

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 creates ionic concentrations gradients $C_{right_side}/C_{left_side}$.

Electrochemical reactions across membranes drive E7 class transport enzymes .

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

Metallic Electrode is free electron source storage for 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**;

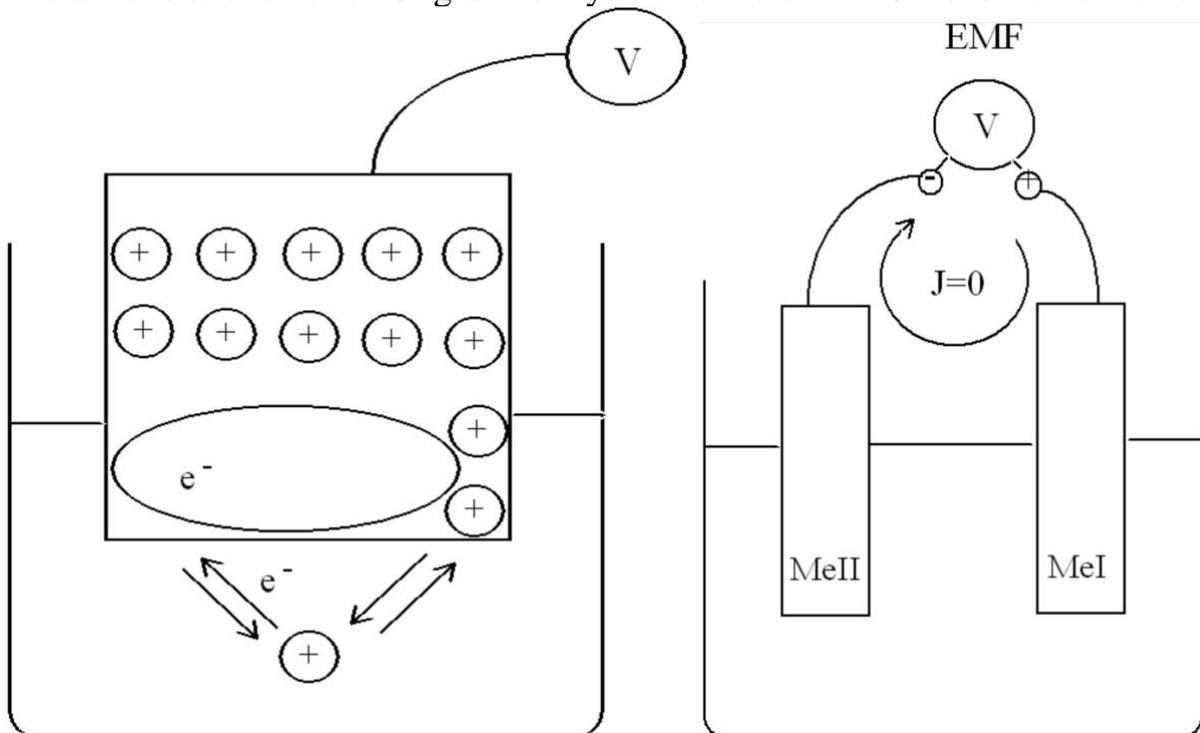
Red-Ox electrode: charged **ions** and free **electrons** transfer through **interface**;

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 :

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

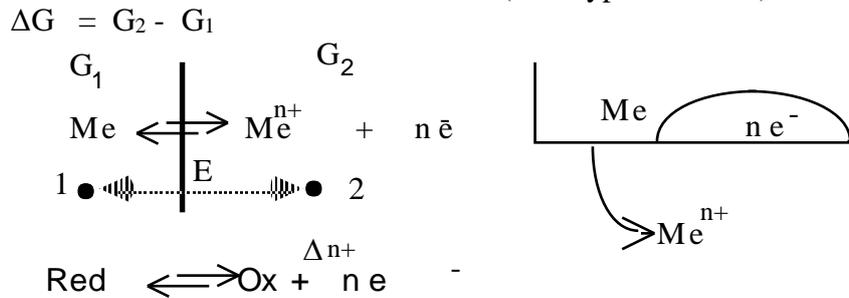
Indicator electrode having E_I – has reactivity with solution - electrode of investigations,

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 oxidized form **Ox** is the Hess law calculated free energy change work W of one mol 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 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

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

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

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:

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

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: $\mu = \Delta G^\circ_A + RT \ln(N_A)$, were N_A is substance A concentration (mol fraction). ΔG° 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 μ :

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

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

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

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

change ΔG_{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** **Oxidizing 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 Δn^+ positively charged ions **Ox** $^{\Delta n^+}$. Electrons **ne** leaves at metal electron gas. Such Δn^+ positive charge entrance into solution as oxidized 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 **H(Pt)** interface / to its cations **H₃O⁺** solution application

Attractor pH=7.36 staying at equilibrium have true pOH=6.64 value as pK_w=14= pH+pOH =7.36 +6.64. Disaccount the water mass [H₂O]=963/18=53.5 M over liter [H₂SO₄]=[H₃O⁺]=1 M solution with 1.061 g/mL density in Nernst equations for **hydrogen electrode** has classic standard potential E_{o, classic}=0 V reference zero:

H(Pt)=H⁺+e⁻; E_{classic}=E_{o, classic}+0.0591•logK^o_{classicH(Pt)}=0+0.0591•log[H⁺]=0+0.0591•log(1 M)=0 Volts. [11] Thermodynamic account Hydroxonium ions demand the water: **H(Pt)+H₂O<=>H₃O⁺+e⁻** and E^o_H=0.10166 V. The ratio [H₃O⁺]/([H₂O]-[H₃O⁺])=1 M/52.5 M=X_{H₃O⁺}/X_{H₂O} is mol fraction instead molarity [H⁺]=1 M at classic potential expression. The water account gave thermodynamic standard E^o_H=0.10166 V on potential scale.

Nernst's expression with classic zero measurement demands thermodynamic standard potential E^o_H=0.10166 V :

$$E = E^o_H + \ln(10) \cdot R \cdot T / F \cdot 1 \cdot \log(X_{H_3O^+} / X_{H_2O}) = E_o + E^o_H + 0.0591 \cdot \log(1/52.5) = 0.10166 - 0.10166 = 0 \text{ V.}$$

As ratio **1=K_{H(Pt)}=X_{H₃O⁺}/X_{H₂O}** is one than E^o_H=0.10166 V is thermodynamic standard potential:

$$E = E^o_H + \frac{\ln(10) \cdot R \cdot T}{F \cdot 1} \cdot \log \frac{X_{H_3O^+}}{X_{H_2O}} = 0.10166 + 0.0591 \cdot \log(1) = 0.10166 \text{ V.}$$

Metal oxidation free energy change minimum is different endoergic ΔG_{eq}=E^o_H•F•1=0.10166•96485•1=9.81 kJ/mol instead Alberty is exoergic.

Alberty Hess value is in did exoergic: ΔG_{Hess, eq}=G_{H₃O⁺}+G_{e⁻}-(G_{H(Pt)} +G_{H₂O})=22.44+0-(**48.56**+0)=-**26.12** kJ/mol .

Free energy changes are determined on water and carbon dioxide gas as zero G_{H₂O}=G_{CO₂gas}=G_{e⁻}=0 kJ/mol reference scale. Absolute scale hydrogen standard potential is: E^o_H=ΔG_{eq}/F/1=-**26.12**/96485/1=-0.27073 Volts. Equilibrium free energy change minimum is exoergic: ΔG_{eq}=E^o_H•F•1=-0.27073•96485•1=-**26.12** kJ/mol coincident with Alberty data. Absolute potential scale decreases about ΔE=-0.27073-0.10166=-0,37239 Volts relative to classic zero scale. Nernst's equilibrium constant is grater as one for metal oxidation to hydroxonium ion: **K_{H(Pt)_Red}=[H₃O⁺]*[e⁻]/[H₂O]/[H(Pt)]=EXP(-ΔG_{Alberty}/R/T)=EXP(**26120**/8,3144/298,15)=37675,6.**

I type electrode Metal interface **H(Pt)** / on its cation **H₃O⁺** solution application.

High rate protolysis attractors [H₃O⁺]=10^{-7.36} M , pH=7.36 and water mass [H₂O]=996/18=55.3 M account in liter shows metal hydrogen strong reducing potential: E_{pH=7.36}=-0.27073+0.0591•log(10^{-7.36}/55.3)=-0.8087 V and free energy change minimum ΔG_{eqpH, 7.36}=E^o_H•F•1=-0.8087•96485•1/1000=-78,03 kJ/mol .

Nernst's half reaction metal reduction potential E^o_H=-0.27073 V has energy change ΔG_{eq}=-**26.12** kJ/mol.

Platinum sheet immersed in hydroxonium ions [H⁺]=[H₃O⁺]=[H₂SO₄]=1 M sulfuric acid solutions **H(Pt)<=>H⁺+e⁻**: E=E^o+0.0591•log[H⁺]=**0.0**+0.0591•log(1 M)=**0** V is classic.

Ratio [H₃O⁺]/[H₂O]=1/52.5=X_{H₃O⁺}/X_{H₂O} instead zero **0** classic give thermodynamic standard potential: E^o_H=0.10166 V and from Alberty data on absolute scale

the absolute standard potential is E^o_H=-0.27073 Volts.

$$\text{absolute } E^o_H = -0.27073 \text{ V} \qquad \text{classic zero } E^o_H = 0 \text{ V} \qquad \text{thermodynamic } E^o_H = 0.10166 \text{ V}$$

$$E_{(Pt)H^+} = E^o_H + 0.0591 \cdot \log\left(\frac{X_{H_3O^+}}{X_{H_2O}}\right) \qquad E_{H, \text{classic}} = E^o_H + 0.0591 \cdot \log([H_3O^+])$$

Absolute standard potential E^o_H=-0.27073 V based on Alberty data G_{H₂gas}=**85.64** kJ/mol and G_{H₂aq}=**103.24** kJ/mol for hydrogen, which was detected on water and carbon dioxide gas G_{H₂O}=G_{CO₂gas}=G_{e⁻}=0 kJ/mol as zero scale reference. Reducing agent metal hydrogen at

pH=7.36, [H₃O⁺]=10^{-7.36} M with potential E_{pH=7.36}=-0.27073+0.0591•log(10^{-7.36}/55.3)=-0.8087 V is strong reductant. Free energy content in one mol metal hydrogen is: G_{H(Pt)}=**48.56** kJ/mol .

Substance	ΔH ^o _H , kJ/mol	ΔS ^o _H , J/mol/K	ΔG ^o _H , kJ/mol
H₂O	-285.85	69.9565	-237.191
H₂O	-286.65	-453.188	-151.549
H₃O⁺	-285.81	-3.854	-213.2746
H₂(aq)	23.4	-130	99.13
H(Pt)(aq)	E ^o _H =	-0,27073	48,56
H₂(aq)	-5.02	-363.92	103.24
O₂aqua	-11.70	-94.2	16.4

CRC 2010

2006, Massachusetts Technology Inst. Alberty pH=7,36 [8]

Mischenko 1972, Himia, Leningrad [26]

CRC 2010 [1]

ΔG_{Hess, eq}=G_{H₃O⁺}-(G_{H(Pt)} +G_{H₂O})=22.44-(**48.56**+0)=-**26.12** kJ/mol.

2006, Massachusetts Technology Inst. Alberty pH=7,36 [8]

The solubility of gaseous hydrogen $\text{H}_{2\text{gas}}+\text{H}_2\text{O}=\text{H}_{2\text{aq}}$ compensates ($\text{H}_{2\text{gas}}+2\text{H}_2\text{O}=\text{H}_{2\text{aq}}+\text{H}_2\text{O}=2\text{H}_3\text{O}^++2\text{e}^-$ water molecule in Nernst's oxidation to hydroxonium and is spontaneous, because **absolute** free energy change is negative. $\Delta G_{\text{Hess}_\text{H}_3\text{O}^+}=2G_{\text{H}_3\text{O}^+}+2G_{\text{e}^-}-(G_{\text{H}_{2\text{aq}}}+G_{\text{H}_2\text{O}})=2*22.44+2*0-(103.24+0)=-58.36 \text{ kJ/mol}$.

With graphite oxidizes $\text{H}_{2\text{aq}}$ solution to hydroxonium with standard **absolute** potential is

$$E^\circ_{\text{H}_{2\text{aq}}}=-58.36*1000/96485/2=-0.3024 \text{ V.}$$

Sum of Nernst and inverse half-reactions: $\text{H}_{2\text{aq}}+\text{H}_2\text{O}=2\text{H}_3\text{O}^++2\text{e}^-$; $2\text{H}_3\text{O}^++2\text{e}^-=2\text{H(Pt)}+2\text{H}_2\text{O}$

shows solubility of hydrogen in lattice of platinum $\text{H}_{2\text{aq}}=2\text{H(Pt)}+\text{H}_2\text{O}$;

Oxidation of hydrogen solution $\text{H}_{2\text{aq}}+\text{H}_2\text{O}=2\text{H}_3\text{O}^++2\text{e}^-$ potential $E^\circ_{\text{H}_{2\text{aq}}}=-0.302 \text{ V}$ plus inverse potential $E^\circ_{\text{H(Pt)}}=+0.27072 \text{ V}$ of metal electrochemical solubility in platinum lattice $2\text{H}_3\text{O}^++2\text{e}^-=\text{H(Pt)}+2\text{H}_2\text{O}$ shows the solubility of hydrogen mole fraction $[\text{H}_{2\text{aq}}]/[\text{H}_2\text{O}]$ from solution to platinum lattice exoergic, spontaneous:

$$\Delta G_{\text{spH(Pt)}}=\Delta E^\circ_{\text{spH(Pt)}}*F*2=(E^\circ_{\text{H}_{2\text{aq}}}-E^\circ_{\text{H(Pt)}})*F*2=(-0.302+0.27073)*96485*2=-0.03128*96485*2=-6.03 \text{ kJ/mol};$$

$$K_{\text{spH(Pt)}}=[\text{H(Pt)}]^2/[\text{H}_{2\text{aq}}]=\text{EXP}(-\Delta G_{\text{spH(Pt)}}/R/T)=\text{EXP}(6036/8.3144/298.15)=11.415 .$$

Solubility product in platinum H(Pt) from water $\text{H}_{2\text{aq}}=2\text{H(Pt)}+\text{H}_2\text{O}$ shows hydrogen solubility product in to metal slightly more exoergic favored: $\Delta G_{\text{sp}_\text{H(Pt)}}=2G_{\text{H(Pt)}}+G_{\text{H}_2\text{O}}-(G_{\text{H}_{2\text{aq}}})=2*48.56+0-(103.24)=-6.12 \text{ kJ/mol}$ and constant more favored:

$$K_{\text{sp}_\text{H(Pt)}}=[\text{H(Pt)}]^2*[\text{H}_2\text{O}]/[\text{H}_{2\text{aq}}]=\text{EXP}(-\Delta G_{\text{spH(Pt)}}/R/T)=\text{EXP}(6120/8.3144/298.15)=11.808 .$$

The ratio $K_{\text{H}_{2\text{sp}}}=[\text{H}_{2\text{aq}}]/[\text{H}_2\text{O}]/X_{\text{H}_{2\text{gas}}}=\text{EXP}(-\Delta G_{\text{H}_{2\text{sp}}}/R/T)=\text{EXP}(-17600/8.3144/298.15)=0.0008253$ gives solubility $[\text{H}_{2\text{aq}}]=K_{\text{H}_{2\text{sp}}}*\text{[H}_2\text{O}]*X_{\text{H}_{2\text{gas}}}=0.0008253*55.3*1=0.04564 \text{ M}$, if pure gas mol fraction is one $X_{\text{H}_{2\text{gas}}}=1$.

As **Alberty's** Application of Mathematical Data in Biochemistry, the unit-free solubility product of mole fractions is $K_{\text{H}_{2\text{sp}}}=[\text{H}_{2\text{aq}}]/[\text{H}_2\text{O}]/X_{\text{H}_{2\text{gas}}}=\text{EXP}(-\Delta G_{\text{H}_{2\text{sp}}}/R/T)=\text{EXP}(-17600/8.3144/298.15)=0.0008253$ endoergic, unfavored: $\Delta G_{\text{H}_{2\text{sp}}\text{Alberty}}=G_{\text{H}_{2\text{aq}}}-G_{\text{H}_{2\text{gas}}}-G_{\text{H}_2\text{O}}=103.24-85.64-0=17.6 \text{ kJ/mol}$ for gas solubility $\text{H}_{2\text{gas}}+\text{H}_2\text{O}=\text{H}_{2\text{aq}}$.

From the ratio $[\text{H(Pt)}]^2/[\text{H}_{2\text{aq}}]=K_{\text{sp}_\text{H(Pt)}}/[\text{H}_2\text{O}]=11.808/55.3=0.213526$ obtains mol fraction of H(Pt) square:

$$[\text{H(Pt)}]^2=K_{\text{spH(Pt)}}/[\text{H}_2\text{O}]*[\text{H}_{2\text{aq}}]=11.808/55.3*0.04564=0.009745. \text{ Saturated solubility in platinum lattice}$$

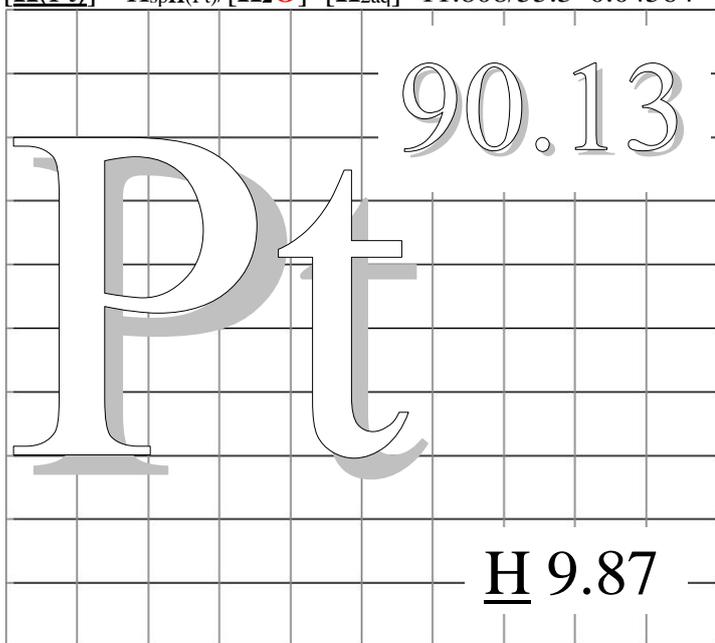
$$[\text{H(Pt)}]=\text{SQRT}(0.009745)=0.0987 \text{ in mol fraction}$$

units is hydrogen atom surface fraction 9.87% shared with platinum atoms fraction 90.13% on total 100% platinum lattice surface. $\text{H}_{2\text{aq}}\text{Alberty}=2\text{H(Pt)}+\text{H}_2\text{O}$; Solubility mol fractions concentrations are unit less as constant too $K_{\text{sp}_\text{H(Pt)}}=11.808$.

Atom radiuses are Pt 0.135 nm, H 0.053 nm. Area square of radiuses Pt 0.0729 nm², H 0.0112 nm² on surface 0.0729+0.0112=0.0841 nm² of lattice.

Common are shared surface total area 100% progress for Platinum atom has 0.0729/0.0841=86.7% and 0.0112/0.0841=9.53% own H hydrogen atom. [25]

H(Pt) solubility in water $2\text{H(Pt)}+\text{H}_2\text{O}=\text{H}_{2\text{aq}}\text{Alberty}$ is less as one $K_{\text{spH(Pt)}_\text{H}_{2\text{aq}}}=[\text{H}_{2\text{aq}}]/[\text{H(Pt)}]^2/[\text{H}_2\text{O}]=0.0846$ and $\Delta G_{\text{Alberty}}=G_{\text{H}_{2\text{aq}}}-2G_{\text{H(Pt)}}-G_{\text{H}_2\text{O}}=6.12 \text{ kJ/mol}$ positive, unfavored, non-spontaneous. It keeps metal lattice saturated with hydrogen 9.87%, because is positive



$$K_{\text{spH(Pt)}_\text{H}_{2\text{aq}}}=[\text{H}_{2\text{aq}}]/[\text{H(Pt)}]^2/[\text{H}_2\text{O}]=\text{EXP}(-\Delta G_{\text{sp}_\text{H(Pt)}}/R/T)=\text{EXP}(-6120/8.3144/298.15)=0.08469 \text{ unfavored.}$$

Water oxidation to oxygen aqua $\text{O}_{2\text{aqua}}$ half reaction $5\text{H}_2\text{O}=\text{O}_{2\text{aq}}+4\text{H}_3\text{O}^++4\text{e}^-$ Hess free energy change is:

$$\Delta G_{\text{O}_{2\text{aq}}\text{Alberty}}=G_{\text{O}_{2\text{aq}}}+4G_{\text{H}_3\text{O}^+}-5G_{\text{H}_2\text{O}}=329.68-4*22.44-5*0=419.44 \text{ kJ/mo} , \text{ because aqua mol fraction:}$$

$\text{O}_{2\text{gas}}\text{AIR}+\text{H}_2\text{O}=\text{O}_{2\text{aq}}$ compensate one water molecule of six $6\text{H}_2\text{O}=\text{O}_{2\text{gas}}\text{AIR}+\text{H}_2\text{O}+4\text{H}_3\text{O}^++4\text{e}^-$ and Nernst's half reaction have five: $5\text{H}_2\text{O}=\text{O}_{2\text{aq}}+4\text{H}_3\text{O}^++4\text{e}^-$ with absolute standard potential $E^\circ_{\text{O}_{2\text{aq}}}=1.0868 \text{ V}$.

It is identical to electrochemical calculation of free energy change minimum using absolute Nernst's standard potential: $\Delta G_{\text{eqO}_{2\text{aq}}}=\text{E}^\circ_{\text{O}_{2\text{aq}}}\cdot F\cdot n_{\text{e}^-}=1.0868*96485*4=419.44 \text{ kJ/mol} .$

Hydrogen metal H(Pt) half reaction $\text{H(Pt)}+\text{H}_2\text{O}=\text{H}_3\text{O}^++\text{e}^-$ Hess free energy change is:

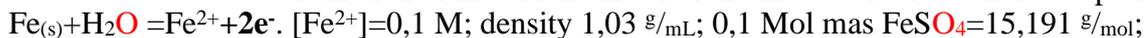
$$\Delta G_{\text{H(Pt)}\text{eqAlberty}}=G_{\text{H}_3\text{O}^+}+G_{\text{e}^-}-(G_{\text{H(Pt)}}+G_{\text{H}_2\text{O}})=22.44+0-(48.56+0)=-26.12 \text{ kJ/mol} .$$

It is coincident with electrochemical calculation of free energy change minimum using **absolute** Nernst's standard potential $E^\circ_{\text{H(Pt)}}=-0.27073 \text{ Volts}$:

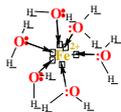
$$\Delta G_{\text{eqH(Pt)}}=\text{E}^\circ_{\text{H(Pt)}}\cdot F\cdot n_{\text{e}^-}=-0.27073*96485*1=-26.12 \text{ kJ/mol} \text{ coinciding with Alberty data. [8,15]}$$

Metal immersed in its ions solution by Nernst's oxidation half reaction first type Electrode potential in Volts.

Coordination of metal ions in solution bind water with donor-acceptor bonds.



$E_{\text{Fe}/\text{Fe}^{2+}} = E_{\text{Fe}}^{\circ} - 0,0591/2 * \log(1/([\text{H}_2\text{O}])) = -0,4402 - 0,0591/2 * \log(1/55,3) + 0,10166 - 0,37239 = -0,6594 \text{ V}$.



$E_{\text{Fe}} = E_{\text{Fe}/\text{Fe}^{2+}} + 0,0591/2 * \log([\text{Fe}^{2+}]/[\text{Fe}]/([\text{H}_2\text{O}])) = -0,65943 + 0,0591/2 * \log(0,1/1/(55,3)) = -0,74048 \text{ V}$;

Distinguish $-0,74048 \text{ V}$ has $4 - 0,74059 \text{ V}$. $\Delta G_{\text{eq, Fe}} = E_{\text{Fe}}^{\circ} \cdot F \cdot 2 = -0,65943 * 96485 * 2 = -127,25 \text{ kJ/mol}$,

$\Delta G_{\text{eq, Fe}} = G_{\text{Fe}^{2+}} - (G_{\text{Fe}} + G_{\text{H}_2\text{O}}) = -82,14 - (50,08 + 0) = -127,25 \text{ kJ/mol}$;

$G_{\text{Fe}} = G_{\text{Fe}^{2+}} - (\Delta G_{\text{eq, Fe}} + G_{\text{H}_2\text{O}}) = -82,14 - (-127,25 + 0) = 45,11 \text{ kJ/mol}$;

$E_{\text{Fe}} = E_{\text{Fe}/\text{Fe}^{2+}} + 0,0591/2 * \log([\text{Fe}^{2+}]/[\text{Fe}]/([\text{H}_2\text{O}] - 6[\text{Fe}^{2+}])) = -0,658382 + 0,0591/2 * \log(0,1/1/(56,38 - 0,6)) = -0,7395 \text{ V}$;

$[\text{H}_2\text{O}] = 55,3 \text{ M} = (996 \text{ g/L}) / (18 \text{ g/mol})$; $m_{\text{H}_2\text{O}} = m_{\text{L}} - m_{\text{FeSO}_4} = 1030 - 15,191 = 1284,8 \text{ g}$; $[\text{H}_2\text{O}] = 1014,8 \text{ g} / 18 \text{ g/mol} = 56,38 \text{ M}$.

Substance	$\Delta H_{\text{H}}^{\circ} \text{ kJ/mol}$	$\Delta S_{\text{H}}^{\circ} \text{ J/molK}$	$\Delta G_{\text{H}}^{\circ} \text{ kJ/mol}$
Fe	$E_{\text{Fe}}^{\circ} =$	-0.6594 V	45,11
Fe^{2+}	-87.45	-17.8	-82.14
Fe^{2+}	-89.1	-137.7	-78.9
Fe^{3+}	-44.79	-110	-11.99
Fe^{3+}	-48.5	-315.9	-4.7
Cu	$E_{\text{Cu}}^{\circ} =$	0,1243 V	70,02
Cu^{2+}	64.8	-98	94,0187
Zn	$E_{\text{Zn}}^{\circ} =$	-0,98098 V	68,65
Zn^{2+}	-153.39	-109.8	-120,653

$G_{\text{Fe}} = G_{\text{Fe}^{2+}} - (\Delta G_{\text{eq, Fe}} + G_{\text{H}_2\text{O}}) = -82,14 - (-127,25 + 0) = 45,11 \text{ kJ/mol}$;

BioThermodynamic 2006

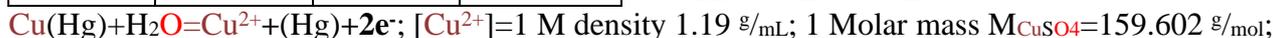
CRC 2010

$G_{\text{Cu}} = G_{\text{Cu}^{2+}} - (\Delta G_{\text{eq, Cu}} + G_{\text{H}_2\text{O}}) = 94,0187 - (24,0 + 0) = 70,02 \text{ kJ/mol}$;

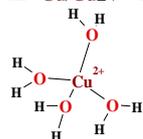
$\Delta G_{\text{Cu}^{2+}} = \Delta H_{\text{H}} - T * \Delta S_{\text{H}} = 64,8 - 298,15 * -0,098 = 94,0187 \text{ kJ/mol}$;

$G_{\text{Zn}} = G_{\text{Zn}^{2+}} - (\Delta G_{\text{eq, Zn}} + G_{\text{H}_2\text{O}}) = -120,653 - (-189,3 + 0) = 68,65 \text{ kJ/mol}$;

$\Delta G_{\text{Zn}^{2+}} = \Delta H_{\text{H}} - T * \Delta S_{\text{H}} = -153,39 - 298,15 * -0,1098 = -120,65 \text{ kJ/mol}$;



$E_{\text{Cu}/\text{Cu}^{2+}} = E_{\text{Cu}}^{\circ} + 0,0591/2 * \log(1/([\text{H}_2\text{O}])) = 0,3435 - 0,0591/2 * \log(1/55,3) + 0,10166 - 0,371339 = 0,1243 \text{ V}$.



$E_{\text{Cu}} = E_{\text{Cu}}^{\circ} + 0,0591/2 * \log([\text{Cu}^{2+}]/[\text{Cu}]/([\text{H}_2\text{O}])) = 0,1243 + 0,0591/2 * \log(1/1/(55,3)) = 0,0728 \text{ V}$;

Distinguish on number $0,0728 \text{ V}$ in the second sign $0,0733 \text{ V}$

$m_{\text{H}_2\text{O}} = (m_{\text{L}} - m_{\text{CuSO}_4}) / 18 = 1190 - 159,602 = 1030,4 / 18 = 57,24 - 4 = 53,24 \text{ mol}$;

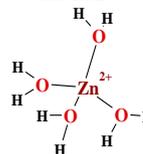
$E_{\text{Cu}} = E_{\text{Cu}}^{\circ} + 0,0591/2 * \log([\text{Cu}^{2+}]/[\text{Cu}]/([\text{H}_2\text{O}] - 4[\text{Cu}^{2+}])) = 0,1243 + 0,0591/2 * \log(1 \text{ M} / 1 / (57,24 - 4)) = 0,0733 \text{ V}$;

$\Delta G_{\text{eq, Cu}} = E_{\text{Cu}}^{\circ} \cdot F \cdot 2 = 0,1243 * 96485 * 2 = 24,0 \text{ kJ/mol}$; $\Delta G_{\text{eq, Cu}} = G_{\text{Cu}^{2+}} - (G_{\text{Cu}} + G_{\text{H}_2\text{O}}) = 94,0187 - (G_{\text{Cu}} + 0) = 24,0 \text{ kJ/mol}$;

$G_{\text{Cu}} = G_{\text{Cu}^{2+}} - (\Delta G_{\text{eq, Cu}} + G_{\text{H}_2\text{O}}) = 94,0187 - (24,0 + 0) = 70,02 \text{ kJ/mol}$;



$E_{\text{Zn}/\text{Zn}^{2+}} = E_{\text{Zn}}^{\circ} + 0,0591/2 * \log(1/([\text{H}_2\text{O}])) = -0,7628 - 0,0591/2 * \log(1/55,3) + 0,10166 - 0,371339 = -0,98098 \text{ V}$.



$E_{\text{Zn}} = E_{\text{Zn}/\text{Zn}^{2+}} + 0,0591/2 * \log([\text{Zn}^{2+}]/[\text{Zn}]/([\text{H}_2\text{O}])) = -0,980981 + 0,0591/2 * \log(2/1/(55,3)) = -1,0215 \text{ V}$

Distinguish on number $-1,0215 \text{ V}$ in the forth sign $-1,02358 \text{ V}$ 2M ;

Solubility $57,7 \text{ g/100g}$ in hundreds grams of voter; $w\% = 57,7 / 157,7 * 100 = 36,6\%$;

$m_{\text{H}_2\text{O}} = m_{\text{L}} - m_{\text{ZnSO}_4} = 1310 - 161,44 * 2 = 987,12 \text{ g}$; $m_{\text{ZnSO}_4} = 2 * 161,44 = 322,88 \text{ g}$; $[\text{H}_2\text{O}] = 987,12 \text{ g} / 18 \text{ g/mol} = 54,84 \text{ M}$.



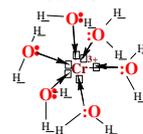
$E_{\text{Zn}} = E_{\text{Zn}/\text{Zn}^{2+}} + 0,0591/2 * \log \frac{[\text{Zn}^{2+}]}{[\text{Zn}] \cdot ([\text{H}_2\text{O}] - 4 \cdot [\text{Zn}^{2+}])} = -0,980981 + 0,0591/2 * \log(2/1/(54,84 - 4 * 2)) = -1,02358 \text{ V}$;

$\Delta G_{\text{eq, Zn}} = E_{\text{Zn}}^{\circ} \cdot F \cdot 2 = -0,980981 * 96485 * 2 = -189,3 \text{ kJ/mol}$; $\Delta G_{\text{eq, Zn}} = G_{\text{Zn}^{2+}} - (G_{\text{Zn}} + G_{\text{H}_2\text{O}}) = -120,653 - (G_{\text{Zn}} + 0) = -189,3 \text{ kJ/mol}$

$G_{\text{Zn}} = G_{\text{Zn}^{2+}} - (\Delta G_{\text{eq, Zn}} + G_{\text{H}_2\text{O}}) = -120,653 - (-189,3 + 0) = 68,65 \text{ kJ/mol}$;



$E_{\text{Cr}/\text{Cr}^{3+}} = E_{\text{Cr}}^{\circ} + 0,0591/3 * \log(1/([\text{H}_2\text{O}])) = -0,744 - 0,0591/3 * \log(1/55,3) + 0,10166 - 0,371339 = -0,9793 \text{ V}$.



$E_{\text{Cr}} = E_{\text{Cr}}^{\circ} + 0,0591/3 * \log([\text{Cr}^{3+}]/[\text{Cr}]/([\text{H}_2\text{O}])) = -0,9793 + 0,0591/3 * \log(1/1/55,3) = -1,0136 \text{ V}$;

Distinguish on number $-1,0136 \text{ V}$ in the fourth sign $-1,01246 \text{ V}$ 1M ; $2,32 \text{ M}$;

$m_{\text{H}_2\text{O}} = m_{\text{L}} - m_{\text{Cr}_2(\text{SO}_4)_2} = 1172 - 196,08 = 975,92 \text{ g}$; $m_{\text{Cr}_2(\text{SO}_4)_2} = 392,16 / 2 = 196,08$;

$[\text{Cr}^{3+}] = 2 * C_{\text{Cr}_2(\text{SO}_4)_2} = 1 \text{ M}$ density $1,172 \text{ g/mL}$; $m_{\text{Cr}_2(\text{SO}_4)_2} = 196,08 \text{ g}$; $[\text{H}_2\text{O}] = 975,92 \text{ g} / 18 \text{ g/mol} = 54,21778 \text{ M}$



$E_{\text{Cr}} = E_{\text{Cr}}^{\circ} + 0,0591/3 * \log \frac{[\text{Cr}^{3+}]}{[\text{Cr}] \cdot ([\text{H}_2\text{O}] - 6 \cdot [\text{Cr}^{3+}])} = -0,9793 + 0,0591/3 * \log(1/1/(54,21778 - 6 * 1)) = -1,01246 \text{ V}$;

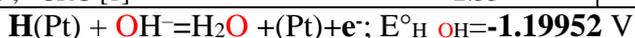
Solubility 64 g/100g in hundred grams of water; $w\% = 64 / 164 * 100 = 39\%$;

$39 / 100 \text{ g} = X / 1172 \text{ g/L}$; $39 / 100 * 1172 = 457,07 = X \text{ g/L}$; $C_{\text{Cr}_2(\text{SO}_4)_2} = 457,07 / 392,16 = 1,1655 \text{ M}$ $\text{Cr}_2(\text{SO}_4)_3$;

$m_{\text{H}_2\text{O}} = m_{\text{L}} - m_{\text{Cr}_2(\text{SO}_4)_2} = 1172 - 457,07 = 714,93 \text{ g}$; $m_{\text{Cr}_2(\text{SO}_4)_2} = 457,07 \text{ g}$; $[\text{H}_2\text{O}] = 714,93 \text{ g} / 18 \text{ g/mol} = 39,718 \text{ M}$

Table 1. Nernst's half reactions Standard Electrode Potentials classic, Thermodynamic, Absolute Volts.

	Reduced form = Oxidized form + n e ⁻ ; [classic references]	H ₂ O disaccount classic zero E _o	Thermodynamic scale on H ₂ O account	Absolute scale -0,37239
H	<u>H</u> (Pt) + H ₂ O = H ₃ O ⁺ + (Pt) + e ⁻ ; general reference CRC [1]	classic zero 0	0.10166	-0.27073
	<u>H</u> (Pt) + OH ⁻ = H ₂ O + (Pt) + e ⁻ ; classic CRC [1]	-0.8277	-0.8282	-1.1995
	<u>H</u> (Pt) + OH ⁻ = H ₂ O + (Pt) + e ⁻ ; corrected CRC -0.8277 + 0.10449	-0.9322	-0.93375	-1.30508
	H₂aq + H₂O = 2H₃O⁺ + 2e⁻; graphite electrode	-0.1343	0.07039	-0.302
O	5H ₂ O = O ₂ aq + 4H ₃ O ⁺ + 4e ⁻ ; Suchotina [17]	1.2288	1.45924	1.0868
	H ₂ O ₂ + 2H ₂ O = O ₂ aq + 2H ₃ O ⁺ + 2e ⁻ ; David A. Harris [21]	1.2764	1,4811	1,1087
	4H ₂ O = H ₂ O ₂ + 2 H ₃ O ⁺ + 2e ⁻ ; Suchotina [17]	1.776	2.0837	1.7113
	H₂O₂aq + 2H₂O = O₂aq + 2H₃O⁺ + 2e⁻; University Alberta [19]	0.6945	0.8992	0.5268
CHO	C₆H₁₂O₆ + 42H₂O = 24H₃O⁺ + 6H₃O⁺ + 6HCO₃⁻ + 24e⁻;	-0.04915	0.2328	-0.13964
	HOO⁻ + H₂O = O₂aq + H₃O⁺ + 2e⁻;	0.3155	0.4686	0.09625
N	NO₂⁻ + 2OH⁻ = NO₃⁻ + H₂O + 2e⁻; pH > 3.15 Suchotina [17]	0.01	0.0602	-0.3122
	HNO₂ + 4H₂O = NO₃⁻ + 3H₃O⁺ + 2e⁻; pH < 3.15 [18]	0.94	1.2477	0.8753
	NO₂⁻ + 3H₂O = NO₃⁻ + 2H₃O⁺ + 2e⁻ David A. Harris [21]	0.835	1.09115	0.7188
	NO_{aq} + 5H₂O = NO₃⁻ + 4H₃O⁺ + 3e⁻; pH > 3.15 [18]	0.96	1.2333	0.8609
	NH₄⁺ + 13H₂O = NO₃⁻ + 10H₃O⁺ + 8e⁻; Suchotina [17]	0.87	1.1391	0.7667
Br	2Br = Br₂(aq) + 2e⁻; CRC [1]	1.0873	1.18896	0.8176
Bi	BiO⁺ + 6H₂O = BiO₃ + 4H₃O⁺ + 2e⁻; 1 < pH < 7 Suchotina [17]	1.80	2.21065	1.8383
Mn H⁺	Mn²⁺ + 12H₂O = MnO₄⁻ + 8H₃O⁺ + 5e⁻; Kortly, Shucha [18]	1.51	1.85885	1.4865
	MnO₂↓ + 4OH⁻ = MnO₄⁻ + 2H₂O + 3e⁻; Suchotina [17]	0.603	0.6360	0.2636
	MnO₄²⁻ = MnO₄⁻ + e⁻; Suchotina [17]	0.558	0.65966	0.2873
Pb	Pb²⁺ + 6H₂O = PbO₂(s) + 4H₃O⁺ + 2e⁻; Kortly, Shucha [18]	1.455	1.86565	1.4933
	Pb + H₂O = Pb²⁺ + 2e⁻; pH < 7 Kortly, Shucha [18]	-0.126	0.02716	-0.3452
S	SO₂^s + H₂O = H₂SO₃aq; H₂SO₃ + 3H₂O = HSO₄⁻ + 3H₃O⁺ + 2e⁻; [17]	0.172	0.42815	0.10726
	HSO₃⁻ + 4H₂O = SO₄²⁻ + 3H₃O⁺ + 2e⁻; 2 = < pH < 7 Suchotina [17]	0.172	0.47965	0.10726
	SO₃²⁻ + 2OH⁻ = SO₄²⁻ + H₂O + 2e⁻; pH > 7 Suchotina [17]	-0.93	-0.87984	-1.2522
	S²⁻ = S_{rombic} + H₂O + 2 e⁻; CRC [1]	-0.4763	-0.4261	-0.7985
	HS⁻ + OH⁻ = S_{rombic} + 2H₂O + 2e⁻; CRC [1]	-0.478	-0.4793	-0.8517
	H₂S_{aq} + 2H₂O = S_{rombic} + 2H₃O⁺ + 2e⁻; CRC [1]; Suchotina [17]	0.142	0.3467	-0.025735
	2S₂O₃²⁻ = S₄O₆²⁻ + 2e⁻; Suchotina [17]	0.08	0.1817	-0.1907
Fe	Fe²⁺ = Fe³⁺ + e⁻; Suchotina [17]	0.769	0.8707	0.4983
	Fe(s) + H₂O = Fe²⁺ + 2e⁻; Suchotina [17]	-0.4402	-0.2870	-0.6594
Ag	Ag + H₂O = Ag⁺ + e⁻; Kortly, Shucha [18]	0.7994	1.00406	0.6317
	Ag(s) + Cl⁻ = AgCl(s) + H₂O + e⁻; Kortly, Shucha [18]	0.2223	0.2210	-0.1514
	Ag + 2NH₃aq = Ag(NH₃)₂⁺ + H₂O + e⁻; Suchotina [17]	0.373	0.57766	0.2053
	2Ag + 2OH⁻ = Ag₂O(s) + H₂O + 2e⁻; Suchotina [17]	0.345	0.39516	0.02277
Hg	2Hg + H₂O = Hg₂²⁺ + 2e⁻; Kortly, Shucha [18]	0.907	1.0602	0.6888
	2Hg + 2Cl⁻ = Hg₂Cl₂(s) + 2H₂O + 2e⁻; Suchotina ; [17]	0.2676	0.2663	-0.1059
	2Hg + SO₄²⁻ = Hg₂SO₄(s) + H₂O + 2e⁻; Kortly, Shucha ; [18]	0.614	0.6642	0.2918
	Hg + 2OH⁻ = HgO + H₂O + 2e⁻; Suchotina ; [17]	0.098	0.1482	-0.2242
I	3I⁻ = I₃⁻ + 2e⁻; Kortly, Shucha [18]	0.6276	0.72926	0.35687
Cu	Cu(Hg) + H₂O = Cu²⁺ + (Hg) + 2e⁻; Kortly, Shucha [18]	0.3435	0.4967	0.1243
F	2F⁻ = F₂(g) + 2e⁻; Kortly, Shucha [18]	2.87	2.97166	2.5993
Cl	2Cl⁻ = Cl₂(g) + 2e⁻; Kortly, Shucha [18]	1.358	1.45966	1.0873
Cl	Cl₂(g) + 4H₂O = 2HOCl + 2H₃O⁺ + 2e⁻; Kortly, Shucha [18]	1.63	1.93765	1.5653
Cr	2Cr³⁺ + 21H₂O = Cr₂O₇²⁻ + 14H₃O⁺ + 6e⁻; 1 < pH < 7 [18]	1.33	1.7921	1.41975
	Cr³⁺ + 11H₂O = HCrO₄⁻ + 7H₃O⁺ + 3e⁻; pH > 7 [18]	1.20	1.6793	1.30692
	Cr(OH)₃↓ + 5OH⁻ = CrO₄²⁻ + 4H₂O + 3e⁻; pH > 9 ; Suchotina [17]	-0.13	-0.1657	-0.53806
C	H₂C₂O₄ + 2H₂O = 2CO₂ + 2H₃O⁺ + 2e⁻; pH < 1,25 Suchotina [17]	-0.49	-0.2853	-0.6577
Cr	Cr + H₂O = Cr³⁺ + 3e⁻; Suchotina [17]	-0.744	-0.60801	-0.97935
Zn	Zn + H₂O = Zn²⁺ + 2e⁻; Kortly, Shucha [18]	-0.763	-0.6096	-0.98098
Al	Al + H₂O = Al³⁺ + 3e⁻; CRC [1]	-1.662	-1.5260	-1.8984
	Al + 4OH⁻ = H₂AlO₃⁻ + H₂O + 3e⁻; CRC [1]	-2.33	-2.2627	-2.63506



The absolute potential is corrected by accounting for the absolute free energy of hydroxide $G_{\text{OH}^-} = 77,36 \text{ kJ/mol}$ in the Hess calculation: $\Delta G_{\text{AlbertyH,OH}} = G_{\text{H}_2\text{O}} - (G_{\text{H}(\text{Pt})} + G_{\text{OH}^-}) = 0 - (48.56025 + 77.36) = -125.92 \text{ kJ/mol}$ and calculated in terms of the corrected absolute potential: $E^\circ_{\text{H}} = \Delta G_{\text{eq}}/F/1 = -125.92/96485/1 = -1.30508 \text{ V}$.

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 g/mL density the **hydrogen electrode** has classic $E_{o,\text{classic}} = -0.8277 \text{ V}$ [17] and absolute standard potential:

$$E^\circ_{\text{H,OH}} = E^\circ - 0.0591/1 * \lg([\text{H}_2\text{O}]^1) + 0.10166 - 0,37239 - 0.8277 - 0.0591/1 * \lg(53.5^1) + 0.10166 - 0,37239 = -1.1995 \text{ V}$$

data corrected $\Delta G_{\text{eqH,OH}} = E^\circ_{\text{H,OH}} \cdot F \cdot 1 = -1.30508 * 96485 * 1 = -125.92 \text{ kJ/mol}$ to $E^\circ_{\text{H}} = -0.8277 - 0.10556 = -0.9322 \text{ V}$.

$$E^\circ_{\text{H,OH}} = E^\circ - 0.0591/1 * \lg([\text{H}_2\text{O}]^1) + 0.10166 - 0,37239 - 0.9322 - 0.0591/1 * \lg(53.5^1) + 0.10166 - 0,37239 = -1.30508 \text{ V};$$

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

Oxygen gas solubility $O_{2gas}+H_2O=O_{2aq}$ compensate one water molecule $6H_2O=O_{2gas}+H_2O+4H_3O^++4e^-$ on Nernst's half reaction $5H_2O=O_{2aq}+4H_3O^++4e^-$, forming absolute standard potential $E^{\circ}_{5HOH}=1.0868$ V.

$$E^{\circ}_{5HOH}=E^{\circ}-0.0591/4*\lg(1/[H_2O]^5)+0.10166-0.37239=1.2288-0.0591/4*\lg(1/53.5^{^5})+0.10166-0.37239=1.0868$$
 V.

Substance	$\Delta H^{\circ}_H, \text{kJ/mol}$	$\Delta S^{\circ}_H, \text{J/mol/K}$	$\Delta G^{\circ}_H, \text{kJ/mol}$
H₂O	-285.85	69.9565	-237.191
H₂O	-286.65	-453.188	-151.549
H₃O⁺	-285.81	-3.854	-213.2746
H₂(aq)	23.4	-130	99.13
H(Pt)(aq)	$E^{\circ}_H-E^{\circ}_{O2}$	-1.3575	48.56
H₂(aq)	-5.02	-363.92	103.24
O₂aqua	-11.70	-94.2	16.4
O₂aqua	-11.715	110.876	16.4

$\Delta G_{Hess}=2\Delta G^{\circ}_{H_2O}-4\Delta G^{\circ}_{(Pt)H}-\Delta G^{\circ}_{O_2aqua}=-689=2*(-344.521)$ kJ/mol;
 $=2*(-237.191)-(4*99.13/2+16.4)=-689=2*344.5$ kJ/mol. CRC 2010
 2006, Massachusetts Technology Inst. Albany [8]
[Mischenko](#) 1972, Himia, Leningrad [26]
 CRC 2010 [1]
 $G_{H(Pt)}=(2G_{H_2O}-\Delta G_{eq2H_2O}-G_{O_2aqua})/4=48.56$ kJ/mol;
 2006, Massachusetts Technology Inst. Albany [8]
 Water concentration $[H_2O]^5$ logarithm extracted from $E^{\circ}_{classic}=1.2288$ V
 absolute standard potential of Nernst's $E^{\circ}_{5HOH}=1.0868$ V.

Oxygen solution $O_{2aq}+4H_3O^++4e^-=5H_2O$ is strong oxidant with inverse standard potential $-E^{\circ}_{5HOH}=-1.0868$ V.

The oxidized form of oxygen attracts four free electrons with hydroxonium ions, forming four water molecules in the reduced form as products. The free energy content increases when dissolved in water:

$$G_{O2aq}=G_{O2gas}+G_{O2sk}=303.1+26.58=330$$
 kJ/mol.

Oxygen solubility free energy change Hess law solution is exothermic and endoergic $O_{2gas}+H_2O=O_{2aq}$, which mol fraction in air $1=[O_{2gas}]>[O_{2air}]=0.2095$ and in water has unit less value for concentration $[O_{2aq}]/[H_2O]=1.22*10^{(-3)}/55.3$ M= $2.206*10^{-5}$ and for constant too; $K_{speq}=[O_{2aq}]/[O_{2gas}]/[H_2O]=1.22*10^{(-3)}/55.3=2.206*10^{-5}$. Energy change is positive $\Delta G_{Hess}=\Delta G^{\circ}_{O_2aqua}-\Delta G^{\circ}_{H_2O}-\Delta G^{\circ}_{O_2gas}=16.4-(0-237.191)=253.6$ kJ/mol, so positive on scale of absolute expressions $\Delta G_{AlbertyO2aq}=G_{O2aq}-(G_{H_2O}+G_{O2gas})=330-(0+303.1)=26.58$ kJ/mol

and $\Delta G_{speq}=-R\cdot T\cdot \ln(K_{speq})=-8.3144*298.15*\ln(2.205*10^{-5})=26.58$ kJ/mol.

$[O_2]$ solubility Hess free energy change is positive $\Delta G_{Hess}=\Delta G_{solubility}=253.6$ kJ/mol, but minimized at equilibrium mixture $K_{sp}=[O_{2aq}]/[O_{2gas}]/[H_2O]=2.206*10^{-5}=10^{-4.656}$.

Equilibrium state is Prigogine attractor for all non-equilibrium states.

Free energy change minimum ΔG_{min} reaching establishes equilibrium. [53rd page](#).

Osmolar $C_{osm}=0$ M and ionic force $I=0$ M in water from air 20.95% oxygen solubility is $[O_{2aq}]=0.00025546$ M:

$$[O_{2aq}]=K_{sp}*[O_{2air}]*[H_2O]=2.205*10^{-5}*0.2095*55.3=0.00025546$$
 M.

Pure 1atm mol fraction $[O_{2gas}]=1$. Osmolar $C_{osm}=0.305$ M, ionic force $I=0.25$ M, air 20.95% oxygen dissolve $[O_{2aq}]=9.768\cdot 10^{-5}$ M. Therefore $K_{O2spBlood}=[O_{2aq}]/[O_{2air}]=9.768\cdot 10^{-5}/0.2095=4.663\cdot 10^{-4}$ M is physiologic solubility constant.

Arterial $[O_{2aq}]=6\cdot 10^{-5}$ M and venous $[O_{2aq}]=0.426\cdot 10^{-5}$ M isooxia is maintained by osmosis oxygen molecules, which cross membranes through aquaporins channels against osmolar concentration gradient $C_{osm}=0.305$ M.

Inverse: $O_{2aqua}+4H_3O^++4e^-=6H_2O$; $-E^{\circ}_{O2}=-1.0868$ V; Nernst's: $4(Pt)H+4H_2O=4H_3O^++4e^-$; $E^{\circ}_H=-0.27073$ V;

$O_{2aqua}+4(Pt)H=2H_2O$ electrodes standard potential sum give standard free energy change:

$$\Delta G_{eq}=(E^{\circ}_H-E^{\circ}_{O2})\cdot F\cdot 1\cdot 4=(-0.27073-1.0868)*96485*4=-1.3575*96485*4/1000=2*261.96=-523.925$$
 kJ/mol;

Knowing equilibrium value $\Delta G_{eq2H_2O}=2G_{H_2O}-4G_{(Pt)H}-G_{O_2aqua}=2*0-(4*G_{(Pt)H}+329.68)=-523.925$ kJ/mol, hydrogen metal free energy is $G_{H(Pt)}=(2G_{H_2O}-\Delta G_{eq2H_2O}-G_{O_2aqua})/4=(2*0+523.925-329.68)/4=194.251/4=48.56$ kJ/mol.

$G_{H_3O^++OH}=G_{H_3O^+}+G_{OH}=22.44+77.36=99.8$ kJ/mol of water protolysis $H_2O+H_2O<=>H_3O^++OH$

Biochemistry oxygen O_{2aqua} decreases free energy content $G_{O_2aqua}=329.68$ kJ/mol to $G_{O_2Biochemistry}=88.22$ kJ/mol.

Arterial $[O_{2aqua}]=6\cdot 10^{-5}$ M and pH=7.36 concentrations $[H_3O^+]=10^{-7.36}$ M potential is decreasing

$$E_{O2}=E^{\circ}+0.0591/4*\lg([O_{2aqua}]*[H_3O^+]^4/[H_2O]^5)=1.0868+0.0591/4*\lg(6*10^{(-5)}*10^{(-7.36*4)}/55.346^{^5})=0.46174$$
 V
 by $\Delta E_{arterial}=(E_{O2}-E^{\circ}_{O2})=-1.0868+0.46174=-0.62506$ Volts and

free energy content by $\Delta G_{arterial}=\Delta E_{H_2O}\cdot F\cdot n=0.62506*96485*4/1000=-241.24$ kJ/mol.

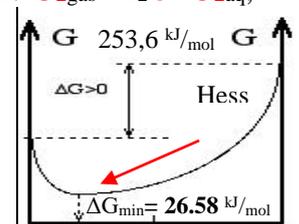
The free energy content of O_{2gas} AIR+ $H_2O=O_{2Blood}$ with solubility contribution increases by:

$$K_{speq}=\frac{[O_{2aqua}]}{[O_{2gas}]\cdot [H_2O]}=2.205*10^{-5}; G_{O2speq}=-R\cdot T\cdot \ln(K_{speq})=-8.3144*298.15*\ln(2.205*10^{-5})=26.58$$
 kJ/mol.

Protolysis decreases free energy to $G_{O2Biochem_arterial}=G_{O2aq}+G_{O2sp}+\Delta G_{arterial}=303.1+26.58-241.456=88.22$ kJ/mol and oxygen becomes fire safe biochemical oxidant, forming [arterial concentration](#) $[O_{2aqua}]=6\cdot 10^{-5}$ M as safe Bioenergetic sustaining normal isooxia. [3];

1) Water 55.346 M decreases potential from **1.0868 V** about **-0.1288 V=0.9580-1.0868=ΔE_{H2O}**.

$$E_{O2}=E^{\circ}_{O2}+0.0591/4*\lg(1/[H_2O]^5)=1.0868+0.01478*\lg(1/55.346^{^5})=0.95805$$
 V ;



A + B 50% C + D
 Reactants
 $O_{2gas}+H_2O_{Blood}$
 product $O_{2aq-Blood}$.

- 2) Acid H_3O^+ increases 10 times the potential and free energy content increases about $\Delta E_{\text{H}_3\text{O}^+} = 0.05912 \text{ V}$
 $\Delta E_{\text{H}_3\text{O}^+} = 0.01478 \cdot \lg([\text{H}^+]^4) = 0.05912 \text{ V}$ and $\Delta G_{\text{max}} = \Delta E_{\text{H}_3\text{O}^+} \cdot F \cdot n = 0.05912 \cdot 96485 \cdot 4 / 1000 = 22.817 \text{ kJ/mol}$;
- 3) Air 20.95% replaced with 100% oxygen [$\text{O}_{2\text{aqua}}$] concentration 5 times increase potential about
 $\Delta E_{\text{O}_2 100\%} = 0.01478 \cdot \lg(100\% [\text{O}_{2\text{aqua}}]) = 0.01478 \cdot \lg(5) = +0.0103 \text{ V}$. Free energy content for oxygen increases about $\Delta G_{\text{max}} = \Delta E_{\text{H}_3\text{O}^+} \cdot F \cdot n = 0.01033 \cdot 96485 \cdot 4 / 1000 = 3.987 \text{ kJ/mol}$. [6th page](#).
 NASA Apollo Moon project closes 1972 because of oxidative stress and technical hazards risk.

In the Nernst half-reaction of glucose oxidation, the absolute standard potential is negative because the strong of 24-electron donor, what reduce the six oxygen molecules in Nernst's reaction $\text{O}_{2\text{aqua}} + 4\text{H}_3\text{O}^+ + 4e^- = 5\text{H}_2\text{O}$ with an inverse absolute standard potential $-E^\circ = -1.0868 \text{ V}$. From the classic of glucose standard potential $E^\circ = -0.04915 \text{ V}$, by extracting by the logarithm $\log(1/55.3^{42})$ 42 water molecules, the absolute Nernst standard potential of glucose is $E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} = -0,04915 - 0,0591/24 \cdot \log(1/55,3^{42}) + 0,10166 - 0,37239 = -0,13964 \text{ V}$.



Glucose and inverse oxygen absolute standard potentials sum ΔE° :

$$\Delta E^\circ = (E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} - E^\circ_{\text{O}_2}) = \Delta G_{\text{Lehninger}} / F / n = -2840000 / 96485 / 24 = -1.2264 \text{ V}$$
 give the absolute free energy change $\Delta G_{\text{Lehninger}} = \Delta E^\circ \cdot F \cdot n = (E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} - E^\circ_{\text{O}_2}) \cdot F \cdot n = (-0.13958 - 1.086865) \cdot 96485 \cdot 24 = -2840 \text{ kJ/mol}$ for the reaction by published data $\text{C}_6\text{H}_{12}\text{O}_6 + 12\text{H}_2\text{O} + 6\text{O}_{2\text{aqua}} = 6\text{H}_3\text{O}^+ + 6\text{HCO}_3^-$. [1,6]

The sum of the absolute standard potentials $(E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} - E^\circ_{\text{O}_2}) = (E_{\text{C}_6\text{H}_{12}\text{O}_6} - 1,086865) = -1,22644 \text{ V}$ of glucose and oxygen allows us to determine the absolute standard potential for glucose

$E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} = \Delta E + E^\circ_{\text{O}_2} = -1,22644 + 1,086865 = -0,139575 \text{ V}$, which is calculated from the value of the inverse Nernst's half reaction absolute standard potential of oxygen $\text{O}_{2\text{aqua}} + 4\text{H}_3\text{O}^+ + 4e^- = 5\text{H}_2\text{O}$; $-E^\circ_{\text{O}_2} = -1.0868 \text{ V}$.

Arterial oxygen [$\text{O}_{2\text{arteriāla}}$] = $6 \cdot 10^{(-5)} \text{ M}$; hydroxonium [H_3O^+] = $10^{(-7,36 \cdot 30)} \text{ M}$ and [$\text{C}_6\text{H}_{12}\text{O}_6$] = $0,005 \text{ M}$ glucose concentration produce very negative arterial potential:

$$E_{\text{C}_6\text{H}_{12}\text{O}_6\text{arterial}} = E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} + 0,0591/24 \cdot \lg([\text{HCO}_3^-]^6 \cdot [\text{H}_3\text{O}^+]^{30} / [\text{H}_2\text{O}]^{42} / [\text{C}_6\text{H}_{12}\text{O}_6]) = -0,13958 + 0,0591/24 \cdot \lg(0,0154 \cdot 10^{(-7,36 \cdot 30)} / 0,005/55,346^{42}) = -0,86237 \text{ V}$$

and inverse Nernst's half reaction absolute arterial potential of oxygen is

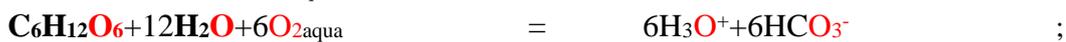
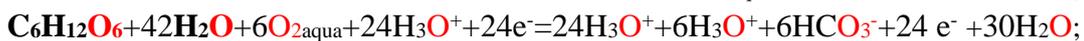
$$E_{\text{O}_2\text{arterial}} = E^\circ_{\text{O}_2} + 0,0591/4 \cdot \lg([\text{H}_2\text{O}]^5 / [\text{O}_{2\text{aqua}}] / [\text{H}_3\text{O}^+]^4) = -1,086865 + 0,0591/4 \cdot \lg(55,346^5 / 6 / 10^{(-5)} / 10^{(-7,36 \cdot 4)}) = -0,46074 \text{ V}.$$

Homeostasis potential sum is more negative $\Delta E_{\text{arterial}} = E_{\text{C}_6\text{H}_{12}\text{O}_6\text{arterial}} + E_{\text{O}_2\text{arterial}} = -0,86237 - 0,46074 = -1,3231 \text{ Volts}$.

Free energy change $\Delta G_{\text{arterial}}$ is more negative as standard value $\Delta G_{\text{Lehninger}}$:

$$\Delta G_{\text{arterial}} = \Delta E \cdot F \cdot n = (E_{\text{C}_6\text{H}_{12}\text{O}_6\text{arterial}} - E_{\text{O}_2\text{arterial}}) \cdot F \cdot n = (-0,86237 - 0,46074) \cdot 96485 \cdot 24 = -3063,846 \text{ kJ/mol}.$$

One mol glucose oxidize six mols of oxygen producing six mols bicarbonate $6\text{H}_3\text{O}^+ + 6\text{HCO}_3^-$:



$$\text{GH}_3\text{O}^+ + \text{HC}_3\text{O}_3^- = \text{GH}_3\text{O}^+ + \text{GHC}_3\text{O}_3^- = 22,44 + 56,08 = 78,52 \text{ kJ/mol},$$

[Glc](#) 6th page Formation from elements $\text{C} + 6\text{H}_2\text{gas} + 3\text{O}_2\text{gas} = \text{C}_6\text{H}_{12}\text{O}_6$ free energy change calculates from Albery data at pH=7.36 $\Delta G^\circ_{\text{Albery}} = \text{G}_{\text{C}_6\text{H}_{12}\text{O}_6} - (6\text{G}_{\text{Cgraph}} + 6\text{G}_{\text{H}_2\text{gas}} + 3\text{G}_{\text{O}_2\text{gas}}) = -402.05 \text{ kJ/mol}$;

Substance	$\Delta H^\circ_{\text{H}} / \text{kJ/mol}$	$\Delta S^\circ_{\text{H}} / \text{mol/K}$	$\Delta G^\circ_{\text{H}} / \text{kJ/mol}$
$\text{C}_6\text{H}_{12}\text{O}_{6\text{aq}}$	-1263,78	269,45	-919,96
Glc	-1267,13	-2901,49	-402,05

2006, Massachusetts Technology Inst. Albery [8] pH=7,36. CRC 2010 $\Delta G^\circ_{\text{Albery}} + (6\text{G}_{\text{Cgraph}} + 6\text{G}_{\text{H}_2\text{gas}} + 3\text{G}_{\text{O}_2\text{gas}}) = \text{G}_{\text{C}_6\text{H}_{12}\text{O}_6} = 1568 \text{ kJ/mol}$;

Calculation of free energy in glucose oxidation $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_{2\text{aqua}} + 12\text{H}_2\text{O} = 6\text{H}_3\text{O}^+ + 6\text{HCO}_3^-$ in three ways:

1) Albery data at pH=7.36 $\Delta G^\circ_{\text{Albery}} = \text{G}_{\text{C}_6\text{H}_{12}\text{O}_6} - (6\text{G}_{\text{Cgraph}} + 6\text{G}_{\text{H}_2\text{gas}} + 3\text{G}_{\text{O}_2\text{gas}}) = -402,05 \text{ kJ/mol}$ standard free energy content in the mole is:

$$\text{G}_{\text{C}_6\text{H}_{12}\text{O}_6} = \Delta G^\circ_{\text{Albery}} + (6\text{G}_{\text{Cgraph}} + 6\text{G}_{\text{H}_2\text{gas}} + 3\text{G}_{\text{O}_2\text{gas}}) = -402,05 + (6 \cdot 91,26 + 6 \cdot 85,6 + 3 \cdot 303) = 1568 \text{ kJ/mol},$$

2) Lehninger's $\Delta \text{G}_{\text{C}_6\text{H}_{12}\text{O}_6} = 6 \cdot \text{G}_{\text{H}_3\text{O}^+} + 6 \cdot \text{G}_{\text{HCO}_3^-} - (\text{G}_{\text{StandardC}_6\text{H}_{12}\text{O}_6} + 6 \cdot \text{G}_{\text{O}_2\text{aqua}} + 12 \cdot \text{G}_{\text{H}_2\text{O}}_{\text{Biochem}}) = -2840 \text{ kJ/mol}$ standard content in the mole of glucose $\text{G}_{\text{StandardC}_6\text{H}_{12}\text{O}_6} = 6 \cdot (22,44 + 56,08) - (-2840 + 6 \cdot 330 + 12 \cdot 0) = 1331 \text{ kJ/mol}$ and

3) free energy content $\Delta \text{G}_{\text{arterial_C}_6\text{H}_{12}\text{O}_6} = 6 \cdot \text{G}_{\text{H}_3\text{O}^+} + 6 \cdot \text{G}_{\text{HCO}_3^-} - (\text{G}_{\text{arterial_C}_6\text{H}_{12}\text{O}_6} + 6 \cdot \text{G}_{\text{O}_2\text{aqua}} + 12 \cdot \text{G}_{\text{H}_2\text{O}}) = -3064 \text{ kJ/mol}$ per mole of glucose at homeostasis $\text{G}_{\text{arterial_C}_6\text{H}_{12}\text{O}_6} = 6 \cdot (22,44 + 56,08) - (-3064 + 6 \cdot 88,22 + 12 \cdot 85,64) = 1978 \text{ kJ/mol}$.

Generated $6\text{HCO}_3^- + 6\text{H}_3\text{O}^+$ ions drive reactants $6\text{O}_{2\text{aqua}}$ and $6\text{H}_2\text{O}$ through membranes aquaporins channels by osmosis against the concentration gradients but transporting ions $6\text{HCO}_3^- + 6\text{H}_3\text{O}^+$ opposite down the gradients through bicarbonate and proton channels consuming produced free energy $\Delta \text{G}_{\text{arterial}} = -3064 \text{ kJ/mol}$.

Absolute potential and free energy values include accounting for hydroxonium H_3O^+ and water H_2O .

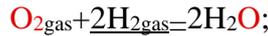
Inverse half reaction of oxygen with free energy $G_{O_2\text{aqua}}=330 \text{ kJ/mol}$ reduction $O_{2\text{aqua}}+4H_3O^++4e^-=5H_2O$ with standard potential $-E_{O_2}=-1.0868 \text{ V}$: oxidize four metal hydrogen atoms with free energy $G_{H(Pt)}=48.56 \text{ kJ/mol}$ within Nernst's half reaction: $4(Pt)H+4H_2O=4H_3O^++4e^-$ and with standard potential $E_{H}^{\circ}=-0.27073 \text{ V}$. Standard free energy change in reaction $O_{2\text{aqua}}+4(Pt)H=2H_2O$ is

$$\Delta G_{Hess\ 2H_2O}=2G_{H_2O}-4G_{H(Pt)}-G_{O_2\text{aqua}}=2*0-(4*48.56+330)=-524.24=2*-262 \text{ kJ/mol}.$$

Standard potentials sum

$\Delta G_{eq}=(E_{H}^{\circ}-E_{O_2}^{\circ})\cdot F\cdot 4=(-0.27073-1.0868)*96485*4=-1.3575*96485*4=-523.925=2*-262 \text{ kJ/mol}$ let independently from Hess law calculate formation from free elements oxygen $O_{2\text{aqua}}$ and metal hydrogen (Pt)H free absolute energy change $\Delta G_{eq(Pt)H\ H_2O}=-262 \text{ kJ/mol}$, which is coincident with absolute free energy $G_{H(Pt)}=48.56 \text{ kJ/mol}$ determination for free elements $O_{2\text{aqua}}$, (Pt)H and using absolute standard potential for oxidation – reduction.

Hydrogen standard free energy in water solution $G_{H_2\text{aqua}}=103.24 \text{ kJ/mol}$ is from Alberty data pH=7,36. [8]



$$\Delta G_{Hess\ CRC\ \text{aqua}}=2\Delta G^{\circ}_{H_2O}-2\Delta G^{\circ}_{H_2\text{aqua}}-\Delta G^{\circ}_{O_2\text{aqua}}=2*(-237,191)-(2*99,13/2+16,4)=-589,91=2*-295 \text{ kJ/mol}. [1]$$

Substance	$\Delta H^{\circ}_H, \text{ kJ/mol}$	$\Delta S^{\circ}_H, \text{ J/mol/K}$	$\Delta G^{\circ}_H, \text{ kJ/mol}$
H_2O	-285.85	69.9565	-237.191
H_2O	-286.65	-453.188	-151.549
H_3O^+	-285.81	-3.854	-213.2746
$H_2(\text{aq})$	23.4	-130	99.13
$H_2(\text{aq})$	-5.02	-363.92	103.24
$E^{\circ}(Pt)H$	-0.27073	-1.0868	48,56
$O_{2\text{aqua}}$	-11.70	-94.2	16.4
$O_{2\text{aqua}}$	-11.715	110.876	16.4

CRC

$$\Delta G_{eq}=-262 \text{ kJ/mol}; \Delta G_{Hess}=-295 \text{ kJ/mol}$$

The reaction $4(Pt)H+O_{2\text{aqua}}=2H_2O$; absolute free energy change

$$\text{is } |\Delta G_{eq}=-262 \text{ kJ/mol}| < |\Delta G_{Hess}=-295 \text{ kJ/mol}|;$$

2006, Massachusetts Technology Inst. Alberty [8]

$$G_{H(Pt)}=(2G_{H_2O}-\Delta G_{eq\ 2H_2O}-G_{O_2\text{aqua}})/4=48,56 \text{ kJ/mol}$$

$$K_{eq\ 2H_2O}=K_{OxRed}=\exp(-\Delta G_{OxRed}/R/T)=\exp(261960.6/8.3144/298.15)=\exp(105.675)=7.832*10^{45};$$

Exothermic and exoergic $O_{2\text{aqua}}$ reduction with metallic hydrogen

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

$\Delta G_{Hess\ \text{Aqua}\ H_2O}=-295 \text{ kJ/mol}$, $\Delta G_{Alberty\ H_2O_2}=-246 \text{ kJ/mol}$, but minimized reaching equilibrium $\Delta G_{eq\ 2H_2O}=-262 \text{ kJ/mol}$ and $\Delta G_{eq\ \text{Standart}\ H_2O_2}=-228.6 \text{ kJ/mol}$ mixtures constants $K_{eq\ 2H_2O}=7.832*10^{45}$ and $K_{eq\ \text{Standard}\ H_2O_2}=1.11*10^{40}$.

The equilibrium state minimum is Prigogine attractor for all irreversible states.

Free energy change minimum reaching establish equilibrium state.

Red $H_2O_2+2H_2O=O_{2\text{aqua}}+2H_3O^++2e^-$; $E^{\circ}_{H_2O_2}=0.5268 \text{ V}$ Alberta University

Edmonton Canada. [19] Peroxide H_2O_2 in medium pH=7.36 absolute inverse

standard $H_2O_2+2H_3O^++2e^-=4H_2O$ potential is $-E^{\circ}_{Ox}=-1.7113 \text{ V}$ Suhotina [17]

Summary dismutation $2H_2O_{2aq}=>O_{2\text{aqua}}+2H_2O+Q+\Delta G$;



$$\text{Standard sum } \Delta G_{eq\ \text{Standart}\ H_2O_2}=(E_{Red}-E_{Ox})\cdot F\cdot n=(0.5268-1.7113)*96485*2=(-1.1845)*96485*2=-228.57 \text{ kJ/mol};$$

$$K_{eq\ \text{Standart}\ H_2O_2}=\frac{[O_{2\text{aqua}}]\cdot[H_2O]^2}{[H_2O_2]_{\text{aqua}}^2}=K_{H_2O_2}=\exp(-\Delta G_{eq}/R/T)=\exp(228573/8.3144/298.15)=1.11*10^{40}\dots\dots$$

$$E^{\circ}_{H_2O_2}=E^{\circ}-0,0591/2*\lg(1/[H_2O]^2)+0,10166-0,372=0,6945-0,02955*\lg(1/55,3^2)+0,10166-0,37239=0,5268 \text{ V};$$

$$E^{\circ}_{H_2O_2\text{Ox}}=E^{\circ}-0,0591/2*\lg(1/[H_2O]^4)+0,10166-0,372=1,776-0,02955*\lg(1/55,3^4)+0,10166-0,37239=1,7113 \text{ V};$$

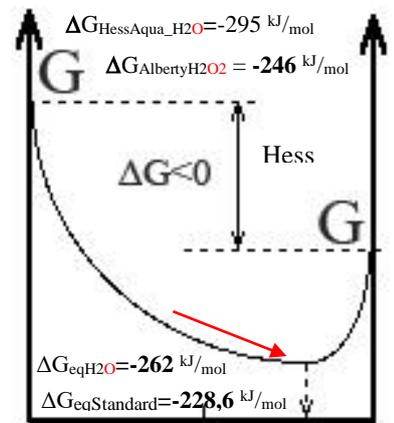
$$E_{H_2O_2}=E^{\circ}+0,0591/2*\lg([O_{2\text{aqua}}]\cdot[H_3O^+]^2/[H_2O_2]/[H_2O]^2)=0,5278+0,0591/2*\lg(6*10^{(-5)}*10^{(-7.36*2)}/1/55,3^2)=-0,1349 \text{ V}$$

$$E_{Ox}=E^{\circ}_{H_2O_2\text{Ox}}+0,0591/2*\lg([H_2O]^4/[H_2O_2]/[H_3O^+]^2)=-1,7123+0,0591/2*\lg(55,3^4/1/10^{(-7.36*2)})=-1,0713 \text{ V}$$

Summary of Nernst's + inverse reaction for homeostasis is

$$\Delta G_{eq\ \text{BioChem}}=(E_{Red}-E_{Ox})\cdot F\cdot n=(-0.13493-1.0703)*96485*2=(-1.2062)*96485*2=-232.76 \text{ kJ/mol};$$

$$G_{\text{Homeostasis}\ H_2O_2}=(G_{O_2\ \text{Biochem}\ \text{arteriaj}}+2*G_{H_2O\ \text{BioChemistry}}-\Delta G_{Alberty})/2=(88.04+2*85.64+232.76)/2=246.04 \text{ kJ/mol};$$



Sulfur / H₂S_{aq} red-ox systems. H₃O⁺ and [H₂O]=55.3 M accounting on absolute free energy and potential scale.

Substance	ΔH ^o _H kJ/mol	ΔS ^o _H J/mol/K	ΔG ^o _H kJ/mol
H ₂ S	-38.6	126	-76.167
HS ⁻	-16.3	67	-36.276
HS ⁻	E ^o _{↓/HS2-} =	-0.8517 V	1.35
HS ⁻	pK _{a1} =7.05	pK _{a1} =7.05	-3.072
H ₂ S	E ^o _{↓/H2S-} =	-0.9290 V	-61.09
H ₂ S	E ^o _{↓/H2S} =	-0.6715 V	88.82
H ₂ S	E ^o _{↓/H2S} =	-0.025735 V	-35.794
S _{rhombic} +	<u>2(Pt)H</u> =	H ₂ S _{aq}	-35.997
S ²⁻	E ^o _{↓/S2-} =	-0.79853V	68.45
S ²⁻	pK _{a2} =19	pK _{a2} =19	92.868

$$\Delta G_{HS-} = \Delta H_{HS-} - T \cdot \Delta S_{HS-} = -38.6 - 298.15 \cdot 0.126 = -76.167 \text{ kJ/mol};$$

$$\Delta G_{HS-} = \Delta H_{HS-} - T \cdot \Delta S_{HS-} = -16.3 - 298.15 \cdot 0.067 = -36.276 \text{ kJ/mol};$$

$$G_{HS-aq} = G_{S_{rhombic}} + 2G_{H_2O} - (\Delta G_{eqHS-aq} + G_{OH}) = 1.35 \text{ kJ/mol};$$

$$G_{HS-} = \Delta G_{eq} - G_{H_3O^+} + (G_{H_2S} + G_{H_2O}) = 50.188 - 22.44 + (-30.82 + 0) = -3.072 \text{ kJ/mol};$$

$$G_{H_2S-aq} = G_{S_{rhombic}} + 3G_{H_2O} - (\Delta G_{eqH_2S-aq} + 2G_{OH}) = -61.09 \text{ kJ/mol};$$

$$G_{H_2S-aq} = G_{S_{rhombic}} + 2G_{H_3O^+} - (\Delta G_{Hess_H_2S-aq} + 2G_{H_2O}) = 88.82 \text{ kJ/mol};$$

$$G_{H_2S-aq} = G_{S_{rhombic}} + 2G_{H_3O^+} - (\Delta G_{Hess_H_2S-aq} + 2G_{H_2O}) = -35.794 \text{ kJ/mol};$$

$$G_{H_2S-aq} = \Delta G_{HessH_2S} + (2G_{H(Pt)} + G_{S_{rhombic}}) = -35.997 \text{ kJ/mol};$$

$$G_{S_{2-aq}} = G_{S_{rhombic}} + G_{H_2O} - (\Delta G_{eqS_{2-aq}}) = 68.45 \text{ kJ/mol};$$

$$G_{S_{2-}} = \Delta G_{eq} - G_{H_3O^+} + (G_{HS-} + G_{H_2O}) = 118.38 - 22.44 + (-3.072 + 0) = 92.868 \text{ kJ/mol};$$

$$S_{2-} = S_{rhombic} + H_2O + 2e^-; E_{\downarrow/S_{2-}} = -0.79853 \text{ V Kortly, Shucha};$$

$$E_{\downarrow/S_{2-}} = E^o - 0.0591/2 \cdot \lg([H_2O]^1) + 0.10166 - 0.37239 = -0.4763 - 0.02955 \cdot \lg(55.3^{^1}) + 0.10166 - 0.37239 = -0.79853 \text{ V};$$

$$\Delta G_{eqS_{2-}} = E^o_{S_{2-}} \cdot F \cdot n = -0.79853 \cdot 96485 \cdot 2 = -154.09 \text{ kJ/mol}; G_{S_{rhombic}} = -85.64 \text{ kJ/mol};$$

$$\Delta G_{eqS_{2-aq}} = G_{S_{rhombic}} + G_{H_2O} - (G_{S_{2-aq}}) = -85.64 + 0 - (68.25) = -154.09 \text{ kJ/mol};$$

$$G_{S_{2-aq}} = G_{S_{rhombic}} + G_{H_2O} - (\Delta G_{eqS_{2-aq}}) = -85.64 + 0 - (-154.09) = 68.25 \text{ kJ/mol};$$

$$HS^- + OH^- = S_{rhombic} + 2H_2O + 2e^-; CRC 2010 E^o_{\downarrow/HS-} = -0.8517 \text{ V};$$

$$E^o_{\downarrow/HS-} = E^o - 0.0591/2 \cdot \lg([H_2O]^2) + 0.10166 - 0.37239 = -0.478 - 0.02955 \cdot \lg(55.3^{^2}) + 0.10166 - 0.37239 = -0.8517 \text{ V};$$

$$\Delta G_{eqHS-} = E_{HS-} \cdot F \cdot n = -0.8517 \cdot 96485 \cdot 2 = -164.35 \text{ kJ/mol};$$

$$\Delta G_{eqHS-aq} = G_{S_{rhombic}} + 2G_{H_2O} - (G_{HS-aq} + G_{OH}) = -85.64 + 2 \cdot 0 - (1.35 + 77.36) = -164.35 \text{ kJ/mol};$$

$$G_{HS-aq} = G_{S_{rhombic}} + 2G_{H_2O} - (\Delta G_{eqHS-aq} + G_{OH}) = -85.64 + 2 \cdot 0 - (-164.35 + 77.36) = 1.35 \text{ kJ/mol};$$

$$H_2S_{aq} + 2H_2O = S_{rhombic} + 2H_3O^+ + 2e^-; E^o_{\downarrow/H_2S} = -0.025735 \text{ V Suchotina}_1 < pH < 7;$$

$$E^o_{\downarrow/H_2S} = E^o - 0.0591/2 \cdot \lg(1/[H_2O]^2) + 0.10166 - 0.37239 = 0.142 - 0.02955 \cdot \lg(1/55.3^{^2}) + 0.10166 - 0.37239 = -0.025735 \text{ V};$$

$$\Delta G_{eqH_2S} = E^o_{H_2S} \cdot F \cdot n = -0.025735 \cdot 96485 \cdot 2 = -4.966 \text{ kJ/mol};$$

$$\Delta G_{eqH_2S-aq} = G_{S_{rhombic}} + 2G_{H_3O^+} - (G_{H_2S-aq} + 2G_{H_2O}) = -85.64 + 2 \cdot 22.44 - (-35.794 + 2 \cdot 0) = -4.966 \text{ kJ/mol};$$

$$G_{H_2S-aq} = G_{S_{rhombic}} + 2G_{H_3O^+} - (\Delta G_{Hess_H_2S-aq} + 2G_{H_2O}) = -85.64 + 2 \cdot 22.44 - (-4.966 + 2 \cdot 0) = -35.794 \text{ kJ/mol};$$

pK_a=7.0 Wikipedia; CRC2010 pK_{a1}=7.05; pK_{a2}=19

$$pK_{a1} = 7.05 \quad H_2S + H_2O = HS^- + H_3O^+; K_{eq1} = K_{a1}/[H_2O] = 10^{-(7.05)}/55.3 = 0.000000001612;$$

$$\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = -8.3144 \cdot 298.15 \cdot \ln(0.000000001612) = G_{HS-} + G_{H_3O^+} - (G_{H_2S} + G_{H_2O}) = 50.188 \text{ kJ/mol};$$

$$\Delta G_{eq} = G_{HS-} + G_{H_3O^+} - (G_{H_2S} + G_{H_2O}) = -3.072 + 22.44 - (-30.82 + 0) = 50.188 \text{ kJ/mol};$$

$$G_{HS-} = \Delta G_{eq} - G_{H_3O^+} + (G_{H_2S} + G_{H_2O}) = 50.188 - 22.44 + (-30.82 + 0) = -3.072 \text{ kJ/mol};$$

$$pK_{a2} = 19 \quad HS^- + H_2O = S^{2-} + H_3O^+; K_{eq1} = K_{a1}/[H_2O] = 10^{-(19)}/55.3 = 10^{-(20.74)};$$

$$\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = -8.3144 \cdot 298.15 \cdot \ln(10^{-(20.74)}) = G_{S_{2-}} + G_{H_3O^+} - (G_{HS-} + G_{H_2O}) = 118.38 \text{ kJ/mol};$$

$$\Delta G_{eq} = G_{S_{2-}} + G_{H_3O^+} - (G_{HS-} + G_{H_2O}) = 92.868 + 22.44 - (-3.072 + 0) = 118.38 \text{ kJ/mol};$$

$$G_{S_{2-}} = \Delta G_{eq} - G_{H_3O^+} + (G_{HS-} + G_{H_2O}) = 118.38 - 22.44 + (-3.072 + 0) = 92.868 \text{ kJ/mol};$$

Sulfur reduction inverse potential: S_{rhombic} + 2H₃O⁺ + 2e⁻ = H₂S_{aq} + 2H₂O; -E^o_s = -0.025735 V;

$$2(Pt)H + 2H_2O = 2H_3O^+ + 2e^-; E^o_H = -0.27073 \text{ V}; S_{rhombic} + 2(Pt)H = H_2S_{aq};$$

$$\Delta G_{eq} = (E^o_H - E^o_s) \cdot F \cdot 1 \cdot 2 = (-0.27073 + 0.025735) \cdot 96485 \cdot 2 = -0.244995 \cdot 96485 \cdot 2 = -47.277 \text{ kJ/mol};$$

$$G_{H_2S-aq} = \Delta G_{HessH_2S} + (2G_{H(Pt)} + G_{S_{rhombic}}) = -47.277 + (2 \cdot 48.46 - 85.64) = -35.997 \text{ kJ/mol}; \text{ 2nd page.}$$

Nernst's half: H₂S_{aq} + 2H₂O = S_{rhombic} + 2H₃O⁺ + 2e⁻ has absolute standard potential E^o_{H₂S} = -0.025735 V

for free energy change: ΔG_{eqH₂S} = E^o_{H₂S} · F · n = -0.025735 · 96485 · 2 = -4.966 kJ/mol

Expression value from Hess law for free energy change to hydrogen sulfide aqua solution in half reaction is

$$\Delta G_{Hess_H_2S-aq} = G_{S_{rhombic}} + 2G_{H_3O^+} - (G_{H_2S-aq} + 2G_{H_2O}) = -85.64 + 2 \cdot 22.44 - (-35.794 + 2 \cdot 0) = -4.966 \text{ kJ/mol};$$

than absolute value is: G_{H₂S-aq} = G_{S_{rhombic}} + 2G_{H₃O⁺} - (ΔG_{Hess_{H₂S-aq}} + 2G_{H₂O}) = -85.64 + 2 · 22.44 - (-4.966 + 2 · 0) = -35.794 kJ/mol.

Formation from elements S_{rhombic} + H₂gas = H₂S_{gas} shows energy content in one mol G_{S_{rhombic}} = -85.64 kJ/mol; [1,6]

Formation energy change is ΔG_{Hess_{H₂S-gas}} = G^o_{H₂S-gas} - (HessG^o_{S_{rhombic}} + HessG^o_{H₂}) = -20.6 - (0 + 0) = -20.6 kJ/mol. [1]

Sulfur energy content in mol is G_{S_{rhombic}} = G^o_{H₂S-gas} - (ΔG_{Hess_{H₂S-gas}} + G_{H₂gas}) = -20.6 - (-20.6 + 85.64) = -85.64 kJ/mol;

Absolute potential and free energy values include accounting for hydroxonium H_3O^+ and water H_2O .

Alberty data are given on absolute values for elements:

$G_{\text{S}_{\text{rombic}}} = -85.64$ kJ/mol; $G_{\text{O}_2\text{gas}} = 303$ kJ/mol; $G_{\text{H}_2\text{gas}} = -85.6$ kJ/mol; $\Delta G^\circ_{\text{SO}_4\text{Form}} = -747.75$ kJ/mol relative to water and carbon dioxide gas as zero $G_{\text{H}_2\text{O}} = G_{\text{CO}_2\text{gas}} = G_{\text{e}} = 0$ kJ/mol reference scale. Formation from elements sulfuric acid and sulfates: $\text{S}_{\text{rombic}} + 2\text{O}_2\text{gas} + \text{H}_2\text{gas} = \text{H}_2\text{SO}_4\text{aq}$; $\Delta G^\circ_{\text{H}_2\text{SO}_4\text{Form}} = G_{\text{H}_2\text{SO}_4} - (G_{\text{S}_{\text{rombic}}} + 2G_{\text{O}_2} + G_{\text{H}_2\text{gas}}) = -690.0$ kJ/mol; [1]

$$G_{\text{H}_2\text{SO}_4} = \Delta G^\circ_{\text{H}_2\text{SO}_4\text{Form}} + (G_{\text{S}_{\text{rombic}}} + 2G_{\text{O}_2} + G_{\text{H}_2\text{gas}}) = -690.0 + (-85.64 + 2 \cdot 303 + 85.6) = -84.04 \text{ kJ/mol}.$$

$$\text{S}_{\text{rombic}} + 2\text{O}_2\text{gas} + \text{H}_2\text{gas}/2 = \text{HSO}_4^-; \Delta G^\circ_{\text{HSO}_4\text{Form}} = G_{\text{HSO}_4^-} - (G_{\text{S}_{\text{rombic}}} + 2G_{\text{O}_2} + 0.5G_{\text{H}_2\text{gas}}) = -755.9 \text{ kJ/mol}.$$

$$G_{\text{HSO}_4^-} = \Delta G^\circ_{\text{HSO}_4\text{Form}} + (G_{\text{S}_{\text{rombic}}} + 2G_{\text{O}_2} + 0.5G_{\text{H}_2\text{gas}}) = -755.9 + (-85.64 + 2 \cdot 303 + 85.6/2) = -192.74 \text{ kJ/mol};$$

$$\text{S}_{\text{rombic}} + 2\text{O}_2\text{gas} = \text{SO}_4^{2-}; \Delta G^\circ_{\text{SO}_4\text{Form}} = G_{\text{SO}_4^{2-}} - (G_{\text{S}_{\text{rombic}}} + 2G_{\text{O}_2}) = -747.75 \text{ kJ/mol};$$

$$G_{\text{SO}_4^{2-}} = \Delta G^\circ_{\text{SO}_4\text{Form}} + (G_{\text{S}_{\text{rombic}}} + 2G_{\text{O}_2}) = -747.75 - 85.64 + 2 \cdot 303 = -227.39 \text{ kJ/mol};$$

Equilibrium constants in mole fractions $K_{\text{eq}} = K_a/[\text{H}_2\text{O}]$ calculate dividing the acid constant by water $[\text{H}_2\text{O}]$.

Protolysis $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} = \text{HSO}_4^- + \text{H}_3\text{O}^+$ acid $\text{p}K_{a1} = -2.8$ and equilibrium is $K_{\text{eq}1} = K_{a1}/[\text{H}_2\text{O}] = 10^{-(2.8)}/55.3 = 11.41$;

$$\Delta G_{\text{eqH}_2\text{SO}_4} = -R \cdot T \cdot \ln(K_{\text{eq}1}) = -8.3144 \cdot 298.15 \cdot \ln(11.41) = G_{\text{HSO}_4^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{H}_2\text{SO}_4} + G_{\text{H}_2\text{O}}) = -6.035 \text{ kJ/mol};$$

$$\Delta G_{\text{eqH}_2\text{SO}_4} = G_{\text{HSO}_4^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{H}_2\text{SO}_4} + G_{\text{H}_2\text{O}}) = G_{\text{HSO}_4^-} + 22,44 - (-84,04 - 151,549) = -6,035 \text{ kJ/mol};$$

$$G_{\text{HSO}_4^-} = G_{\text{HSO}_4^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{H}_2\text{SO}_4} + G_{\text{H}_2\text{O}}) = -6,035 - 22,44 + (-84,04 - 151,549) = -264,06 \text{ kJ/mol};$$

$\text{HSO}_4^- + \text{H}_2\text{O} = \text{SO}_4^{2-} + \text{H}_3\text{O}^+$; $\text{p}K_{a2} = 1.99$; $K_{\text{eq}2} = K_{a2}/[\text{H}_2\text{O}] = 10^{-(1.99)}/55.3 = 0.0001850$;

$$\Delta G_{\text{eqHSO}_4} = -R \cdot T \cdot \ln(K_{\text{eq}2}) = -8.3144 \cdot 298.15 \cdot \ln(0.0001850) = G_{\text{SO}_4^{2-}} + G_{\text{H}_3\text{O}^+} - (G_{\text{HSO}_4^-} + G_{\text{H}_2\text{O}}) = 21.307 \text{ kJ/mol};$$

$$\Delta G_{\text{eqHSO}_4} = G_{\text{SO}_4^{2-}} + G_{\text{H}_3\text{O}^+} - (G_{\text{HSO}_4^-} + G_{\text{H}_2\text{O}}) = -747,75 + 22,44 - (G_{\text{HSO}_4^-} - 151,549) = 21,307 \text{ kJ/mol};$$

$$G_{\text{HSO}_4^-} = G_{\text{SO}_4^{2-}} + G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqHSO}_4} + G_{\text{H}_2\text{O}}) = -747,75 + 22,44 - (21,307 - 151,549) = -595,068 \text{ kJ/mol};$$

$$\Delta G_{\text{eqHSO}_4} = G_{\text{SO}_4^{2-}} + G_{\text{H}_3\text{O}^+} - (G_{\text{HSO}_4^-} + G_{\text{H}_2\text{O}}) = G_{\text{SO}_4^{2-}} + 22,44 - (-264,06 - 151,549) = 21,307 \text{ kJ/mol};$$

$$G_{\text{SO}_4^{2-}} = \Delta G_{\text{eqHSO}_4} - G_{\text{H}_3\text{O}^+} + (G_{\text{HSO}_4^-} + G_{\text{H}_2\text{O}}) = 21,307 - 22,44 + (-264,06 - 151,549) = -416,74 \text{ kJ/mol};$$

Formation from free elements $\text{S}_{\text{rombic}} + 1.5\text{O}_2\text{gas} + \text{H}_2\text{gas} = \text{H}_2\text{SO}_3\text{aq}$ and solubility $\text{SO}_2^{\text{gas}} + \text{H}_2\text{O} = \text{H}_2\text{SO}_3\text{aq}$.

$$\Delta G^\circ_{\text{H}_2\text{SO}_3\text{Form}} = G_{\text{H}_2\text{SO}_3} - (G_{\text{S}_{\text{rombic}}} + 1.5\Delta G_{\text{O}_2} + G_{\text{H}_2\text{gas}}) = G_{\text{H}_2\text{SO}_3} - (-85.64 + 1.5 \cdot 303 + 85.6) = -527.3675 \text{ kJ/mol};$$

$$G_{\text{H}_2\text{SO}_3} = \Delta G^\circ_{\text{H}_2\text{SO}_3\text{Form}} + (G_{\text{S}_{\text{rombic}}} + 1.5\Delta G_{\text{O}_2} + G_{\text{H}_2\text{gas}}) = -527.3675 + (-85.64 + 1.5 \cdot 303 + 85.6) = -72.9075 \text{ kJ/mol};$$

$$G_{\text{HSO}_3^-} = \Delta G^\circ_{\text{HSO}_3\text{Form}} + (G_{\text{S}_{\text{rombic}}} + 1.5\Delta G_{\text{O}_2} + G_{\text{H}_2\text{gas}}/2) = -486.5 + (-85.64 + 1.5 \cdot 303 + 85.6/2) = -74.84 \text{ kJ/mol};$$

$$G_{\text{SO}_3} = \Delta G^\circ_{\text{SO}_3\text{Form}} + G_{\text{S}_{\text{rombic}}} + 1.5\Delta G_{\text{O}_2} = -490.38 - 85.64 + 1.5 \cdot 303 = -121.52 \text{ kJ/mol};$$

Equilibrium constants in mole fractions $K_{\text{eq}} = K_a/[\text{H}_2\text{O}]$ calculate dividing the acid constant by water $[\text{H}_2\text{O}]$.

$$\text{H}_2\text{SO}_3 + \text{H}_2\text{O} = \text{HSO}_3^- + \text{H}_3\text{O}^+; \text{p}K_{a1} = 1.85; K_{\text{eq}1} = K_{a1}/[\text{H}_2\text{O}] = 10^{-(1.85)}/55.3 = 0.0002554;$$

$$\Delta G_{\text{eqH}_2\text{SO}_3} = -R \cdot T \cdot \ln(K_{\text{eq}1}) = -8.3144 \cdot 298.15 \cdot \ln(0.0002554) = G_{\text{HSO}_3^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{H}_2\text{SO}_3} + G_{\text{H}_2\text{O}}) = 20.5075 \text{ kJ/mol};$$

$$G_{\text{H}_2\text{SO}_3} = G_{\text{HSO}_3^-} + G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqH}_2\text{SO}_3} + G_{\text{H}_2\text{O}}) = -74.84 + 22.44 - (20.5075 + 0) = -72.9075 \text{ kJ/mol};$$

$$\text{HSO}_3^- + \text{H}_2\text{O} = \text{SO}_3^{2-} + \text{H}_3\text{O}^+; \text{p}K_{a2} = 7.21; K_{\text{eq}2} = K_{a2}/[\text{H}_2\text{O}] = 10^{-(7.21)}/55.3 = 0.000000001115;$$

$$\Delta G_{\text{eqHSO}_3} = -R \cdot T \cdot \ln(K_{\text{eq}2}) = -8.3144 \cdot 298.15 \cdot \ln(0.000000001115) = G_{\text{SO}_3^{2-}} + G_{\text{H}_3\text{O}^+} - (G_{\text{HSO}_3^-} + G_{\text{H}_2\text{O}}) = 51.1 \text{ kJ/mol};$$

$$G_{\text{HSO}_3^-} = G_{\text{SO}_3^{2-}} + G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqHSO}_3} + G_{\text{H}_2\text{O}}) = -121.52 + 22.44 - (51.1 + 0) = -150.2 \text{ kJ/mol};$$

Oxidation standard potential of sulfurous acid electrode $\text{H}_2\text{SO}_3 + 4\text{H}_2\text{O} = \text{HSO}_4^- + 3\text{H}_3\text{O}^+ + 2\text{e}^-$ $E^\circ_{\text{H}_2\text{SO}_3} = 0.1073$ V.

$$E^\circ_{\text{H}_2\text{SO}_3} = E^\circ + 0.10166 - 0.0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^4) - 0.37239 = 0.172 - 0.0591/2 \cdot \lg(1/55.3^4) + 0.10166 - 0.37239 = 0.10726 \text{ V};$$

$$E_{\text{H}_2\text{SO}_3} = E^\circ_{\text{H}_2\text{SO}_3} + \frac{0.0591}{2} \cdot \log \frac{[\text{HSO}_4^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{H}_2\text{SO}_3] \cdot [\text{H}_2\text{O}]^5} = 0.10726 \text{ V} + \frac{0.0591}{2} \cdot \log \frac{[\text{HSO}_4^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{H}_2\text{SO}_3] \cdot [\text{H}_2\text{O}]^5}$$

$$\Delta G_{\text{eqH}_2\text{SO}_3} = E^\circ_{\text{HSO}_3^-} \cdot F \cdot 2 = 0.107260 \cdot 96485 \cdot 2 = 20.69796 \text{ kJ/mol};$$

$$\Delta G_{\text{eqHS}_2\text{O}_3} = G_{\text{HSO}_3^-} + 3G_{\text{H}_3\text{O}^+} - (G_{\text{H}_2\text{SO}_3} + 4G_{\text{H}_2\text{O}}) = -192.74 + 3 \cdot 22.44 - (-146.118 + 4 \cdot 0) = 20.69796 \text{ kJ/mol};$$

$$G_{\text{H}_2\text{SO}_3} = G_{\text{HSO}_4^-} + 3G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqH}_2\text{SO}_3} + 4G_{\text{H}_2\text{O}}) = -192.74 + 3 \cdot 22.44 - (20.69796 + 4 \cdot 0) = -146.118 \text{ kJ/mol};$$

$$G_{\text{HSO}_4^-} = \Delta G_{\text{eqH}_2\text{SO}_3} - 3G_{\text{H}_3\text{O}^+} + (G_{\text{H}_2\text{SO}_3} + 4G_{\text{H}_2\text{O}}) = 20.69796 - 3 \cdot 22.44 + (-146.118 + 4 \cdot 0) = -192.74 \text{ kJ/mol};$$

Solubility constants in mol fractions $K_{\text{eq}} = K_{\text{sp}}/[\text{H}_2\text{O}]$ calculate dividing saturate product with water $[\text{H}_2\text{O}]$.

$\text{SO}_2^{\text{gas}} + \text{H}_2\text{O} = \text{H}_2\text{SO}_3\text{aq}$; $K_{\text{sp}} = [\text{H}_2\text{SO}_3]/[\text{SO}_2^{\text{gas}}]/[\text{H}_2\text{O}] = 1.46724/1/51.64 = 0.028413$, as saturated state dissolute

94 g/L SO_2 $M = 64.066$ g/mol $[\text{SO}_2] = 94/64.066 = 1.46724$ M sulfurous acid $M_{\text{H}_2\text{SO}_3} = 82.075$ g/mol with density

1.05 g/mL $m_{\text{solution}} = 1050$ g/L and $m_{\text{acid}} = [\text{SO}_2] \cdot M_{\text{H}_2\text{SO}_3} = 1.46724 \text{ M} \cdot 82.075 \text{ g/mol} = 120.4327$ g/L.

Water concentration is $m_{\text{H}_2\text{O}} = 1050 - 120.4327 = 929.5673$ g; $n_{\text{H}_2\text{O}} = 929.5673/18 = 51.64$ M. Free energy change is:

$$\Delta G_{\text{spH}_2\text{SO}_3} = -R \cdot T \cdot \ln(K_{\text{sp}}) = -8.3144 \cdot 298.15 \cdot \ln(0.028413) = G_{\text{H}_2\text{SO}_3} - (G_{\text{SO}_2} + G_{\text{H}_2\text{O}}) = 8.82727 \text{ kJ/mol};$$

Formation from free elements $S_{\text{rombic}} + O_{2\text{gas}} = SO_2$; $\Delta G^{\circ}_{SO_2\text{Form}} = G_{SO_2} - (-85.64 + 303) = -370.82 \text{ kJ/mol}$;

$$G_{SO_2} = \Delta G^{\circ}_{SO_2\text{Form}} + (G_{S_{\text{rombiks}}} + G_{O_2}) = -370.82 + (-85.64 + 303) = -153.46 \text{ kJ/mol}$$

$$\Delta G_{\text{spH}_2\text{SO}_3} = G_{\text{H}_2\text{SO}_3} - (G_{SO_2} + G_{\text{H}_2\text{O}}) = -72.9075 - (-81.73477 + 0) = 8.82727 \text{ kJ/mol}$$

$$G_{SO_2} = G_{\text{H}_2\text{SO}_3} - (\Delta G_{\text{spH}_2\text{SO}_3} + G_{\text{H}_2\text{O}}) = -72.9075 - (8.82727 + 0) = -81.73477 \text{ kJ/mol}$$

$$\text{HSO}_3^- + 4\text{H}_2\text{O} = \text{SO}_4^{2-} + 3\text{H}_3\text{O}^+ + 2\text{e}^-; \text{ Suchotina } 2 = \text{pH} < 7 \text{ } E^{\circ}_{\text{HSO}_4^-} = 0.10726 \text{ V}$$

$$E^{\circ}_{\text{SO}_4} = E^{\circ} + 0.10166 - 0.0591/2 * \lg(1/[\text{H}_2\text{O}]^4) - 0.37239 = 0.172 - 0.0591/2 * \lg(1/55.3^4) + 0.10166 - 0.37239 = 0.10726 \text{ V}$$

$$E_{\text{HSO}_4} = E^{\circ}_{\text{HSO}_4} + 0.0591/2 * \log([\text{HSO}_4^-] * [\text{H}_3\text{O}^+]^3 / [\text{H}_2\text{SO}_3\text{aq}] / [\text{H}_2\text{O}]^4) = 0.10726 \text{ V} + 0.0591/2 * \log \frac{[\text{SO}_4^{2-}] \cdot [\text{H}_3\text{O}^+]^3}{[\text{HSO}_3^-] \cdot [\text{H}_2\text{O}]^4}$$

$$\Delta G_{\text{eqSO}_4} = E^{\circ}_{\text{HSO}_4} \cdot F \cdot 2 = 0.10726 * 96485 * 2 = 20.69796 \text{ kJ/mol}$$

$$\Delta G_{\text{eqSO}_4} = G_{SO_4} + 3G_{\text{H}_3\text{O}^+} - (G_{\text{HSO}_3} + 4G_{\text{H}_2\text{O}}) = -119.5295 + 3 * 22.44 - (-72.9075 + 4 * 0) = 20.69796 \text{ kJ/mol}$$

$$G_{\text{HSO}_3} = G_{SO_4} + 3G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqSO}_4} + 4G_{\text{H}_2\text{O}}) = -119.5295 + 3 * 22.44 - (20.69796 + 4 * 0) = -72.9075 \text{ kJ/mol}$$

$$G_{SO_4} = \Delta G_{\text{eqSO}_4} - 3G_{\text{H}_3\text{O}^+} + (G_{\text{HSO}_3} + 4G_{\text{H}_2\text{O}}) = 20.69796 - 3 * 22.44 + (-72.9075 + 4 * 0) = -119.5295 \text{ kJ/mol}$$

Substance	$\Delta H^{\circ}_H, \text{kJ/mol}$	$\Delta S^{\circ}_H, \text{J/mol/K}$	$\Delta G^{\circ}_H, \text{kJ/mol}$	
H ₂ SO ₄	-814,0	156,9	-690,0	CRC;
H ₂ SO ₄		formation	-84,04	$G_{\text{H}_2\text{SO}_4} = \Delta G^{\circ}_{\text{H}_2\text{SO}_4} + G_{S_{\text{rombiks}}} + 2\Delta G_{O_2} + G_{\text{H}_2\text{gas}} + G_{\text{H}_2\text{O}} = -84,04 \text{ kJ/mol}$;
H ₂ SO ₄		pK _{a1} = -2,8	-415,04	$G_{\text{H}_2\text{SO}_4} = G_{\text{HSO}_4^-} + G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqH}_2\text{SO}_4} + G_{\text{H}_2\text{O}}) = -415,04 \text{ kJ/mol}$;
HSO ₄ ⁻	-887,3	131,8	-755,9	CRC
HSO ₄ ⁻	-	pK _{a1} = -2,8	-264,06	$G_{\text{HSO}_4^-} = \Delta G_{\text{eqH}_2\text{SO}_4} - G_{\text{H}_3\text{O}^+} + (G_{\text{H}_2\text{SO}_4} + G_{\text{H}_2\text{O}}) = -264,06 \text{ kJ/mol}$;
HSO ₄ ⁻	-	pK _{a2} = 1,99	-595,068	$G_{\text{HSO}_4^-} = G_{SO_4^{2-}} + G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqHSO}_4} + G_{\text{H}_2\text{O}}) = -595,068 \text{ kJ/mol}$;
HSO ₄ ⁻		formation	-192,74	$G_{\text{HSO}_4^-} = \Delta G^{\circ}_{\text{HSO}_4^-} + G_{S_{\text{rombiks}}} + 2\Delta G_{O_2} + G_{\text{H}_2\text{gas}}/2 = -192,74 \text{ kJ/mol}$;
HSO ₄ ⁻	E [°] _{HSO₃ =}	0,10726	-192,74	$G_{\text{HSO}_4^-} = \Delta G_{\text{eqHSO}_3} - 3G_{\text{H}_3\text{O}^+} + (G_{\text{H}_2\text{SO}_3} + 4G_{\text{H}_2\text{O}}) = -192,74 \text{ kJ/mol}$;
SO ₄ ²⁻	-907,62	-536,2	-747,75	BioTherm2006; $\Delta G_{SO_4^{2-}} = \Delta H - T * \Delta S = -907,62 - 298,15 * -0,5362 = -747,75 \text{ kJ/mol}$;
SO ₄ ²⁻	-	formation	-227,39	$G_{SO_4^{2-}} = \Delta G^{\circ}_{SO_4\text{Form}} + G_{S_{\text{rombiks}}} + 2\Delta G_{O_2} = -747,75 - 85,64 + 2 * 303 = -227,39 \text{ kJ/mol}$;
SO ₄ ²⁻	-	pK _{a2} = 1,99	-416,74	$G_{SO_4^{2-}} = \Delta G_{\text{eqHSO}_4} - G_{\text{H}_3\text{O}^+} + (G_{\text{HSO}_4^-} + G_{\text{H}_2\text{O}}) = -416,74 \text{ kJ/mol}$;
SO ₄ ²⁻	E [°] _{HSO₃ =}	0,10726	-119,53	$G_{SO_4^{2-}} = \Delta G_{\text{eqHSO}_3} - 3G_{\text{H}_3\text{O}^+} + (G_{\text{HSO}_3} + 4G_{\text{H}_2\text{O}}) = -119,5295 \text{ kJ/mol}$;
SO ₄ ²⁻	E [°] _{SO₃₂ =}	-1,2522	-213,4	$G_{SO_4^{2-}} = \Delta G_{\text{eqSO}_32-OH} - G_{\text{H}_2\text{O}} + (G_{SO_32} + 2G_{OH}) = -213,4 \text{ kJ/mol}$;
SO ₄ ²⁻	-909,3	20,1	-744,5	CRC
SO ₂ ^{gas}	-296,81	248,223	-370,82	$\Delta G_H = \Delta H_H - T * \Delta S_H = -296,81 - 298,15 * 0,248223 = -370,82 \text{ kJ/mol}$;
SO ₂ ^{gas}		formation	-153,46	$G_{SO_2} = \Delta G^{\circ}_{SO_2\text{Form}} + (G_{S_{\text{rombiks}}} + G_{O_2}) = -153,46 \text{ kJ/mol}$;
SO ₂ ^{gas}	$\Delta G_{K_{sp}} = 8,827$	0,028413	-81,735	$\Delta G_{SO_2} = G_{\text{H}_2\text{SO}_3} - (\Delta G_{\text{spH}_2\text{SO}_3} + G_{\text{H}_2\text{O}}) = -72,9075 - (8,82727 + 0) = -81,73477 \text{ kJ/mol}$;
H ₂ SO ₃		formation	-72,9075	$G_{\text{H}_2\text{SO}_3} = \Delta G^{\circ}_{\text{H}_2\text{SO}_3\text{Form}} + (G_{S_{\text{rombiks}}} + 1,5\Delta G_{O_2} + G_{\text{H}_2\text{gas}}) = -72,9075 \text{ kJ/mol}$;
H ₂ SO ₃		pK _{a1} = 1,85	-72,9075	$G_{\text{H}_2\text{SO}_3\text{aq}} = -74,84 + 22,44 - (20,5075 + 0) = -72,9075 \text{ kJ/mol}$;
H ₂ SO ₃	E [°] _{HSO₃ =}	0,10726	-146,118	$G_{\text{H}_2\text{SO}_3} = G_{\text{HSO}_4^-} + 3G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqHSO}_3} + 4G_{\text{H}_2\text{O}}) = -146,11796 \text{ kJ/mol}$;
HSO ₃ ⁻		formation	-74,84	$G_{\text{HSO}_3^-} = \Delta G^{\circ}_{\text{HSO}_3^-} + G_{S_{\text{rombiks}}} + 1,5\Delta G_{O_2} + G_{\text{H}_2\text{gas}}/2 = -74,84 \text{ kJ/mol}$;
HSO ₃ ⁻		pK _{a2} = 7,21	-150,2	$G_{\text{HSO}_3\text{-aq}} = -121,52 + 22,44 - (51,1 + 0) = -150,2 \text{ kJ/mol}$;
HSO ₃ ⁻	E [°] _{HSO₃ =}	0,10726	-72,9075	$G_{\text{HSO}_3^-} = G_{SO_4} + 3G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqHSO}_3} + 4G_{\text{H}_2\text{O}}) = -72,9075 \text{ kJ/mol}$;
HSO ₃ ⁻	-635,5	-29	-486,5	CRC
SO ₃ ²⁻	-632,19	-474,05	-490,38	BioTherm2006 $\Delta G_{H_2SO_32} = \Delta H_H - T * \Delta S_H = -632,1888 - 298,15 * -0,47405 = -490,85 \text{ kJ/mol}$;
SO ₃ ²⁻	-	formation	-121,52	$G_{SO_3^{2-}} = \Delta G_{\text{Form}} = \Delta G^{\circ}_{SO_3} + G_{S_{\text{rombiks}}} + 1,5\Delta G_{O_2} = -121,52 \text{ kJ/mol}$;
SO ₃ ²⁻	E [°] _{SO₃₂-OH =}	-1,2522	-126,48	$G_{SO_3^{2-}} = G_{SO_4^{2-}} + G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqSO}_32-OH} + 2G_{OH}) = -126,483 \text{ kJ/mol}$;

$$G_{\text{H}_2\text{SO}_3} = \Delta G^{\circ}_{\text{H}_2\text{SO}_3\text{Form}} + (G_{S_{\text{rombic}}} + 1,5\Delta G_{O_2} + G_{\text{H}_2\text{gas}}) = -72.9075 \text{ kJ/mol}$$

$$SO_3^{2-} + 2OH^- = SO_4^{2-} + H_2O + 2e^-; \text{pH} > 7; E^{\circ}_{SO_4^{2-}} = -1.2522 \text{ V Suchotina}$$

$$E^{\circ}_{SO_32-OH} = E^{\circ} + 0.10166 + 0.0591/2 * \lg(1/[\text{H}_2\text{O}]) = -0.93 + 0.10166 + 0.02955 * \lg(1/55.3) - 0.37239 = -1.2522 \text{ V}$$

$$E_{SO_32-OH} = E^{\circ}_{SO_32-OH} + \frac{0.0591}{2} \cdot \log \frac{[\text{SO}_4^{2-}] \cdot [\text{H}_2\text{O}]}{[\text{SO}_3^{2-}] \cdot [\text{OH}]^2} = -1.2522 \text{ V} + \frac{0.0591}{2} \cdot \log \frac{[\text{SO}_4^{2-}] \cdot [\text{H}_2\text{O}]}{[\text{SO}_3^{2-}] \cdot [\text{OH}]^2}$$

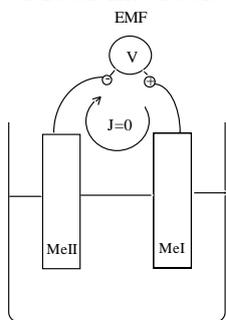
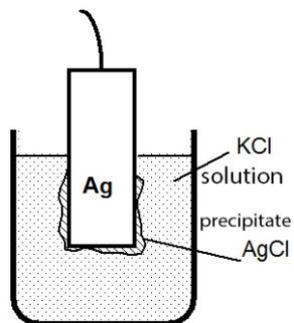
$$\Delta G_{\text{eqSO}_42-OH} = E^{\circ}_{SO_32-OH} \cdot F \cdot 2 = -1.2522 * 96485 * 2 = -241.637 \text{ kJ/mol}$$

$$\Delta G_{\text{eqSO}_32-OH} = G_{SO_4^{2-}} + G_{\text{H}_2\text{O}} - (G_{SO_3^{2-}} + 2G_{OH}) = -213.4 + 0 - (-126.483 + 2 * 77.36) = -241.637 \text{ kJ/mol}$$

$$G_{SO_3^{2-}} = G_{SO_4^{2-}} + G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqSO}_32-OH} + 2G_{OH}) = -213.4 + 0 - (-241.637 + 2 * 77.36) = -126.483 \text{ kJ/mol}$$

$$G_{SO_4^{2-}} = \Delta G_{\text{eqSO}_32-OH} - G_{\text{H}_2\text{O}} + (G_{SO_3^{2-}} + 2G_{OH}) = -241.637 - 0 + (-126.483 + 2 * 77.36) = -213.4 \text{ kJ/mol}$$

Metal/insoluble salt/ solution of salt ions II-type electrode



K^+Cl^- solution, counter-ions Cl^- of $AgCl$ insoluble salt. Nernst's half reactions for silver metal Ag . Electric potential in volt measurement by couple of electrodes **Electric Motion Force** EMF in Volts. 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 **EI** –has reactivity with solution that electrode of investigations, Standard reference electrode $EII = \text{constant}$, because chloride concentration is constant.



$E_{Ag/Ag^+}=E^\circ-0.0591/1*\lg(1/[H_2O]^1)+0.10166-0.37239=0.7994-0.0591/1*\lg(1/55.3^1)+0.10166-0.37239=\mathbf{0.6317 V}$;

$\Delta G_{eq_Ag}=E^\circ_{Ag}\cdot F\cdot 2=\mathbf{0.6317}\cdot 96485\cdot 1=\mathbf{60.95 kJ/mol}$. $\Delta G_{eq_As}=G_{Ag^+}-(G_{Ag}+G_{H_2O})=77.1-(G_{Ag}+0)=\mathbf{60.95 kJ/mol}$;

$G_{Ag}=G_{Ag^+}-(\Delta G_{eq_Ag}+G_{H_2O})=77.1-(\mathbf{60.95}+0)=\mathbf{16.15 kJ/mol}$;

$G_{Ag^+}=G_{Ag}+(\Delta G_{eq_Ag}+G_{H_2O})=\mathbf{103.8}-(\mathbf{60.95}+0)=\mathbf{42.85 kJ/mol}$;

$G_{Ag^+}=\Delta G_{eq_As}+(G_{Ag}+G_{H_2O})=\mathbf{60.95}+(\mathbf{42.855}+0)=\mathbf{103.8 kJ/mol}$;

Solubility equilibrium in mol fractions $AgCl(s)+2H_2O=Ag^++Cl^-$; $AgCl(s)+2H_2O-Cl^-=Ag^+$ absolute constant :

$K_{AbsoluteAgCl}=K_{spAgCl}/[H_2O]^2=[Ag^+][Cl^-]/[AgCl(s)]=1.77\cdot 10^{(-10)}/55.3^2=5.79\cdot 10^{-14}$;

$\Delta G_{AbsoluteAgCl}=-R\cdot T\cdot \ln(K_{AbsoluteAgCl})=-8.3144\cdot 298.15\cdot \ln(5.788\cdot 10^{(-14)})=\mathbf{75.559 kJ/mol}$;

$\Delta G_{spAgCl}=G_{Ag^+}+G_{Cl^-}-(G_{AgCl}+2G_{H_2O})=\mathbf{103.8}-183,955-(\mathbf{-155,714}+2\cdot 0)=\mathbf{75,559 kJ/mol}$;

$G_{AgCl}=G_{Ag^+}+G_{Cl^-}-(\Delta G_{spAgCl}+2G_{H_2O})=\mathbf{103.8}-183,955-(\mathbf{75,559}+2\cdot 0)=\mathbf{-155,714 kJ/mol}$;

compensate solubility water molecule on summary $Ag(s)+H_2O=Ag^++e^-$; $Ag(s)+H_2O+Cl^-=AgCl(s)+2H_2O+e^-$;

reaction $Ag(s)+Cl^-=AgCl(s)+H_2O+e^-$ with absolute standard potential $E^\circ_{Ag/AgCl}=\mathbf{-0.1514 V}$ of

$[Cl^-]=0.1 M=[K^+Cl^-]$ potassium chloride solution; [18]

$E_{Ag/AgCl}=E^\circ-0.0591/1*\lg([H_2O]^1)+0.10166-0.37239=0.2223-0.0591/1*\lg(55.3^1)+0.10166-0.37239=\mathbf{-0.1514 V}$;

$\Delta G_{eq_Ag}=E^\circ_{Ag}\cdot F\cdot 1=\mathbf{-0.1514}\cdot 96485\cdot 1=\mathbf{-14.61 kJ/mol}$,

$\Delta G_{eq_Ag}=G_{AgCl}+G_{H_2O}-(G_{Ag}+G_{Cl^-})=\mathbf{-155.71}+0-(\mathbf{G_{Ag}-183.955})=\mathbf{-14.61 kJ/mol}$;

$G_{Ag}=G_{AgCl}+G_{H_2O}-(\Delta G_{eq_Ag}+G_{Cl^-})=\mathbf{-155.71}+0-(\mathbf{-14.61-183.955})=\mathbf{42.855 kJ/mol}$;

Solubility NH_3 gas and Ag compensate each one water molecule in Nernst's half reaction products



$Ag+2NH_3\text{aq}=Ag(NH_3)_2^++H_2O+e^-$; absolute potential $E^\circ_{Ag/Ag(NH_3)_2^+}=\mathbf{0.000725 V}$; Suchotina classic $E^\circ=0.373 V$;

$E^\circ_{Ag/Ag(NH_3)_2^+}=E^\circ-0.0591/1*\lg([H_2O]^1)+0.10166-0.3=0.373-0.0591/1*\lg(55.3^1)+0.10166-0.37239=\mathbf{-0.000725 V}$;

$\Delta G_{Ag/Ag(NH_3)_2^+}=E^\circ_{Ag/Ag(NH_3)_2^+}\cdot F\cdot 1=\mathbf{-0.000725}\cdot 96485\cdot 1=\mathbf{-0.06995 kJ/mol}$;

$G_{Ag(NH_3)_2^+}=\Delta G_{Ag/Ag(NH_3)_2^+}-G_{H_2O}+(G_{Ag}+2G_{NH_3\text{aq}})=\mathbf{-0.06995}-0+(\mathbf{42.855-2\cdot 91.1})=\mathbf{-139.415 kJ/mol}$;

$2Ag+2OH^-=Ag_2O(s)+H_2O+2e^-$; absolute potential $E^\circ_{2Ag/Ag_2O}=\mathbf{0.02277 V}$; Suchotina classic $E^\circ=0.345 V$;

$E^\circ_{2Ag/Ag_2O}=E^\circ-0.0591/2*\lg([H_2O]^1)+0.10166-0.37239=0.345-0.0591/2*\lg(55.3^1)+0.10166-0.37239=\mathbf{0.02277 V}$

$\Delta G_{Ag/Ag_2O}=E^\circ_{Ag/Ag_2O}\cdot F\cdot 2=\mathbf{0.02277}\cdot 96485\cdot 2=\mathbf{4.394 kJ/mol}$;

$\Delta G_{Ag/Ag_2O}=G_{Ag_2O}+G_{H_2O}-(2G_{Ag}+2G_{OH^-})=G_{Ag_2O}+0-(2\cdot \mathbf{42.855}-2\cdot \mathbf{77.36})=\mathbf{4.394 kJ/mol}$;

$G_{Ag_2O}=\Delta G_{Ag/Ag_2O}-G_{H_2O}+(2G_{Ag}+2G_{OH^-})=\mathbf{4.394}-0+(2\cdot \mathbf{42.855}-2\cdot \mathbf{77.36})=\mathbf{-64.616 kJ/mol}$;

$E^\circ_{Ag/Ag(NH_3)_2^+}=\mathbf{0.000725 V} + \frac{[Ag(NH_3)_2^+]}{[Ag]\cdot ([NH_3]^{-2}\cdot [Ag(NH_3)_2^+])^2} E^\circ_{2Ag/Ag_2O}=\mathbf{0.02277 V} + \frac{[Ag_2O][H_2O]}{[Ag]^2\cdot [OH^-]^2}$

Viela	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
Ag	-	-	16.15
Ag	E°_{Ag/Ag^+}	-0.6317 V	42,85
Ag	$E^\circ_{Ag/AgCl}$	-0.1514 V	42.855
Ag+	105.6	72.7	77.1
Ag+	E°_{Ag}	0.6317 V	103.8
AgCl(s)	-127.01	96.25	-155.71
Cl-	-167.08	56.6	-183.955
$Ag(NH_3)_2^+$	$E^\circ_{Ag(NH_3)_2^+}$	-0.000725	-139.415
AgCl	-	-	-155.71
AgCl	ΔG_{spAgCl}	K_{spAgCl}	-155,714
Cl-	-	-	-183.955
$Ag_2O(s)$	-31.1	121.3	-11.2
$Ag_2O(s)$	E°_{Ag/Ag_2O}	0.02277V	-64.616

$G_{Ag}=G_{Ag^+}-(\Delta G_{eq_Ag}+G_{H_2O})=77.1-(\mathbf{60.95}+0)=\mathbf{16.15 kJ/mol}$;

$G_{Ag^+}=G_{Ag}+(\Delta G_{eq_Ag}+G_{H_2O})=\mathbf{103.8}-(\mathbf{60.95}+0)=\mathbf{42,85 kJ/mol}$;

$G_{Ag}=G_{AgCl}+G_{H_2O}-(\Delta G_{eq_Ag}+G_{Cl^-})=\mathbf{-155.71}+0-(\mathbf{-14.51-183.955})=\mathbf{42.855 kJ/mol}$;

CRC;

$G_{Ag^+}=\Delta G_{eq_As}+(G_{Ag}+G_{H_2O})=\mathbf{60.95}+(\mathbf{42.855}+0)=\mathbf{103.8 kJ/mol}$;

$\Delta G_{AgCl}=\Delta H_H-T\cdot \Delta S_H=-127.01-298.15\cdot 0.09625=\mathbf{-155.71 kJ/mol}$;

$\Delta G_{Cl^-}=\Delta H_H-T\cdot \Delta S_H=-167.08-298.15\cdot 0.0566=\mathbf{-183.955 kJ/mol}$;

$G_{Ag(NH_3)_2^+}=\Delta G_{Ag/Ag(NH_3)_2^+}-G_{H_2O}+(G_{Ag}+2G_{NH_3\text{aq}})=\mathbf{-139.415 kJ/mol}$;

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$G_{AgCl}=G_{Ag^+}+G_{Cl^-}-(\Delta G_{spAgCl}+2G_{H_2O})=\mathbf{-155,714 kJ/mol}$;

BioThermodynamic 2006

CRC;

$G_{Ag_2O}=\Delta G_{Ag/Ag_2O}-G_{H_2O}+(2G_{Ag}+2G_{OH^-})=\mathbf{-64.616 kJ/mol}$;

Nernst's potential studies $\underline{\text{Hg}}/\text{Hg}_2^{2+}/\text{Hg}^{2+}$, Hg_2Cl_2 , $\text{Hg}_2\text{SO}_4(\text{s})$, HgO accounting hydroxonium H_3O^+ , water H_2O .

Substance	$\Delta H^\circ_{\text{H}}$, kJ/mol	$\Delta S^\circ_{\text{H}}$, J/mol/K	$\Delta G^\circ_{\text{H}}$, kJ/mol
$\underline{\text{Hg}}$	$\text{HgO} ; \text{H}_2\text{O}_2$	75.9	35.885
$\underline{\text{Hg}}$	$E^\circ_{\text{HgCl}_2=}$	-0.1059 V	35.8
Hg_2^{2+}	-166.87	66.74	-146.97
Hg_2^{2+}	$E^\circ_{\text{Hg}/\text{Hg}_2^{2+}=}$	0.6888 V	204.52
Hg^{2+}	-170.21	-36.19	-
$\text{Hg}_2\text{SO}_4(\text{s})$	-743.1	200.7	-625.8
$\text{Hg}_2\text{SO}_4(\text{s})$	$K_{\text{AbsoluteHg}_2\text{SO}_4=}$	$10^{(-9.673)}$	-598.44
SO_4^{2-}	-907.62	-536.2	-747.75
SO_4^{2-}	$E^\circ_{\text{Hg}_2\text{SO}_4=}$	0.2918 V	-726.54
SO_4^{2-}	-909.3	20.1	-744.5
$\text{Hg}_2\text{Cl}_2(\text{s})$	-265.37	191.6	-210.7
$\text{Hg}_2\text{Cl}_2(\text{s})$	$E^\circ_{\text{HgCl}_2=}$	-0.1059 V	197.76
$\text{Hg}_2\text{Cl}_2(\text{s})$	$E^\circ_{\text{HgCl}_2=}$	-0.1059 V	255.1
$\text{HgCl}_2(\text{s})$	-224.3	146	-178.6
Cl-	-167.08	56.6	-183.955
Cl-	$K_{\text{AbsoluteHg}_2\text{Cl}_2=}$	$10^{(-23.1)}$	-112.825
$\text{HgO}(\text{s})$	-99.79	70.25	-60.3675
$\text{HgO}(\text{s})$	-90.8	70.3	-58.5
$\text{HgO}(\text{s})$	-	formation	142.3
$\text{HgO}(\text{s})$	$E^\circ_{\text{HgO}=}$	0.22423 V	147.15

$$(E^\circ_{\text{H}_2\text{O}_2\text{aqRed}} - E^\circ_{\text{HgO}}) \cdot F \cdot n = (0.5278 + 0.22318) = 0.7510 \text{ V}$$

$$G_{\text{Hg}} = G_{\text{eqRedOx}_2\text{H}_2\text{O}_2} - G_{\text{O}_2\text{aqua}} + (G_{\text{HgO}} + G_{\text{H}_2\text{O}_2}) = 35.885 \text{ kJ/mol};$$

$$G_{\text{Hg}} = (G_{\text{Hg}_2\text{Cl}_2} + G_{\text{H}_2\text{O}} - (2G_{\text{Cl}} + \Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2})) / 2 = 35.8 \text{ kJ/mol};$$

$$\Delta G_{\text{Hg}_2^{2+}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -166.87 - 298.15 \cdot 0.06674 = -146.97 \text{ kJ/mol};$$

$$G_{\text{Hg}_2^{2+}} = \Delta G_{\text{eq}_\text{Hg}^+} + (2G_{\text{Hg}} + G_{\text{H}_2\text{O}}) = 132.92 + (2 \cdot 35.702 + 0) = 204.32 \text{ kJ/mol};$$

CRC

CRC

$$G_{\text{Hg}_2\text{SO}_4} = G_{\text{Hg}_2^{2+}} + G_{\text{SO}_4^{2-}} - (\Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4} + 2G_{\text{H}_2\text{O}}) = -598.44 \text{ kJ/mol};$$

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$$G_{\text{SO}_4} = G_{\text{Hg}_2\text{SO}_4} - (2G_{\text{Hg}} + \Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4}) = -726.54 \text{ kJ/mol}$$

CRC

CRC

$$G_{\text{Hg}_2\text{Cl}_2(\text{s})} = \Delta G^\circ_{\text{Hg}_2\text{Cl}_2\text{Form}} + (G_{\text{Hg}_2^{2+}} + 2 \cdot G_{\text{Cl}}) = 197.76 \text{ kJ/mol};$$

$$G_{\text{Hg}_2\text{Cl}_2} = \Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} - 2G_{\text{H}_2\text{O}} + (2G_{\text{Cl}} + 2G_{\text{Hg}}) = 255.1 \text{ kJ/mol};$$

CRC

$$\Delta G_{\text{Cl}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -167.08 - 298.15 \cdot 0.0566 = -183.955 \text{ kJ/mol};$$

$$G_{\text{Cl}} = (-G_{\text{Hg}_2^{2+}} + \Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} + (G_{\text{Hg}_2\text{Cl}_2} + 3G_{\text{H}_2\text{O}})) / 2 = -112.825 \text{ kJ/mol};$$

$$\Delta G_{\text{HgO}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -99.79 - 298.15 \cdot 0.07025 = 2 \cdot -60.3675 \text{ kJ/mol};$$

$$\text{CRC } \Delta G_{\text{HgO}} = -58.5 \text{ kJ/mol};$$

$$2G_{\text{HgO}} = 2\Delta G_{\text{HgO}} + (2 \cdot G_{\text{Hg}} + G_{\text{O}_2}) = 2 \cdot 142.2 \text{ kJ/mol}$$

$$G_{\text{HgO}} = \Delta G_{\text{eq}_\text{HgO}} - 2G_{\text{H}_2\text{O}} + (G_{\text{Hg}} + 2G_{\text{OH}}) = 147.15 \text{ kJ/mol};$$

$2\underline{\text{Hg}} + \text{H}_2\text{O} = \text{Hg}_2^{2+} + 2e^-$; absolute standard potential $E^\circ_{\text{Hg}} = 0.6888 \text{ V}$; Kortly, Shucha ; [18]

$$E^\circ_{\text{Hg}} = E^\circ - 0.0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^1) + 0.10166 - 0.3713 = 0.907 - 0.0591/2 \cdot \lg(1/55.3^1) + 0.10166 - 0.37239 = 0.6888 \text{ V};$$

$$\Delta G_{\text{eq}_\text{Hg}} = E^\circ_{\text{Hg}} \cdot F \cdot 2 = 0.6888 \cdot 96485 \cdot 2 = 132.92 \text{ kJ/mol};$$

$$\Delta G_{\text{eq}_\text{Hg}} = G_{\text{Hg}_2^{2+}} + (2G_{\text{Hg}} + G_{\text{H}_2\text{O}}) = G_{\text{Hg}_2^{2+}} + (2 \cdot 35.8 + 0) = 204.52 - (2 \cdot 35.8 + 0) = 132.92 \text{ kJ/mol};$$

$$G_{\text{Hg}_2^{2+}} = \Delta G_{\text{eq}_\text{Hg}} + (2G_{\text{Hg}} + G_{\text{H}_2\text{O}}) = 132.92 + (2 \cdot 35.8 + 0) = 204.52 \text{ kJ/mol};$$

Solubility equilibrium $\text{Hg}_2\text{Cl}_2(\text{s}) + 3\text{H}_2\text{O} = \text{Hg}_2^{2+} + 2\text{Cl}^-$; $2\underline{\text{Hg}} + \text{H}_2\text{O} = \text{Hg}_2^{2+} + 2e^-$; absolute solubility constant :

$$K_{\text{AbsoluteHg}_2\text{Cl}_2} = K_{\text{spHg}_2\text{Cl}_2} / [\text{H}_2\text{O}]^3 = [\text{Hg}_2^{2+}] \cdot [\text{Cl}^-]^2 / [\text{Hg}_2\text{Cl}_2(\text{s})] / [\text{H}_2\text{O}]^3 = 1.43 \cdot 10^{(-18)} / 1/55.3^3 = 10^{-23.1};$$

$$\Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} = -R \cdot T \cdot \ln(K_{\text{AbsoluteHg}_2\text{Cl}_2}) = -8.314 \cdot 298.15 \cdot \ln(10^{(-23.1)}) = 131.85 \text{ kJ/mol};$$

$$\Delta G_{\text{Hg}_2\text{Cl}_2} = G_{\text{Hg}_2^{2+}} + 2G_{\text{Cl}} - (G_{\text{Hg}_2\text{Cl}_2} + 3G_{\text{H}_2\text{O}}) = 204.52 + 2G_{\text{Cl}} - (276.61 + 3 \cdot 0) = 204.52 + 2 \cdot 101.97 - (276.61 + 3 \cdot 0) = 131.85 \text{ kJ/mol};$$

$$G_{\text{Cl}} = (-G_{\text{Hg}_2^{2+}} + \Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} + (G_{\text{Hg}_2\text{Cl}_2} + 3G_{\text{H}_2\text{O}})) / 2 = (-204.52 + 131.85 + (276.61 + 3 \cdot 0)) / 2 = 101.97 \text{ kJ/mol};$$

$$\text{Hg}_2^{2+} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2(\text{s}); G_{\text{Hg}_2\text{Cl}_2(\text{s})} = \Delta G^\circ_{\text{Hg}_2\text{Cl}_2\text{Form}} + (G_{\text{Hg}_2^{2+}} + 2 \cdot G_{\text{Cl}}) = -210.7 + (204.52 + 2 \cdot 101.97) = 197.76 \text{ kJ/mol};$$

$$\text{Formation Hg}_2^{2+} + 2\text{Cl}^-; G_{\text{Hg}_2\text{Cl}_2(\text{s})} = G_{\text{Hg}_2\text{Cl}_2(\text{s})} - (G_{\text{Hg}_2^{2+}} + 2 \cdot G_{\text{Cl}}) = 276.61 - (204.52 + 2 \cdot 101.97) = -131.85 \text{ kJ/mol};$$

$2\underline{\text{Hg}} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{H}_2\text{O} + 2e^-$; absolute standard potential $E^\circ_{\text{HgCl}_2} = -0.1059 \text{ V}$; Suchotina ; [18]

$$E^\circ_{\text{HgCl}_2} = E^\circ - 0.0591/2 \cdot \lg([\text{H}_2\text{O}]^2) + 0.10166 - 0.37239 = 0.2678 - 0.0591/2 \cdot \lg(55.3^2) + 0.10166 - 0.37239 = -0.1059 \text{ V};$$

$$\Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} = E^\circ_{\text{Hg}_2\text{Cl}_2} \cdot F \cdot 2 = -0.1059 \cdot 96485 \cdot 2 = -20.44 \text{ kJ/mol};$$

$$\Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} = G_{\text{Hg}_2\text{Cl}_2} + 2G_{\text{H}_2\text{O}} - (2G_{\text{Cl}} + 2G_{\text{Hg}}) = 255.1 + 2 \cdot 0 - (2 \cdot 101.97 + 2 \cdot 35.8) = -20.44 \text{ kJ/mol};$$

$$G_{\text{Hg}_2\text{Cl}_2} = \Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} - 2G_{\text{H}_2\text{O}} + (2G_{\text{Cl}} + 2G_{\text{Hg}}) = -20.44 - 2 \cdot 0 + (2 \cdot 101.97 + 2 \cdot 35.8) = 255.1 \text{ kJ/mol};$$

$$G_{\text{Hg}} = (G_{\text{Hg}_2\text{Cl}_2} + G_{\text{H}_2\text{O}} - (2G_{\text{Cl}} + \Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2})) / 2 = (255.1 + 0 - (2 \cdot 101.97 - 20.44)) / 2 = 35.8 \text{ kJ/mol};$$

Solubility equilibrium $\text{Hg}_2\text{SO}_4(\text{s}) + 2\text{H}_2\text{O} = \text{Hg}_2^{2+} + \text{SO}_4^{2-}$; $2\underline{\text{Hg}} + 2\text{H}_2\text{O} = \text{Hg}_2^{2+} + 2e^-$; absolute solubility constant:

$$K_{\text{AbsoluteHg}_2\text{SO}_4} = K_{\text{spHg}_2\text{SO}_4} / [\text{H}_2\text{O}]^2 = [\text{Hg}_2^{2+}] \cdot [\text{SO}_4^{2-}] / [\text{Hg}_2\text{SO}_4(\text{s})] / [\text{H}_2\text{O}]^2 = 6.5 \cdot 10^{(-7)} / 1/55.3^2 = 10^{-9.673};$$

$$\Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4} = -R \cdot T \cdot \ln(K_{\text{AbsoluteHg}_2\text{SO}_4}) = -8.314 \cdot 298.15 \cdot \ln(10^{(-9.673)}) = 55.21 \text{ kJ/mol};$$

$$\Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4} = G_{\text{Hg}_2^{2+}} + G_{\text{SO}_4^{2-}} - (G_{\text{Hg}_2\text{SO}_4} + 2G_{\text{H}_2\text{O}}) = 209.09 - 747.75 - (G_{\text{Hg}_2\text{SO}_4} + 2 \cdot 0) = 55.21 \text{ kJ/mol};$$

$$G_{\text{Hg}_2\text{SO}_4} = G_{\text{Hg}_2^{2+}} + G_{\text{SO}_4^{2-}} - (\Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4} + 2G_{\text{H}_2\text{O}}) = 209.09 - 747.75 - (55.21 + 2 \cdot 0) = -593.87 \text{ kJ/mol};$$

$$\text{Hg}_2\text{SO}_4(\text{s}) + 2\text{H}_2\text{O} = \text{Hg}_2^{2+} + \text{SO}_4^{2-}; 2\underline{\text{Hg}} + \text{H}_2\text{O} = \text{Hg}_2^{2+} + 2e^-;$$

$2\underline{\text{Hg}} + \text{SO}_4^{2-} = \text{Hg}_2\text{SO}_4(\text{s}) + \text{H}_2\text{O} + 2e^-$; absolute standard potential $E^\circ_{\text{HgSO}_4} = 0.291772 \text{ V}$; Kortly, Shucha ; [18]

$$E^\circ_{\text{HgSO}_4} = E^\circ - 0.0591/2 \cdot \lg([\text{H}_2\text{O}]^1) + 0.10166 - 0.37239 = 0.614 - 0.0591/2 \cdot \lg(55.3^1) + 0.10166 - 0.37239 = 0.2918 \text{ V};$$

$$\Delta G_{\text{eq}_\text{HgSO}_4} = E^\circ_{\text{HgSO}_4} \cdot F \cdot 2 = 0.291772 \cdot 96485 \cdot 2 = 56.30 \text{ kJ/mol};$$

$$\Delta G_{\text{eq}_\text{HgSO}_4} = G_{\text{Hg}_2\text{SO}_4} - (2G_{\text{Hg}} + G_{\text{SO}_4}) = -593.87 - (2 \cdot 35.7 + G_{\text{SO}_4}) = 56.30 \text{ kJ/mol};$$

$$G_{\text{SO}_4} = G_{\text{Hg}_2\text{SO}_4} - (2G_{\text{Hg}} + \Delta G_{\text{eq}_\text{HgSO}_4}) = -593.87 - (2 \cdot 35.7 + 56.3) = -721.57 \text{ kJ/mol};$$

$$\text{Formation } 2\underline{\text{Hg}} + \text{O}_2 \text{ aqua} = 2\underline{\text{HgO}}; 2G_{\text{HgO}} = 2\Delta G_{\text{HgO}} + (2 \cdot G_{\text{Hg}} + G_{\text{O}_2}) = 2 \cdot -58.5 + (2 \cdot 35.8 + 330) = 2 \cdot 142.3 \text{ kJ/mol};$$

Formation $2\text{Hg} + \text{O}_2 \text{ aqua} = 2\text{HgO}$; $2\Delta G_{\text{HgO}} = 2G_{\text{HgO}} - (2 \cdot 35.7 + 330) = 2 \cdot -58.5 = -117 \text{ kJ/mol}$;

$2G_{\text{HgO}} = 2\Delta G_{\text{HgO}} + (2 \cdot G_{\text{Hg}} + G_{\text{O}_2}) = 2 \cdot -58.5 + (2 \cdot 35.7 + 330) = 2 \cdot 142.2 \text{ kJ/mol}$;

$\Delta G_{\text{eqHgO}} = G_{\text{HgO}} + 2G_{\text{H}_2\text{O}} - (G_{\text{Hg}} + 2G_{\text{OH}}) = -58.5 + 2 \cdot 0 - (35.7 + 2 \cdot 77.36) = -53.20 \text{ kJ/mol}$

$\text{Hg} + 2\text{OH}^- = \text{HgO} + \text{H}_2\text{O} + 2e^-$, Nernst's absolute standard potential $E^\circ_{\text{HgO}} = -0.2242 \text{ V}$;

$E_{\text{HgO}} = E^\circ - 0.0591/2 \cdot \lg([\text{H}_2\text{O}]^1) + 0.10166 - 0.37239 = 0.098 - 0.0591/2 \cdot \lg(55.3^1) + 0.10166 - 0.37239 = -0.22423 \text{ V}$;

$\Delta G_{\text{eqHgO}} = E^\circ_{\text{HgO}} \cdot F \cdot n = -0.22423 \cdot 96485 \cdot 2 = -43.27 \text{ kJ/mol}$;

$\Delta G_{\text{eqHgO}} = G_{\text{HgO}} + G_{\text{H}_2\text{O}} - (G_{\text{Hg}} + 2G_{\text{OH}}) = G_{\text{HgO}} + 0 - (35.8 + 2 \cdot 77.36) = 147.25 + 0 - (35.8 + 2 \cdot 77.36) = -43.27 \text{ kJ/mol}$;

$G_{\text{HgO}} = \Delta G_{\text{eqHgO}} - G_{\text{H}_2\text{O}} + (G_{\text{Hg}} + 2G_{\text{OH}}) = -43.27 - 0 + (35.8 + 2 \cdot 77.36) = 147.25 \text{ kJ/mol}$;

Reduction $\text{HgO} + 2\text{H}_2\text{O} + 2e^- = \text{Hg} + 2\text{OH}^-$, inverse standard potential $-E^\circ_{\text{HgO}} = 0.22423 \text{ V}$.

Oxidation $\text{H}_2\text{O}_2 \text{ aqua} + 2\text{H}_2\text{O} = \text{O}_2 \text{ aqua} + 2\text{H}_3\text{O}^+ + 2e^-$ Nernst's absolute standard potential $E^\circ_{\text{RedH}_2\text{O}_2} = 0.5278 \text{ V}$;

$\text{HgO} + 2\text{H}_2\text{O} + 2e^- + \text{H}_2\text{O}_2 \text{ aqua} + 2\text{H}_2\text{O} = \text{Hg} + 2\text{OH}^- + \text{O}_2 \text{ aqua} + 2\text{H}_3\text{O}^+ + 2e^-$;

$\text{HgO} + \text{H}_2\text{O}_2 \text{ aqua} + 4\text{H}_2\text{O} = \text{Hg} + \text{O}_2 \text{ aqua} + (2\text{OH}^- + 2\text{H}_3\text{O}^+)$; $\text{HgO} + \text{H}_2\text{O}_2 \text{ aqua} + 4\text{H}_2\text{O} = \text{Hg} + \text{O}_2 \text{ aqua} + (4\text{H}_2\text{O})$;

Summary: $\text{HgO} + \text{H}_2\text{O}_2 \text{ aqua} = \text{Hg} + \text{O}_2 \text{ aqua}$ catalase; $G_{\text{H}_2\text{O}_2} = 279.285 \text{ kJ/mol}$;

$\Delta G_{\text{eqRedOx}_2\text{H}_2\text{O}_2} = (E^\circ_{\text{H}_2\text{O}_2 \text{ aqua Red}} - E^\circ_{\text{HgO}}) \cdot F \cdot n = (0.5278 + 0.22318) \cdot 96485 \cdot 2 = (0.7510) \cdot 96485 \cdot 2 = 144.9166 \text{ kJ/mol}$;

$\Delta G_{\text{eqRedOx}_2\text{H}_2\text{O}_2} = G_{\text{Hg}} + G_{\text{O}_2 \text{ aqua}} - (G_{\text{HgO}} + G_{\text{H}_2\text{O}_2}) = 35.7 + 330 - (-58.5 + 279.285) = 144.9166 \text{ kJ/mol}$;

HgO ; $G_{\text{Hg}} = G_{\text{eqRedOx}_2\text{H}_2\text{O}_2} - G_{\text{O}_2 \text{ aqua}} + (G_{\text{HgO}} + G_{\text{H}_2\text{O}_2}) = 144.9166 - 330 + (-58.5 + 279.285) = 35.70 \text{ kJ/mol}$;

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$G_{\text{Pb}} = G_{\text{Pb}_2} - (\Delta G_{\text{eqPb}_2\text{Pb}^+} + G_{\text{H}_2\text{O}}) = -415.895 - (-66.42 + 0) = -349.07 \text{ kJ/mol}$;

$G_{\text{Pb}^{2+}} = G_{\text{PbO}_2} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqPbO}_2\text{Pb}^{2+}} + 6G_{\text{H}_2\text{O}}) = -415.69 \text{ kJ/mol}$;

$\Delta G^\circ_{\text{Pb}^{2+}} = \Delta H^\circ_{\text{H}} - T \cdot \Delta S^\circ_{\text{H}} = 0.92 - 298.15 \cdot 0.0185 = -4.596 \text{ kJ/mol}$;

$G_{\text{PbO}_2} = \Delta G_{\text{eqPbO}_2\text{Pb}^{2+}} - 4G_{\text{H}_3\text{O}^+} + (G_{\text{Pb}^{2+}} + 6G_{\text{H}_2\text{O}}) = -217.3 \text{ kJ/mol}$;

$G_{\text{Al}} = G_{\text{Al}_3} - (\Delta G_{\text{eqAl/Al}_3} + G_{\text{H}_2\text{O}}) = -441.5 - (-549.5 + 0) = 108 \text{ kJ/mol}$;

$\Delta G^\circ_{\text{Pb}^{2+}} = \Delta H^\circ_{\text{H}} - T \cdot \Delta S^\circ_{\text{H}} = -538.4 - 298.15 \cdot -0.325 = -441.5 \text{ kJ/mol}$;

$G_{\text{H}_2\text{AlO}_3^-} = \Delta G_{\text{eqH}_2\text{AlO}_3\text{Al}^-} - G_{\text{H}_2\text{O}} + (G_{\text{Al}} + 4G_{\text{OH}}) = -345.29 \text{ kJ/mol}$;

$G_{\text{NaAlO}_2} = -1133.2 \text{ kJ/mol}$;

$G_{\text{Al}^{3+}} = -538.4 \text{ kJ/mol}$;

$G_{\text{H}_2\text{AlO}_3^-} = -2.63506 \text{ kJ/mol}$;

$G_{\text{NaAlO}_2} = -1133.2 \text{ kJ/mol}$;

$\text{Pb}^{2+} + 6\text{H}_2\text{O} = \text{PbO}_2(\text{s}) + 4\text{H}_3\text{O}^+ + 2e^-$; Nernst's half reaction absolute standard potential $E^\circ_{\text{PbO}_2} = 1.49326 \text{ V}$;

$E_{\text{PbO}_2} = E^\circ - 0.0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^6) + 0.10166 - 0.37239 = 1.455 - 0.0591/2 \cdot \lg(1/55.3^6) + 0.10166 - 0.37239 = 1.49326 \text{ V}$;

$\Delta G_{\text{eqPbO}_2\text{Pb}^{2+}} = E^\circ_{\text{PbO}_2\text{Pb}^{2+}} \cdot F \cdot 3 = 1.49326 \cdot 96485 \cdot 3 = 288.15 \text{ kJ/mol}$;

$\Delta G_{\text{eqPbO}_2\text{Pb}^{2+}} = G_{\text{PbO}_2} + 4G_{\text{H}_3\text{O}^+} - (G_{\text{Pb}^{2+}} + 6G_{\text{H}_2\text{O}}) = -217.3 + 4 \cdot 22.44 - (-415.69 + 6 \cdot 0) = 288.15 \text{ kJ/mol}$;

$G_{\text{PbO}_2} = \Delta G_{\text{eqPbO}_2\text{Pb}^{2+}} - 4G_{\text{H}_3\text{O}^+} + (G_{\text{Pb}^{2+}} + 6G_{\text{H}_2\text{O}}) = 288.15 - 4 \cdot 22.44 + (-415.69 + 6 \cdot 0) = -217.3 \text{ kJ/mol}$;

$G_{\text{Pb}^{2+}} = G_{\text{PbO}_2} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqPbO}_2\text{Pb}^{2+}} + 6G_{\text{H}_2\text{O}}) = -217.3 + 4 \cdot 22.44 - (288.15 + 6 \cdot 0) = -415.69 \text{ kJ/mol}$;

$$E_{\text{PbO}_2\text{Pb}^{2+}} = E^\circ_{\text{PbO}_2\text{Pb}^{2+}} + \frac{0.0591}{2} \cdot \lg \frac{[\text{PbO}_2][\text{H}_3\text{O}^+]^4}{[\text{Pb}^{2+}][\text{H}_2\text{O}]^6} = 1.4674 \text{ V} + \frac{0.0591}{2} \cdot \lg \frac{[\text{PbO}_2][\text{H}_3\text{O}^+]^4}{[\text{Pb}^{2+}][\text{H}_2\text{O}]^6} ;$$

$\text{Pb} + \text{H}_2\text{O} = \text{Pb}^{2+} + 2e^-$; $\text{pH} < 7$ Nernst's half reaction absolute standard potential $E^\circ_{\text{Pb/Pb}^{2+}} = -0.3452 \text{ V}$;

$E_{\text{Pb/Pb}^{2+}} = E^\circ - 0.0591/2 \cdot \lg(1/[\text{H}_2\text{O}]) + 0.10166 - 0.37239 = -1.26 - 0.0591/2 \cdot \lg(1/55.3^1) + 0.10166 - 0.37239 = -0.3452 \text{ V}$;

$\Delta G_{\text{eqPb}_2\text{Pb}^{2+}} = E^\circ_{\text{Pb}_2\text{Pb}^{2+}} \cdot F \cdot n = -0.34523 \cdot 96485 \cdot 2 = -66.62 \text{ kJ/mol}$;

$\Delta G_{\text{eqPb}_2\text{Pb}^{2+}} = G_{\text{Pb}_2} - (G_{\text{Pb}} + G_{\text{H}_2\text{O}}) = -415.69 - (G_{\text{Pb}} + 0) = -71.59 = -66.62 \text{ kJ/mol}$;

$G_{\text{Pb}} = G_{\text{Pb}_2} - (\Delta G_{\text{eqPb}_2\text{Pb}^{2+}} + G_{\text{H}_2\text{O}}) = -415.69 - (-66.62 + 0) = -349.07 \text{ kJ/mol}$;

$\text{Al} + \text{H}_2\text{O} = \text{Al}^{3+} + 3e^-$; CRC Nernst's half reaction absolute standard potential $E^\circ_{\text{Pb/Pb}^{2+}} = -1.8984 \text{ V}$;

$E_{\text{Al/Al}^{3+}} = E^\circ - 0.0591/2 \cdot \lg(1/[\text{H}_2\text{O}]) + 0.10166 - 0.37239 = -1.662 - 0.0591/3 \cdot \lg(1/55.3^1) + 0.10166 - 0.37239 = -1.8984 \text{ V}$;

$\Delta G_{\text{eqAl/Al}^{3+}} = E^\circ_{\text{Al/Al}^{3+}} \cdot F \cdot 3 = -1.8984 \cdot 96485 \cdot 3 = -549.5 \text{ kJ/mol}$;

$\Delta G_{\text{eqAl/Al}^{3+}} = G_{\text{Al}_3} - (G_{\text{Al}} + G_{\text{H}_2\text{O}}) = -441.5 - (108 + 0) = -549.5 \text{ kJ/mol}$;

$G_{\text{Al}} = G_{\text{Al}_3} - (\Delta G_{\text{eqAl/Al}^{3+}} + G_{\text{H}_2\text{O}}) = -441.5 - (-549.5 + 0) = 108 \text{ kJ/mol}$;

$\text{Al} + 4\text{OH}^- = \text{H}_2\text{AlO}_3^- + \text{H}_2\text{O} + 3e^-$; CRC Nernst's half reaction absolute standard potential $E^\circ_{\text{H}_2\text{AlO}_3\text{-Al}} = -2.63506 \text{ V}$;

$E_{\text{H}_2\text{AlO}_3\text{-Al}} = E^\circ - 0.0591/2 \cdot \lg([\text{H}_2\text{O}]) + 0.10166 - 0.37239 = -2.33 - 0.0591/3 \cdot \lg(55.3^1) + 0.10166 - 0.37239 = -2.63506 \text{ V}$;

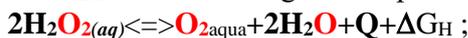
$\Delta G_{\text{eqH}_2\text{AlO}_3\text{Al}^-} = E^\circ_{\text{H}_2\text{AlO}_3\text{Al}^-} \cdot F \cdot 3 = -2.63506 \cdot 96485 \cdot 3 = -762.73 \text{ kJ/mol}$;

$\Delta G_{\text{eqH}_2\text{AlO}_3\text{Al}^-} = G_{\text{H}_2\text{AlO}_3^-} + G_{\text{H}_2\text{O}} - (G_{\text{Al}} + 4G_{\text{OH}}) = -345.29 + 0 - (108 + 4 \cdot 77.36) = -762.73 \text{ kJ/mol}$;

$G_{\text{H}_2\text{AlO}_3^-} = \Delta G_{\text{eqH}_2\text{AlO}_3\text{Al}^-} - G_{\text{H}_2\text{O}} + (G_{\text{Al}} + 4G_{\text{OH}}) = -762.73 - 0 + (108 + 4 \cdot 77.36) = -345.29 \text{ kJ/mol}$;

$$E_{\text{AlO}_2\text{-Al}} = E^\circ_{\text{AlO}_2\text{-Al}} + \frac{0.0591}{3} \cdot \lg \frac{[\text{H}_2\text{AlO}_3^-][\text{H}_2\text{O}]}{[\text{Al}][\text{OH}^-]^4} = -2.63506 \text{ V} + \frac{0.0591}{3} \cdot \lg \frac{[\text{H}_2\text{AlO}_3^-][\text{H}_2\text{O}]}{[\text{Al}][\text{OH}^-]^4} ;$$

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



Red: $\text{H}_2\text{O}_2 + 2\text{H}_2\text{O} = \text{O}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^-$; $E^\circ_{\text{Red}} = E^\circ_{\text{RedH}_2\text{O}_2} = 0.5268 \text{ V}$ Nernst's absolute potential Alberta University;

Ox: $\text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^- = 4\text{H}_2\text{O}$; $E^\circ_{\text{OxH}_2\text{O}_2} = -1.7113 \text{ V}$ inverse standard potential Suhotina;

$$\Delta G_{\text{eqStandarta}_2\text{H}_2\text{O}_2} = (E^\circ_{\text{H}_2\text{O}_2\text{aqRed}} - E^\circ_{\text{H}_2\text{O}_2\text{aqOx}}) * F * n = (0.5268 - 1.7113) * 96485 * 2 = (-1.1845) * 96485 * 2 = -228.57 \text{ kJ/mol};$$

$$\Delta G_{\text{Alberty}_2\text{H}_2\text{O}_2} = G_{\text{O}_2\text{aq}} + 2 * G_{\text{H}_2\text{O}} - 2 * G_{\text{H}_2\text{O}_2} = 330 + 2 * 0 - 2 * G_{\text{H}_2\text{O}_2} = -228.57 \text{ kJ/mol}; \text{ exoergic}$$

$$G_{\text{H}_2\text{O}_2} = (G_{\text{O}_2\text{aq}} + 2 * G_{\text{H}_2\text{O}} + \Delta G_{\text{Alberty}_2\text{H}_2\text{O}_2}) / 2 = (330 + 2 * 0 + 228.57) / 2 = 558.57 / 2 = 279.285 \text{ kJ/mol};$$

$$K_{\text{eqStandart}} = \frac{[\text{O}_2]_{\text{aq}} * [\text{H}_2\text{O}]^2}{[\text{H}_2\text{O}_2]_{\text{aq}}^2} = K_{\text{H}_2\text{O}_2} = \exp(-\Delta G_{\text{eq}} / R / T) = \exp(228573 / 8.3144 / 298.15) = 1.11 * 10^{40} \dots\dots$$

Half reactions RedOx Nernst's reduction and oxidation electrons balance 2 e^- at $\text{pH}=7.36$, $[\text{O}_{\text{aq}}] = 6 * 10^{-5} \text{ M}$.
 $E_{\text{Red}} = E^\circ_{\text{H}_2\text{O}_2} + 0.0591 / 2 * \lg([\text{O}_{\text{aq}}] * [\text{H}_3\text{O}^+]^2 / [\text{H}_2\text{O}_2] / [\text{H}_2\text{O}]^2) = 0.5268 + 0.0591 / 2 * \lg(6 * 10^{(-5)} * 10^{(-7.36 * 2)} / 1 / 55.3^{(2)}) = -0.13493 \text{ V};$
 $E_{\text{Ox}} = -E^\circ_{\text{H}_2\text{O}_2\text{Ox}} + 0.0591 / 2 * \lg([\text{H}_2\text{O}_2] * [\text{H}_3\text{O}^+]^2 / [\text{H}_2\text{O}]^4) = -1.7113 + 0.0591 / 2 * \lg(1 * 10^{(-7.36 * 2)} / 55.3^{(4)}) = -1.0703 \text{ V};$
 Energy change is $\Delta G_{\text{Homeostasis}} = (E_{\text{Red}} - E_{\text{Ox}}) * F * n = (-0.13493 - 1.0703) * 96485 * 2 = (-1.2062) * 96485 * 2 = -232.76 \text{ kJ/mol};$

$$G_{\text{HomeostasisH}_2\text{O}_2} = (G_{\text{O}_2\text{Biochem_arteriaj}} + 2 * G_{\text{H}_2\text{OBioChemistry}} - \Delta G_{\text{Alberty}}) / 2 = (88.04 + 2 * 85.64 + 232.76) / 2 = 246.04 \text{ kJ/mol}$$

Substance	$\Delta H^\circ_H, \text{kJ/mol}$	$\Delta S^\circ_H, \text{J/mol/K}$	$\Delta G^\circ_H, \text{kJ/mol}$
H_3O^+	-285.81	-3.854	-213.275
$\text{O}_{2\text{aq}}$	-11.715	110.876	16.4
$\text{O}_{2\text{aq}}$	-11.70	-94.2	16.40
H_2O	-285.85	69.9565	-237.191
H_2O	-286.65	-453.188	-151.549
$\text{H}_2\text{O}_2(\text{aq})$	-191.99	-481.688	-48.39
$\text{H}_2\text{O}_2(\text{aq})$	-191.17	143.9	-134.03
$\text{H}_2\text{O}_2\text{aq}$	Formation	-48.39	340.25
$\text{H}_2\text{O}_2\text{aq}$	Formation	-134.03	254.61
$\text{H}_2\text{O}_2(\text{aq})$	$\Delta E^\circ_{\text{H}_2\text{O}_2\text{RedOx}}$	-1.1845	279.285
HOO^-	$\text{pK}_a = 11.75$	77.016	333.866
$\text{H}_2\text{O}_2\text{l}$	-237.129	69.91	-237.129

$G_{\text{H}_2\text{O}_2} = 279.285 \text{ kJ/mol}; G_{\text{HOO}^-} = 333.866 \text{ kJ/mol};$
 $\Delta G^\circ_{\text{H}_3\text{O}^+}, \text{kJ/mol}$ [Mischenko](#) 1972, Himia, Leningrad [26]
 CRC 2010; $G_{\text{O}_2\text{aq}} = 330 \text{ kJ/mol}; G_{\text{H}_2\text{O}} = 0 \text{ kJ/mol};$
 $\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{O}_2} + 2\Delta H^\circ_{\text{H}_2\text{O}} - 2\Delta H^\circ_{\text{H}_2\text{O}_2} = -201.02 \dots = -201.06 \dots \text{kJ/mol}$
 $= -11.7 - 2 * 286.65 - (2 * -191.99) = -201.02 \dots \text{kJ/mol}$ eksotermiska..
 $= -11.7 - 2 * 285.85 - (2 * -191.17) = -201.06 \dots \text{kJ/mol}$
Biochem. Thermodynamic 2006 Massachusetts Technology Inst. University Alberta 1997.
 $G_{\text{H}_2\text{O}_2\text{aq}} = \Delta G_{\text{H}_2\text{O}_2\text{Alberty}} + (G_{\text{O}_2\text{gas}} + G_{\text{H}_2\text{gas}} + G_{\text{H}_2\text{O}}) = 340.25 \text{ kJ/mol};$
 $G_{\text{H}_2\text{O}_2\text{aq}} = \Delta G_{\text{H}_2\text{O}_2\text{Alberty}} + (G_{\text{O}_2\text{gas}} + G_{\text{H}_2\text{gas}} + G_{\text{H}_2\text{O}}) = 254.61 \text{ kJ/mol};$
 $G_{\text{H}_2\text{O}_2} = (G_{\text{O}_2\text{aq}} + 2 * G_{\text{H}_2\text{O}} + \Delta G_{\text{Alberty}_2\text{H}_2\text{O}_2}) / 2 = 558.57 / 2 = 279.285 \text{ kJ/mol};$
 $G_{\text{HOO}^-} = -G_{\text{H}_3\text{O}^+} + \Delta G_{\text{aH}_2\text{O}_2} + (G_{\text{H}_2\text{O}_2} + G_{\text{H}_2\text{O}}) = 333.866 \text{ kJ/mol};$
 CRC

$\text{H}_2\text{O}_2 + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HOO}^-$; $\text{pK}_a = 11.75$; $G_{\text{H}_2\text{O}_2} = 279.29 \text{ kJ/mol}; G_{\text{HOO}^-} = 333.866 \text{ kJ/mol};$
 $\Delta G_{\text{aH}_2\text{O}_2} = -R * T * \ln(K_a / [\text{H}_2\text{O}]) = -8.3144 * 298.15 * \ln(10^{(-11.75)} / 55.3) = -8.3144 * 298.15 * -31.07 = 77.016 \text{ kJ/mol};$
 $\Delta G_{\text{aH}_2\text{O}_2} = G_{\text{H}_3\text{O}^+} + G_{\text{HOO}^-} - (G_{\text{H}_2\text{O}_2} + G_{\text{H}_2\text{O}}) = 22.44 + G_{\text{HOO}^-} - (279.29 + 0) = 77.016 \text{ kJ/mol};$
 $G_{\text{HOO}^-} = -G_{\text{H}_3\text{O}^+} + \Delta G_{\text{aH}_2\text{O}_2} + (G_{\text{H}_2\text{O}_2} + G_{\text{H}_2\text{O}}) = -22.44 + 77.016 + (279.29 + 0) = 333.866 \text{ kJ/mol};$

$\text{HOO}^- + \text{H}_2\text{O} = \text{O}_{2\text{aq}} + \text{H}_3\text{O}^+ + 2\text{e}^-$; Absolute peroxide anion standard potential is $E^\circ_{\text{NernstHOO}^-} = 0.09625 \text{ Volts}$.

$$\Delta G_{\text{NernstHOO}^-} = G_{\text{O}_2\text{aq}} + G_{\text{H}_3\text{O}^+} - (G_{\text{HOO}^-} + G_{\text{H}_2\text{O}}) = 330 + 22.44 - (333.866 + 0) = 18.574 \text{ kJ/mol};$$

Absolute Nernst's reaction standard potential is $E^\circ_{\text{NernstHOO}^-} = \Delta G_{\text{NernstHOO}^-} / F = 18574 / 96485 / 2 = 0.09625 \text{ V}$.

$$E^\circ_{\text{HOO}^-} = E^\circ - 0.0591 / 2 * \lg(1 / [\text{H}_2\text{O}]^1) + 0.10166 - 0.37 = 0.31548 - 0.02955 * \lg(1 / 55.3^{(1)}) + 0.10166 - 0.37239 = 0.09625 \text{ V};$$

$$E^\circ_{\text{HOO}^-} = E^\circ + 0.372 = 0.09625 + 0.37239 = 0.46864 \text{ V}; E^\circ_{\text{HOO}^-} = 0.46864 - 0.10166 = 0.36698 \text{ V};$$

$$E^\circ_{\text{HOO}^-} = 0.36698 + 0.0591 / 2 * \lg(1 / 55.3^{(1)}) = 0.31548 \text{ V};$$

Exothermic and exoergic $\text{H}_2\text{O}_2(\text{aq})$ dismutation Hesa free energy change $\Delta G_{\text{Alberty}_2\text{H}_2\text{O}_2} = -246 \text{ kJ/mol}$ and in Homeostasis $\Delta G_{\text{Homeostasis}} = -232.76 \text{ kJ/mol}$ is negative, but minimized

$\Delta G_{\text{eqStandart}} = -228.6 \text{ kJ/mol}$ reaching standard equilibrium mixture constant $K_{\text{eq}} = 1.11 * 10^{40}$.

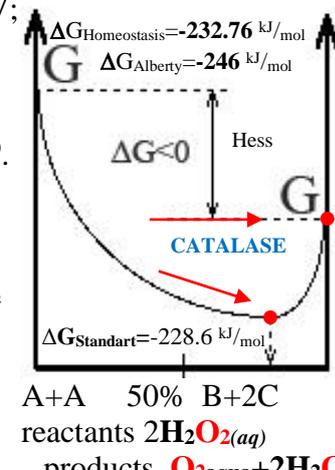
Le Chatelier principle is Prigogine attractor as free energy change minimum ΔG_{min} reaching. High rate protolysis attractors $\text{pH}=7.36$, oxygen 20.95% in air stay at equilibrium, while homeostasis irreversibly continues, as are non equilibrium state. Prigogine attractors are Nobel Prize in Chemistry 1977th. CATALASE erase peroxide molecules H_2O_2 reaching 100% efficiency for $\omega=6$, $\omega=3$ fatty acids C20:4 elongation synthesis in peroxisomes. CATALASE reactivity is indispensable irreversible homeostasis Brownian molecular engine for evolution and survival.

Formation from elements $\text{O}_{2\text{gas}} + \text{H}_{2\text{gas}} + \text{H}_2\text{O} = \text{H}_2\text{O}_2\text{aq};$

$$\text{Catalase}; G_{\text{H}_2\text{O}_2\text{aq}} = \Delta G_{\text{H}_2\text{O}_2\text{Alberty}} + (G_{\text{O}_2\text{gas}} + G_{\text{H}_2\text{gas}} + G_{\text{H}_2\text{O}}) = -134.03 + (85.64 + 303 + 0) = 254.61 \text{ kJ/mol};$$

$$\text{Catalase}; G_{\text{H}_2\text{O}_2\text{aq}} = \Delta G_{\text{H}_2\text{O}_2\text{Alberty}} + (G_{\text{O}_2\text{gas}} + G_{\text{H}_2\text{gas}} + G_{\text{H}_2\text{O}}) = -48.39 + (85.64 + 303 + 0) = 340.25 \text{ kJ/mol};$$

$$41^{\text{st}}, 54^{\text{th}} \text{ page [1,8,20]} \Delta G^\circ_{\text{UnivAlberta}} = -134.03 \text{ kJ/mol}; \Delta G^\circ_{\text{Alberty}} = -48.39 \text{ kJ/mol};$$



Solubility $N_{2gas}+H_2O+\Delta G=N_{2aq}$ increases molar nitrogen energy from $G_{N_{2gas}}=-9.55$ kJ/mol to $G_{N_{2aq}}=18.7$ kJ/mol.

Published content of Alberty dissolve nitrogen **absolute** free energy in one mol is $G_{N_{2aqua}}=18.7$ kJ/mol, if pure gas mol fraction is one $[N_{2gas}]=1$. [8] Hundred grams of water dissolve nitrogen gas 0.00175 g/100g H_2O density has 996 g/L. [1] Solubility $[N_{2aqua}]=0.00175/100.00175*996=0.01743/28.02=0.01743=10^{-3.206}$ M and the solubility constant in mole fractions is less than one $K_{sp}=10^{-(3.206)}/[H_2O]=10^{-(3.206)}/55.3=10^{-4.949}$, which free energy change minimum in reaction is

$$\Delta G_{sp}=-R\cdot T\cdot\ln(K_{sp})=-8.3144*298.15*\ln(10^{-(4.949)})=28.25 \text{ kJ/mol.}$$

Hess law energy change coincides $\Delta G_{spHessN_{2aqua}}=G_{N_{2aqua}}-(G_{N_{2gas}}+G_{H_2O})=18.7-(-9.55+0)=28.25$ kJ/mol within absolute free energy scale. Mole $G_{N_{2gas}}=G_{N_{2aqua}}-(\Delta G_{spHessN_{2aqua}}+G_{H_2O})=18.7-(28.25+0)=-9.55$ kJ/mol contains the free energy below the zero reference scale for water. Dissolute nitrogen mol of energy content is positive $G_{N_{2aqua}}=18.7$ kJ/mol. [1,8]

Prigogine energy change in solubility product reaction coincides with Hess law free energy change by data of Alberty: $\Delta G_{Hess_sp_N_{2aqua}}=G_{N_{2aqua}}-(G_{N_{2gas}}+G_{H_2O})=18.7-(G_{N_{2gas}}-0)=28.25$ kJ/mol.

Expressed nitrogen gas free energy content on the zero reference scale for water $G_{H_2O}=0$ kJ/mol is negative

$$G_{N_{2gas}}=G_{N_{2aqua}}-(\Delta G_{Hess_sp_N_{2aqua}}+G_{H_2O})=18.7-(28.25+0)=-9.55 \text{ kJ/mol.}$$

$$\Delta G_{spN_{2aqua}}=G_{N_{2aqua}}-(G_{N_{2gas}}+G_{H_2O})=18.7-(-9.55+0)=28.25 \text{ kJ/mol; [8]}$$

Substance	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
N_{2gas}	$G_{N_{2gas}}=$	form NH_3	107.285
N_{2aq}	-10.54	98.1	18.7
N_{2gas}	$N_{2gas}+H_2O$	$=N_{2aq}$	-9.55

$$G_{N_{2gas}}=2G_{NH_3gas}-(2\Delta G_{Hess_NH_3gas}+3*G_{H_2gas})=107.285 \text{ kJ/mol;}$$

$$G_{N_{2gas}}=2*165.6593-(-32.8+3*85.64)=107.285 \text{ kJ/mol; [1,8];}$$

Solution N_{2aq} at pH=7.36 [8].

$$G_{N_{2gas}}=G_{N_{2aqua}}-(\Delta G_{Hess_sk_N_{2aqua}}+G_{H_2O})=18.7-(28.25+0)=-9.55 \text{ kJ/mol;}$$

Formation from aqua elements $N_{2aq}+3H_{2aq}>2NH_{3aq}$ with absolute energy $G_{N_{2aq}}=18.7$ kJ/mol; $G_{H_{2aq}}=103.24$ kJ/mol shows exoergic reaction $2\Delta G_{Hess_NH_3aq}=2G_{NH_3aq}-(G_{N_{2aq}}+3*G_{H_{2aq}})=2*91.1056-(18.7+3*103.24)=-146.2$ kJ/mol. [8] Formation from elements $N_{2gas}+3H_{2gas}>2NH_{3gas}$ energies $G_{N_{2gas}}=-9.55$ kJ/mol; $G_{H_{2gas}}=85.64$ kJ/mol shows negative data $2\Delta G_{Hess_NH_3gas}=2G_{NH_3gas}-(G_{N_{2gas}}+3*G_{H_{2gas}})=2G_{NH_3gas}-(-9.55+3*85.64)=2*-16.4=-32.8$ kJ/mol. Ammonia gas has energy $2G_{NH_3gas}=2\Delta G_{Hess_NH_3gas}+(G_{N_{2gas}}+3*G_{H_{2gas}})=2*-16.4+(-9.55+3*85.64)=-214.57=2*107.285$ kJ/mol content. Classically, Hess assumed zero energy for free elements zero values are CRC data exoergic change:

$$2\Delta G_{Hess_NH_3gas}=2G^{\circ}_{NH_3gas}-(G^{\circ}_{N_{2gas}}+3*G^{\circ}_{H_2})=2*-16.4-(0+3*0)=-32.8 \text{ kJ/mol. [1]}$$

Solubility $NH_{3gas}+H_2O=NH_{3aq}$; $G_{NH_{3aq}}=91.1$ kJ/mol; Ammonia at pH=7.36 [8]

$$\Delta H_{Hydration}=\Delta H^{\circ}_{NH_{3aq}}-\Delta H^{\circ}_{NH_{3gas}}-\Delta H^{\circ}_{H_2O}=-132.5608+45.94-286.65=373.3 \text{ kJ/mol;}$$

$$S_{Hydration}=\Delta S^{\circ}_{NH_{3aqua}}-\Delta S^{\circ}_{NH_{3gas}}-\Delta S^{\circ}_{H_2O}=-739.2922-192.77-69.9565=-1002 \text{ J/mol/K;}$$

$$\Delta G_{Hydrations}=\Delta H_{Hydrations}-T*\Delta S_{Hydration}=-373.3-298.15*-1.002=-74.5537 \text{ kJ/mol;}$$

$$K_{sp}=\exp(-\Delta G_{Hydration}/R/T)=\exp(74553.7/8.3144/298.15)=10^{13.06};$$

Alberty solutions for ammonia at pH=7.36 $G_{NH_{3aq}}=91.1056$ kJ/mol and Hess hydration with change in energy $\Delta G_{Hydrations}=-74.5537$ kJ/mol calculate the absolute energy content of the gas NH_{3gas} coincidentally as follows: $G_{NH_{3gas}}=G_{NH_{3aq}}-(\Delta G_{Hydration}+G_{H_2O})=91.1056-(-74.5537+0)=165.7$ kJ/mol; and

$$G_{NH_{3gas}}=(2\Delta G_{Hess_NH_3gas}+(G_{N_{2gas}}+3*G_{H_{2gas}}))/2=(-32.8+(107.2+3*85.64))/2=165.7 \text{ kJ/mol; [1,8] CRC, Alberty}$$

$$G_{NH_{3gas}}=(\Delta G_{Hess_NH_3gas}+(G_{N_{2gas}}+3*G_{H_{2gas}}))/2=(-32.8+(-9.55+3*85.64))/2=107.285 \text{ kJ/mol;}$$

The energy for the one mol element hydrogen $G_{H_{2gas}}=85.64$ kJ/mol, for the gas $G_{NH_{3gas}}=165.7$ kJ/mol, with energy of formation o -32.8 kJ/mol $G_{N_{2gas}}=2G_{NH_{3gas}}-(2\Delta G_{Hess_NH_3gas}+3*G_{H_{2gas}})=2*165.7-(2*-16.4+3*85.64)=107.28$ kJ/mol calculate the one mol nitrogen gas energy content.

Solubility $NH_{3gas}+H_2O=NH_{3aq}$; $G_{NH_{3aq}}=91.1$ kJ/mol; $G_{NH_{3gas}}=107.285$ kJ/mol on absolute energy scale is exoergic too $\Delta G_{Hydration}=G_{NH_{3aq}}-(G_{NH_{3gas}}+G_{H_2O})=91.1056-(107.285+0)=-16.18$ kJ/mol. [1,8] CRC, Alberty Solubility product is favored $K_{sp}=\exp(-\Delta G_{Hydration}/R/T)=\exp(16179.4/8.3144/298.15)=683.17$ greater as one.

Weak acid $G_{NH_4^+}=50.81$ kJ/mol protolysis progress $NH_4^++H_2O=NH_{3aq}+H_3O^+$; $pK_{eq}=10.99$; shows energy change $\Delta G_{eq}=-R\cdot T\cdot\ln(K_{eq})=-8.3144*298.15*\ln(10^{-(10.99)})=G_{NH_3Hydration}+G_{H_3O}-G_{NH_4^+}-G_{H_2O}=62.73$ kJ/mol, [16th page](#): $\Delta G_{eq}=G_{NH_{3aq}}+G_{H_3O}-(G_{NH_4^+}+G_{H_2O})=91.1+22.44-G_{NH_4^+}-0=62.73$ kJ/mol.

Ammonium free energy content is $G_{NH_4^+}=G_{NH_{3aq}}+G_{H_3O}-(\Delta G_{eq}+G_{H_2O})=91.1+22.44-62.73-0=50.81$ kJ/mol.

Protolysis classic acid constant is $NH_4^+=H^++NH_{3aqua}$ $pK_a=9.25$;

Formation from elements HNO_2 $\Delta G^{\circ}_{HNO_2}=-46$ kJ/mol and HNO_3 $\Delta G^{\circ}_{HNO_3}=-250.53$ kJ/mol:

$$G_{HNO_2}=\Delta G^{\circ}_{HNO_2}+0.5N_{2gas}+O_{2gas}+0.5H_{2gas}=-46+(0.5*-9.55+303+0.5*85.6)=295.025 \text{ kJ/mol;}$$

$$G_{N_{2gas}}=G_{N_{2aqua}}-(\Delta G_{Hess_sk_N_{2aqua}}+G_{H_2O})=18.7-(28.25+0)=-9.55 \text{ kJ/mol; } G_{H_2gas}=85.6 \text{ kJ/mol Alberty; } G_{O_2gas}=303 \text{ kJ/mol;}$$

$$G_{NO_2Form}=\Delta G^{\circ}_{NO_2aq}+0.5G_{N_{2gas}}+G_{O_2gas}+G_{H_2O}=-33.01+0.5*-9.55+1*303+0=265.2 \text{ kJ/mol;}$$

$$G_{HNO_3Form}=\Delta G^{\circ}_{HNO_3}+(0.5G_{N_{2gas}}+1.5G_{O_2gas}+0.5G_{H_2gas})=-250.53+(0.5*-9.55+1.5*303)=199.195 \text{ kJ/mol;}$$

Acid and protolysis equilibrium constant $K_{eq}=K_a/[H_2O]$ calculate dividing the acid constant by water $[H_2O]$.

- $HNO_2+H_2O=NO_2^-+H_3O^+$; $pK_a=3.15$; $K_{eq}=K_a/[H_2O]=10^{(-3.15)}/55.3=0.00001280$;
 $\Delta G_{eqHNO_2}=-R\cdot T\cdot\ln(K_{eq})=-8.3144\cdot 298.15\cdot\ln(0.0000128)=G_{NO_2^-}+G_{H_3O^+}-(G_{HNO_2}+G_{H_2O})=27.927$ kJ/mol;
 $\Delta G_{eqHNO_2}=G_{NO_2^-}+G_{H_3O^+}-(G_{HNO_2}+G_{H_2O})=265.2+22.44-(259.713+0)=27.927$ kJ/mol;
 $G_{NO_2^-}=\Delta G_{eqHNO_2}-G_{H_3O^+}+(G_{HNO_2}+G_{H_2O})=27.927+22.44-(259.713+0)=265.2$ kJ/mol;
 $G_{HNO_2}=G_{NO_2^-}+G_{H_3O^+}-(\Delta G_{eqHNO_2}+G_{H_2O})=265.2+22.44-(27.927+0)=259.713$ kJ/mol;
- $HNO_3+H_2O=NO_3^-+H_3O^+$; $pK_a=-1.4$; $K_{eq}=K_a/[H_2O]=10^{(1.4)}/55.3=0.4542$;
 $\Delta G_{eqHNO_3}=-R\cdot T\cdot\ln(K_{eq})=-8.3144\cdot 298.15\cdot\ln(0.4542)=G_{NO_3^-}+G_{H_3O^+}-(G_{HNO_3}+G_{H_2O})=1.956$ kJ/mol;
 $\Delta G_{eqHNO_3}=G_{NO_3^-}+G_{H_3O^+}-(G_{HNO_3}+G_{H_2O})=340.2+22.44-(360.684+0)=1.956$ kJ/mol;
 $G_{HNO_3}=G_{NO_3^-}+G_{H_3O^+}-(\Delta G_{eqHNO_3}+G_{H_2O})=340.2+22.44-(1.956+0)=360.7$ kJ/mol;
 $G_{NO_3^-}=\Delta G_{eqHNO_3}-G_{H_3O^+}+(G_{HNO_3}+G_{H_2O})=1.956-22.44+(360.684+0)=340.2$ kJ/mol;

Substance	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
HNO_2	$E^\circ_{NO_3^-H_3O^+}=0.8763$ V	0.8763 V	238.42
HNO_2	-	$pK_a=3.15$	259.713
HNO_2	-79.5	254.1	-46.0
HNO_2	-	formation	295.025
NO_2^-	-	formation	265.2
NO_2^-	-	$pK_a=3.15$	265.2
NO_2^-	-104.19	-238.7	-33.01
NO_2^-	-	-	482.3
HNO_3	-207	146	-250.53
HNO_3	-	formation	199.195
HNO_3	-	$pK_a=-1.4$	360.7
NO_3^-	$E^\circ_{NH_4^+H_2O}=0.7677$ V	0.7677 V	601.06
NO_3^-	-206.85	146.7	-250.5886
NO_3^-	-	formation	340.2
NO_3^-	-	$pK_a=-1.4$	340.2
NO_3^-	$E^\circ_{NO_3^-OH}=-0.3112$ V	-0.3112 V	359.87
NO_3^-	-204.59	-318.8	-109.55
NO_{gas}	91.3	210.8	87.6
NO_{gas}	Solubility product -	-	61.024
NO_{aq}	BioTherm 2006	-	86.55
NO_{aq}	$E^\circ_{NO(g)H_3O^+}=-0.8963$	-0.8963	170.52
NH_3_{gas}	$\Delta G_{Hydration}$	-74.5537	165.7
NH_3_{gas}	[1,8] CRC	Alberty	107.285
NH_3_{gas}	-45.9	192.77	-16.4
NH_3_{aq}	-132.5608	-739.2922	91.1056
NH_3_{aq}	$pK_{beq}=6.49475$	-	91.1
NH_4^+	$pK_{aeq}=10.99$	-	50.81

$$G_{HNO_2}=G_{NO_3^-}+3G_{H_3O^+}-(\Delta G_{eqNO_3}+4G_{H_2O})=238.42$$
 kJ/mol;
 $G_{HNO_2}=G_{NO_2^-}-G_{H_3O^+}+(\Delta G_{eqHNO_2}+G_{H_2O})=259.713$ kJ/mol;
 CRC
 $G_{HNO_2_{gas}}=\Delta G^\circ_{HNO_2_{gas}}+0.5N_{2_{gas}}+O_{2_{gas}}+0.5H_{2_{gas}}=295.025$ kJ/mol
 $G_{NO_2_{form}}=\Delta G^\circ_{NO_2_{aq}}+0.5G_{N_{2_{gas}}}+G_{O_{2_{gas}}}+G_{H_2O}=265.2$ kJ/mol;
 $G_{NO_2^-}=\Delta G_{eqHNO_2}-G_{H_3O^+}+(G_{HNO_2}+G_{H_2O})=265.2$ kJ/mol;
BioTherm2006
 $G_{NO_3^-}=\Delta G_{eqNH_4^+H_2O}-10G_{H_3O^+}+(G_{NH_4^+}-13G_{H_2O})=580.31$ kJ/mol
 Wikiped $G^\circ_{NO_3^-}=\Delta H_H-T\cdot\Delta S_H=-207-298.15\cdot 0.146=-250.5886$ kJ/mol;
 $G_{HNO_3_{Form}}=\Delta G^\circ_{HNO_3}+(0.5G_{N_{2_{gas}}}+1.5G_{O_{2_{gas}}}+0.5G_{H_{2_{gas}}})=199.195$ kJ/mol;
 $G_{HNO_3}=G_{NO_3^-}+G_{H_3O^+}-(\Delta G_{eqHNO_3}+G_{H_2O})=360.7$ kJ/mol;
 $G_{NO_3^-}=\Delta G_{eqNH_4^+H_2O}-10G_{H_3O^+}+(G_{NH_4^+}-13G_{H_2O})=601.06$ kJ/mol;
 $\Delta G^\circ_{NO_3^-}=\Delta H_H-T\cdot\Delta S_H=-206.85-298.15\cdot 0.1467=-250.5886$ kJ/mol;
 $G_{NO_3_{Form}}=\Delta G^\circ_{HNO_3_{aq}}+(0.5G_{N_{2_{gas}}}+1.5G_{O_{2_{gas}}}+G_{H_2O})=340.2$ kJ/mol;
 $G_{NO_3^-}=\Delta G_{eqHNO_3}-G_{H_3O^+}+(G_{HNO_3}+G_{H_2O})=340.2$ kJ/mol;
 $G_{NO_3^-}=\Delta G_{eqNO_3-OH}-G_{H_2O}+(G_{NO_2^-}+2G_{OH})=359.87$ kJ/mol;
BioTherm2006
 CRC
 $G_{NO_{gas}}=G_{NO_{aq}}-(G_{H_2O}+\Delta G_{sp})=86.55-(0+25.526)=61.024$ kJ/mol;
 $G_{NO_{aq}}=G_{NO_3^-}+4G_{H_3O^+}-(\Delta G_{eqNO(g)H_3O^+}+6G_{H_2O})=170.52$ kJ/mol;
 $G_{NH_3_{gas}}=\Delta G_{NH_3_{aq}}-(\Delta G_{Hydrations}+G_{H_2O})=91.1056-(-74.5537+0)=165.7$ kJ/mol;
 $2G_{NH_3_{gas}}=2\Delta G_{Hess_NH_3_{gas}}+(G_{N_{2_{gas}}}+3\cdot G_{H_{2_{gas}}})=2\cdot 107.285$ kJ/mol;
 $2G_{NH_3_{gas}}=2\cdot -16.4+(-9.55+3\cdot 85.64)=-214.57=2\cdot 107.285$ kJ/mol;
 Ammonia pH=7.36 [8] **Alberty**; $NH_{3_{aq}}$ formation
 $G_{NH_3_{aq}}=G_{NH_4^+}+G_{OH^-}-(\Delta G_{beq}+G_{H_2O})=91.1$ kJ/mol; [Wikipedia](#) [28]
 $G_{NH_4^+}=G_{NH_3_{aq}}+G_{H_3O^+}-(\Delta G_{aeq}+G_{H_2O})=91.1+22.44-62.73-0=50.81$ kJ/mol;

Protolysis $NH_{3aq}+H_2O=NH_4^++OH^-$ constant $K_{beq}=K_b/[H_2O]=10^{(-)}/55.3=3.20\cdot 10^{(-7)}=10^{(-6.4947)}$ $pK_{beq}=6.4947$ in classic expressed without water account is $K_b=[NH_4^+]\cdot[OH^-]/[NH_3aq]=10^{(-4.752)}=1.77\cdot 10^{(-5)}$; $pK_b=4.752$.

Energy accumulates endoergic in products $G_{NH_4^+}+G_{OH^-}=50.81+77.36=128.17$ kJ/mol;

$$\Delta G_{beq}=-R\cdot T\cdot\ln(K_{beq})=-8.3144\cdot 298.15\cdot\ln(10^{(-6.4947)})=G_{NH_4^+}+G_{OH^-}-(G_{NH_3aq}+G_{H_2O})=37.07$$
 kJ/mol .

$$\Delta G_{Hess_beq}=G_{NH_4^+}+G_{OH^-}-(G_{NH_3aq}+G_{H_2O})=50.81+77.36-(91.1056+0)=37.064$$
 kJ/mol;

$$G_{NH_3aq}=G_{NH_4^+}+G_{OH^-}-(\Delta G_{Hess_beq}+G_{H_2O})=50.81+77.36-(37.07+0)=91.1$$
 kJ/mol;

The energy expressed for the gas solubility are $NH_{3gas}+H_2O=NH_{3aq}$ are $G_{NH_3aq}=91.1$ kJ/mol, $G_{NH_3gas}=107.3$ kJ/mol.

Weak acid $G_{NH_4^+}=50.81$ kJ/mol protolysis $NH_4^++H_2O=NH_{3aq}+H_3O^+$ $pK_{eq}=10.99$ shows endoergic energy change

positive $\Delta G_{aeq}=-R\cdot T\cdot\ln(K_{aeq})=-8.3144\cdot 298.15\cdot\ln(10^{(-10.99)})=G_{NH_3_{Hydration}}+G_{H_3O^+}-G_{NH_4^+}-G_{H_2O}=62.73$ kJ/mol .

Ammonium free energy content in one mol is $G_{NH_4^+}=G_{NH_3aq}+G_{H_3O^+}-(\Delta G_{aeq}+G_{H_2O})=91.1+22.44-(62.73+0)=50.81$ kJ/mol .

Nernst's potential $\text{NO}_3^-/\text{NO}_2^-$ red-ox system behaving in acidic H_3O^+ water and basic OH^- medium

$\text{HNO}_2 + 4\text{H}_2\text{O} = \text{NO}_3^- + 3\text{H}_3\text{O}^+ + 2\text{e}^-$; $E^\circ_{\text{NO}_3^-/\text{HNO}_2} = 0.8753$ V Kortly, Shucha pH<3.15;

$$E^\circ_{\text{NO}_3^-/\text{HNO}_2} = E^\circ + 0.10166 - 0.0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^4) - 0.37239 = 0.94 + 0.10166 - 0.02955 \cdot \lg(1/55.3^{14}) - 0.37239 = 0.8753 \text{ V};$$

$$E_{\text{NO}_3^-/\text{HNO}_2} = E^\circ_{\text{NO}_3^-/\text{HNO}_2} + \frac{0.0591}{2} \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^3}{[\text{HNO}_2] \cdot [\text{H}_2\text{O}]^4} = 0.8753 \text{ V} + \frac{0.0591}{2} \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^3}{[\text{HNO}_2] \cdot [\text{H}_2\text{O}]^4}$$

$$\Delta G_{\text{eqNO}_3} = E^\circ_{\text{NO}_3} \cdot F \cdot 2 = 0.8753 \cdot 96485 \cdot 2 = 168.9 \text{ kJ/mol};$$

$$\Delta G_{\text{eqNO}_3} = G_{\text{NO}_3^-} + 3G_{\text{H}_3\text{O}^+} - (G_{\text{HNO}_2} + 4G_{\text{H}_2\text{O}}) = 340.2 + 3 \cdot 22.44 - (238.62 + 4 \cdot 0) = 168.9 \text{ kJ/mol};$$

$$G_{\text{HNO}_2} = G_{\text{NO}_3^-} + 3G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqNO}_3} + 4G_{\text{H}_2\text{O}}) = 340.2 + 3 \cdot 22.44 - (168.9 + 4 \cdot 0) = 238.62 \text{ kJ/mol};$$

$\text{NO}_2^- + 2\text{OH}^- = \text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^-$; $E^\circ_{\text{NO}_3^-/\text{NO}_2^-} = -0.3122$ V; pH>3.15 Suchotina

$$E^\circ_{\text{NO}_3^-/\text{NO}_2^-} = E^\circ + 0.10166 - 0.0591/2 \cdot \lg([\text{H}_2\text{O}]) - 0.37239 = 0.01 + 0.10166 - 0.02955 \cdot \lg(55.3^{14}) - 0.37239 = -0.3122 \text{ V};$$

$$E_{\text{NO}_3^-/\text{NO}_2^-} = E^\circ_{\text{NO}_3^-/\text{NO}_2^-} + \frac{0.0591}{2} \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_2\text{O}]}{[\text{NO}_2^-] \cdot [\text{OH}^-]^2} = -0.3122 \text{ V} + \frac{0.0591}{2} \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_2\text{O}]}{[\text{NO}_2^-] \cdot [\text{OH}^-]^2}$$

$$\Delta G_{\text{eqNO}_3-\text{O}_2} = E^\circ_{\text{NO}_3-\text{O}_2} \cdot F \cdot 2 = -0.3122 \cdot 96485 \cdot 2 = -60.245 \text{ kJ/mol};$$

$$\Delta G_{\text{eqNO}_3-\text{O}_2} = G_{\text{NO}_3^-} + G_{\text{H}_2\text{O}} - (G_{\text{NO}_2^-} + 2G_{\text{OH}^-}) = 359.675 + 0 - (265.3 + 2 \cdot 77.36) = -60.245 \text{ kJ/mol};$$

$$G_{\text{NO}_3^-} = \Delta G_{\text{eqNO}_3-\text{O}_2} - G_{\text{H}_2\text{O}} + (G_{\text{NO}_2^-} + 2G_{\text{OH}^-}) = -60.245 - 0 + (265.3 + 2 \cdot 77.36) = 359.775 \text{ kJ/mol};$$

$$G_{\text{NO}_2^-} = G_{\text{NO}_3^-} + G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqNO}_3-\text{O}_2} + 2G_{\text{OH}^-}) = 359.675 + 0 - (-60.245 + 2 \cdot 77.36) = 265.3 \text{ kJ/mol};$$

$\text{NO}_2 + 3\text{H}_2\text{O} = \text{NO}_3^- + 2\text{H}_3\text{O}^+ + 2\text{e}^-$; David Harris; absolute standard potential $E^\circ_{\text{NO}_3^-} = 0.7188$ V

$$E^\circ_{\text{NO}_3^-} = E^\circ + 0.10166 - 0.0591/2 \cdot \lg([\text{H}_2\text{O}]^3) - 0.371339 = 0.835 + 0.10166 - 0.02955 \cdot \lg(1/55.3^{14}) - 0.371339 = 0.7188 \text{ V}$$

Molarity $M_{\text{NO}} = 30.006$ g/mol; solubility $\text{NO}^{(\text{g})}$ 0.00562 g/99.6g 20 C; w% = 0.00562/(0.00562+99.6)*100 = 0.00562%;

product $[\text{NO}_{\text{aq}}] = (0.00562/100 \cdot 99.6)/30.006 = 0.001865$ M, if pure gas mol fraction is one $[\text{NO}^{(\text{g})}] = 1$;

Equilibrium $\text{NO}_{\text{gas}} + \text{H}_2\text{O} = \text{NO}_{\text{aq}}$ constant is $K_{\text{eq}} = [\text{NO}_{\text{aq}}]/[\text{NO}^{(\text{g})}][\text{H}_2\text{O}] = 0.001865/1/55.3 = 10^{-(4.472)}$.

Equilibrium minimum is $\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8.3144 \cdot 298.15 \cdot \ln(10^{-(4.472)}) = -8.3144 \cdot 298.15 \cdot -10.297 = 25.526$ kJ/mol

$$\Delta G_{\text{eq}} = G_{\text{NO}_{\text{aq}}} - (G_{\text{H}_2\text{O}} + G_{\text{NO}_{\text{gas}}}) = 86.55 - (0 + G_{\text{NO}_{\text{gas}}}) = 25.526 \text{ kJ/mol};$$

$$G_{\text{NO}_{\text{gas}}} = G_{\text{NO}_{\text{aq}}} - (G_{\text{H}_2\text{O}} + \Delta G_{\text{eq}}) = 86.55 - (0 + 25.526) = 61.024 \text{ kJ/mol}, \text{ if equilibrium minimum is } \Delta G_{\text{eq}} = 25.526 \text{ kJ/mol};$$

Solubility of gas NO_{gas} compensate water molecule on Nernst's expression from six $6\text{H}_2\text{O}$ to five $5\text{H}_2\text{O}$:

$\text{NO}_{\text{aq}} + 5\text{H}_2\text{O} = \text{NO}_3^- + 4\text{H}_3\text{O}^+ + 3\text{e}^-$; $E^\circ_{\text{NO}^{(\text{g})}/\text{NO}_{\text{aq}}} = 0.8609$ V; Kortly, Shucha;

$$E^\circ_{\text{NO}^{(\text{g})}/\text{NO}_{\text{aq}}} = E^\circ + 0.10166 - 0.0591/3 \cdot \lg(1/[\text{H}_2\text{O}]^5) - 0.37239 = 0.96 + 0.10166 - 0.0197 \cdot \lg(1/55.3^{15}) - 0.37239 = 0.8609 \text{ V};$$

$$E_{\text{NO}^{(\text{g})}/\text{NO}_{\text{aq}}} = E^\circ_{\text{NO}^{(\text{g})}/\text{NO}_{\text{aq}}} + 0.0591/3 \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{NO}_{\text{aq}}] \cdot [\text{H}_2\text{O}]^6} = 0.8609 \text{ V} + 0.0197 \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{NO}_{\text{aq}}] \cdot [\text{H}_2\text{O}]^6}$$

$$\Delta G_{\text{eqNO}^{(\text{g})}/\text{NO}_{\text{aq}}} = E^\circ_{\text{NO}^{(\text{g})}/\text{NO}_{\text{aq}}} \cdot F \cdot 3 = 0.8609 \cdot 96485 \cdot 3 = 249.19 \text{ kJ/mol};$$

$$\Delta G_{\text{eqNO}^{(\text{g})}/\text{NO}_{\text{aq}}} = G_{\text{NO}_3^-} + 4G_{\text{H}_3\text{O}^+} - (G_{\text{NO}_{\text{aq}}} + 5G_{\text{H}_2\text{O}}) = 340.2 + 4 \cdot 22.44 - (180.77 + 5 \cdot 0) = 249.19 \text{ kJ/mol};$$

$$G_{\text{NO}_{\text{aq}}} = G_{\text{NO}_3^-} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqNO}^{(\text{g})}/\text{NO}_{\text{aq}}} + 5G_{\text{H}_2\text{O}}) = 340.2 + 4 \cdot 22.44 - (249.19 + 5 \cdot 0) = 180.77 \text{ kJ/mol};$$

$\text{NH}_4^+ + 13\text{H}_2\text{O} = \text{NO}_3^- + 10\text{H}_3\text{O}^+ + 8\text{e}^-$; $E^\circ_{\text{NH}_4^+/\text{NO}_3^-} = 0.7667$ V Suchotina

$$E^\circ_{\text{NH}_4^+/\text{NO}_3^-} = E^\circ + 0.10166 - 0.0591/8 \cdot \lg(1/[\text{H}_2\text{O}]^{13}) - 0.371339 = 0.87 + 0.10166 - 0.00739 \cdot \lg(1/55.3^{13}) - 0.371339 = 0.7667 \text{ V};$$

$$E_{\text{NH}_4^+/\text{NO}_3^-} = E^\circ_{\text{NH}_4^+/\text{NO}_3^-} + 0.0591/8 \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^{10}}{[\text{NH}_4^+] \cdot [\text{H}_2\text{O}]^{13}} = 0.7666879 \text{ V} + 0.00739 \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^{10}}{[\text{NH}_4^+] \cdot [\text{H}_2\text{O}]^{13}}$$

$$\Delta G_{\text{eqNH}_4^+/\text{NO}_3^-} = E^\circ_{\text{NH}_4^+/\text{NO}_3^-} \cdot F \cdot 8 = 0.7666879 \cdot 96485 \cdot 8 = 592.56 \text{ kJ/mol};$$

$$\Delta G_{\text{eqNH}_4^+/\text{NO}_3^-} = G_{\text{NO}_3^-} + 10G_{\text{H}_3\text{O}^+} - (G_{\text{NH}_4^+} + 13G_{\text{H}_2\text{O}}) = 601.06 + 10 \cdot 22.44 - (232.9 + 13 \cdot 0) = 592.56 \text{ kJ/mol};$$

$$G_{\text{NO}_3^-} = \Delta G_{\text{eqNH}_4^+/\text{NO}_3^-} - 10G_{\text{H}_3\text{O}^+} + (G_{\text{NH}_4^+} + 13G_{\text{H}_2\text{O}}) = 592.56 - 10 \cdot 22.44 + (232.9 + 13 \cdot 0) = 601.06 \text{ kJ/mol};$$

Nernst's potential studies $\underline{5(Pt)H} + MnO_4^-$ on hydroxonium H_3O^+ and water H_2O account

Inverse Nernst's standard potential: $MnO_4^- + 8H_3O^+ + 5e^- = Mn^{2+} + 12H_2O$; $-E^\circ_{Mn^{2+}/MnO_4^-} = -1.4865V$.

Twelve water molecules account $[H_2O] = 55.3 M = (996 \frac{g}{L}) / (18 \frac{g}{mol})$ increase potential to:

$$E^\circ_{Mn^{2+}/MnO_4^-} = E^\circ - 0.0591/5 \cdot \log(1/[H_2O]^{12}) = 1.51 - 0.0591/5 \cdot \log(1/55.3^{12}) + 0.10166 - 0.37239 = 1.4865 V.$$

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

Reductant oxidation Nernst's: $\underline{5(Pt)H} + 5H_2O = 5H_3O^+ + 5e^-$; absolute standard potential $E^\circ_H = -0.27073 V$.

$$E_{MnO_4^-} = -1.4865 V + 0.0591/5 \cdot \log([H_2O]^{12} \cdot [Mn^{2+}] / [MnO_4^-] \cdot [H_3O^+]^8);$$

$$E_H = E^\circ_H + 0,0591 \cdot \log([H_3O^+] / [H_2O]) = -0,27073 V + 0,0591 \cdot \log([H_3O^+] / [H_2O]);$$

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

$$\Delta G_{HessPtH} = \Delta G^\circ_{Mn^{2+}} + 7\Delta G^\circ_{H_2O} - (\Delta G^\circ_{MnO_4^-} + 3\Delta G^\circ_{H_3O^+} + 5G_{(Pt)H}) = -228,1 + 7 \cdot (-237,191) - (3 \cdot (-213,2746) - 447,2 + 5 \cdot 48,56) = -1044,21 \text{ kJ/mol};$$

$$\Delta G_{HessCRC} = \Delta G^\circ_{Mn^{2+}} + 7\Delta G^\circ_{H_2O} - (\Delta G^\circ_{MnO_4^-} + 3\Delta G^\circ_{H_3O^+} + 5/2\Delta G^\circ_{H_2}) = -228,1 + 7 \cdot (-237,191) - (3 \cdot (-213,2746) - 447,2 + 5 \cdot 99,13/2) = -1049 \text{ kJ/mol};$$

$$\Delta G_{Alberty} = \Delta G^\circ_{Mn^{2+}} + 7\Delta G^\circ_{H_2O} - (\Delta G^\circ_{MnO_4^-} + 3\Delta G^\circ_{H_3O^+} + 5/2G_{H_2}) = -228,1 + 7 \cdot (-237,191) - (3 \cdot (-213,2746) - 447,2 + 5 \cdot 103,24/2) = -1059,5 \text{ kJ/mol};$$

Substan	$\Delta H^\circ_H, \text{kJ/mol}$	$\Delta S^\circ_H, \text{J/mol/K}$	$\Delta G^\circ_H, \text{kJ/mol}$
H_2O	-285.85	69.9565	-237.191
H_2O	-286.65	-453.188	-151.549
H_3O^+	-285.81	-3.854	-213.2746
$H_2(aq)$	23.4	-130	99.13
$H_2(aq)$	-5.02	-363.92	103.24
$H(Pt)(aq)$	-	-	48.56
MnO_4^-	-541.4	-191.2	-447.2
Mn^{2+}	-220.8	-73.6	-228.1
O_{2aqua}	-11.7	-94.2	16.4

CRC Handbook of Chemistry and Physics, 2010. D.Lide

Biochem. Thermodyn, Alberty, 2006, Massachusetts Techn. Inst.

$\Delta G^\circ_{H_3O^+}, \text{kJ/mol}$ Mischenko 1972, Himia, Leningrad [26]

Alberty 2006 Biochem. Thermodyn. Massachusetts Technology Inst.

$$\Delta G_{eq} = -847.7 \text{ kJ/mol}; \Delta G_{HessOxRed} = -1044.2 \text{ kJ/mol}$$

$$|\Delta G_{eq} = -847.7 \text{ kJ/mol}| < |\Delta G_{Hess} = -1044.2 \text{ kJ/mol}|;$$

$$\Delta G_{eqH/MnO_4^-} = (E^\circ_H - E^\circ_{MnO_4^-}) \cdot F \cdot 1 \cdot 5 = (-0,27073 - 1,4865) \cdot 96485 \cdot 5 = -1,757 \cdot 96485 \cdot 5 = -847,7 \text{ kJ/mol}.$$

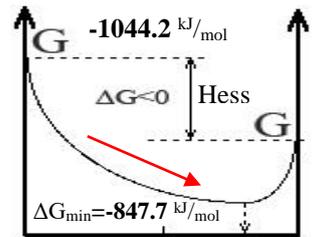
$$K_{eq} = \exp(-\Delta G_{eq} / R/T) = \exp(847732 / 8,3144 / 298,15) = \exp(341,96) = 10^{148,5};$$

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

$\Delta G_{Hess} = \Delta G_{OxRed} = -1043.7 \text{ kJ/mol}$, but minimizes $\Delta G_{min} = \Delta G_{eqOxRed} = -847.7 \text{ kJ/mol}$ reaching

$$\text{equilibrium mixture } 10^{148.5} = K_{eq} = \frac{[H_2O]^7 \cdot [Mn^{2+}]}{[(Pt)H]^5 \cdot [MnO_4^-] \cdot [H_3O^+]^3};$$

Prigogine attractor is free energy change minimum ΔG_{min} reaching. Free energy change minimum reaching establishes equilibrium. Equilibrium state is attractor for all infinite non-equilibrium states.



5A + B + 3C 50% D + 8E

reactants $\underline{5(Pt)H} + MnO_4^- + 3H_3O^+$

products $Mn^{2+} + 7H_2O$

$MnO_2 + 4OH^- = MnO_4^- + 2H_2O + 3e^-$; Reductant Nernst's absolute standard potential: $E^\circ_{MnO_2/MnO_4^-} = 0.26465 V$,

$E^\circ_{MnO_2/MnO_4^-} = E^\circ - 0.0591/3 \cdot \log([H_2O]^2) + 0.10166 - 0.37239 = 0.603 - 0.0591/3 \cdot \log(55.3^2) + 0.10166 - 0.37239 = 0.26465 V$;

$MnO_4^{2-} = MnO_4^- + e^-$; Reductant Nernst's absolute standard potential: $E^\circ_{MnO_2/MnO_4^-} = 0.2883 V$;

$E^\circ_{MnO_4^{2-}/MnO_4^-} = E^\circ - 0.0591/3 \cdot \log([H_2O]^0) + 0.10166 - 0.37239 = 0.558 - 0.0591/3 \cdot \log(55.3^0) + 0.10166 - 0.37239 = 0.2883 V$;

2) Carbonic anhydrase CA generate free energy from zero $G_{CO_2+2H_2O} = 0 \text{ kJ/mol}$ to $G_{H_3O^+ + HCO_3^-} = 78,52 \text{ kJ/mol}$.

Solubility in water creates free energy from zero level $CO_{2gas} + H_2O = CO_{2aqua}$ to $G_{CO_{2aqua}} = 18,38 \text{ kJ/mol}$ constant:

$$K_{eqCO_{2aqua}} = [CO_{2aqua}] / [CO_{2gas}] \cdot [H_2O] = \exp(-G_{CO_{2aqua}} / R/T) = \exp(-18382,746 / 8,3144 / 298,15) = 0,000601808$$

increasing free energy by $\Delta G_{CO_{2aqua}} = -R \cdot T \cdot \ln(K_{eqCO_{2aqua}}) = -8,3144 \cdot 298,15 \cdot \ln(0,000601808) = 18,38 \text{ kJ/mol}$.

Reaction $CO_{2aqua} + 2H_2O + \Delta G + Q = v \xrightarrow{CA} H_3O^+ + HCO_3^-$ velocity constant is

$k_{1CO_{2aqua}} = 1,5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ and protolytic acid CO_{2aqua} equilibrium value of constant is

$$\frac{[HCO_3^-]_{aqua} \cdot [H_3O^+]}{[CO_2]_{aqua} \cdot [H_2O]^2} = K_{eqCAHCO_3aqua} = K_{aCO_2aqua} / [H_2O]^2 = 10^{-7,0512} / 55,3^2 = 2,906 \cdot 10^{-11}. [9]$$

CA high rate protolysis constant accumulate free energy in products $H_3O^+ + HCO_3^-$ activating its:

$$\Delta G_{eqCACO_{2aqua}} = -R \cdot T \cdot \ln(K_{eqCACO_{2aqua}}) = -8,3144 \cdot 298,15 \cdot \ln(2,906 \cdot 10^{-11}) / 1000 = 60,14 \text{ kJ/mol}.$$

Total free energy increases by activation reaching equilibrium state with high rate protolysis and solubility:

$$G_{H_3O^+ + HCO_3^-} = G_{H_3O^+} + G_{HCO_3^-} = 22,44 + 56,08 = G_{CO_{2aqua}} + \Delta G_{eqCACO_{2aqua}} = 18,38 + 60,14 = 78,52 \text{ kJ/mol}. [1,8,14]$$

High rate protolysis attractor is $pH = 7,36$. Deviation from the attractor disrupts the order of irreversible homeostasis processes, creating disorder and chaos.

Carbonic anhydrase CA synthesis indispensable active Biosphere attractor.

The reactivity of carbonic anhydrase and the equilibrium-attractor value of the generated physiological buffer solution protolysis $\text{pH}=7.36$ is a self-organizing biosphere attractor. The accumulated free energy of the reaction $\text{CO}_2+2\text{H}_2\text{O}$ in the products $(\text{CO}_2\text{aqua}) \text{H}_3\text{O}^++\text{HCO}_3^-$ accumulate free energy $G_{\text{H}_3\text{O}^++\text{HCO}_3^-}=18.38+60.14=78.38$ kJ/mol is necessary for the functional activity of the bicarbonate buffer system for the perfect order of reactions in the complex processes of irreversible homeostasis.

CO_2 no reaction with water H_2O at absence of CA. CO_2 is weak soluble and slow react with OH^- ions. [Wikipedia](#) [27] mol mass $M_{\text{CO}_2}=44.009$ g/mol. Solubility $\text{CO}_2\text{gas}+\text{H}_2\text{O}=\text{CO}_2\text{aqua}$ 1.45 g/L at 0.99 atm and at 1 atm $m_{\text{CO}_2}=100*1.45/99=1.4646$ g/L has concentration $[\text{CO}_2\text{aqua}]=m_{\text{CO}_2}/M_{\text{CO}_2}=1.4646/44.009=0.03328$ M.

Solubility product is $K_{\text{spCO}_2\text{aqua}}=[\text{CO}_2\text{aqua}]/[\text{CO}_2\text{gas}]=0.03328$ M but equilibrium constant in mol fractions is $K_{\text{eqCO}_2\text{aqua}}=[\text{CO}_2\text{aqua}]/[\text{CO}_2\text{gas}]/[\text{H}_2\text{O}]=K_{\text{spCO}_2\text{aqua}}/[\text{H}_2\text{O}]=0.03328/55.3=0.000601808$.

Free energy $\Delta G_{\text{eqCO}_2\text{aqua}}=-R\cdot T\cdot\ln(K_{\text{eqCO}_2\text{aqua}})=-8.3144*298.15*\ln(0.000601808)/1000=18.38$ kJ/mol has minimum value at solubility equilibrium $G_{\text{CO}_2\text{aqua}}=\Delta G_{\text{eqCO}_2\text{aqua}}+(G_{\text{CO}_2\text{gas}}+G_{\text{H}_2\text{O}})=18.38+(0+0)=18.38$ kJ/mol .

From air 0.04 % mol fraction $[\text{CO}_2\text{gas}]=0.0004$ creates dissolved concentration:

$$[\text{CO}_2\text{aqua}]=K_{\text{eqCO}_2\text{aqua}}*[\text{H}_2\text{O}]*[\text{CO}_2\text{gas}]=0.000601808*55.3457*0.0004=0.000753$$
 M.

Carbon dioxide CO_2aqua reacts with OH^- ions times $10^{16.54}$ slower as bicarbonate HCO_3^- neutralization reaction: $\text{H}_3\text{O}^++\text{HCO}_3^-=\text{CO}_2\text{aqua}+2\text{H}_2\text{O}$, because neutralization velocity constant is $k_2=5.16885*10^{18}$ $\text{M}^{-2}\text{s}^{-1}$, but OH^- ions $\text{CO}_2\text{aqua}+\text{OH}^-=\text{HCO}_3^-$ have velocity constant $k_{1\text{OH}}=1.5*10^2$ $\text{M}^{-2}\text{s}^{-1}$. Reaction has favored equilibrium constant:

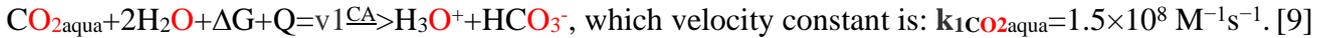
$$\Delta G_{\text{HessHCO}_3^-}=G_{\text{HCO}_3^-}-(G_{\text{CO}_2\text{aqua}}+G_{\text{OH}^-})=56.08-(18.38+77.36)=-39.66$$
 kJ/mol

$$k_{1\text{OH}}/k_{2\text{HCO}_3^-}=[\text{HCO}_3^-]/[\text{CO}_2\text{aqua}]/[\text{OH}^-]=K_{\text{eqHCO}_3^-}=\text{EXP}(-\Delta G_{\text{eqHCO}_3^-}/R/T)=\text{EXP}(39660/8.3144/298.15)=8875.3$$

and produce exothermic heat Q: $\Delta H_{\text{Hess}}=\Delta H^\circ_{\text{HCO}_3^-}-\Delta H^\circ_{\text{CO}_2}-\Delta H^\circ_{\text{OH}^-}=-48.68$ kJ/mol . Inverse $\text{HCO}_3^-=\text{CO}_2\text{aqua}+\text{OH}^-$ reaction has $k_{2\text{HCO}_3^-}=k_{1\text{OH}}/K_{\text{eqHCO}_3^-}=1.5*10^2/8875.3=0.0169$ unfavored constant. Decomposition $\text{HCO}_3^-=\text{CO}_2\text{aqua}+\text{OH}^-$ velocity constant $k_{2\text{HCO}_3^-}$ is then billion 10^{10} times slower as CA velocity constant $k_{1\text{CO}_2\text{aqua}}=1.5*10^8$ $\text{M}^{-1}\text{s}^{-1}$. [9]

CA protolytic reactivity creates functional active bicarbonate buffer self-organizing attractor $\text{pH}=7.36$ with generate concentrations gradients for transport of H_3O^+ , HCO_3^- , CO_2aqua and of O_2aqua , H_2O by osmose through aquaporin channels. [9]

CA high rate protolysis require CO_2aqua react with two water molecules:



Neutralization $\text{H}_3\text{O}^++\text{HCO}_3^-=\text{CO}_2\text{aqua}+2\text{H}_2\text{O}$ velocity constant is CA independent times $10^{10.54}$ greater about CA velocity constant: $k_2/k_{1\text{CO}_2\text{aqua}}=5.16885*10^{18}/1.5/10^8=34407299853=10^{10.54}$.

CA protolysis equilibrium constant evaluate ratio of velocity constants in expression:

$$K_{\text{eqCAHCO}_3\text{aqua}}=k_{1\text{CO}_2\text{aqua}}/k_2=K_{\text{aCO}_2\text{aqua}}/[\text{H}_2\text{O}]^2=10^{-(7.0512)}/55.3^2=2.906*10^{-11}=10^{-10.54}$$

Bicarbonate buffer acid protolysis constant $\text{pK}_{\text{aCO}_2\text{aqua}}=7.0512$ is friendly to attractor value $\text{pH}=7.36$:

$$K_{\text{aCO}_2\text{aqua}}=K_{\text{eqCAHCO}_3\text{aqua}}*[\text{H}_2\text{O}]^2=\frac{[\text{HCO}_3^-]_{\text{aqua}}*[\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}}}=10^{-7.0512}=10^{-\text{pK}_{\text{aCO}_2\text{aqua}}}$$
. Original $\text{pK}_{\text{aCO}_2\text{aqua}}=7.0512$ value

obtained and calculated for [BUFFER](#) solutions. Hess free energy change is exoergic negative:

$$\Delta G_{\text{Hess}}=2\Delta G^\circ_{\text{H}_2\text{O}}+\Delta G^\circ_{\text{CO}_2}-(\Delta G^\circ_{\text{H}_3\text{O}^+}+\Delta G^\circ_{\text{HCO}_3^-})=2*(-237.191-385.98)-(-213.2746-544.9688)=-102$$
 kJ/mol . [1]

Neutralization: $\text{H}_3\text{O}^++\text{HCO}_3^-=\text{CO}_2\text{aqua}+2\text{H}_2\text{O}$ constant is inverse to protolysis and favored:

$$K_{\text{eqNeutralization}}=1/K_{\text{eqCAHCO}_3\text{aqua}}=[\text{HCO}_3^-]*[\text{H}_3\text{O}^+]/[\text{CO}_2\text{aqua}]/[\text{H}_2\text{O}]^2=1/2.90636/10^{(-11)}=34407299853.$$

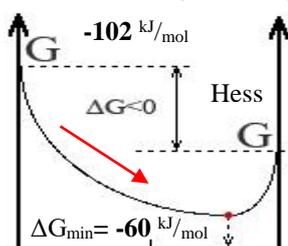
$$\Delta G_{\text{Absolute_Neutralization}}=2G_{\text{H}_2\text{O}}+G_{\text{CO}_2\text{aqua}}-G_{\text{H}_3\text{O}^+}-G_{\text{HCO}_3^-}=2*0+18.38-22.44-56.08=-60.14$$
 kJ/mol and

enthalpy Hess change in reaction is exothermic: $\Delta H_{\text{Hess}}=2\Delta H^\circ_{\text{H}_2\text{O}}+\Delta H^\circ_{\text{CO}_2}-\Delta H^\circ_{\text{H}_3\text{O}^+}-\Delta H^\circ_{\text{HCO}_3^-}=-7.2$ kJ/mol .

Neutralization is favored reaction. Free energy change on minimum expression is negative:

$$\Delta G_{\text{eqNeutralization}}=-R\cdot T\cdot\ln(K_{\text{eqNeutralization}})=-8.3144*298.15*\ln(34407299853)=-60.14$$
 kJ/mol , but CO_2aqua protolysis minimum as inverse reaction of neutralization is positive:

$$\Delta G_{\text{eqCAHCO}_3\text{aqua}}=-R\cdot T\cdot\ln(K_{\text{eqCAHCO}_3\text{aqua}})=-8.3144*298.15*\ln(1/34407299853)=60.14$$
 kJ/mol .



A+B 50 % C+2D.

Attractor Fig. 2. Exothermic and exoergic neutralization Hess free energy change $\Delta G_{\text{HessNeutralization}}$ is negative -102 kJ/mol , but $\Delta G_{\text{eqNeutralization}}=-60.14$ kJ/mol minimized reaching equilibrium mixture $K_{\text{eq}}=34407299853$ at presence of CA carbonic anhydrase. Carbon dioxide reaction with hydroxide anions is slow, because of small factors: $k_{1\text{OH}}=1.5*10^2$ $\text{M}^{-2}\text{s}^{-1}$ velocity constant and concentrations $[\text{CO}_2\text{aqua}]=0.0007512$ M, $[\text{OH}^-]=10^{-6.64}$ M. Carbonic anhydrase synthesis resolves perfect order of bioenergetic homeostasis as self-organization attractor. [3.4] Reactants $\text{H}_3\text{O}^++\text{HCO}_3^-$, products $\text{CO}_2\text{aqua}+2\text{H}_2\text{O}$.

2CO₂ / H₂C₂O₄ / CH_{4gas} solubility and protolysis require hydroxonium H₃O⁺ and water H₂O account.

Formation from free elements of carbon dioxide C_{gr}+O_{2gas}=CO_{2gas} standard free energy change is exoergic negative ΔG_{Hess_CO2gas}=-394.36 kJ/mol. [1] If background level for biochemistry absolute energy scale is zero than in Hess law for graphite the absolute free energy content is G_{gr}=ΔG^o_{Hess_CO2gas}-G_{O2gas}=394.36-303.1=91.26 kJ/mol.

The standard free energy change for methane formation from free elements C_{gr}+2H_{2gas}>CH_{4gas} [1,8] is

$$\Delta G_{\text{Hess_CH4gas}} = G_{\text{CH4gas}} - (G_{\text{Cgr}} + 2 * G_{\text{H2}}) = G_{\text{CH4gas}} - (91.26 + 2 * 85.64) = -50.5 \text{ kJ/mol and}$$

the free energy content per mole of methane remaining unused from free elements in Hess's law is

$$G_{\text{CH4gas}} = \Delta G_{\text{Hess_CH4gas}} + (G_{\text{Cgr}} + 2 * G_{\text{H2}}) = -50.5 + (91.26 + 2 * 85.64) = 212.04 \text{ kJ/mol.}$$

This allows us to calculate the absolute free energy per mole of the element graphite using Alberty's energy data:

$$G^{\circ}_{\text{CgrCH4gas}} = G^{\circ}_{\text{CH4gas}} - \Delta G_{\text{Hess_CH4gas}} - 2 * G^{\circ}_{\text{H2gas}} = 212.04 - (-50.5 + 2 * 85.64) = 91.26 \text{ kJ/mol ,}$$

which coincides with the zero background of carbon dioxide gas G^o_{CO2gas}=0 kJ/mol on the absolute energy scale.

Solubility of methane CH_{4gas}+H₂O=CH_{4aq} is 22.7 mg/L and methane molar mas is M_{CH4}=16.043 g/mol. Water account [H₂O]=996/18=55.3 M give constant K_{eq}=K_{sp}/[H₂O]=0.001414947 M/55.3 M=10^{^-4.592}. Alberty given data calculate solubility energy change ΔG_{eqCH4aq}=G_{CH4aq}-(G_{CH4gas}+G_{H2O})=238.25-(212.04+0)=26.21 kJ/mol .

$$G_{\text{CH4aq}} = \Delta G_{\text{eqCH4}} + (G_{\text{H2O}} + G_{\text{CH4}^{\text{gas}}}) = 26.21 + (0 + 212.04) = 238.25 \text{ kJ/mol;}$$

Methane solubility [CH₄]=0.0227/16.043=0.001414947 M equilibrium absolute free energy change is

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8.3144 \cdot 298.15 \cdot \ln(0.001414947/55.3) = -8.3144 \cdot 298.15 \cdot -6.592 = 26.21 \text{ kJ/mol .}$$

Equilibrium energy change ΔG_{eqCH4}=G_{CH4aq}-(G_{H2O}+G_{CH4^{gas}})=G_{CH4aq}-(0+212.04)=26.21 kJ/mol let us calculate

absolute free energy content for methane in water (aqua): G_{CH4aq}=G_{CH4gas}+G_{CH4sp}=212.04+26.21=238.25 kJ/mol;

Substance	ΔH ^o _H kJ/mol	ΔS ^o _H J/mol/K	ΔG ^o _H kJ/mol	ΔG _{H2C2O4} =ΔH _H -T*ΔS _H =-829.9-298.15*-0.1098=-747.75 kJ/mol;
H ₂ O	-285.85	69.9565	-237.191	CRC
H ₃ O ⁺	-285.81	-3.854	-213.2746	CRC Mischenko 1972, Himia, Leningrad [26]
H ₂ C ₂ O _{4cr}	-829.9	-109.8	-797.16	CRC
H ₂ C ₂ O _{4cr}	formation		76.96	G _{H2C2O4cr} =ΔG ^o _{H2C2O4crForm} +(2G _{Cgr} +2G _{O2gas} +G _{H2gas})=76.96 kJ/mol;
H ₂ C ₂ O _{4aq}	ΔG _{eq_sp} =	9.0161	85.976	G _{H2C2O4aq} =ΔG _{eq_sp} +(G _{H2O} +G _{H2C2O4^{cr}})=85.976 kJ/mol;
H ₂ C ₂ O _{4aq}	E ^o _{H2C2O4} =	-0.6577 V	171.78	G _{H2C2O4} =2G _{CO2} +2G _{H3O} -(ΔG _{eqH2C2O4} +2G _{H2O})=171.78 kJ/mol;
HC ₂ O _{4⁻}	17.08	pK _{a2} =1.25	80.618	G _{HC2O4} =ΔG _{eq1H2C2O4} -G _{H3O} +(G _{H2C2O4} +ΔG _{H2O})=80.618 kJ/mol ;
HC ₂ O _{4⁻}	E ^o _{HC2O4} =	-0.7092 V	159.028	G _{HC2O4} =2G _{CO2} +G _{H3O} -(ΔG _{eqHC2O4} +G _{H2O})=159.028 kJ/mol;
C ₂ O _{4²⁻}	-	-	-677.14	Alberty 2006 Biochem.Thermodyn Massachusetts Techn. Inst.
C ₂ O _{4²⁻}	33.578	pK _{a2} =4.14	91.756	G _{C2O4} =ΔG _{eq2HC2O4} -G _{H3O} +(G _{HC2O4} +G _{H2O})=91.756 kJ/mol ;
C ₂ O _{4²⁻}	E ^o _{C2O4} =	-0.7607 V	146.79	G _{C2O4} =2G _{CO2} -(ΔG _{eqC2O4})=2*0-(-146.79)=146.79 kJ/mol;
CH _{4gas}	-74.6	186.3	-50.5	Wikipedia CRC [1]
CH _{4gas}	formation	-50.5	212.04	G _{CH4gas} =ΔG _{Hess_CH4gas} +(G _{Cgr} +2*G _{H2})=212.04 kJ/mol;
CH _{4gas}	Alberty	2006	120.56	G ^o _{CgrCH4gas} =G ^o _{CH4gas} -G _{Hess_CH4gas} -2*G ^o _{H2gas} =91.26 kJ/mol;
CH _{4aq}	Solubility	26.21	238.25	G _{CH4aq} = G _{CH4gas} + G _{CH4sp} =212.04+26.21=238.25 kJ/mol;
CH _{4aq}	Alberty	2006	136.95	Alberty 2006 Biochem.Thermodyn Massachusetts Techn. Inst.
C _{gr}	background	Biochemistry	91.26	G ^o _{Cgr0CO2} =-ΔG ^o _{Hess_CO2gas} -G ^o _{O2gas0} =394.36-303.1=91.26 kJ/mol;
CO _{2gas}	-393.509	213.74	-394.359	CRC [1]
CO _{2aq}	-413.798	117.5704	-385.98	CRC [1]
CO _{2aq}	E ^o _{H2C2O4} =	-0.6577 V	-42.90	2G _{CO2} = ΔG _{eqH2C2O4} -2G _{H3O} +(G _{H2C2O4} +2G _{H2O})=2*-42.902 kJ/mol;
CO _{2aq}	E ^o _{HC2O4} =	-0.7092 V	-97.514	2G _{CO2} = ΔG _{eqHC2O4} -G _{H3O} +(G _{HC2O4} +G _{H2O})=2*-97.514 kJ/mol;
CO _{2aq}	E ^o _{C2O4} =	-0.7607 V	-27.517	2G _{CO2} =ΔG _{eqC2O4} +(G _{C2O4})=-27.517 kJ/mol;
CO _{2aq}	K _{eqCO2aqua}	šķīdība	18.38	G _{CO2aqua} =ΔG _{eqCO2aqua} +(G _{CO2gas} +G _{H2O})=18.38+(0+0)=18.38 kJ/mol .

Formation from free elements $2C_{gr}+2O_{2gas}+H_{2gas}=H_2C_2O_{4cr}$ and solubility $H_2C_2O_{4cr}+H_2O=H_2C_2O_{4aq}$:
 $G_{H_2C_2O_{4cr}}=\Delta G^\circ_{H_2C_2O_{4cr}Form}+(2G_{C_{gr}}+2G_{O_{2gas}}+G_{H_{2gas}})=-797.16+(2*91.26+2*303+85.6)=76.96$ kJ/mol.

Solubility of oxalic acid 118 g/L $H_2C_2O_{4cr}+H_2O=H_2C_2O_{4aq}$ constant is calculated from CRC, Wikipedia data

$$K_{eq_sp}=[H_2C_2O_{4aq}]/[H_2C_2O_{4cr}]/[H_2O]=1.3106/1/49.77=0.026329. [1,29]$$

Molar mass $M_{H_2C_2O_4}=90.034$ g/mol; $[H_2O]=982/18=49.777$ M; concentration $[H_2C_2O_4]=118/90.034=1.3106$ M and mass fraction in percent $w\%=118/(118+982)*100=10.7272\%$, if pure solid mol fraction is one $[H_2C_2O_{4cr}]=1$.

Oxalic acid solubility free energy change for unfavored equilibrium $K_{eq_sp}=0.026329$ is positive:

$$\Delta G_{eq_sp}=-R\cdot T\cdot\ln(K_{eq_sp})=-8.3144*298.15*\ln(0.026329)=-8.3144*298.15*-3.637=9.0161$$
 kJ/mol .

Hess law for change $\Delta G_{eq_sp}=G_{H_2C_2O_{4aq}}-(G_{H_2O}+G_{H_2C_2O_{4cr}})=G_{H_2C_2O_{4aq}}-(0+76.96)=9.0161$ kJ/mol let us calculate free energy content: $G_{H_2C_2O_{4aq}}=\Delta G_{eq_sp}+(G_{H_2O}+G_{H_2C_2O_{4cr}})=9.0161+(0+76.96)=85.976$ kJ/mol [29] [Wikipedia](#).

1. Weak acid protolysis $H_2C_2O_4+H_2O=HC_2O_4^-+H_3O^+$; $pK_{a1}=1.25$; $K_{eq1}=K_{a1}/[H_2O]=10^{-(1.25)}/55.3=0.0010169$;
 $\Delta G_{eq1H_2C_2O_4}=-R\cdot T\cdot\ln(K_{eq1})=-8.3144*298.15*\ln(0.0010169)=\Delta G_{HC_2O_4}+\Delta G_{H_3O}-(\Delta G_{H_2C_2O_4}+\Delta G_{H_2O})=17.08$ kJ/mol;
 $\Delta G_{eq1H_2C_2O_4}=G_{HC_2O_4}+G_{H_3O}-(G_{H_2C_2O_4}+\Delta G_{H_2O})=G_{HC_2O_4}+22.44-(85.976+0)=17.082$ kJ/mol;
 $G_{HC_2O_4}=\Delta G_{eq1H_2C_2O_4}-G_{H_3O}+(G_{H_2C_2O_4}+\Delta G_{H_2O})=17.082-22.44+(85.976+0)=80.618$ kJ/mol;

2. Weak acid protolysis $HC_2O_4^-+H_2O=C_2O_4^{2-}+H_3O^+$; $pK_{a2}=4.14$; $K_{eq2}=K_{a2}/[H_2O]=10^{-(4.14)}/55.3=0.000001310$;
 $\Delta G_{eq2HC_2O_4}=-R\cdot T\cdot\ln(K_{eq2})=-8.3144*298.15*\ln(0.000001310)=\Delta G_{C_2O_4}+\Delta G_{H_3O}-(\Delta G_{HC_2O_4}+\Delta G_{H_2O})=33.578$ kJ/mol;
 $\Delta G_{eq2HC_2O_4}=G_{C_2O_4}+G_{H_3O}-(G_{HC_2O_4}+\Delta G_{H_2O})=G_{C_2O_4}+22.44-(80.618+0)=33.578$ kJ/mol;
 $G_{C_2O_4}=\Delta G_{eq2HC_2O_4}-G_{H_3O}+(G_{HC_2O_4}+\Delta G_{H_2O})=33.578-22.44+(80.618+0)=91.756$ kJ/mol;

$pH\leq 1.25$ $H_2C_2O_4+2H_2O=2CO_2+2H_3O^++2e^-$; $E^\circ_{H_2C_2O_4}=-0.6577$ V Suchotina [17]

$$E^\circ_{H_2C_2O_4}=E^\circ+0.10166-0.0591/2*\lg(1/[H_2O]^2)-0.37239=-0.49+0.10166-0.02955*\lg(1/55.3^2)-0.37239=-0.6577$$
 V;

Absolute Nernst's Standard potential $E^\circ_{H_2C_2O_4}=-0.6577$ V; Suchotina [17]

$$E_{H_2C_2O_4}=E^\circ_{H_2C_2O_4}+\frac{0.0591}{2}\cdot\lg\frac{[CO_2]^2\cdot[H_3O^+]^2}{[H_2C_2O_4]\cdot[H_2O]^2}=-0.6577$$
 V + $\frac{0.0591}{2}\cdot\lg\frac{[CO_2]^2\cdot[H_3O^+]^2}{[H_2C_2O_4]\cdot[H_2O]^2}$

$$\Delta G_{eqH_2C_2O_4}=E^\circ_{H_2C_2O_4}\cdot F\cdot 2=-0.6577*96485*2=-126.9$$
 kJ/mol;

$$\Delta G_{eqH_2C_2O_4}=2G_{CO_2}+2G_{H_3O}-(G_{H_2C_2O_4}+2G_{H_2O})=2*0+2*22.44-(85.976+2*0)=-126.9$$
 kJ/mol ;

$$G_{H_2C_2O_4}=2G_{CO_2}+2G_{H_3O}-(\Delta G_{eqH_2C_2O_4}+2G_{H_2O})=2*0+2*22.44-(-126.9+2*0)=171.78$$
 kJ/mol ;

$1.25<pH\leq 4.14$; $HC_2O_4^-+H_2O=2CO_2+H_3O^++2e^-$;

Absolute Nernst's Standard potential $E^\circ_{HC_2O_4}=-0.7092$ V Suchotina [17]

$$E^\circ_{HC_2O_4}=E^\circ+0.10166-0.0591/2*\lg(1/[H_2O]^1)-0.37239=-0.49+0.10166-0.0591/2*\lg(1/55.3^1)-0.37239=-0.709$$
 V;

$$\Delta G_{eqHC_2O_4}=E^\circ_{HC_2O_4}\cdot F\cdot 2=-0.7092*96485*2=-136.85$$
 kJ/mol;

$$\Delta G_{eqHC_2O_4}=2G_{CO_2}+G_{H_3O}-(G_{HC_2O_4}+G_{H_2O})=2*0+22.44-(80.618+0)=-136.85$$
 kJ/mol;

$$G_{HC_2O_4}=2G_{CO_2}+G_{H_3O}-(\Delta G_{eqHC_2O_4}+G_{H_2O})=2*0+22.44-(-136.85+0)=159.028$$
 kJ/mol;

$4.14 < pH$; $C_2O_4^{2-}=2CO_2+2e^-$; Absolute Nernst's Standard potential $E^\circ_{C_2O_4}=-0.7607$ V; Suchotina [17]

$$E^\circ_{C_2O_4}=E^\circ+0.10166-0.0591/2*\lg([1/H_2O]^0)-0.37239=-0.49+0.10166-0.0591/2*\lg(1/55.3^0)-0.37239=-0.7607$$
 V;

$$\Delta G_{eqC_2O_4}=E^\circ_{C_2O_4}\cdot F\cdot 2=-0.7607*96485*2=-146.79$$
 kJ/mol;

$$\Delta G_{eqC_2O_4}=2G_{CO_2}-(G_{C_2O_4})=2*0-(G_{C_2O_4})=-146.79$$
 kJ/mol;

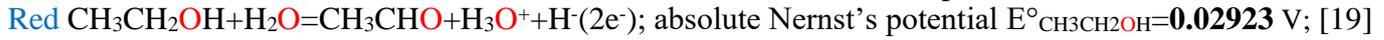
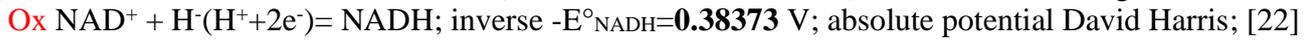
$$G_{C_2O_4}=2G_{CO_2}-(\Delta G_{eqC_2O_4})=2*0-(-146.79)=146.79$$
 kJ/mol;

Nernst's potential studies reducing with vitamin B₃ ethanal H₃CCH=O and oxidizing H₃CCH₂OH ethanol



$$\Delta G_{Hess} = \Delta G^\circ_{H_3O} + \Delta G^\circ_{CH_3CHO} + \Delta G^\circ_{NADH} - \Delta G^\circ_{CH_3CH_2OH} - \Delta G^\circ_{H_2O} - \Delta G^\circ_{NAD^+} = 159.1 \text{ kJ/mol};$$

$$\Delta G_{Hess} = 32.2824 + 1175.5732 - 151.549 - (75.2864 + 1059.11 - 237.191) = 159.1 \text{ kJ/mol endoergic. Anaerobic:}$$



$$E^\circ_{C_2H_5OH} = E^\circ - 0,0591/2 \cdot \log(1/[H_2O]^1) = 0,19 - 0,0591/2 \cdot \log(1/55,3^1) + 0,10166 - 0,37239 = \mathbf{0,02923 \text{ V}};$$

$$\text{Sum: } E^\circ_{C_2H_5OH} - E^\circ_{NAD^+} = \mathbf{0,02923 + 0,38373 = 0.3545 \text{ V}, n=2; \Delta G_{eq} = \Delta E^\circ \cdot F \cdot n = 0.3545 \cdot 96485 \cdot 2 = \mathbf{68,4 \text{ kJ/mol}};$$

By convention balanced n=2=m number of electrons 2e⁻ donors E^o_{NADH} = **-0.38373 V** plus acceptors of electrons -E^o_{C₂H₅OH} = **0.02923 V**, as -E^o_{NAD⁺} = **0.38373 V** accepting electrons from ethanol E^o_{C₂H₅OH} = **-0.02923 V**:

$$\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = \mathbf{68,4 \text{ kJ/mol}}; K_{eq} = \frac{[NADH] \cdot [CH_3CHO] \cdot [H_3O^+]}{[NAD^+] \cdot [CH_3CH_2OH] \cdot [H_2O]} = e^{-\frac{\Delta G_{eq}}{R \cdot T}} = e^{-\frac{68408}{8.314 \cdot 298.15}} = 1.036 \cdot 10^{-12} = 10^{-11.985}$$



$$\Delta G_{Hess} = \Delta G^\circ_{CH_3CH_2OH} + \Delta G^\circ_{H_2O} + \Delta G^\circ_{NAD^+} - \Delta G^\circ_{H_3O} - \Delta G^\circ_{CH_3CHO} - \Delta G^\circ_{NADH} = -159.1 \text{ kJ/mol};$$

$$\Delta G_{Hess} = 75.2864 + 1059.11 - 237.191 - (32.2824 + 1175.5732 - 151.549) = -159.1 \text{ kJ/mol endoergiska};$$



Sum:

$$\Delta E^\circ = E^\circ_{NADH} - E^\circ_{CH_3CHO} = \mathbf{-0,38373 + 0,02923 = -0.3545 \text{ V}, \Delta G_{eq} = \Delta E^\circ \cdot F \cdot n = -0.3545 \text{ V} \cdot 2 \text{ mol} \cdot 96485 \text{ C/mol} = \mathbf{-68,4 \text{ kJ/mol}};$$

By convention balanced n=2=m number of electrons 2e⁻ ΔE^o donors E^o_{NADH} = **-0.38373 V** plus electrons acceptor -E^o_{CH₃CHO} = **0.02923 V**, as -E^o_{CH₃CHO} = **0.02923 V** accepting electrons from vitamin E^o_{NADH} = **-0.38373 V**.

$$\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = \mathbf{-68.408 \text{ kJ/mol}}; K_{eq} = \frac{[NAD^+] \cdot [CH_3CH_2OH] \cdot [H_2O]}{[NADH] \cdot [CH_3CHO] \cdot [H_3O^+]} = e^{-\frac{\Delta G_{eq}}{R \cdot T}} = e^{-\frac{-68408}{8.314 \cdot 298.15}} = 9.65 \cdot 10^{11} = 10^{11.985}.$$

In aerobic organisms NADH oxidase with O₂ aqua perform ratio [NAD⁺]/[NADH]=10⁶;

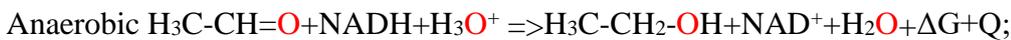
$$\Delta G_{Homeostasis} = \mathbf{-68.408} + R \cdot T \cdot \ln(10^6 \cdot 1/1 \cdot 10^{-7.36}/55.3) = \mathbf{68.408 - 86.2 = -17.8 \text{ kJ/mol}}.$$

$$[NAD^+]/[NADH] = 10^3; \Delta G_{Homeostasis} = \mathbf{68.408 - 69.08 = -0.676 \text{ kJ/mol}}.$$

Equilibrium is shifted far to reactants as aerobic constant K_{eq} = 10^{-11.985} and inverse anaerobic constant K_{eq} = 10^{11.985}. Aerobic endothermic and endoergic vitamin B₃ ethanal oxidation Hess law free energy change positive ΔG_{Hess} = 159 kJ/mol and inverse ethanal anaerobic reduction negative ΔG_{Hess} = -159 kJ/mol, but minimizes reaching

equilibrium aerobic ΔG_{min} = ΔG_{eq} = 68.4 kJ/mol and anaerobic reactants -
ΔG_{min} = ΔG_{eq} = **-68.4 kJ/mol** reaching equilibrium mixture products -
constants 10^{-11.985} = K_{eq} aerobic and anaerobic 10^{11.985} = K_{eq}.

Prigogine attractor is free energy change absolute minimum ΔG_{min} reaching equilibrium ΔG_{min} = **68.4 kJ/mol** = |ΔG_{eq}| < |ΔG_{Hess}| = 159 kJ/mol.



$$\text{Anaerobic } \Delta G_{eq} = \Delta E^\circ \cdot F \cdot n = -0.3545 \text{ V} \cdot 2 \text{ mol} \cdot 96485 \text{ C/mol} = \mathbf{-68.408 \text{ kJ/mol}} \text{ favored.}$$

Insufficient low O₂ aqua concentration hypoxia to anaerobic alcohol oxidation unflavored but ethanal reduction to ethanol favored [H₃CCH₂OH]/[H₃CCH=O]=1/10 homeostasis reduction with NADH reductase enzyme as negative free energy change

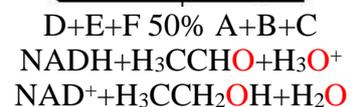
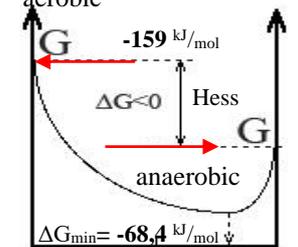
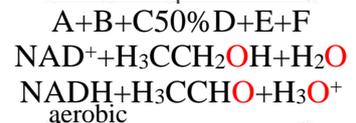
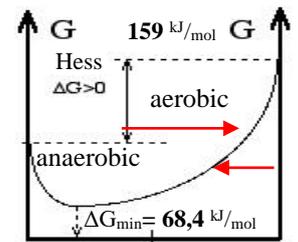
$$\Delta G_{Homeostasis} = -27.86 \text{ kJ/mol}$$

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

$$\Delta G_{Homeostasis} = -68.41 + 8.3144 \cdot 298.15 \cdot \ln(K_{Homeostasis}) = -68.41 + 40.54 = -27.86 \text{ kJ/mol}$$

$$\Delta G_{Homeostasis} = -68.41 + 8.3144 \cdot 298.15 \cdot \ln\left(\frac{1}{10} \frac{1}{10} \frac{55.333}{10^{-7.36}}\right) = -27.86 \text{ kJ/mol}; K_{Homeostasis} = \frac{[NAD^+] \cdot [CH_3CH_2OH] \cdot [H_2O]}{[NADH] \cdot [CH_3CHO] \cdot [H_3O^+]}$$

$$[NADH]/[NAD^+] = 1/770; \Delta G_{Homeostasis} = 68.408 + 8.3144 \cdot 298.15 \cdot \ln(700/1 \cdot 1/1 \cdot 55.3457/10^{-7.36}) = 0.028 \text{ kJ/mol}.$$



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 (SiO_2) crystalline in protolysis of silicic acid reaction:

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

On glass surface locate silicic anions functional groups $\downarrow \text{SiO}_2\text{-SiO}_3^-$. On glass surface establishes protolytic equilibrium state between crystalline silicic acid $\text{SiO}_2\text{-SiO}_3\text{H}$ and anionic groups of silicate $\text{SiO}_2\text{-SiO}_3^-$. Silicic acid is water insoluble acid and therefore weak protolyte:



As crystalline membrane has inner surface equilibrium and outer surface of membrane has outer equilibrium, where last depends on tested medium H_3O^+ concentration.



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

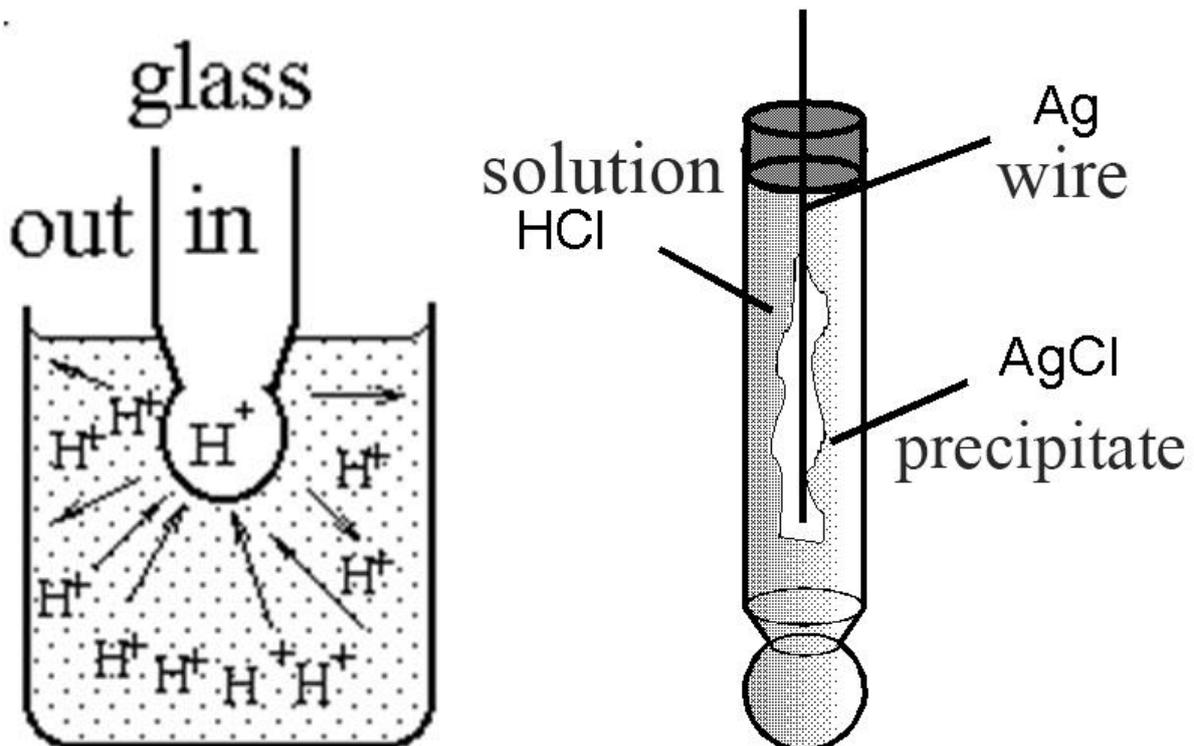
$$K_{\text{inner}} = \frac{[\text{H}_2\text{O}]}{[\text{H}_3\text{O}^+]_{\text{inner}}}; \quad K_{\text{outer}} = \frac{[\text{H}_3\text{O}^+]_{\text{outer}}}{[\text{H}_2\text{O}]}; \quad K_{\text{inner}} \bullet K_{\text{outer}} = K_{\text{membr}} = \frac{[\text{H}_3\text{O}^+]_{\text{outer}}}{[\text{H}_3\text{O}^+]_{\text{inner}}};$$

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

where $n=+1$ hydrogen ion charge H^+ , but logarithm of concentrations ratio is subtraction two logarithms from concentration ratio. Ions concentration inside membrane is constant $E_{\text{const}} = -0,0591 \bullet \log[\text{H}_3\text{O}^+]_{\text{inner}}$. Membrane potential depends only on solution $\text{H}_3\text{O}^+_{\text{outer}}$ and $\text{pH} = -\log[\text{H}_3\text{O}^+]_{\text{outer}}$.

$$E_{\text{membr}} = E_{\text{const}} + 0,0591 \bullet \log[\text{H}_3\text{O}^+]_{\text{outer}}.$$

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 immerses one silver wire, that forms second type electrode 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) measure for closed electric circle. That achieved in outer solution coupled reference electrode with standard potential E_{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 immersed AgCl electrode potential $E_{\text{AgCl inner}}$;
- 2) glass membrane electrode $E_{\text{membr.}} = E_{\text{const.}} + 0.0591 \cdot \log[\text{H}_3\text{O}^+_{\text{outer}}] = E_{\text{const.}} - 0.0591 \cdot \text{pH}$;
- 3) reference electrode with standard potential E_{AgCl} .

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

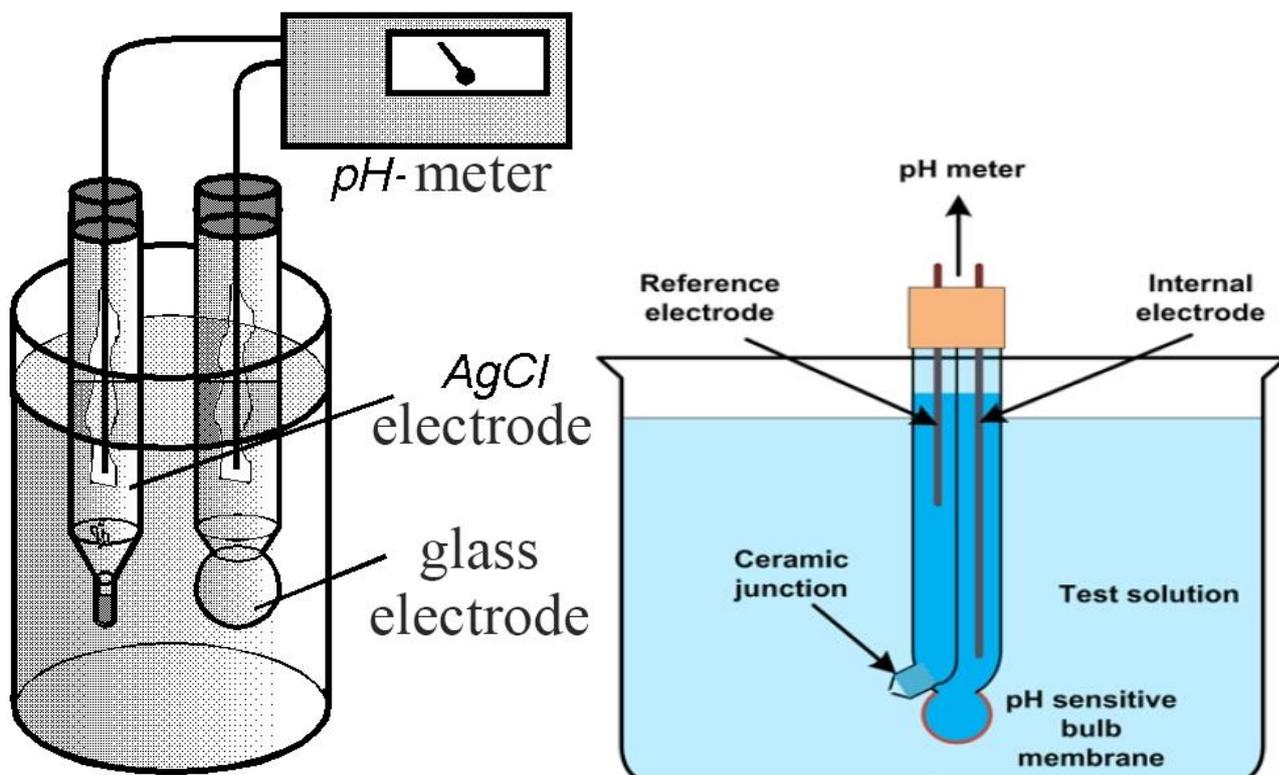
$$\text{EDS} = E_{\text{AgCl}} + E_{\text{membr.}} + E_{\text{AgCl inner}} = (E_{\text{AgCl}} + E_{\text{AgCl inner}} + E_{\text{const.}}) + 0.0591 \cdot \lg [\text{H}_3\text{O}^+_{\text{inner}}] = E'_{\text{const.}} - 0.0591 \cdot \text{pH}$$

$$\text{EDS} = E'_{\text{const.}} - 0.0591 \cdot \text{pH} .$$

Measured Electric Motion Force (EMF) is proportional to pH value in solution.

pH measurement by glass electrodes have some advantages:

- 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 depend 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 $\text{Cr}_2\text{O}_7^{2-} / 2\text{Cr}^{3+}$ red-ox system behaving in acidic H_3O^+ , water medium

Nernst's absolute standard potential. $\log K_D=2.05$; $K_D=10^{2.05}$; $2\text{HCrO}_4^- = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$;

$$\Delta G_D = -R \cdot T \cdot \ln(K_D \cdot [\text{H}_2\text{O}]) = -8.3144 \cdot 298.15 \cdot \ln(10^{2.05} \cdot 55.3) = G_{\text{Cr}_2\text{O}_7} + G_{\text{H}_2\text{O}} - (2G_{\text{HCrO}_4}) = \mathbf{-21.65 \text{ kJ/mol}}$$

$$2G_{\text{HCrO}_4} = G_{\text{Cr}_2\text{O}_7} + G_{\text{H}_2\text{O}} - (\Delta G_D) = G_{\text{Cr}_2\text{O}_7} + 0 - (-21.65) = \text{??? kJ/mol}$$

$$pK_a = 1.8; \text{HCrO}_4^- + \text{H}_2\text{O} = \text{Cr}_2\text{O}_7^{2-} + \text{H}_3\text{O}^+; K_{eq} = K_a / [\text{H}_2\text{O}] = 10^{-(1.8)} / 55.3 = 0.0002866;$$

$$\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = -8.3144 \cdot 298.15 \cdot \ln(0.0002866) = G_{\text{Cr}_2\text{O}_7} + G_{\text{H}_3\text{O}} - (G_{\text{HCr}_2\text{O}_7} + G_{\text{H}_2\text{O}}) = \mathbf{20.22 \text{ kJ/mol}}$$

$$G_{\text{HCr}_2\text{O}_7} = G_{\text{Cr}_2\text{O}_7} + G_{\text{H}_3\text{O}} - (\Delta G_{eq} + G_{\text{H}_2\text{O}}) = G_{\text{Cr}_2\text{O}_7} + 22.44 - (20.22 + 0) = \text{??? kJ/mol}$$

Instability constant $[\text{Cr(OH)}]^{2+} + \text{H}_2\text{O} = \text{Cr}^{3+} + \text{OH}^-$; $K_{inst} = 10^{-(9.77)}$; $K_{eq} = K_{inst} / [\text{H}_2\text{O}] = 10^{-(9.88)} / 55.3 = 10^{-(11.51)}$;

$$\Delta G_{eqinst} = -R \cdot T \cdot \ln(K_{eqinst}) = -8.3144 \cdot 298.15 \cdot \ln(10^{-(11.51)}) = G_{\text{Cr}^{3+}} + G_{\text{OH}^-} - (G_{[\text{Cr(OH)}]^{2+}} + G_{\text{H}_2\text{O}}) = \mathbf{65.7 \text{ kJ/mol}}$$

$$G_{[\text{Cr(OH)}]^{2+}} = G_{\text{Cr}^{3+}} + G_{\text{OH}^-} - (\Delta G_{eqinst} + G_{\text{H}_2\text{O}}) = G_{\text{Cr}^{3+}} + 77.36 - (65.7 + 0) = \text{??? kJ/mol}$$

Instability $[\text{Cr(OH)}_2]^{+} + 2\text{H}_2\text{O} = \text{Cr}^{3+} + 2\text{OH}^-$; $K_{inst} = 10^{-(17.3)}$; $K_{eqinst} = K_{inst} / [\text{H}_2\text{O}]^2 = 10^{-(17.3)} / 55.3^2 = 10^{-(20.785)}$;

$$\Delta G_{eqinst} = -R \cdot T \cdot \ln(K_{eqinst}) = -8.3144 \cdot 298.15 \cdot \ln(10^{-(20.785)}) = G_{\text{Cr}^{3+}} + 2G_{\text{OH}^-} - (G_{\text{Cr(OH)}_2} + 2G_{\text{H}_2\text{O}}) = \mathbf{118.64 \text{ kJ/mol}}$$

$$G_{\text{Cr(OH)}_2} = G_{\text{Cr}^{3+}} + 2G_{\text{OH}^-} - (\Delta G_{eqinst} + 2G_{\text{H}_2\text{O}}) = G_{\text{Cr}^{3+}} + 2 \cdot 77.36 - (118.64 + 2 \cdot 0) = \text{??? kJ/mol}$$

Instability constant $[\text{Cr(OH)}_3] + 3\text{H}_2\text{O} = \text{Cr}^{3+} + 3\text{OH}^-$; $K_{inst} = 10^{-(24)}$; $K_{eq} = K_{inst} / [\text{H}_2\text{O}] = 10^{-(24)} / 55.3 = 10^{-(29.23)}$;

$$\Delta G_{eqinst} = -R \cdot T \cdot \ln(K_{eqinst}) = -8.3144 \cdot 298.15 \cdot \ln(10^{-(29.23)}) = G_{\text{Cr}^{3+}} + 3G_{\text{OH}^-} - (G_{[\text{Cr(OH)}_3]} + 3G_{\text{H}_2\text{O}}) = \mathbf{166.8 \text{ kJ/mol}}$$

$$G_{[\text{Cr(OH)}_3]} = G_{\text{Cr}^{3+}} + 3G_{\text{OH}^-} - (\Delta G_{eqinst} + 3G_{\text{H}_2\text{O}}) = G_{\text{Cr}^{3+}} + 3 \cdot 77.36 - (166.8 + 3 \cdot 0) = \text{??? kJ/mol}$$

$2\text{Cr}^{3+} + 21\text{H}_2\text{O} = \text{Cr}_2\text{O}_7^{2-} + 14\text{H}_3\text{O}^+ + 6e^-$; $1 < \text{pH} < 7$; Standard potential $E^\circ_{\text{Cr}_2\text{O}_7} = \mathbf{1,41975 \text{ V}}$ Kortly, Shucha [18]

$$E^\circ_{\text{Cr}_2\text{O}_7} = E^\circ + 0,10166 - 0,0591/6 \cdot \lg(1/[\text{H}_2\text{O}]^{21}) - 0,372 = 1,33 + 0,10166 - 0,0591/6 \cdot \lg(1/55,3^{21}) - 0,37239 = \mathbf{1,41975 \text{ V}}$$

$$E_{\text{Cr}_2\text{O}_7 - / 2\text{Cr}^{3+}} = E^\circ_{\text{Cr}_2\text{O}_7 - / 2\text{Cr}^{3+}} + \frac{0.0591}{6} \cdot \lg \frac{[\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{H}_3\text{O}^+]^{14}}{[\text{Cr}^{3+}]^2 \cdot [\text{H}_2\text{O}]^{21}} = \mathbf{1,41975 \text{ V}} + \frac{0.0591}{6} \cdot \lg \frac{[\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{H}_3\text{O}^+]^{14}}{[\text{Cr}^{3+}]^2 \cdot [\text{H}_2\text{O}]^{21}}$$

$$\Delta G_{eq\text{Cr}_2\text{O}_7 - / 2\text{Cr}^{3+}} = E^\circ_{\text{Cr}_2\text{O}_7 - / 2\text{Cr}^{3+}} \cdot F \cdot 6 = \mathbf{1,41975 \cdot 96485 \cdot 6 = 821,9 \text{ kJ/mol}}$$

$$\Delta G_{eq\text{Cr}_2\text{O}_7 - / 2\text{Cr}^{3+}} = G_{\text{Cr}_2\text{O}_7} - 14G_{\text{H}_3\text{O}} - (2G_{2\text{Cr}^{3+}} + 21G_{\text{H}_2\text{O}}) = G_{\text{Cr}_2\text{O}_7} - 14 \cdot 22,44 - (2G_{2\text{Cr}^{3+}} + 21 \cdot 0) = \mathbf{821,9 \text{ kJ/mol}}$$

$$2G_{2\text{Cr}^{3+}} = G_{\text{Cr}_2\text{O}_7} - 14 \cdot 22,44 - (821,9 + 21 \cdot 0) = \text{??? kJ/mol}$$

$\text{Cr}^{3+} + 11\text{H}_2\text{O} = \text{HCrO}_4^- + 7\text{H}_3\text{O}^+ + 3e^-$; $\text{pH} > 7$; Standard potential $E^\circ_{\text{Cr}_2\text{O}_7} = \mathbf{1,30692 \text{ V}}$ Kortly, Shucha [18]

$$E^\circ_{\text{CrO}_4} = E^\circ + 0,10166 - 0,0591/3 \cdot \lg(1/[\text{H}_2\text{O}]^{11}) - 0,37239 = 1,2 + 0,10166 - 0,0591/3 \cdot \lg(1/55,3^{11}) - 0,37239 = \mathbf{1,30692 \text{ V}}$$

$$\Delta G_{eq\text{CrO}_4 / \text{Cr}^{3+}} = E^\circ_{\text{CrO}_4 / \text{Cr}^{3+}} \cdot F \cdot 3 = \mathbf{1,30692 \cdot 96485 \cdot 3 = 378,3 \text{ kJ/mol}}$$

$$\Delta G_{eq\text{H}_2\text{C}_2\text{O}_4} = G_{\text{CrO}_4} + 14G_{\text{H}_3\text{O}} - (2G_{2\text{Cr}^{3+}} + 21G_{\text{H}_2\text{O}}) = G_{\text{CrO}_4} + 14 \cdot 22,44 - (2G_{2\text{Cr}^{3+}} + 21 \cdot 0) = \mathbf{378,3 \text{ kJ/mol}}$$

$$2G_{2\text{Cr}^{3+}} = G_{\text{CrO}_4} + 14 \cdot 22,44 - (378,3 + 21 \cdot 0) = \text{??? kJ/mol}$$

$\text{Cr(OH)}_3 \downarrow + 5\text{OH}^- = \text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3e^-$; $\text{pH} > 9$; $E^\circ_{\text{CrO}_4 - \text{OH}} = \mathbf{-0,53806 \text{ V}}$ Suchotina [17]

$$E^\circ_{\text{CrO}_4 - \text{OH}} = E^\circ - 0,0591/3 \cdot \lg([\text{H}_2\text{O}]^4) + 0,10166 - 0,37239 = -0,13 - 0,0591/3 \cdot \lg(55,3^4) + 0,10166 - 0,37239 = \mathbf{-0,53806 \text{ V}}$$

$$\Delta G_{eq\text{CrO}_4 - \text{OH}} = E^\circ_{\text{CrO}_4 - \text{OH}} \cdot F \cdot 3 = \mathbf{-0,53806 \cdot 96485 \cdot 3 = -155,74 \text{ kJ/mol}}$$

$$\Delta G_{eq\text{CrO}_4 - \text{OH}} = G_{\text{CrO}_4} + 4G_{\text{H}_3\text{O}} - (G_{\text{Cr(OH)}_3} + 5G_{\text{OH}^-}) = G_{\text{CrO}_4} + 4 \cdot 22,44 - (G_{\text{Cr(OH)}_3} + 5 \cdot 77,36) = \mathbf{-155,74 \text{ kJ/mol}}$$

$$G_{\text{Cr(OH)}_3} = G_{\text{CrO}_4} + 14 \cdot 22,44 - (-155,74 + 21 \cdot 0) = \text{??? kJ/mol}$$

$$E_{\text{CrO}_4 - / \text{Cr(OH)}_3 \downarrow} = E^\circ_{\text{CrO}_4 - / \text{Cr(OH)}_3 \downarrow} + \frac{0.0591}{3} \cdot \lg \frac{[\text{CrO}_4^{2-}] \cdot [\text{H}_2\text{O}]^4}{[\text{Cr(OH)}_3] \cdot [\text{OH}^-]^5} = \mathbf{-0,563806 \text{ V}} + \frac{0.0591}{3} \cdot \lg \frac{[\text{CrO}_4^{2-}] \cdot [\text{H}_2\text{O}]^4}{[\text{Cr(OH)}_3] \cdot [\text{OH}^-]^5} \text{ V}$$

Solubility product $\text{Cr(OH)}_3 + 4\text{H}_2\text{O} = \text{Cr}^{3+} + 3\text{OH}^-$; $K_{sp} = 6,7 \cdot 10^{-(31)}$; $K_{eq} = K_{sp} / [\text{H}_2\text{O}]^4 = 6,7 \cdot 10^{-(31)} / 55,3^4 = 10^{-(37,145)}$;

$$\Delta G_{sp} = -R \cdot T \cdot \ln(K_{sp}) = -8,3144 \cdot 298,15 \cdot \ln(10^{-(37,145)}) = G_{\text{Cr}^{3+}} + 3G_{\text{OH}^-} - (G_{\text{Cr(OH)}_3} + 4G_{\text{H}_2\text{O}}) = \mathbf{212,02 \text{ kJ/mol}}$$

$$G_{\text{Cr(OH)}_3} = G_{\text{Cr}^{3+}} + 3G_{\text{OH}^-} - (\Delta G_{sp} + 4G_{\text{H}_2\text{O}}) = G_{\text{Cr}^{3+}} + 3 \cdot 77,36 - (212,02 + 4 \cdot 0) = \text{??? kJ/mol}$$

Substance	$\Delta H^\circ_{\text{H}} \text{ kJ/mol}$	$\Delta S^\circ_{\text{H}} \text{ J/mol/K}$	$\Delta G^\circ_{\text{H}} \text{ kJ/mol}$
$\text{CrCl}_2(\text{cr})$	-395.4	115.3	-356
$\text{CrCl}_3(\text{cr})$	-556.5	123	-486.1
Cr	-	23.8	-
$\text{CrO}_3(\text{l})$	-292.9	266.2	-
$\text{Cr}_2\text{O}_3(\text{cr})$	-1139.7	81.2	1058.1

$$2G_{\text{HCrO}_4} = G_{\text{Cr}_2\text{O}_7} + 0 - (-21.65) = \text{??? kJ/mol}$$

$$G_{\text{HCr}_2\text{O}_7} = G_{\text{Cr}_2\text{O}_7} + 22.44 - (20.22 + 0) = \text{??? kJ/mol}$$

$$G_{[\text{Cr(OH)}]^{2+}} = G_{\text{Cr}^{3+}} + 77.36 - (65.7 + 0) = \text{??? kJ/mol}$$

$$G_{\text{Cr(OH)}_2} = G_{\text{Cr}^{3+}} + 2 \cdot 77.36 - (118.64 + 2 \cdot 0) = \text{??? kJ/mol}$$

$$G_{[\text{Cr(OH)}_3]} = G_{\text{Cr}^{3+}} + 3 \cdot 77.36 - (166.8 + 3 \cdot 0) = \text{??? kJ/mol}$$

$$2G_{2\text{Cr}^{3+}} = G_{\text{Cr}_2\text{O}_7} - 14 \cdot 22,44 - (806,9 + 21 \cdot 0) = \text{??? kJ/mol}$$

$$2G_{2\text{Cr}^{3+}} = G_{\text{CrO}_4} + 14 \cdot 22,44 - (370,8 + 21 \cdot 0) = \text{??? kJ/mol}$$

$$G_{\text{Cr(OH)}_3} = G_{\text{CrO}_4} + 14 \cdot 22,44 - (163,2 + 21 \cdot 0) = \text{??? kJ/mol}$$

$$G_{\text{Cr(OH)}_3} = G_{\text{Cr}^{3+}} + 3 \cdot 77.36 - (211,99 + 4 \cdot 0) = \text{??? kJ/mol}$$

Nernst's potential $\text{BiO}_3^- / \text{Bi}^{3+}$ $2\text{Bi}+6\text{OH}=\text{Bi}_2\text{O}_3+3\text{H}_2\text{O}+6\text{e}^-$; $\text{pH}>7$; [7]

$$E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}}=E^\circ-0,0591/6*\lg([\text{H}_2\text{O}]^3)+0,10166-0,37239=-0,46-0,0591/6*\lg(55,3^{\wedge}3)+0,10166-0,37239=-\mathbf{0,78223\text{ V}} ;$$

$$E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}}=E^\circ-0,0591/6*\lg(1/[\text{H}_2\text{O}]^3)+0,10166-0,37239=-0,46-0,0591/6*\lg(1/55,3^{\wedge}3)+0,10166-0,37239=-\mathbf{0,67923\text{ V}} ;$$

Substance	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol
Bi^{3+}	-	82.8	-
Bi	$E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}}$	-0,78223V	-249,6
Bi	$E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}}$	-0,67923V	-132,6
Bi	$E^\circ_{\text{BiCl}_3/\text{Bi}}$	-0,21372V	298,725
Bi	$E^\circ_{\text{BiCl}_4/\text{Bi}}$	-0,17939V	288,795
Bi	$E^\circ_{\text{BiClO}/\text{Bi}}$	-0,007735V	-91,03
Bi	-74,125	56.7	-91,03
Bi_2	219,7	-	-
BiOH^{2+}	-	-146.4	-
Cl^-	-167.08	56.6	-183.955
Cl(g)	-121.301	165.19	-
Cl_2	-	223.081	-
$\text{BiCl}_{3(\text{s})}$	-379.1	177	-315.0
$\text{BiClO}_{(\text{s})}$	-366.9	120.5	-322.1
Bi_2O_3	-573.9	151.5	-493.7
Bi(OH)_3	-711.3	-	-



$$G_{\text{Bi}}=(G_{\text{Bi}_2\text{O}_3}+3G_{\text{H}_2\text{O}}-(\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}}+6G_{\text{OH}}))/2=-\mathbf{249,6\text{ kJ/mol}};$$

$$G_{\text{Bi}}=(G_{\text{Bi}_2\text{O}_3}+3G_{\text{H}_3\text{O}}-(\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}}+3G_{\text{OH}}+3G_{\text{H}_2\text{O}}))/2=-\mathbf{132,6\text{ kJ/mol}};$$

$$G_{\text{Bi}}=G_{\text{BiCl}_3}+3G_{\text{H}_2\text{O}}-(\Delta G_{\text{eqBiCl}_3/\text{Bi}}+3G_{\text{Cl}})=\mathbf{298,725\text{ kJ/mol}};$$

$$G_{\text{Bi}}=G_{\text{BiCl}_3}+2G_{\text{H}_2\text{O}}-(\Delta G_{\text{eqBiCl}_3/\text{Bi}}+3G_{\text{Cl}})=\mathbf{288,795\text{ kJ/mol}};$$

$$G_{\text{Bi}}=G_{\text{BiClO}}+2G_{\text{H}_3\text{O}}-(\Delta G_{\text{eqBiClO}/\text{Bi}}+3\text{H}_2\text{O}+G_{\text{Cl}})=\mathbf{-91,03\text{ kJ/mol}};$$

$$\Delta H_{\text{Bi}_2\text{O}_3/\text{Bi}}=\Delta G+\Delta S*T=-\mathbf{91,03}+0,0567*298,15=-\mathbf{74,125\text{ kJ/mol}};$$

$$E_{\text{Bi}_2\text{O}_3/\text{Bi}}=E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}}+\frac{0,0591}{6}*\lg\frac{[\text{Bi}_2\text{O}_3][\text{H}_2\text{O}]^3}{[\text{Bi}]^2[\text{OH}]^6} =$$

$$=-\mathbf{0,78223}+0,0591/6*\lg([\text{Bi}_2\text{O}_3]*[\text{H}_2\text{O}]^3/[\text{Bi}]^2/[\text{OH}]^6)$$

$$G_{\text{Bi}}=G_{\text{BiCl}}+3G_{\text{H}_2\text{O}}-(\Delta G_{\text{eqBiCl}_3/\text{Bi}}+3G_{\text{Cl}})=\mathbf{306,2\text{ kJ/mol}};$$

$$G_{\text{Bi}}=G_{\text{BiClO}}+2G_{\text{H}_3\text{O}}-(\Delta G_{\text{eqBiClO}/\text{Bi}}+3\text{H}_2\text{O}+G_{\text{Cl}})=\mathbf{291,44\text{ kJ/mol}};$$

$$=-\mathbf{0,8337}+0,0591/6*\lg([\text{Bi}_2\text{O}_3]*[\text{H}_2\text{O}]^6/[\text{Bi}]^2/[\text{OH}]^6)$$

$$E_{\text{Bi}_2\text{O}_3/\text{Bi}}=E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}}+\frac{0,0591}{6}*\lg\frac{[\text{Bi}_2\text{O}_3][\text{H}_2\text{O}]^6}{[\text{Bi}]^2[\text{OH}]^6} =$$

$$\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}}=E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}}*F*6=-\mathbf{0,78223*96485*6}=-\mathbf{458,63\text{ kJ/mol}};$$

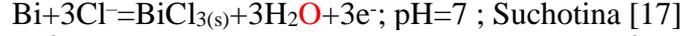
$$\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}}=G_{\text{Bi}_2\text{O}_3}+3G_{\text{H}_2\text{O}}-(2G_{\text{Bi}}+6G_{\text{OH}})=-493,7+3*0-(2*G_{\text{Bi}}+6*77,36)=-\mathbf{458,63\text{ kJ/mol}};$$

$$G_{\text{Bi}}=(G_{\text{Bi}_2\text{O}_3}+3G_{\text{H}_2\text{O}}-(\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}}+6G_{\text{OH}}))/2=(-493,7+3*0-(-458,63+6*77,36))/2=-\mathbf{249,6\text{ kJ/mol}};$$

$$\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}}=E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}}*F*6=-\mathbf{0,67923*96485*6}=-\mathbf{393,2\text{ kJ/mol}};$$

$$\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}}=G_{\text{Bi}_2\text{O}_3}+3G_{\text{H}_3\text{O}}-(2G_{\text{Bi}}+3G_{\text{OH}}+3G_{\text{H}_2\text{O}})=-493,7+3*22,44-(2*G_{\text{Bi}}+3*77,36+3*0)=-\mathbf{393,2\text{ kJ/mol}};$$

$$G_{\text{Bi}}=(G_{\text{Bi}_2\text{O}_3}+3G_{\text{H}_3\text{O}}-(\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}}+3G_{\text{OH}}+3G_{\text{H}_2\text{O}}))/2=(-493,7+3*22,44-(-393,2+3*77,36+3*0))/2=-\mathbf{132,6\text{ kJ/mol}};$$

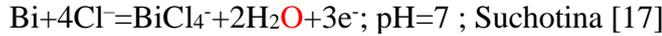


$$E^\circ_{\text{BiCl}_3/\text{Bi}}=E^\circ-0,0591/3*\lg([\text{H}_2\text{O}]^3)+0,10166-0,37239=0,16-0,0591/3*\lg(55,3^{\wedge}3)+0,10166-0,37239=-\mathbf{0,21372\text{ V}} ;$$

$$\Delta G_{\text{eqBiCl}_3/\text{Bi}}=E^\circ_{\text{eqBiCl}_3/\text{Bi}}*F*3=-\mathbf{0,21372*96485*3}=-\mathbf{69,32\text{ kJ/mol}};$$

$$\Delta G_{\text{eqBiCl}_3/\text{Bi}}=G_{\text{BiCl}}+3G_{\text{H}_2\text{O}}-(G_{\text{Bi}}+3G_{\text{Cl}})=-315+3*0-(G_{\text{Bi}}+3*-\mathbf{183,955})=-\mathbf{69,32\text{ kJ/mol}};$$

$$G_{\text{Bi}}=G_{\text{BiCl}_3}+3G_{\text{H}_2\text{O}}-(\Delta G_{\text{eqBiCl}_3/\text{Bi}}+3G_{\text{Cl}})=-315+3*0-(-\mathbf{69,32}+3*-\mathbf{183,955})=\mathbf{298,725\text{ kJ/mol}};$$

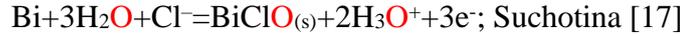


$$E^\circ_{\text{BiCl}_4/\text{Bi}}=E^\circ-0,0591/3*\lg([\text{H}_2\text{O}]^2)+0,10166-0,37239=0,16-0,0591/3*\lg(55,3^{\wedge}2)+0,10166-0,37239=-\mathbf{0,17939\text{ V}} ;$$

$$\Delta G_{\text{eqBiCl}_4/\text{Bi}}=E^\circ_{\text{eqBiCl}_4/\text{Bi}}*F*3=-\mathbf{0,17939*96485*3}=-\mathbf{51,93\text{ kJ/mol}};$$

$$\Delta G_{\text{eqBiCl}_4/\text{Bi}}=G_{\text{BiCl}}+2G_{\text{H}_2\text{O}}-(G_{\text{Bi}}+3G_{\text{Cl}})=-315+3*0-(G_{\text{Bi}}+3*-\mathbf{183,955})=-\mathbf{51,93\text{ kJ/mol}};$$

$$G_{\text{Bi}}=G_{\text{BiCl}_3}+2G_{\text{H}_2\text{O}}-(\Delta G_{\text{eqBiCl}_4/\text{Bi}}+3G_{\text{Cl}})=-315+3*0-(-\mathbf{51,93}+3*-\mathbf{183,955})=\mathbf{288,795\text{ kJ/mol}};$$

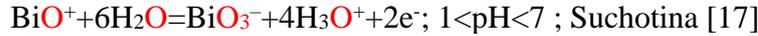


$$E^\circ_{\text{BiClO}/\text{Bi}}=E^\circ-0,0591/3*\lg(1/[\text{H}_2\text{O}]^3)+0,10166-0,37239=0,16-0,0591/3*\lg(1/55,3^{\wedge}3)+0,10166-0,37239=-\mathbf{0,007735\text{ V}} ;$$

$$\Delta G_{\text{eqBiClO}/\text{Bi}}=E^\circ_{\text{eqBiClO}/\text{Bi}}*F*3=-\mathbf{0,007735*96485*3}=-\mathbf{2,2389\text{ kJ/mol}};$$

$$\Delta G_{\text{eqBiClO}/\text{Bi}}=G_{\text{BiClO}}+2G_{\text{H}_3\text{O}}-(G_{\text{Bi}}+3\text{H}_2\text{O}+G_{\text{Cl}})=-322,1+2*22,44-(G_{\text{Bi}}+3*0-\mathbf{183,955})=-\mathbf{2,2389\text{ kJ/mol}};$$

$$G_{\text{Bi}}=G_{\text{BiClO}}+2G_{\text{H}_3\text{O}}-(\Delta G_{\text{eqBiClO}/\text{Bi}}+3\text{H}_2\text{O}+G_{\text{Cl}})=-322,1+2*22,44-(-\mathbf{2,2389}+3*0-\mathbf{183,955})=-\mathbf{91,03\text{ kJ/mol}};$$



$$E^\circ_{\text{BiO}_3/\text{BiO}^+}=E^\circ-0,0591/2*\lg(1/[\text{H}_2\text{O}]^6)+0,10166-0,37239=1,80-0,0591/2*\lg(1/55,3^{\wedge}6)+0,10166-0,37239=\mathbf{1,83826\text{ V}} ;$$

$$E_{\text{BiO}_3/\text{BiO}^+}=E^\circ_{\text{BiO}_3/\text{BiO}^+}+\frac{0,0591}{2}*\lg\frac{[\text{BiO}_3^-][\text{H}_3\text{O}^+]^4}{[\text{BiO}^+][\text{H}_2\text{O}]^6}=\mathbf{1,83826V}+\frac{0,0591}{2}*\lg\frac{[\text{BiO}_3^-][\text{H}_3\text{O}^+]^4}{[\text{BiO}^+][\text{H}_2\text{O}]^6}$$

$$\Delta G_{\text{eqBiO}_3/\text{BiO}^+}=E^\circ_{\text{eqBiO}_3/\text{BiO}^+}*F*3=\mathbf{1,83826*96485*2}=\mathbf{354,73\text{ kJ/mol}};$$

$$\Delta G_{\text{eqBiO}_3/\text{BiO}^+}=G_{\text{BiO}_3}+4G_{\text{H}_3\text{O}}-(G_{\text{BiO}^+}+6\text{H}_2\text{O})=G_{\text{BiO}_3}+4*22,44-(G_{\text{BiO}^+}+6*0)=\mathbf{354,73\text{ kJ/mol}};$$

$$G_{\text{BiO}^+}=G_{\text{BiO}_3}+4G_{\text{H}_3\text{O}}-(\Delta G_{\text{eqBiO}_3/\text{BiO}^+}+6\text{H}_2\text{O})=G_{\text{BiO}_3}+4*22,44-(\mathbf{354,73}+6*0)=\text{???}\text{ kJ/mol};$$

$$G_{\text{Bi}}=-\mathbf{249,6\text{ kJ/mol}}; G_{\text{Bi}}=-\mathbf{132,6\text{ kJ/mol}}; G_{\text{Bi}}=\mathbf{298,7\text{ kJ/mol}}; G_{\text{Bi}}=\mathbf{288,8\text{ kJ/mol}}; G_{\text{Bi}}=-\mathbf{91,0\text{ kJ/mol}}; G_{\text{Bi}}=-\mathbf{83,57\text{ kJ/mol}};$$

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