O = 2HOCl + 2H<sub>3</sub>O<sup>+</sup> + 2e<sup>-</sup> ;</b> Kortly, Shucha <b>2Cr<sup>3+</sup> + 21H<sub>2</sub>O = Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> + 14H<sub>3</sub>O<sup>+</sup> + 6e<sup>-</sup> ;</b> Kortly, Shucha	1.63 1.33	1.93765 1.7921	1.53945 1.3939
<b>C</b>	<b>Cr<sup>3+</sup> + 11H<sub>2</sub>O = HCrO<sub>4</sub><sup>-</sup> + 7H<sub>3</sub>O<sup>+</sup> + 3e<sup>-</sup> ;</b> Kortly, Shucha	1.20	1.6793	1.2811
<b>Cr</b>	<b>H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + 2H<sub>2</sub>O = 2CO<sub>2</sub> + 2H<sub>3</sub>O<sup>+</sup> + 2e<sup>-</sup> ;</b> Suchotina	-0.49	-0.2853	-0.6835
<b>Zn</b>	<b>Cr = Cr<sup>3+</sup> + 3e<sup>-</sup> ;</b> Suchotina	-0.744	-0.6423	-1.0405
<b>Al</b>	<b>Zn = Zn<sup>2+</sup> + 2e<sup>-</sup> ;</b> Kortly, Shucha	-0.7628	-0.6611	-1.0593
<b>H. C</b>	Ubiquinol + 2H <sub>2</sub> O = Ubiquinone + 2H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup> Succinate <sup>2-</sup> + 2H <sub>2</sub> O = Fumarate <sup>2-</sup> + 2H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup> Ascorbic Acid + 2H <sub>2</sub> O = C <sub>6</sub> H <sub>6</sub> O <sub>6</sub> + 2H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup> glycolate + 2H <sub>2</sub> O = Glyoxylate + 2H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup> CH <sub>3</sub> CH <sub>2</sub> OH + H <sub>2</sub> O = CH <sub>3</sub> CHO + H <sub>3</sub> O <sup>+</sup> + H <sup>-</sup> C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> + 42H <sub>2</sub> O = 30H <sub>3</sub> O <sup>+</sup> + 6HCO <sub>3</sub> <sup>-</sup> + 24e <sup>-</sup> ; Kaksis	0.459 0.445 0.390 0.324 0.190 0.0701	0.664 0.650 0.595 0.529 0.343 0.2590	0.2656 0.2516 0.1965 0.1305 -0.0550 -0.1392

Reaction  $O_{2aq} + 2H_{2aq} \Rightarrow 2H_2O$  is  $\Delta G_{HessH_2OBio} = (2G_{H_2O} - (2G_{H_2aq} + G_{O_{2aq}})) / 2 = (2*0 - (2*103 + 330)) / 2 = -268$  kJ/mol;

Oxygen half reaction:  $O_{2aq} + 4H_3O^+ + 4e^- \Leftrightarrow 6H_2O$  standard potential  $E^\circ_{O_2} = 1.485$  Volts produces the water :

$E_{O_2} = E^\circ_{O_2} + 0.0591/4 \cdot \log([O_{2aq}] \cdot [H_3O^+]^4 / [H_2O]^6) = 1.485$  V + 0.0148 • log([O<sub>2</sub>aq] • [H<sub>3</sub>O<sup>+</sup>]<sup>4</sup> / [H<sub>2</sub>O]<sup>6</sup>) with four

reducing Nernst's half reactions:  $4(Pt)H + 4H_2O \Leftrightarrow 4H_3O^+ + 4e^-$ ;  $E^\circ_H = 0.1016$  V give free energy change

$\Delta G_{eq} = (E^\circ_H - E^\circ_{O_2}) \cdot F \cdot 1 \cdot 4 = (0.10166 - 1.485) \cdot 96485 \cdot 4 = -1.38334 \cdot 96485 \cdot 4 / 1000 = -533.9 = 2 \cdot 266.94$  kJ/mol of water

formation  $O_{2aq} + 4(Pt)H \Rightarrow 2H_2O$  from elements free energy content  $G_{H(Pt)} = 51$  kJ/mol,  $G_{O_{2aq}} = 330$  kJ/mol:

Equilibrium value  $\Delta G_{eq2H_2O} = 2G_{H_2O} - 4G_{(Pt)H} - G_{O_{2aq}} = 2*0 - (4*G_{(Pt)H} + 329.68) = -533.9 = 2* -266.94$  kJ/mol,

expresses metal free energy  $G_{H(Pt)} = (2G_{H_2O} - \Delta G_{eq2H_2O} - G_{O_{2aq}}) / 4 = (2*0 + 533.886 - 329.68) / 4 = 204.2 / 4 = 51.05$  kJ/mol ;

**Ox:**  $2H_3O^+ + H_2O + 2e^- \Leftrightarrow H_{2aq} + 2H_2O$ ;  $\Delta G_{Hess_H_3O^+} = G_{H_{2aq}} + 2G_{H_2O} - (2G_{H_3O^+} + 2G_{e^-}) = 103.24 + 2*0 - (2*22.44 + 2*0) = 58.36$  kJ/mol;

Graphite electrode oxidizes hydrogen liberate (Pt) lattice  $E^\circ_{H_3O^+} = 58.36 \cdot 1000 / 96485 / 2 = 0.302$  V

**Red** Nernst's:  $2H(Pt) + 2H_2O \Leftrightarrow 2H_3O^+ + 2e^-$ ; **H(Pt)** oxidation half reaction standard potential  $E^\circ_H = 0.1016$  V.

**Ox+Red** summary  $2H_3O^+ + H_2O + 2e^- \Leftrightarrow H_{2aq} + 2H_2O$ ;  $(Pt)H + 2H_2O \Leftrightarrow 2H_3O^+ + 2e^-$ ;

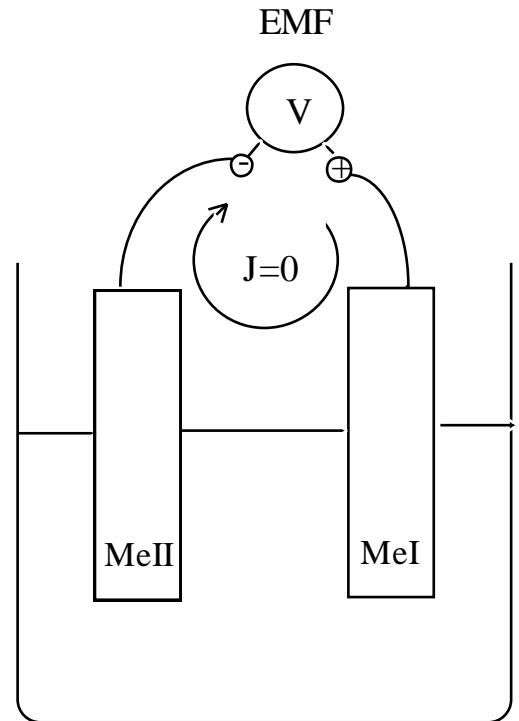
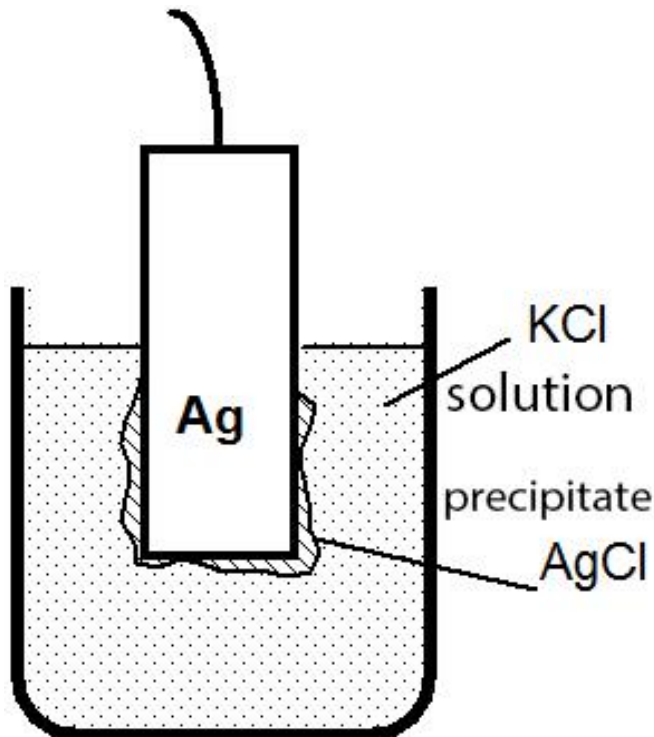
is metal **H(Pt)** hydrogen spontaneous solubility product equilibrium:  $2(Pt)H + H_2O \Leftrightarrow H_{2aq}$ ;

$\Delta E^\circ_{Hess\_sp\_H(Pt)} = E^\circ_H + E^\circ_{H_2Ox} = 0.10166 - 0.302 = -0.2$  V;  $\Delta G_{Hess\_sp\_H(Pt)} = \Delta E^\circ_{sp\_H(Pt)} \cdot F \cdot 2 = -0.2 \cdot 96485 \cdot 2 = -38.6$  kJ/mol;

$\Delta G_{Hess\_sp\_H(Pt)} = G_{H_{2aq}} - 2G_{H(Pt)} - G_{H_2O} = 103.24 - 2*51.05 - 0 = 1.14$  kJ/mol .

## Metal/insoluble salt/ion II-type electrode

Silver /silver chloride/chloride ion II-type electrode consists of silver metal, AgCl precipitate insoluble salt and  $K^+Cl^-$  solution, containing the counter-ions  $Cl^-$  of AgCl insoluble salt

$$\underline{AgCl} + e^- \rightleftharpoons Ag^+ + Cl^-$$


$K^+Cl^-$  solution, containing the counter-ions  $Cl^-$  of AgCl insoluble salt.

Red-ox half reaction is:  $\underline{AgCl} + e^- \rightleftharpoons Ag^+ + Cl^-$

Nernst's equation:  $E_{Ag/AgCl} = E_{oAgCl} - 0.0591 \cdot \log [Cl^-]$

The main application of II-type electrodes is their use as reference electrodes, because potential value depends only on chloride ion concentration.

Chloride concentration is precise controlled technology for instruments use.

Between two electrodes MeI (Indicator electrode) and MeII (Reference electrode) on electric circuit linked

can be expressed MeI Indicator EI as sum :  $EI = EMF + EII$

Indicator electrode having EI –has reactivity with solution that electrode of investigations, Standard reference electrode having  $EII = \text{constant}$  , because chloride concentration is constant and has no reactivity with environment into solution.

**Nernst's potential** studies  $\underline{5(Pt)H} + MnO_4^-$  on hydroxonium  $H_3O^+$  and water  $H_2O$  account Oxidant reduction inverse Nernst's potential:  $MnO_4^- + 7H_3O^+ + 5e^- \leftrightarrow Mn^{2+} + 12H_2O$ ;  $E^\circ_{MnO_4} = 1.86$  V.

Reductant oxidation Nernst's potential:  $\underline{5(Pt)H} + 5H_2O \leftrightarrow 5H_3O^+ + 5e^-$ ; standart  $E^\circ_{H} = 0,10166$  V.

Electrones balancing  $+ne^- = 5e^- = -ne^-$  summary Red-Ox reaction:  $\underline{5(Pt)H} + MnO_4^- + 3H_3O^+ \leftrightarrow Mn^{2+} + 7H_2O$ .

$$E_{MnO_4} = E^\circ + \frac{0.0591}{4} \cdot \lg \frac{[H_2O]^{12} \cdot [Mn^{2+}]}{[MnO_4^-] \cdot [H_3O^+]^8} = -1.86 \text{ V} + \frac{0.0591}{4} \cdot \lg \frac{[H_2O]^{12} \cdot [Mn^{2+}]}{[MnO_4^-] \cdot [H_3O^+]^8}; [H_2O] = 55.3 \text{ M} = \frac{996 \text{ g/L}}{18 \text{ g/mol}}$$

$$E_H = E^\circ_H + 0.0591 \cdot \lg \frac{[H_3O^+]}{[H_2O]} = 0.10166 \text{ V} + 0.0591 \cdot \lg \frac{[H_3O^+]}{[H_2O]};$$

Substan	$\Delta H^\circ_H, \text{kJ/mol}$	$\Delta S^\circ_H, \text{J/mol/K}$	$\Delta G^\circ_H, \text{kJ/mol}$	$\Delta G_{Hess} = \Delta G^\circ_{Mn2} + 7\Delta G^\circ_{H2O} - 3\Delta G^\circ_{H3O} - \Delta G^\circ_{MnO4} - 5\Delta G^\circ_{(Pt)H} = -1049 \text{ kJ/mol}$
$H_2O$	-285.85	69.9565	-237.191	$-228.1 + 7 \cdot (-237.191) - (3 \cdot (-213.2746) - 447.2 + 5 \cdot 99.13/2) = -1049 \text{ kJ/mol}$
$H_2O$	<b>-286.65</b>	<b>-453.188</b>	<b>-151.549</b>	Biochem. Thermodyn, Albery, 2006, Massachusetts Technology Inst.
$H_3O^+$	-285.81	-3.854	-213.2746	CRC Handbook of Chemistry and Physics, 2010, D.Lide
$H_2(aq)$	23.4	-130	99.13	$\Delta G_{eq} = -800 \text{ kJ/mol}; \Delta G_{Hess} = -1049 \text{ kJ/mol}$
$MnO_4^-$	-541.4	-191.2	-447.2	for $\underline{5(Pt)H} + MnO_4^- + 8H_3O^+ \leftrightarrow Mn^{2+} + 8H_2O$ as absolute value
$Mn^{2+}$	-220.8	-73.6	-228.1	$ \Delta G_{eq} = -800 \text{ kJ/mol}  <  \Delta G_{Hess} = -1049 \text{ kJ/mol} ;$

Concentration  $[H_2O]^{12}$  exponent 12 included in classic standard potential  $E_o = 1.51$  V as logarithm:

$$E^\circ_{MnO_4} = E_o - 0.0591/5 \cdot \log(1/[H_2O]^{12}) = 1.51 + 0.10166 - 0.0591/5 \cdot \log(1/55.3^{12}) = 1.76 + 0.10166 = 1.859 \text{ V};$$

$$\Delta G_{eqOxRed} = (E^\circ_H + E^\circ_{MnO_4}) \cdot F \cdot 1 \cdot 5 = (0.10166 - 1.86) \cdot 96485 \cdot 5 = -1.758 \cdot 96485 \cdot 5 = -848 \text{ kJ/mol}$$

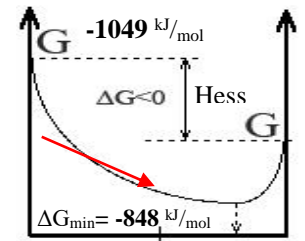
$$K_{eq} = \exp(-\Delta G_{eqOxRed}/R/T) = \exp(848.3/8.3144/298.15) = \exp(342.2) = 4.08 \cdot 10^{148};$$

Exothermic and exoergic  $MnO_4^-$  reduction by  $\underline{5(Pt)H}$  Hess free energy change negative

$\Delta G_{Hess} = \Delta G_{OxRed} = -1049 \text{ kJ/mol}$ , but minimizes  $\Delta G_{min} = \Delta G_{eq} = -848 \text{ kJ/mol}$  reaching

$$\text{equilibrium mixture } 4.08 \cdot 10^{148} = K_{eq} = \frac{[H_2O]^7 \cdot [Mn^{2+}]}{[(Pt)H]^5 [MnO_4^-] [H_3O^+]^3}; \text{ Prigogine attractor is free}$$

energy change minimum  $\Delta G_{min}$  reaching. Free energy change minimum reaching establishes equilibrium.

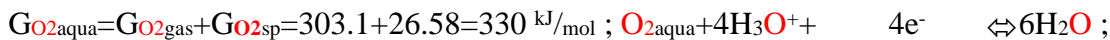


reactants  $\underline{5(Pt)H} + MnO_4^- + 3H_3O^+$   
products  $Mn^{2+} + 7H_2O$

**Nernst's potential**  $O_{2(aqua)}/H_2O$  red-ox system biochemical mechanism of acidosis and oxidative stress (forced oxidizing agent power by potential E increase)

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

Water medium (blood plasma) oxygen is strong oxidant **1.485** V according half reaction:



oxidized form free electrons reduced form;

$$G_{H_3O+OH} = G_{H_3O+} + G_{OH} = 22.44 + 77.36 = 99.8 \text{ kJ/mol of } H_2O + H_2O \leftrightarrow H_3O^+ + OH$$

Biochemistry oxygen  $O_{2(aqua)}$  decreases free energy content  $G_{O_{2(aqua)}} = 329.7 \text{ kJ/mol}$  to  $G_{O_{2(Biochemistry)}} = 78.08 \text{ kJ/mol}$ .

Concentration arterial  $[O_{2(aqua)}] = 6 \cdot 10^{-5} \text{ M}$  and  $pH = 7.36$  concentration  $[H_3O^+] = 10^{-7.36} \text{ M}$ .

$$E_{O_2} = E^\circ + 0.0591/4 \cdot \log([O_{2(aqua)}] \cdot [H_3O^+]^4 / [H_2O]^6) = 1.485 + 0.0591/4 \cdot \log(6 \cdot 10^{-5} \cdot 10^{-29.44} / 55.346^6) = 0.833 \text{ Volts}$$

$$\text{decrease } \Delta E_{arterial} = E^\circ - E_o = 1.485 - 0.833 = -0.652 \text{ V}; \Delta G_{arterial} = \Delta E_{H_2O} \cdot F \cdot n = -0.652 \cdot 96485 \cdot 4 / 1000 = -251.6 \text{ kJ/mol.}$$

Solubility zero value  $O_{2(gas)} \text{ AIR} + H_2O \xrightarrow{\text{Aquaporins}} O_{2(Blood)}$  increases to product level  $G_{O_{2(sp)}} = 26.58 \text{ kJ/mol}$ :

$$\frac{[O_{2(aqua)}]}{[O_{2(gas)}] \cdot [H_2O]} = K_{sp} = 2.205 \cdot 10^{-5}; G_{O_{2(sp)}} = -R \cdot T \cdot \ln(K_{sp}) = -8.3144 \cdot 298.15 \cdot \ln(2.205 \cdot 10^{-5}) = 26.58 \text{ kJ/mol.}$$

Free energy protolysis decreases  $G_{O_{2(Biochem\_arterial)}} = G_{O_{2(aqua)}} + G_{O_{2(sp)}} + \Delta G_{arterial} = 303.1 + 26.58 - 251.6 = 78.08 \text{ kJ/mol}$

and oxygen becomes fire safe biochemical oxidant, forming arterial concentration  $[O_{2(aqua)}] = 6 \cdot 10^{-5} \text{ M}$  as safe

Bioenergetic sustaining normal isooxia. [3];

1) Water 55.346 M decreases potential from **1.485 V** to classic standard **1.383 V** about **-0.155 V** =  $\Delta E_{H_2O}$ .

$$E_{O_2} = E^{\circ}_{O_2} + 0.0591/4 \cdot \log(1/[H_2O]^6) = 1.485 + 0.01478 \cdot \log(1/55.346^6) = 1.383 \text{ V};$$

2) Acid  $H_3O^+$  increases 10 times the potential and free energy content increases about  $\Delta E_{H_3O^+} = 0.05912 \text{ V}$

$$\Delta E_{H_3O^+} = 0.01478 \cdot \lg([H^+]^4) = 0.05912 \text{ V} \text{ and } \Delta G_{\max} = \Delta E_{H_3O^+} \cdot F \cdot n = 0.05912 \cdot 96485 \cdot 4/1000 = 22.817 \text{ kJ/mol};$$

3) Air 20.95% replaced with 100% oxygen  $[O_{2\text{aqua}}]$  concentration 5 times increase potential about

$$\Delta E_{O_2 100\%} = 0.01478 \cdot \lg(100\% [O_{2\text{aqua}}]) = 0.01478 \cdot \lg(5) = +0.0103 \text{ V}. \text{ Free energy content for}$$

oxygen increases about  $\Delta G_{\max} = \Delta E_{H_3O^+} \cdot F \cdot n = 0.01033 \cdot 96485 \cdot 4/1000 = 3.987 \text{ kJ/mol}$ . [6th page](#).

NASA Apollo Moon project closes 1972 because of oxidative stress and technical hazards risk.

Which concentration water  $[H_2O]$ , oxidiser [Ox], reducer [Red], acid  $[H_3O^+]$  changes decrease free energy content or increase free energy content for oxidising reagent? How standard potential  $E^{\circ}$  values change free energy content in oxidants and in reductants! When increases and when decreases content?

Oxygen solubility Prigogine attractor free energy change Hess law solution is exothermic and endoergic



$$\Delta G_H = \Delta G^{\circ}_{H_2O} + \Delta G^{\circ}_{O_{2\text{aqua}}} - \Delta G^{\circ}_{H_2O} - \Delta G^{\circ}_{O_{2\text{gas}}} = 16.4 - (0 - 151,549) = 168 \text{ kJ/mol endoergic};$$

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8.3144 \cdot 298.15 \cdot \ln(2.205 \cdot 10^{-5}) = -8.3144 \cdot 298.15 \cdot 6.414 = 26.58 \text{ kJ/mol}$$

$[O_2]$  solubility Hess free energy change is positive  $\Delta G_{\text{Hess}} = \Delta G_{\text{solubility}} = 168 \text{ kJ/mol}$ ,

but minimized minimised to  $\Delta G_{\min} = \Delta G_{\text{eq}} = 26.58 \text{ kJ/mol}$  reaching

$$\text{equilibrium mixture } K_{\text{eq}} = \frac{[O_{2\text{aqua}}]}{[O_{2\text{air}}] \cdot [H_2O]} = 2.205 \cdot 10^{-5} = 10^{-4.66}$$

Equilibrium reaching is Prigogine attractor free energy change minimum  $\Delta G_{\min}$ .

Free energy change minimum  $\Delta G_{\min}$  reaching establishes equilibrium. [53rd page](#).

Zero osmolar  $C_{\text{osm}} = 0 \text{ M}$  and ionic force  $I = 0 \text{ M}$  in distilled water from air 20.95% solubility is:

$$\text{solubility } [O_{2\text{water}}] = K_{\text{eq}} \cdot [O_{2\text{air}}] \cdot [H_2O] = 2.205 \cdot 10^{-5} \cdot 0.2095 \cdot 55.3 = 2.5567 \cdot 10^{-4} \text{ M}.$$

ELSEVIER, Rotating Electrode Method and Oxygen reduction Electrocatalysts, 2014, p.1-31,

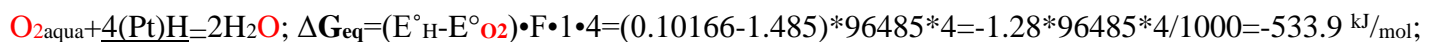
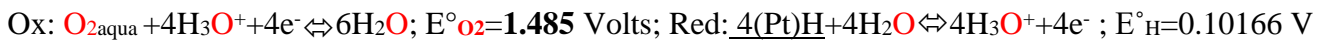
1. WeiXinga, MinYinb, QingLvb, YangHub, ChangpengLiub, JiujunZhangc. Pure 1atm mol fraction  $[O_{2\text{gas}}] = 1$ .

Osmolar  $C_{\text{osm}} = 0.305 \text{ M}$ , ionic force  $I = 0.25 \text{ M}$ , air oxygen 20.95% conditions dissolve  $[O_{2\text{aqua}}] = 9.768 \cdot 10^{-5} \text{ M}$ .

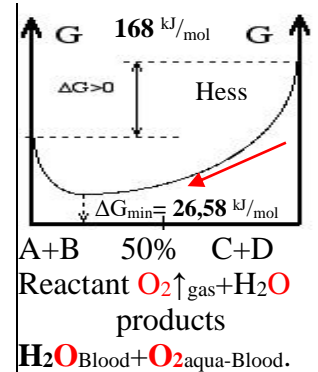
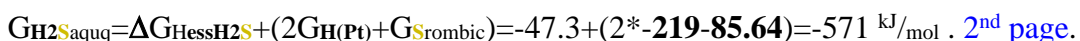
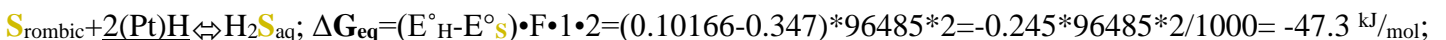
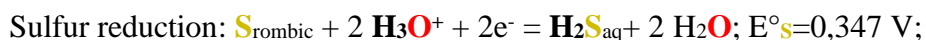
Therefore physiologic equilibrium constant is  $K_{O_2\text{blood}} = [O_{2\text{aqua}}]/[O_{2\text{air}}] = 9.768 \cdot 10^{-5}/0.2095 = 4.663 \cdot 10^{-4} = 10^{-3.3314}$ .

Arterial  $[O_{2\text{aqua}}] = 6 \cdot 10^{-5} \text{ M}$  and venous  $[O_{2\text{aqua}}] = 0.426 \cdot 10^{-5} \text{ M}$  concentration determines  $pK_{O_2\text{blood}} = 3.3314$

by osmosis oxygen molecules crossing through aquaporins membranes against gradient.



Knowing equilibrium value  $\Delta G_{\text{eq}2H_2O} = 2G_{H_2O} - 4G_{(Pt)H} - G_{O_{2\text{aqua}}} = 2 \cdot 0 - (4 \cdot G_{(Pt)H} + 329.68) = -533.9 \text{ kJ/mol}$ , hydrogen metal free energy is  $G_H(Pt) = (2G_{H_2O} - \Delta G_{\text{eq}2H_2O} - G_{O_{2\text{aqua}}})/4 = (2 \cdot 0 + 533,886 - 329,68)/4 = 204,2/4 = 51,05 \text{ kJ/mol}$ ;



**Nernst's potential  $O_{2(aqua)} / H_2O$  |  $(Pt)H / H_3O^+$  un  $H_2O_2 / H_2O$  |  $H_2O_2 / O_2$  studies**

Ox oxidizing reactant half reaction:  $O_{2(aqua)} + 4H_3O^+ + 4e^- \rightleftharpoons 6 H_2O$  ;  $G_H(Pt)=164.82/4 =41.2$  kJ/mol

Red reducing reactant half reaction:  $4(Pt)H + 4H_2O \rightleftharpoons 4 H_3O^+ + 4e^-$  ; metālisks ūdenradis  $G_H(Pt)=41.2$  kJ/mol

$$O_{2(aqua)} + 4(Pt)H \rightleftharpoons 2H_2O ; \Delta G_{eqStandart} = 2G_{H_2O} - 4G_H(Pt) - G_{O_{2(aqua)}} = (2*0 - 4*41.2 - 329.68) = -494.5 \text{ kJ/mol}$$

$$E_{O_2} = E^\circ_{O_2} + 0.0591/4 \cdot \lg([O_{2(aqua)}] \cdot [H_3O^+]^4 / [H_2O]^6) = 1.485 + 0.0591/4 \cdot \lg([O_{2(aqua)}] \cdot [H_3O^+]^4 / [H_2O]^6) ;$$

$$E_H = E^\circ + 0.0591 \cdot \lg([H_3O^+] / [H_2O]) = 0.10166 \text{ V} + 0.0591 \cdot \lg([H_3O^+] / [H_2O]) ;$$

Gas  $O_{2(gas)} + 2H_{2(gas)} \rightleftharpoons 2H_2O$  ;  $\Delta G_{Hess2H_2O} = 2\Delta G^\circ_{H_2O} - (2\Delta G^\circ_{H_2(gas)} + \Delta G^\circ_{O_2(gas)}) = 2* -273.19 - (2*0 + 0) = 2* -273.19 = -546.4$  kJ/mol

$$O_{2(aqua)} + 2H_{2(aqua)} \rightleftharpoons 2H_2O ; \Delta G_{Alberty2H_2O} = 2G_{H_2O} - 2G_{H_{2(aqua)}} - G_{O_{2(aqua)}} = 2*0 - (2*103.24 + 329.68) = -536.4 \text{ kJ/mol} ;$$

Hydrogen energy  $G_{H_{2(aqua)}} = 103$  kJ/mol of Alberty R.A. Biochemical Thermodynamic's 1-463. (2006).

Substance	$\Delta H^\circ_H$ , kJ/mol	$\Delta S^\circ_H$ , J/mol/K	$\Delta G^\circ_H$ , kJ/mol
<b>H<sub>2</sub>O</b>	-285.85	69.9565	-237.191
<b>H<sub>2</sub>O</b>	<b>-286.65</b>	<b>-453.188</b>	<b>-151.549</b>
<b>H<sub>3</sub>O<sup>+</sup></b>	-285.81	-3.854	-213.2746
<b>H<sub>2</sub>(aq)</b>	23.4	-130	99.13
<b>O<sub>2</sub>(aqua)</b>	<b>-11.70</b>	<b>-94.2</b>	<b>16.4</b>
<b>O<sub>2</sub>(aqua)</b>	-11.715	110.876	16.4

$$\Delta G_{Hess} = 2\Delta G^\circ_{H_2O} - 4\Delta G^\circ_{(Pt)H} - \Delta G^\circ_{O_{2(aqua)}} = -689 = 2* -344.521 \text{ kJ/mol} ;$$

$$= 2* -237.191 - (4*99.13/2 + 16.4) = -689 = 2* 344.5 \text{ kJ/mol. CRC 2010}$$

$$\Delta G_{eq} = -494 \text{ kJ/mol} ; \Delta G_{Hess} = -689 \text{ kJ/mol}$$

in reaction  $4(Pt)H + O_{2(aqua)} \rightleftharpoons 2 H_2O$  ; absolute values

$$|\Delta G_{eq} = -534 \text{ kJ/mol}| < |\Delta G_{Hess} = -689 \text{ kJ/mol}| ;$$

Water concentration  $[H_2O]^6$  as logarithm extracted of  $E^\circ_{classic} = 1.229$  V  
Thermodynamic to hydrogen reference  $E^\circ = 1.383 + 0.10166 = 1.485$  V

$$E^\circ_{O_2} = 1.485 \text{ V} ; E_o_{O_2} = E^\circ_{O_2} + 0.0591/4 \cdot \lg(1/[H_2O]^6) = 1.383 \text{ V} ; [H_2O] = 996 \text{ g/L} / 18 \text{ g/mol} = 55.3 \text{ M} ;$$

$$\Delta G_{eq2H_2O} = (E^\circ_H - E^\circ_{O_2}) \cdot F \cdot 4 = (0.10166 - 1.485) \cdot 96485 \cdot 4 = -1.28 \cdot 96485 \cdot 4 = -533,886 = 2* -266,9 \text{ kJ/mol} ;$$

$$K_{eq2H_2O} = K_{OxRed} = \exp(-\Delta G_{OxRed} / R/T) = \exp(533886 / 8.3144 / 298.15) = \exp(215,4) = 3,42 \cdot 10^{93} ;$$

$$G_H(Pt) = (2G_{H_2O} - \Delta G_{eq2H_2O} - G_{O_{2(aqua)}}) / 4 = (2*0 + 533,9 - 329.68) / 4 = 164.82 / 4 = 51,05 \text{ kJ/mol} ;$$

Exothermic and exoergic  $O_{2(aqua)}$  reduction with metallic hydrogen

$4(Pt)H$  and  $H_2O_2$  dismutation Hess free energy change negative

$\Delta G_{Hess2H_2O} = -546$ ..... kJ/mol ,  $\Delta G_{Hess_{H_2O_2}} = -480$ ..... kJ/mol, but minimized

reaching equilibrium  $\Delta G_{eq2H_2O} = -534$  kJ/mol and  $\Delta G_{eqStandart} = -228.6$ ..... kJ/mol mixture

constants  $K_{eq2H_2O} = 3,42 \cdot 10^{93}$ ..... and  $K_{eqStandart} = 1.108 \cdot 10^{40}$ .....

The minimum  $\Delta G_{min}$  is Prigogine attractor. Free energy change minimum reaching establish equilibrium state.

Red  $H_2O_2 + 2 H_2O - 2 e^- = O_{2(aqua)} + 2 H_3O^+$  ;  $E^\circ_{H_2O_2} = 0.899$  V Alberta University ;

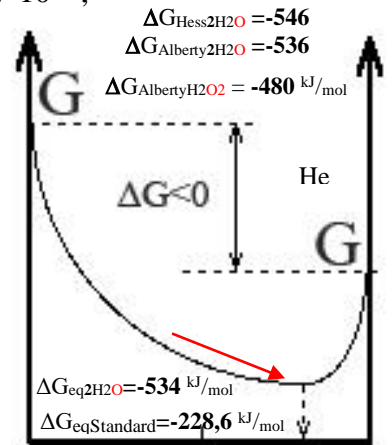
$[H_2O_2] = 1$  M concentration environment pH=7.36. .

Oks  $H_2O_2 + 2 H_3O^+ + 2 e^- = 4 H_2O$  ;  $E^\circ_{Ox} = 2.084$  V Suhotina ;

$$2H_2O_{2(aq)} \Rightarrow O_{2(aqua)} + 2H_2O + Q + \Delta G ;$$

Reactants  $4(Pt)H + O_{2(aqua)}$  and products  $2H_2O$

Reactants  $2H_2O_{2(aq)}$  and products  $O_{2(aqua)} + 2H_2O$



4A+B 50% 2D  
2A 50% B+2C

$$\Delta G_{eqStandart} = (E_{Red} - E_{Ox}) \cdot F \cdot n = (0.7975 - 1.982) \cdot 96485 \cdot 2 = (-1.1845) \cdot 96485 \cdot 2 = -228.6 \text{ kJ/mol} ;$$

$$K_{eqStandart} = \frac{[O_2]_{aqua} \cdot [H_2O]^2}{[H_2O_2]_{aqua}^2} = K_{H_2O_2} = \exp(-\Delta G_{eq} / R/T) = \exp(228573 / 8.3144 / 298.15) = 1.108 \cdot 10^{40} \text{ .....}$$

$$E_{oH_2O_2} = E^\circ_{H_2O_2} + 0.0591/2 \cdot \lg([O_{2(aqua)}] \cdot [H_3O^+]^2 / [H_2O_2] / [H_2O]^2) = 0.899 + 0.0591/2 \cdot \lg(6 \cdot 10^{(-5)} \cdot 10^{(-7.36 \cdot 2)} / 1 / 55.3^2) = 0.2363 \text{ V}$$

$$E_{oOx} = E^\circ_{H_2O_2Ox} + 0.0591/2 \cdot \lg([H_2O_2] \cdot [H_3O^+]^2 / [H_2O]^4) = 2.084 + 0.0591/2 \cdot \lg(1 \cdot 10^{(-7.36 \cdot 2)} / 55.3^4) = 1.443 \text{ V}$$

$$\Delta G_{eqBioChem} = (E_{Red} - E_{Ox}) \cdot F \cdot n = (0.2363 - 1.443) \cdot 96485 \cdot 2 = (-1.207) \cdot 96485 \cdot 2 = -232.86 \text{ kJ/mol}$$

$$\Delta G_{Alberty} = G_{O_2Biochem\_arteriaj} + 2 \cdot G_{H_2OBioChemistry} - 2 \cdot G_{H_2O_2} = 78.08 + 2 \cdot 85.64 - 2 \cdot 364.79 = -480.22 \text{ kJ/mol} ; \text{Alberty}$$

$$1. \Delta H_{Hess} = \Delta H^\circ_{O_2} + 2\Delta H^\circ_{H_2O} - 2\Delta H^\circ_{H_2O_2} = -11.7 - 2 \cdot 286.65 - (2 \cdot -191.99) = -201.02 \text{ kJ/mol} = -11.7 - 2 \cdot 285.85 - (2 \cdot -191.17) = -201.06 \text{ kJ/mol}$$

$$2. \Delta S_{dispersed} = -\Delta H_H / T = -(-201.02) / 298.15 = 674.2 \text{ J/mol/K} ; \Delta S_{dispersed} = -\Delta H_H / T = -(-201.06) / 298.15 = 674.36 \text{ J/mol/K} ;$$

$$\Delta S_{Hess} = \Delta S^\circ_{O_2} + 2\Delta S^\circ_{H_2O} - 2\Delta S^\circ_{H_2O_2} = -94.2 + 2 \cdot -453.188 - (2 \cdot -481.688) = -37.2 \text{ J/mol/K} ;$$

$$\Delta S_{Hess} = \Delta S^\circ_{O_2} + 2\Delta S^\circ_{H_2O} - 2\Delta S^\circ_{H_2O_2} = 110.876 + 2 \cdot 69.9565 - (2 \cdot 143.9) = -37 \text{ J/mol/K} ;$$

$$2. \Delta S_{total} = \Delta S_H + \Delta S_{dispersed} = -37.2 + 674.2 = 637 \text{ ..... J/mol/K} \Delta S_{total} = -37.011 + 674.36 = 637.35 \text{ ..... J/mol/K} ;$$

$$4. \Delta G_{Hess} = \Delta H_H - T \cdot \Delta S_H = -201.02 - 298.15 \cdot -0.0372 = -189.9 \text{ kJ/mol exoergic spontaneous.}$$

$$\Delta G_{Hess} = \Delta H_H - T \cdot \Delta S_H = -201.06 - 298.15 \cdot -0.037 = -190 \text{ kJ/mol} ;$$

$$T \cdot \Delta S_{total} = 0.637 \cdot 298.15 = 189.9 \text{ kJ/mol} ; T \cdot \Delta S_{total} = 0.63735 \cdot 298.15 = 190 \text{ kJ/mol} ;$$

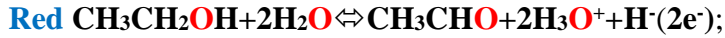


Nernst's potential studies reducing with vitamin B<sub>3</sub> ethanal H<sub>3</sub>CCH=O and oxidising H<sub>3</sub>CCH<sub>2</sub>OH ethanol



ΔG<sub>Hess</sub>=ΔG°<sub>H<sub>3</sub>O</sub>+ΔG°<sub>CH<sub>3</sub>CHO</sub>+ΔG°<sub>NADH</sub>-ΔG°<sub>CH<sub>3</sub>CH<sub>2</sub>OH</sub>-ΔG°<sub>H<sub>2</sub>O</sub>-ΔG°<sub>NAD<sup>+</sup></sub>=159.1 kJ/mol;

ΔG<sub>Hess</sub>=32.2824+1175.5732-151.549-(75.2864+1059.11-237.191)=159.1 kJ/mol endoergic;



E°<sub>H<sub>2</sub>O</sub>=0.190+0.10166+0.0591/2\*log([H<sub>2</sub>O])=0.343 V;

By convention balanced n = 2 = m number of electrons 2e<sup>-</sup>ΔE° is expressed as E°<sub>H<sub>2</sub>O</sub> of the electron donor minus E°<sup>1</sup> of the electron acceptor. Because NAD<sup>+</sup> is accepting electrons from ethanol :

E°<sub>H<sub>2</sub>O</sub>=0.190-0.0591/2\*log([H<sub>2</sub>O])=0.190+0.02955\*log(55.3333)=0.190+0.0515=0.343 V

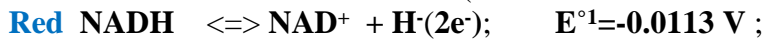
ΔE°=E°<sub>H<sub>2</sub>O</sub>-E°<sup>1</sup>=0.343-(-0.0113)=0.3545 V, n=2; ΔG<sub>eq</sub>=ΔE°•F•n=0.3545 V•2 mol•96485 C/mol=68.408 kJ/mol

ΔG<sub>eq</sub>=-R•T•ln(K<sub>eq</sub>); K<sub>eq</sub>= $\frac{[NADH] \cdot [CH_3CHO] \cdot [H_3O^+]}{[NAD^+] \cdot [CH_3CH_2OH] \cdot [H_2O]}$  = e<sup>-ΔG<sub>eq</sub>/R•T</sup> = e<sup>-68408/(8.314•298.15)}</sup> = 1.036•10<sup>-12</sup>=10<sup>-11.985</sup>



ΔG<sub>Hess</sub>=ΔG°<sub>CH<sub>3</sub>CH<sub>2</sub>OH</sub>+ΔG°<sub>H<sub>2</sub>O</sub>+ΔG°<sub>NAD<sup>+</sup></sub> -ΔG°<sub>H<sub>3</sub>O</sub>-ΔG°<sub>CH<sub>3</sub>CHO</sub>-ΔG°<sub>NADH</sub> = -159.1 kJ/mol;

ΔG<sub>Hess</sub>=75.2864+1059.11-237.191-(32.2824+1175.5732-151.549)= -159.1 kJ/mol endoergiska;



By convention balanced n=2=m number of electrons 2e<sup>-</sup>ΔE° is expressed as E°<sup>1</sup> of the electron donor minus E°<sub>H<sub>2</sub>O</sub> of the electron acceptor. Because CH<sub>3</sub>CHO is accepting electrons from NADH in our example

ΔE°=E°<sup>1</sup>-E°<sub>H<sub>2</sub>O</sub>=-0.0113-0.343=-0.3545 V, n=2; ΔG<sub>eq</sub>=ΔE°•F•n=-0.3545 V•2 mol•96485 C/mol=-68.408 kJ/mol;

ΔG<sub>eq</sub>=-R•T•ln(K<sub>eq</sub>)=- 68,408 kJ/mol; K<sub>eq</sub>= $\frac{[NAD^+] \cdot [CH_3CH_2OH] \cdot [H_2O]}{[NADH] \cdot [CH_3CHO] \cdot [H_3O^+]}$  = e<sup>ΔG<sub>eq</sub>/R•T</sup> = e<sup>-68408/(8.314•298.15)}</sup> = 9.65•10<sup>11</sup>=10<sup>11.985</sup>.

In aerobic organisms NADH oxidase with O<sub>2</sub> aqua perform ratio [NAD<sup>+</sup>]/[NADH]=10<sup>6</sup>;

ΔG<sub>Homeostasis</sub>=68.408+ R•T•ln(10<sup>6</sup>•1/1•10<sup>-7.36</sup>/55.3)=68.408-86.2=-17.8..... kJ/mol.

[NAD<sup>+</sup>]/[NADH]=10<sup>3</sup>; ΔG<sub>Homeostasis</sub>=68.408-69.08=-0.676..... kJ/mol.

Equilibrium is shifted far to reactants as aerobic constant K<sub>eq</sub>=10<sup>-11.985</sup> and inverse

anaerobic constant K<sub>eq</sub>=10<sup>11.985</sup>. Aerobic endothermic and endoergic vitamin B<sub>3</sub> ethanol

oxidation Hess law free energy change positive ΔG<sub>Hess</sub>=159..... kJ/mol and inverse

ethanal anaerobic reduction negative ΔG<sub>Hess</sub>=-159..... kJ/mol , but minimises reaching

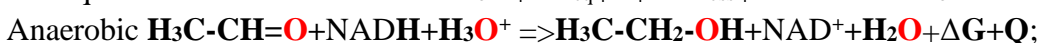
equilibrium aerobic ΔG<sub>min</sub>=ΔG<sub>eq</sub>=68.4..... kJ/mol and anaerobic

ΔG<sub>min</sub>=ΔG<sub>eq</sub>=-68.4..... kJ/mol reaching equilibrium mixture

constants 10<sup>-11.985</sup>=K<sub>eq</sub> aerobic and anaerobic 10<sup>11.985</sup>=K<sub>eq</sub>.

Prigogine attractor is free energy change absolute minimum ΔG<sub>min</sub> reaching

equilibrium ΔG<sub>min</sub>=68.4..... kJ/mol= |ΔG<sub>eq</sub>| < |ΔG<sub>Hess</sub>| = 159..... kJ/mol.



Anaerobic ΔG<sub>eq</sub>=ΔE°•F•n=-0.3545 V•2 mol•96485 C/mol=-68.408..... kJ/mol favored.

Insufficient low O<sub>2</sub> aqua concentration hypoxia to anaerobic alcohol oxidation unflavored

but ethanal reduction to ethanol favored [H<sub>3</sub>CCH<sub>2</sub>OH]/[H<sub>3</sub>CCH=O]=1/10 homeostasis

reduction with NADH reductase enzyme as negative free energy change

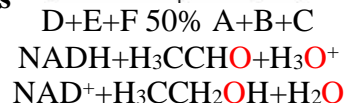
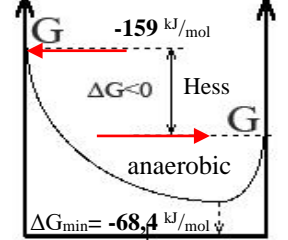
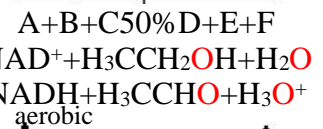
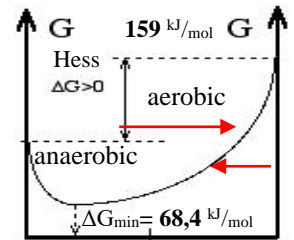
ΔG<sub>Homeostasis</sub>=-27.86..... kJ/mol

Anaerobic homeostasis ratio [NADH]/[NAD<sup>+</sup>]=10 over [NAD<sup>+</sup>] favors reduction:

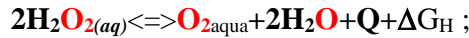
ΔG<sub>Homeostasis</sub>=-68.41+8.3144•298.15•ln(K<sub>Homeostasis</sub>)=-68.41+40.54=-27.86..... kJ/mol

ΔG<sub>Homeostasis</sub>=-68.41+8.3144•298.15•ln( $\frac{1}{10} \frac{1}{10} \frac{55.333}{10^{-7.36}}$ )=-27.86 kJ/mol ; K<sub>Homeostasis</sub>= $\frac{[NAD^+] \cdot [CH_3CH_2OH] \cdot [H_2O]}{[NADH] \cdot [CH_3CHO] \cdot [H_3O^+]}$

[NADH]/[NAD<sup>+</sup>]=1/770; ΔG<sub>Homeostasis</sub>=68.408+8.3144•298.15•ln(700/1•1/1•55.3457/10<sup>-7.36</sup>)=0.028 kJ/mol.



High rate protolysis peroxide anions  $\text{H}^+ + \text{HOO}^- \rightleftharpoons \text{OOH} + \text{H}^+$  collision activation energy is high  $E_a = 79000 \text{ J/mol}$  oposit  $\text{HOO}^- \Rightarrow \text{Fe}^{3+}$  collision activation energy  $E_a = 29 \text{ J/mol}$  is small. Producing  $\omega=6, \omega=3$  fatty acids, oxygen, water and heat:



$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{O}_2} + 2\Delta G^\circ_{\text{H}_2\text{O}} - 2\Delta G^\circ_{\text{H}_2\text{O}_2} = 16.40 + 2*(-237.191) - (2*(-134.03)) = -189.9 \dots \text{kJ/mol} \text{ exoergic}$$

$$\Delta G_{\text{HessAlberty}} = G^\circ_{\text{O}_2} + 2G^\circ_{\text{H}_2\text{O}} - 2G^\circ_{\text{H}_2\text{O}_2} = 303.1 + 2*(0) - (2*364.79) = -426.5/2 \text{kJ/mol} = -213,25 \dots \text{kJ/mol} \text{ exoergic}$$

Substance	$\Delta H^\circ_{\text{H}}$ , kJ/mol	$\Delta S^\circ_{\text{H}}$ , J/mol/K	$\Delta G^\circ_{\text{H}}$ , kJ/mol
$\text{H}_3\text{O}^+$	-285.81	-3.854	-213.275
$\text{O}_2(\text{aq})$	-11.715	110.876	16.4
$\text{O}_2(\text{aq})$	<b>-11.70</b>	<b>-94.2</b>	<b>16.40</b>
$\text{H}_2\text{O}$	-285.85	69.9565	-237.191
$\text{H}_2\text{O}$	<b>-286.65</b>	<b>-453.188</b>	<b>-151.549</b>
$\text{H}_2\text{O}_2(\text{aq})$	<b>-191.99</b>	<b>-481.688</b>	<b>-48.39</b>
$\text{H}_2\text{O}_2(\text{aq})$	-191.17	143.9	-134.03
$\text{H}_2\text{O}_2(\text{l})$	-237.129	69.91	-237.129

1.  $\Delta H^\circ_{\text{Hess}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{reactants}}$ ; 3.  $\Delta G^\circ_{\text{Hess}} = \Delta H^\circ_{\text{H}} - T \cdot \Delta S^\circ_{\text{H}}$ ;  
 Miščenko 1968, Himia, Leningrad 2.  $\Delta S^\circ_{\text{Hess}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{reactants}}$   
 CRC 2010; 2.  $\Delta S^\circ_{\text{Hess}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{reactants}}$   
 $\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{O}_2} + 2\Delta H^\circ_{\text{H}_2\text{O}} - 2\Delta H^\circ_{\text{H}_2\text{O}_2} = -201.02 \dots = -201.06 \dots \text{kJ/mol}$   
 $= -11.7 - 2*286.65 - (2*(-191.99)) = -201.02 \dots \text{kJ/mol} \text{ eksotermiska..}$   
 $= -11.7 - 2*285.85 - (2*(-191.17)) = -201.06 \dots \text{kJ/mol}$   
 Biochem Thermodynamic 2006 Masachusetts Technology institute  
 University Alberta 1997.

$$2. \Delta S_{\text{dispersed}} = -\Delta H_{\text{H}}/T = -(-201.02)/298.15 = 674.2 \dots \text{J/mol/K}; \Delta S_{\text{dispersed}} = -\Delta H_{\text{H}}/T = -(201.06)/298.15 = 674.36 \dots \text{J/mol/K};$$

$$\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{O}_2} + 2\Delta S^\circ_{\text{H}_2\text{O}} - 2\Delta S^\circ_{\text{H}_2\text{O}_2} = -94.2 + 2*110.876 - (2*69.9565) = -37.2 \dots \text{J/mol/K};$$

$$\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{O}_2} + 2\Delta S^\circ_{\text{H}_2\text{O}} - 2\Delta S^\circ_{\text{H}_2\text{O}_2} = 110.876 + 2*69.9565 - (2*143.9) = -37 \dots \text{J/mol/K};$$

$$2. \Delta S_{\text{total}} = \Delta S_{\text{H}} + \Delta S_{\text{dispersed}} = -37.2 + 674.2 = 637 \dots \text{J/mol/K}; \Delta S_{\text{total}} = -37.011 + 674.36 = 637.35 \dots \text{J/mol/K};$$

$$4. \Delta G_{\text{Hess}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -201.02 - 298.15 * -0.0372 = -189.9 \dots \text{kJ/mol} \text{ exoergic} \dots \text{spontaneous} \dots$$

$$\Delta G_{\text{Hess}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -201.06 - 298.15 * -0.037 = -190 \dots \text{kJ/mol};$$

$$T \cdot \Delta S_{\text{total}} = 0.637 * 298.15 = 189.9 \dots \text{kJ/mol}; T \cdot \Delta S_{\text{total}} = 0.63735 * 298.15 = 190 \dots \text{kJ/mol};$$

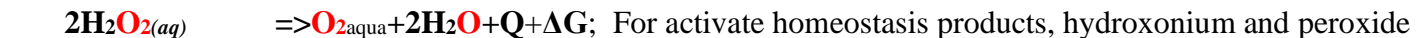
Half reactions RedOx Nernst's reduction and oxidation electrons balance  $2 e^-$  at  $\text{pH}=7.36$ ,  $[\text{O}_{\text{aq}}] = 6 * 10^{-5} \text{ M}$

$$E_{\text{Red}} = E^\circ_{\text{H}_2\text{O}_2} + 0.0591/2 \cdot \lg([\text{O}_2(\text{aq})] * [\text{H}_3\text{O}^+]^2 / [\text{H}_2\text{O}_2] / [\text{H}_2\text{O}]^2) = 0.899 + 0.0591/2 \cdot \lg(6 * 10^{-5} * 10^{-(7.36*2)} / 1 / 55.3^2) = 0.2363 \text{ V}$$

$$E_{\text{Ox}} = E^\circ_{\text{H}_2\text{O}_2\text{Ox}} + 0.0591/2 \cdot \lg([\text{H}_2\text{O}_2] * [\text{H}_3\text{O}^+]^2 / [\text{H}_2\text{O}]^4) = 2.084 + 0.0591/2 \cdot \lg(1 * 10^{-(7.36*2)} / 55.3^4) = 1.443 \text{ V}$$

**Red:**  $\text{H}_2\text{O}_2 + 2 \text{H}_2\text{O} = \text{O}_2 + 2 \text{H}_3\text{O}^+ + 2 e^-$ ;  $E^\circ_{\text{Red}} = E^\circ_{\text{RedH}_2\text{O}_2} = 0.899 \text{ V}$  Alberta University classic  $E_o = 0.694 \text{ V}$ ;

**Ox:**  $\text{H}_2\text{O}_2 + 2 \text{H}_3\text{O}^+ + 2 e^- = 4 \text{H}_2\text{O}$ ;  $E^\circ_{\text{Ox}} = E^\circ_{\text{OxH}_2\text{O}_2} = 2.084 \text{ V}$  Suhotina classic  $E_o = 1.776 \text{ V}$



anions:  $G_{\text{H}_2\text{O}_2} = 364.8 \text{ kJ/mol}$ ;  $G_{\text{H}_3\text{O}^+} + G_{\text{HOO}^-} = 22.44 + 418.32 = 440.76 \text{ kJ/mol}$  free energy referring to water and  $\text{CO}_2(\text{gas})$

zero  $G_{\text{H}_2\text{O}} = G_{\text{CO}_2(\text{gas})} = 0 \text{ kJ/mol}$  appreciate values :

$$\Delta G_{\text{min}} = \Delta G_{\text{eqStandart}} = (E^\circ_{\text{RedH}_2\text{O}_2} - E^\circ_{\text{OxH}_2\text{O}_2}) * F * n = (0.899 - 2.084) * 96485 * 2 = (-1.185) * 96485 * 2 = -228.7 \text{ kJ/mol};$$

$$K_{\text{eqStandart}} = \frac{[\text{O}_2]_{\text{aq}} \cdot [\text{H}_2\text{O}]^2}{[\text{H}_2\text{O}_2]_{\text{aq}}^2} = K_{\text{H}_2\text{O}_2} = \exp(-\Delta G_{\text{eq}}/R/T) = \exp(228670/8.3144/298.15) = 1.15 * 10^{40} \dots$$

$$\text{Homeostasis } \Delta G_{\text{eqBioChem}} = (E_{\text{Red}} - E_{\text{Ox}}) * F * n = (0.2363 - 1.443) * 96485 * 2 = (-1.206) * 96485 * 2 = -232.8 \dots \text{kJ/mol};$$

$$\Delta G_{\text{Alberty}} = G_{\text{O}_2(\text{Biochem\_arteriaj})} + 2 * G_{\text{H}_2\text{O}(\text{BioChemistry})} - 2 * G_{\text{H}_2\text{O}_2} = 78.08 + 2*85.64 - 2*364.79 = -480.22 \text{ kJ/mol}; \text{ Alberty}$$

Exothermic and exoergic  $\text{H}_2\text{O}_2(\text{aq})$  dismutation Hesa free energy change  $\Delta G_{\text{Alberty}}$  and

$\Delta G_{\text{HessAlberty}}$  is negative  $-480 \dots \text{kJ/mol}$ ,  $-426.5 \dots \text{kJ/mol}$ , but minimized

$$\Delta G_{\text{eqStandart}} = -228.7 \dots \text{kJ/mol} \text{ reaching equilibrium mixture constant } K_{\text{eq}} = 1.15 * 10^{40} \dots$$

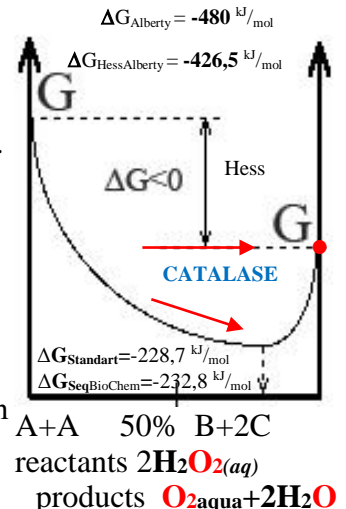
Le Chatelier principle is Prigogine attractor free energy change minimum  $\Delta G_{\text{min}}$

reaching. High rate protolysis attractors  $\text{pH}=7.36$ , oxygen 20.95% in air stay at equilibrium, while homeostasis irreversibly continues, as are non equilibrium state.

Prigogine attractors Nobel Prize Chemistry 1977<sup>th</sup>. CATALASE erase peroxide molecules  $\text{H}_2\text{O}_2$  to 100%  $\omega=6, \omega=3$  fatty acids  $\text{C}_{20:4}$  efficiency elongation synthesis in

peroxisomes. CATALASE reactivity is indispensable irreversible homeostasis

Brownian molecular engine for evolution and survival.



## Glass $\text{SiO}_2 \downarrow \text{SiO}_2 \downarrow \text{SiO}_2$ membrane electrode and pH detection

Glass electrodes are usually applicable to solution pH determination. As membrane electrode its potential forms on surface of silicon dioxide ( $\text{SiO}_2$ ) crystalline in protolysis of silicic acid reaction:

$\text{SiO}_2\text{-SiO}_3\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{SiO}_2\text{-SiO}_3^- + \text{H}_3\text{O}^+$ . So glass electrode potential have formed following.

On glass surface locate silicone anions functional groups  $\text{SiO}_2\text{-SiO}_3^-$ . On thin crystalline glass membrane surface in solution with  $\text{H}^+$  ions (in hydrochloric acid HCl) established protolytic equilibrium between crystalline silicic acid  $\text{SiO}_2\text{-SiO}_3\text{H}$  and anionic group of silicate  $\text{SiO}_2\text{-SiO}_3^-$ . Silicic acid is water insoluble acid and weak electrolyte:  $\text{SiO}_2\text{-SiO}_3\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{SiO}_2\text{-SiO}_3^- + \text{H}_3\text{O}^+$ .

As crystalline membrane has inner surface equilibrium and outer surface of membrane has outer equilibrium, where last depends on tested medium  $\text{H}^+$  concentration.



Product in sequence connected equilibrium constants are membrane equilibrium constant  $K_{\text{inner}} \cdot K_{\text{outer}} = K_{\text{membr}}$ :

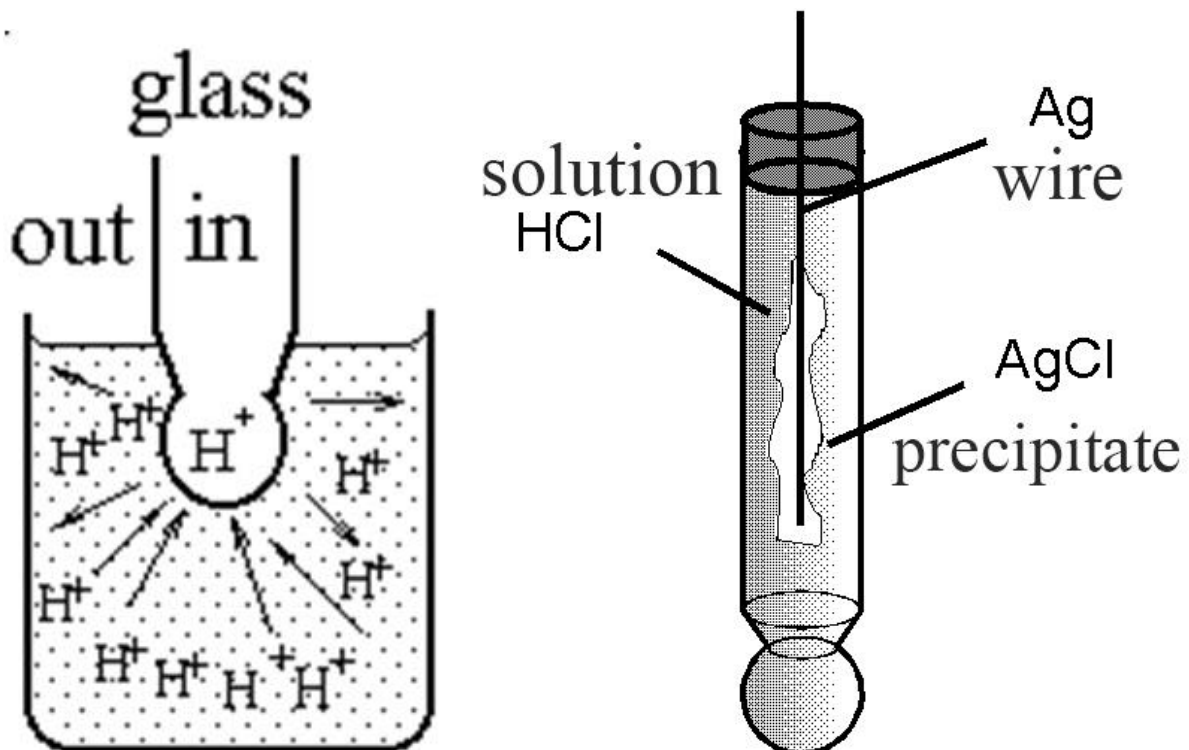
$$K_{\text{inner}} = \frac{[\text{H}_2\text{O}]}{[\text{H}_3\text{O}^+]_{\text{inner}}}; \quad K_{\text{outer}} = \frac{[\text{H}_3\text{O}^+]_{\text{outer}}}{[\text{H}_2\text{O}]}; \quad K_{\text{inner}} \cdot K_{\text{outer}} = K_{\text{membr}} = \frac{[\text{H}_3\text{O}^+]_{\text{outer}}}{[\text{H}_3\text{O}^+]_{\text{inner}}};$$

$$E_{\text{membr}} = \frac{0,0591}{n} \log \frac{[\text{H}_3\text{O}^+]_{\text{outer}}}{[\text{H}_3\text{O}^+]_{\text{inner}}} = 0.0591 (\log[\text{H}_3\text{O}^+]_{\text{outer}} - \log[\text{H}_3\text{O}^+]_{\text{inner}}) = E_{\text{const}} - 0.0591 \cdot \text{pH} \quad (24)$$

where  $n=+1$  hydrogen ion charge  $\text{H}^+$ , but logarithm of concentrations ratio is subtraction two logarithms from concentration ratio. Ions concentration inside membrane is constant  $E_{\text{const}} = -0.0591 \cdot \log[\text{H}_3\text{O}^+]_{\text{inner}}$ . Membrane potential depends only on solution  $\text{H}_3\text{O}^+_{\text{outer}}$  and  $\text{pH} = -\log[\text{H}_3\text{O}^+]_{\text{outer}}$ .

$$E_{\text{membr}} = E_{\text{const}} + 0.0591 \cdot \log[\text{H}_3\text{O}^+]_{\text{outer}} \quad (24)$$

Figure shows on end of glass tube thin bulb, that serves about glass membrane. Inside bulb HCl solution with known concentration. Outside emerge in test solution and measure the pH of solution potentiometric.



Glass membrane  $\text{HSiO}_3\text{-SiO}_2 \downarrow \text{SiO}_2 \downarrow \text{SiO}_2\text{-SiO}_3\text{H}$  and electrodes combination with silver wire.

For electric connection with glass membrane in inner solution deepes one silver wire, that forms second type electroda potential  $E_{\text{AgCl inner}}$  in sequence with membrane potential  $E_{\text{membr.}} + E_{\text{AgCl inner}}$  Potential depends only on outer pH of investigated solution, because hydrochloric acid concentration is constant. EMF (electric motion force) mesure for closed electric cycle. That acheaved in outer solution deeping reference electroda with standard potential  $E_{\text{AgCl}}$ . Electric chain closed at pH-meter contact clumps:

Total EMF potential consist of three electrodes in sequence connected as well from 3 parts:

- 1) inside glass electrode deeped AgCl electrode potential  $E_{\text{AgCl inner}}$ ;
- 2) glass membrane electrode  $E_{\text{membr.}} = E_{\text{const.}} + 0.0591 \cdot \log[\text{H}_3\text{O}^+_{\text{outer}}] = E_{\text{const.}} - 0.0591 \cdot \text{pH}$  (24).;
- 3) reference electrode with standard potential  $E_{\text{AgCl}}$ .

By additive sum of constant values parts is calculated new constant:  $E'_{\text{const.}} = (E_{\text{AgCl}} + E_{\text{AgCl inner}} + E_{\text{const.}})$ .

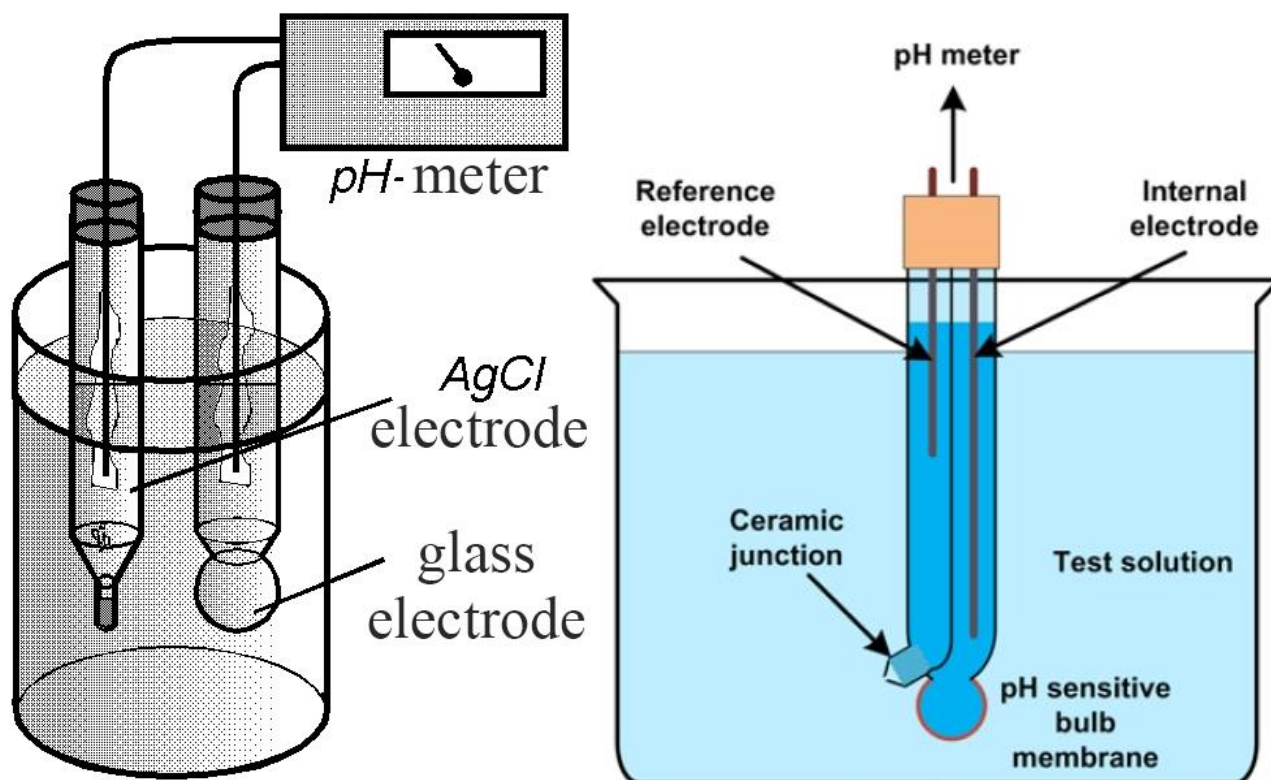
$$E_{\text{DS}} = E_{\text{AgCl}} + E_{\text{membr.}} + E_{\text{AgCl inner}} = (E_{\text{AgCl}} + E_{\text{AgCl inner}} + E_{\text{const.}}) + 0.0591 \cdot \lg [\text{H}_3\text{O}^+_{\text{inner}}] = E'_{\text{const.}} - 0.0591 \cdot \text{pH} \quad (25)$$

$$E_{\text{DS}} = E'_{\text{const.}} - 0.0591 \cdot \text{pH} \quad (26)$$

Measured electric motion force (EMF) is proportional to pH value in solution.

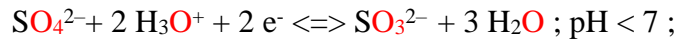
pH measurement by glass electrode has opportunities :

- 1) glass electrode is useable on complete pH interval (from pH = 0 to pH = 14);
- 2) measurement precision reaches 0.001 pH units;
- 3) measurements not depends on oxidation, reduction and proteins in solution;
- 4) permanent direct control of pH by pH-meter.



pH measurement by EMF couple with combined glass and silver chloride electrodes

**Nernst's potential  $\text{SO}_4^{2-}/\text{SO}_3^{2-}$  red-ox system behaving in acidic  $\text{H}_3\text{O}^+$  water and basic  $\text{OH}^-$  medium (forced oxidising agent power by potential E increase in acidosis)**



$$E^\circ = E_o + 0,0591/2 * \lg(1/[\text{H}_2\text{O}]^3) = +0,20 \text{ V} ; E^\circ = E_o - 0,0591/2 * \lg([\text{H}_2\text{O}]^3) = \mathbf{0,3545 \text{ V}} ;$$

$$E^\circ_{\text{SO}_4} = E^\circ + 0,10166 + 0,0591/2 * \lg([\text{H}_2\text{O}]^3) = 0,2 + 0,10166 + 0,02955 * \lg(55,3^3) = \mathbf{0,45615 \text{ V}} ;$$

$$E_{\text{SO}_4} = E^\circ_{\text{SO}_4} + \frac{0,0591}{2} \cdot \lg \frac{[\text{SO}_4^{2-}] \cdot [\text{H}_3\text{O}^+]^2}{[\text{SO}_3^{2-}] \cdot [\text{H}_2\text{O}]^3} = \mathbf{0,456 \text{ V}} + \frac{0,0591}{2} \cdot \lg \frac{[\text{SO}_4^{2-}] \cdot [\text{H}_3\text{O}^+]^2}{[\text{SO}_3^{2-}] \cdot [\text{H}_2\text{O}]^3}$$

$$\text{At pH}=7, [\text{H}_2\text{O}]=55,3 \text{ M} ; 0,02955 * \lg([\text{H}_3\text{O}^+]^2/[\text{H}_2\text{O}]^3) = 0,02955 * \lg(10^{-7*2}/55,3^3) = \underline{-0,56819 \text{ V}}$$

$$E_{\text{SO}_4} = \mathbf{0,456} - \underline{0,5682} + 0,02955 * \lg \frac{[\text{SO}_4^{2-}]}{[\text{SO}_3^{2-}]} = \mathbf{-0,1122} + 0,02955 * \lg \frac{[\text{SO}_4^{2-}]}{[\text{SO}_3^{2-}]} ;$$



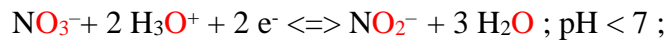
$$E^\circ_{\text{SO}_4} = E^\circ + 0,10166 - 0,0591/2 * \lg([\text{H}_2\text{O}]) = -0,93 + 0,10166 - 0,02955 * \lg(55,3) = -0,981 + 0,10166 = \mathbf{-0,87984 \text{ V}} ;$$

$$E_{\text{SO}_4} = E^\circ_{\text{SO}_4} + \frac{0,0591}{2} \cdot \lg \frac{[\text{SO}_4^{2-}] \cdot [\text{H}_2\text{O}]}{[\text{SO}_3^{2-}] \cdot [\text{OH}^-]^2} = \mathbf{-0,87984 \text{ V}} + \frac{0,0591}{2} \cdot \lg \frac{[\text{SO}_4^{2-}] \cdot [\text{H}_2\text{O}]}{[\text{SO}_3^{2-}] \cdot [\text{OH}^-]^2}$$

$$\text{At pOH}=7, [\text{H}_2\text{O}]=55,3 \text{ M} ; 0,02955 * \lg([\text{H}_2\text{O}]/[\text{OH}^-]^2) = 0,02955 * \lg(55,3/10^{-7*2}) = \underline{+0,4651975 \text{ V}}$$

$$E_{\text{SO}_4} = \mathbf{-0,8798} + \underline{0,46519763} + 0,02955 * \lg([\text{SO}_4^{2-}]/[\text{SO}_3^{2-}]) = \mathbf{-0,4146} + 0,02955 * \lg([\text{SO}_4^{2-}]/[\text{SO}_3^{2-}]);$$

**Nernst's potential  $\text{NO}_3^-/\text{NO}_2^-$  red-ox system behaving in acidic  $\text{H}_3\text{O}^+$  water and basic  $\text{OH}^-$  medium (forced oxidising agent power by potential E increase in acidosis)**



$$E^\circ = E_o + 0,0591/2 * \lg(1/[\text{H}_2\text{O}]^3) = +0,94 \text{ V} ; E_o = E^\circ - 0,0591/2 * \lg([\text{H}_2\text{O}]^3) = 0,99 \text{ V} ;$$

$$E^\circ_{\text{NO}_3} = E^\circ + 0,10166 + 0,0591/2 * \lg([\text{H}_2\text{O}]^3) = 0,94 + 0,10166 + 0,02955 * \lg(55,3^3) = 0,99 + 0,10166 = \mathbf{1,093 \text{ V}} ;$$

$$E_{\text{NO}_3} = E^\circ_{\text{NO}_3} + \frac{0,0591}{2} \cdot \lg \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^2}{[\text{NO}_2^-] \cdot [\text{H}_2\text{O}]^3} = \mathbf{1,093 \text{ V}} + \frac{0,0591}{2} \cdot \lg \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^2}{[\text{NO}_2^-] \cdot [\text{H}_2\text{O}]^3}$$

$$\text{At pH}=7, [\text{H}_2\text{O}]=55,3 \text{ M} ; 0,02955 * \lg([\text{H}_3\text{O}^+]^2/[\text{H}_2\text{O}]^3) = 0,02955 * \lg(10^{-7*2}/55,3^3) = \underline{-0,56819 \text{ V}}$$

$$E_{\text{NO}_3} = \mathbf{1,093} - \underline{0,5682} + 0,02955 * \lg \frac{[\text{NO}_3^-]}{[\text{NO}_2^-]} = \mathbf{0,525} + 0,02955 * \lg \frac{[\text{NO}_3^-]}{[\text{NO}_2^-]} ;$$



$$E^\circ = E_o + 0,0591/2 * \lg([\text{H}_2\text{O}]) = 0,01 \text{ V} = E^\circ ; E_o = E^\circ - 0,0591/2 * \lg([\text{H}_2\text{O}]) = 0,01 + 0,02955 * \lg(55,3) = 0,0615 \text{ V} ;$$

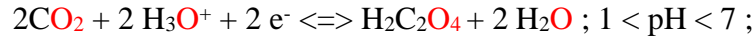
$$E^\circ_{\text{NO}_3} = E^\circ + 0,10166 - 0,0591/2 * \lg([\text{H}_2\text{O}]) = 0,01 + 0,10166 + 0,02955 * \lg(55,3) = 0,0615 + 0,10166 = \mathbf{0,16316 \text{ V}} ;$$

$$E_{\text{NO}_3} = E^\circ_{\text{NO}_3} + \frac{0,0591}{2} \cdot \lg \frac{[\text{NO}_3^-] \cdot [\text{H}_2\text{O}]}{[\text{NO}_2^-] \cdot [\text{OH}^-]^2} = \mathbf{0,16316 \text{ V}} + \frac{0,0591}{2} \cdot \lg \frac{[\text{NO}_3^-] \cdot [\text{H}_2\text{O}]}{[\text{NO}_2^-] \cdot [\text{OH}^-]^2}$$

$$\text{At pOH}=7, [\text{H}_2\text{O}]=55,3 \text{ M} ; 0,02955 * \lg([\text{H}_2\text{O}]/[\text{OH}^-]^2) = 0,02955 * \lg(55,3/10^{-7*2}) = \underline{+0,46519763 \text{ V}}$$

$$E_{\text{NO}_3} = \mathbf{0,16316} + \underline{0,46519763} + 0,02955 * \lg([\text{NO}_3^-]/[\text{NO}_2^-]) = \mathbf{0,527} + 0,02955 * \lg([\text{NO}_3^-]/[\text{NO}_2^-]);$$

**Nernst's potential  $2\text{CO}_2 / \text{H}_2\text{C}_2\text{O}_4$  red-ox system behaving in acidic  $\text{H}_3\text{O}^+$ , water medium**  
(forced oxidising agent power by potential E increase in acidosis)



$$E^\circ = E_o + 0.0591/2 * \lg(1/[\text{H}_2\text{O}]^2) = -0.49 \text{ V}; E_o = -0.49 - 0.0591/2 * \lg(1/55.3^2) = -0.387 \text{ V};$$

$$E^\circ_{\text{H}_2\text{C}_2\text{O}_4} = E^\circ + 0.10166 + 0.0591/2 * \lg([\text{H}_2\text{O}]^2) = -0.49 + 0.10166 - 0.02955 * \lg(1/55.3^2) = \mathbf{-0.285 \text{ V}};$$

$$E_{\text{H}_2\text{C}_2\text{O}_4} = E^\circ_{\text{H}_2\text{C}_2\text{O}_4} + \frac{0.0591}{2} \cdot \lg \frac{[\text{CO}_2]^2 \cdot [\text{H}_3\text{O}^+]^2}{[\text{H}_2\text{C}_2\text{O}_4] \cdot [\text{H}_2\text{O}]^2} = \mathbf{-0.285 \text{ V}} + \frac{0.0591}{2} \cdot \lg \frac{[\text{CO}_2]^2 \cdot [\text{H}_3\text{O}^+]^2}{[\text{H}_2\text{C}_2\text{O}_4] \cdot [\text{H}_2\text{O}]^2}$$

$$\text{At pH}=7, [\text{H}_2\text{O}]=55.3 \text{ M}; 0.02955 * \lg([\text{H}_3\text{O}^+]^2 / [\text{H}_2\text{O}]^2) = 0.02955 * \lg(10^{-7*2} / 55.3^2) = \mathbf{-0.5167 \text{ V}}$$

$$E_{\text{SO}_4} = \mathbf{-0.285 - 0.5167} + 0.02955 * \lg \frac{[\text{CO}_2]^2}{[\text{H}_2\text{C}_2\text{O}_4]} = \mathbf{-0.8017} + 0.02955 * \lg \frac{[\text{CO}_2]^2}{[\text{H}_2\text{C}_2\text{O}_4]};$$

**Nernst's potential  $\text{NO}_3^- / \text{NH}_3$  red-ox system behaving in acidic  $\text{H}_3\text{O}^+$ , water medium**  
(forced oxidising agent power by potential E increase in acidosis)



$$E^\circ = E_o + 0.0591/8 * \lg([\text{H}_2\text{O}]^6) = -0.12 \text{ V}; E_o = -0.12 - 0.0591/8 * \lg([\text{H}_2\text{O}]^6) = \mathbf{-0.1972 \text{ V}};$$

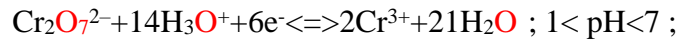
$$E^\circ_{\text{NO}_3^-/\text{NH}_3} = E^\circ + 0.10166 - 0.02955/4 * \lg(55.3^6) = -0.12 + 0.10166 - 0.0772 = -0.1972 + 0.10166 = \mathbf{-0.09554 \text{ V}};$$

$$E_{\text{NO}_3^-/\text{NH}_3} = E^\circ_{\text{NO}_3^-/\text{NH}_3} + \frac{0.0591}{8} \cdot \lg \frac{[\text{NO}_3^-] \cdot [\text{H}_2\text{O}]^6}{[\text{NH}_3] \cdot [\text{OH}^-]^9} = \mathbf{-0.0955 \text{ V}} + \frac{0.0591}{8} \cdot \lg \frac{[\text{NO}_3^-] \cdot [\text{H}_2\text{O}]^6}{[\text{NH}_3] \cdot [\text{OH}^-]^9}$$

$$\text{At pOH}=7, [\text{H}_2\text{O}]=55.3 \text{ M}; 0.02955/4 * \lg([\text{H}_2\text{O}]^6 / [\text{OH}^-]^9) = 0.02955/4 * \lg(55.3^6 / 10^{-7*9}) = \mathbf{+0.5427 \text{ V}}$$

$$E_{\text{NO}_3^-/\text{NH}_3} = \mathbf{-0.0955} + \mathbf{+0.5427} + 0.02955/4 * \lg \frac{[\text{NO}_3^-]}{[\text{NH}_3]} = \mathbf{0.4427} + 0.02955/4 * \lg \frac{[\text{NO}_3^-]}{[\text{NH}_3]};$$

**Nernst's potential  $\text{Cr}_2\text{O}_7^{2-} / 2\text{Cr}^{3+}$  red-ox system behaving in acidic  $\text{H}_3\text{O}^+$ , water medium**  
(forced oxidising agent power by potential E increase in acidosis)



$$E^\circ = E_o + 0.0591/6 * \lg(1/[\text{H}_2\text{O}]^{21}) = 1.33 \text{ V}; E_o = 1.33 - 0.0591/6 * \lg(1/[\text{H}_2\text{O}]^{21}) = 1.6905 \text{ V};$$

$$E^\circ_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}} = E^\circ + 0.10166 - 0.0591/6 * \lg(1/55.3^{21}) = 1.33 + 0.10166 + 0.3605 = 1.6905 + 0.10166 = \mathbf{1.7921 \text{ V}};$$

$$E_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}} = E^\circ_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}} + \frac{0.0591}{6} \cdot \lg \frac{[\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{H}_3\text{O}^+]^{14}}{[\text{Cr}^{3+}]^2 \cdot [\text{H}_2\text{O}]^{21}} = \mathbf{1.6905 \text{ V}} + \frac{0.0591}{6} \cdot \lg \frac{[\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{H}_3\text{O}^+]^{14}}{[\text{Cr}^{3+}]^2 \cdot [\text{H}_2\text{O}]^{21}}$$

$$\text{At pH}=7, [\text{H}_2\text{O}]=55.3 \text{ M}; 0.02955/3 * \lg([\text{H}_3\text{O}^+]^{14} / [\text{H}_2\text{O}]^{21}) = 0.02955/3 * \lg(10^{-7*14} / 55.3^{21}) = \mathbf{1.3258 \text{ V}}$$

$$E_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}} = \mathbf{1.6905} + \mathbf{1.3258} + 0.02955/3 * \lg \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{Cr}^{3+}]^2} = \mathbf{3.0164} + 0.02955/3 * \lg \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{Cr}^{3+}]^2};$$

**Nernst's potential  $\text{CrO}_4^{2-} / \text{Cr}(\text{OH})_3 \downarrow$  red-ox system behaving in acidic  $\text{H}_3\text{O}^+$ , water medium**  
(forced oxidising agent power by potential E increase in acidosis)

$$E^\circ = E_o + 0.0591/3 * \lg([\text{H}_2\text{O}]^4) = -0.13 \text{ V}; E_o = -0.13 - 0.0591/3 * \lg([\text{H}_2\text{O}]^4) = -0.13 - 0.0591/3 * \lg(55.3^4) = -0.2673 \text{ V};$$

$$E^\circ_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}} = E^\circ + 0.10166 - 0.0591/3 * \lg(55.3^4) = -0.13 + 0.10166 - 0.1373267 = -0.2673 + 0.10166 = \mathbf{-0.1657 \text{ V}};$$

$$E_{\text{CrO}_4^{2-}/\text{Cr}(\text{OH})_3 \downarrow} = E^\circ_{\text{CrO}_4^{2-}/\text{Cr}(\text{OH})_3 \downarrow} + \frac{0.0591}{3} \cdot \lg \frac{[\text{CrO}_4^{2-}] \cdot [\text{H}_2\text{O}]^4}{[\text{Cr}(\text{OH})_3] \cdot [\text{OH}^-]^5} = \mathbf{-0.1657 \text{ V}} + \frac{0.0591}{3} \cdot \lg \frac{[\text{CrO}_4^{2-}] \cdot [\text{H}_2\text{O}]^4}{[\text{Cr}(\text{OH})_3] \cdot [\text{OH}^-]^5}$$

$$\text{At pOH}=7, [\text{H}_2\text{O}]=55.3 \text{ M}; 0.0591/3 * \lg([\text{H}_2\text{O}]^4 / [\text{OH}^-]^5) = 0.0591/3 * \lg(55.3^4 / 10^{-7*5}) = \mathbf{+0.8268 \text{ V}}$$

$$E_{\text{CrO}_4^{2-}/\text{Cr}(\text{OH})_3 \downarrow} = \mathbf{-0.1657} + \mathbf{+0.8268} + 0.0591/3 * \lg \frac{[\text{CrO}_4^{2-}]}{[\text{Cr}(\text{OH})_3]} = \mathbf{+0.7483} + 0.0591/3 * \lg \frac{[\text{CrO}_4^{2-}]}{[\text{Cr}(\text{OH})_3]};$$

**Nernst's potential  $\text{BiO}_3^- / \text{Bi}^{3+}$  red-ox system behaving in acidic  $\text{H}_3\text{O}^+$ , water medium**  
(forced oxidising agent power by potential E increase in acidosis)



$$E^\circ = E_o + 0.0591/2 * \lg(1/[\text{H}_2\text{O}]^9) = 1.80 \text{ V} ; E_o = 1.80 - 0.0591/2 * \lg(1/55.3^9) = 2.2635 \text{ V} ;$$

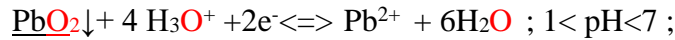
$$E^\circ_{\text{BiO}_3^-/\text{Bi}^{3+}} = E^\circ + 0.10166 + 0.0591/2 * \lg(1/[\text{H}_2\text{O}]^9) = 1.8 + 0.10166 - 0.02955 * \lg(1/55.3^9) = 2.2635 + 0.10166 = \mathbf{2.365 \text{ V}} ;$$

$$E_{\text{BiO}_3^-/\text{Bi}^{3+}} = E^\circ_{\text{BiO}_3^-/\text{Bi}^{3+}} + \frac{0.0591}{2} * \lg \frac{[\text{BiO}_3^-] \cdot [\text{H}_3\text{O}^+]^6}{[\text{Bi}^{3+}] \cdot [\text{H}_2\text{O}]^9} = \mathbf{2.365 \text{ V}} + \frac{0.0591}{2} * \lg \frac{[\text{BiO}_3^-] \cdot [\text{H}_3\text{O}^+]^6}{[\text{Bi}^{3+}] \cdot [\text{H}_2\text{O}]^9}$$

$$\text{At pH}=7, [\text{H}_2\text{O}]=55.3 \text{ M} ; 0.02955 * \lg([\text{H}_3\text{O}^+]^6/[\text{H}_2\text{O}]^9) = 0.02955 * \lg(10^{-7*6}/55.3^9) = \underline{-1.7046 \text{ V}}$$

$$E_{\text{BiO}_3^-/\text{Bi}^{3+}} = \mathbf{2.365} - \underline{1.7046} + 0.02955 * \lg \frac{[\text{BiO}_3^-]}{[\text{Bi}^{3+}]} = \mathbf{0.6604} + 0.02955 * \lg \frac{[\text{BiO}_3^-]}{[\text{Bi}^{3+}]} ;$$

**Nernst's potential  $\text{PbO}_2 \downarrow / \text{Pb}^{2+}$  red-ox system behaving in acidic  $\text{H}_3\text{O}^+$ , water medium**  
(forced oxidising agent power by potential E increase in acidosis)



$$E^\circ = E_o + 0.0591/2 * \lg(1/[\text{H}_2\text{O}]^6) = 1.80 \text{ V} ; E_o = 1.8 - 0.0591/2 * \lg(1/55.3^6) = 2.109 \text{ V} ;$$

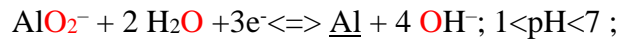
$$E^\circ_{\text{PbO}_2 \downarrow/\text{Pb}^{2+}} = E^\circ + 0.10166 - 0.0591/2 * \lg(1/[\text{H}_2\text{O}]^6) = 1.8 + 0.10166 - 0.02955 * \lg(1/55.3^6) = 2.109 + 0.10166 = \mathbf{2.21066 \text{ V}} ;$$

$$E_{\text{PbO}_2 \downarrow/\text{Pb}^{2+}} = E^\circ_{\text{PbO}_2 \downarrow/\text{Pb}^{2+}} + \frac{0.0591}{2} * \lg \frac{[\text{PbO}_2 \downarrow] \cdot [\text{H}_3\text{O}^+]^4}{[\text{Pb}^{2+}] \cdot [\text{H}_2\text{O}]^6} = \mathbf{2.2106 \text{ V}} + \frac{0.0591}{2} * \lg \frac{[\text{PbO}_2 \downarrow] \cdot [\text{H}_3\text{O}^+]^4}{[\text{Pb}^{2+}] \cdot [\text{H}_2\text{O}]^6}$$

$$\text{At pH}=7, [\text{H}_2\text{O}]=55.3 \text{ M} ; 0.02955 * \lg([\text{H}_3\text{O}^+]^4/[\text{H}_2\text{O}]^6) = 0.02955 * \lg(10^{-7*4}/55.3^6) = \underline{-1.1364 \text{ V}}$$

$$E_{\text{PbO}_2 \downarrow/\text{Pb}^{2+}} = \mathbf{2.2106} - \underline{1.1364} + 0.02955 * \lg \frac{[\text{PbO}_2 \downarrow]}{[\text{Pb}^{2+}]} = \mathbf{0.9726} + 0.02955 * \lg \frac{[\text{PbO}_2 \downarrow]}{[\text{Pb}^{2+}]} ;$$

**Nernst's potential  $\text{AlO}_2^- / \text{Al} \downarrow$  red-ox system behaving in acidic  $\text{H}_3\text{O}^+$ , water medium**  
(forced oxidising agent power by potential E increase in acidosis)



$$E^\circ = E_o + 0.0591/3 * \lg([\text{H}_2\text{O}]^2) = -2.35 \text{ V} ; E_o = E^\circ - 0.0591/3 * \lg(55.3^2) = -2.4187 \text{ V} ;$$

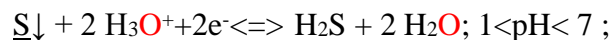
$$E^\circ_{\text{AlO}_2^-/\text{Al} \downarrow} = E^\circ + 0.10166 - 0.0591/3 * \lg([\text{H}_2\text{O}]^2) = -2.35 + 0.10166 - 0.0591/3 * \lg(55.3^2) = -2.4187 + 0.10166 = \mathbf{-2.317 \text{ V}} ;$$

$$E_{\text{AlO}_2^-/\text{Al} \downarrow} = E^\circ_{\text{AlO}_2^-/\text{Al} \downarrow} + \frac{0.0591}{3} * \lg \frac{[\text{AlO}_2^-] \cdot [\text{H}_2\text{O}]^2}{[\text{Al} \downarrow] \cdot [\text{OH}^-]^4} = \mathbf{-2.317 \text{ V}} + \frac{0.0591}{3} * \lg \frac{[\text{AlO}_2^-] \cdot [\text{H}_2\text{O}]^2}{[\text{Al} \downarrow] \cdot [\text{OH}^-]^4}$$

$$\text{At pOH}=7, [\text{H}_2\text{O}]=55.3 \text{ M} ; 0.0591/3 * \lg([\text{H}_2\text{O}]^2/[\text{OH}^-]^4) = 0.0591/3 * \lg(55.3^2/10^{-7*4}) = \underline{+0.6203 \text{ V}}$$

$$E_{\text{AlO}_2^-/\text{Al} \downarrow} = \mathbf{-2.317} + \underline{0.6203} + 0.0591/3 * \lg \frac{[\text{AlO}_2^-]}{[\text{Al} \downarrow]} = \mathbf{+1.6967} + 0.0591/3 * \lg \frac{[\text{AlO}_2^-]}{[\text{Al} \downarrow]} ;$$

**Nernst's potential  $\text{S} \downarrow / \text{H}_2\text{S}$  red-ox system behaving in acidic  $\text{H}_3\text{O}^+$ , water medium**  
(forced oxidising agent power by potential E increase in acidosis)



$$E^\circ = E_o + 0.0591/2 * \lg(1/[\text{H}_2\text{O}]^2) = 0.142 \text{ V} ; E_o = 0.142 - 0.0591/2 * \lg(1/55.3^2) = 0.245 \text{ V} ;$$

$$E^\circ_{\text{S} \downarrow/\text{H}_2\text{S}} = E^\circ + 0.10166 + 0.0591/2 * \lg(1/[\text{H}_2\text{O}]^2) = 0.142 + 0.10166 - 0.02955 * \lg(1/55.3^2) = 0.245 + 0.10166 = \mathbf{0.3467 \text{ V}} ;$$

$$E_{\text{S} \downarrow/\text{H}_2\text{S}} = E^\circ_{\text{S} \downarrow/\text{H}_2\text{S}} + \frac{0.0591}{2} * \lg \frac{[\text{S} \downarrow] \cdot [\text{H}_3\text{O}^+]^2}{[\text{H}_2\text{S}] \cdot [\text{H}_2\text{O}]^2} = \mathbf{0.3467 \text{ V}} + \frac{0.0591}{2} * \lg \frac{[\text{S} \downarrow] \cdot [\text{H}_3\text{O}^+]^2}{[\text{H}_2\text{S}] \cdot [\text{H}_2\text{O}]^2}$$

$$\text{At pH}=7, [\text{H}_2\text{O}]=55.3 \text{ M} ; 0.02955 * \lg([\text{H}_3\text{O}^+]^2/[\text{H}_2\text{O}]^2) = 0.02955 * \lg(10^{-7*2}/55.3^2) = \underline{-0.5167 \text{ V}}$$

$$E_{\text{S} \downarrow/\text{H}_2\text{S}} = \mathbf{0.3467} - \underline{0.5167} + 0.02955 * \lg \frac{[\text{S} \downarrow]}{[\text{H}_2\text{S}]} = \mathbf{-0.17} + 0.02955 * \lg \frac{[\text{S} \downarrow]}{[\text{H}_2\text{S}]} ;$$

## References.

1. [David R. Lide. CRC Handbook of Chemistry and Physics .90th ed. Taylor and Francis Group LLC; 2010 .](#)
2. Prigogine I, Defey R. Chemical Thermodynamics. Longmans Green & co ©; 1954.
3. Prigogine I, Nicolis G. Self-Organization in Non-Equilibrium Systems. Wiley, 1977.
4. [Prigogine I. Time, Structure and Fluctuations. Lecture, The Nobel Praise in Chemistry; 1977.](#)
5. [Kuman M. New light on the attractors creating order out of the chaos. \*Int J Complement Alt Med.\* \*\*11\*\*\(6\), 337, \(2018\) ;](#)
6. [Nelson DL, Cox MM. Lehninger Principles of Biochemistry. 5<sup>th</sup> ed. New York: W.H. Freeman and company; 2008.](#)
7. [Xing W, Yin G, Zhang J. Rotating Electrode Method and Oxygen Reduction Electrocatalysts. \*Elsevier\*; 6 \(2014\) .](#)
8. [Alberty RA. Biochemical Thermodynamic's : Applications of Mathematics. John Wiley & Sons, Inc. 1-463, \(2006\).](#)
9. [Pinard MA, Mahon B, McKenna R. Probing the Surface of Human Carbonic Anhydrase for Clues towards the Design of Isoform Specific Inhibitors. \*BioMed Research International\*; \*\*2015\*\*, 3 \(2015\).](#)
11. Balodis J. PRACTICAL WORKS IN PHYSICAL CHEMISTRY PART II. Izdevniecība «Zvaigzne», Rīga, 1975, p.149. Latvian.
14. [Kaksis A. The Biosphere Self-Organization Attractors drive perfect order homeostasis reactions to link bioenergetic with functionally activate oxygen and carbon dioxide molecules. 7th International Conference on New Trends in Chemistry September 25-26, 2021.27-32.](#)
15. [Kaksis A. HIGH RATE PROTOLYSIS ATTRACTORS ACTIVATE energy over zero  \$\text{GH}\_2\text{O}=\text{GCO}\_2\text{gas}=0\$  kJ/mol of water and carbon dioxide. FREE ENERGY CONTENT as BIOSPHERE Self-ORGANIZATION creates PERFECT ORDER IRREVERSIBLE HOMEOSTASIS PROGRESS. 9th International Conference on New Trends in Chemistry 19-21 May, 2023. 14-19.](#)
16. Loach, P.A. (I 976) In Handbook of Biochemistry and Molecular Biology, 3rd edn (Fasman, G.D. ed.), Physical and Chemical Data, Vol. 1, pp. 122-130 e, CRC Press, Boca Raton, FL
17. A.M. Suchotina, Handbook of Electro-Chemistry, Petersburg ,1981."Chimia"© Russian
18. S.Kortly and L.Shucha. Handbook of chemical equilibria in analytical chemistry. 1985.EllisHorwood Ltd.©
19. University Alberta Data Tables Molar Thermodynamic Properties of Pure Substances 1997.  
<http://www.vhem.ualberta.ca/>
20. Boca Raton, FL. Free **FAD**; FAD bound to a specific flavo-protein (for example succinate dehydrogenase) a different **E°**
21. David A. Harris, "Bio-energetic at a Glance". **b** Blackwell Science Ltd ©, 1995, p.116.
22. Daniel C. Harris, "Quantitative chemical analysis". W.H.Freeman and Company ©, 5th ed.1999, p545
23. E. Newton Harvey, "The oxidation-reduction potential of the Luciferin-Oxyluciferin system". JGP.1927, p385
24. [https://en.wikipedia.org/wiki/Atomic\\_radii\\_of\\_the\\_elements\\_\(data\\_page\)#Atomic radius](https://en.wikipedia.org/wiki/Atomic_radii_of_the_elements_(data_page)#Atomic_radius)