

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

Anniversary Nernst's Nobel Prize in Chemistry 1920:

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

Electrochemical potential both side membrane create ionic concentrations gradients $C_{right_side}/C_{left_side}$.

Electrochemical reactions across membrane drive E7class transport enzymes .

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

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

Are classified such Type **electrodes**:

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

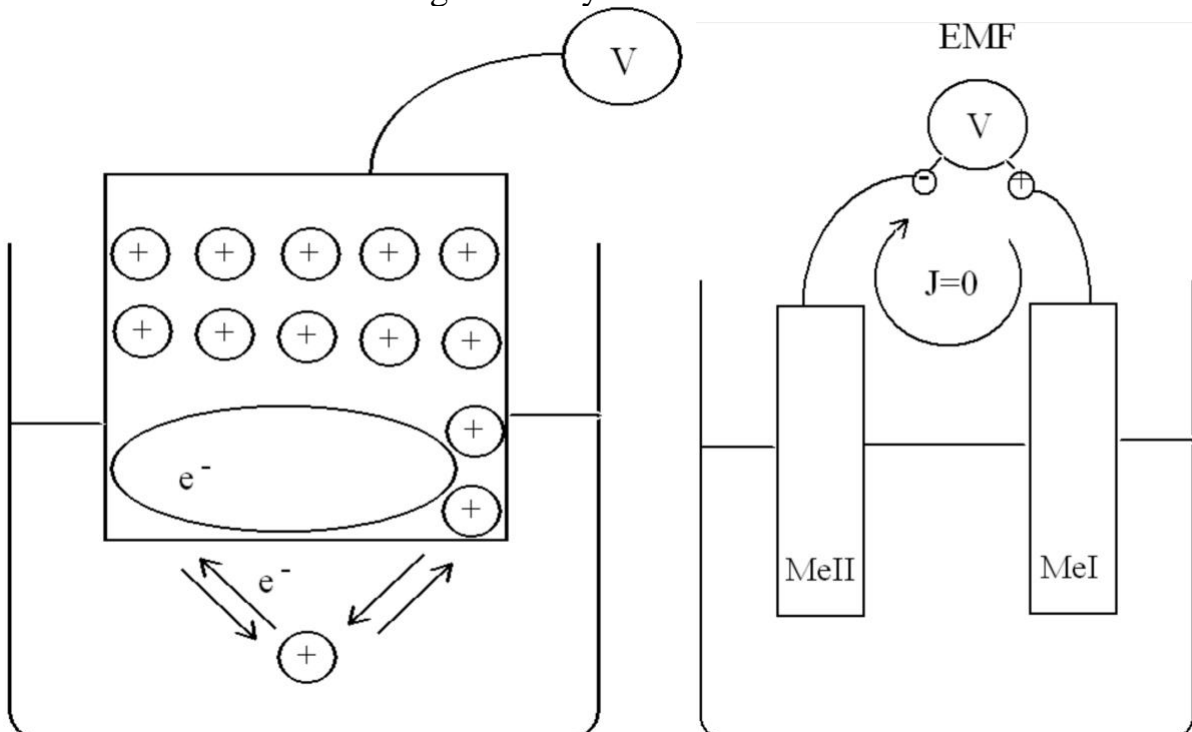
Type II: charged **ions** and free **electrons** transfer through **interface**;

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

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

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

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



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

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

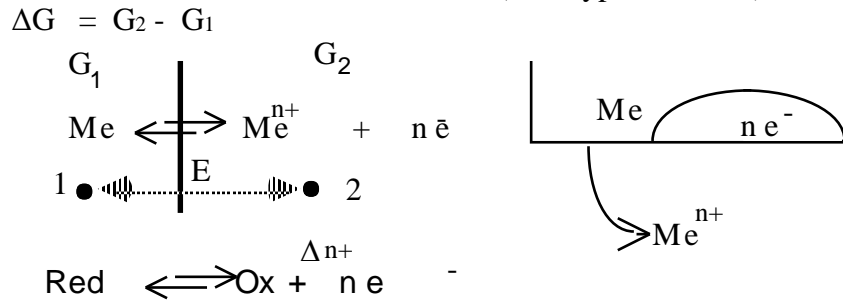
$$EMF = E_I - E_{II} \quad ; \quad E_I = EMF + E_{II}$$

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

Reference

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

(First type electrode)



One **1** mol of the reduced form **Red** transfer from left side to right side in reaction to oxidised form **Ox** is the Hess law calculated free energy change work W of one mol 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

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

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

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

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

Second thermodynamic approach to obtaining Nernst's expression.

When equilibrium is established reactant and product chemical potential sum is equal $\mu_{\text{Red}} + nF = \mu_{\text{Ox}} + n\mu_{e^-}$ but each chemical compound chemical potential is: $\mu = \Delta G^\circ_A + RT \ln(N_A)$, where N_A is substance A concentration (mol fraction). 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 :

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

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

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

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

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** ^{Δn^+} + **ne** **Oxidising form** $E = E^\circ + \frac{0,0591}{n} \cdot \lg \left(\frac{[\text{Ox}]}{[\text{Red}]} \right)$.

In reaction **ne** electron lose (left at metal) exert towards solution transfer Δn^+ positively charged ions **Ox** ^{Δn^+} . Electrons **ne** leaves at metal electron gas. Such Δn^+ positive charge entrance into solution as oxidised form **Ox** ^{Δn^+} 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 H_3O^+ solution application

Attractor $\text{pH}=7.36$ staying at equilibrium have true $\text{pOH}=6.64$ value as $\text{pK}_w=14= \text{pH}+\text{pOH}=7.36+6.64$. Disaccount the water mass $[\text{H}_2\text{O}]=963/18=53.5$ M over liter $[\text{H}_2\text{SO}_4]=[\text{H}_3\text{O}^+]=1$ 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^- ; $E_{\text{classic}}=E_{o_classic}+0.0591\cdot\log K^{\circ}_{\text{classicH(Pt)}}=0+0.0591\cdot\log[\text{H}^+]=0+0.0591\cdot\log(1\text{ M})=0$ Volts. [11] Thermodynamic account Hydroxonium ions demand the water: **H(Pt)**+ $\text{H}_2\text{O}\rightleftharpoons\text{H}_3\text{O}^++\text{e}^-$ and $E^{\circ}_{\text{H}}=0.10166$ V. The ratio $[\text{H}_3\text{O}^+]/([\text{H}_2\text{O}]-[\text{H}_3\text{O}^+])=1\text{ M}/52.5\text{ M}=X_{\text{H}_3\text{O}^+}/X_{\text{H}_2\text{O}}$ is mol fraction instead molarity $[\text{H}^+]=1$ M at classic potential expression. The water account gave thermodynamic standard $E^{\circ}_{\text{H}}=0.10166$ V on potential scale. Nernst's expression with classic zero measurement demands thermodynamic standard potential $E^{\circ}_{\text{H}}=0.10166$ V :

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

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

$$E=E^{\circ}_{\text{H}}+\frac{\ln(10)\cdot R\cdot T}{F\cdot 1}\cdot\log\frac{X_{\text{H}_3\text{O}^+}}{X_{\text{H}_2\text{O}}}=0.10166+0.0591\cdot\log(1)=0.10166\text{ V.}$$
 Metal oxidation free energy change

minimum is different endoergic $\Delta G_{\text{eq}}=E^{\circ}_{\text{H}}\cdot F\cdot 1=0.10166\cdot 96485\cdot 1=9.81$ kJ/mol instead Alberty is exoergic .

Alberty Hess value is exoergic; $\Delta G_{\text{Hess_eq}}=G_{\text{H}_3\text{O}^+}+G_{\text{e}^-}-(G_{\text{H(Pt)}}+G_{\text{H}_2\text{O}})=22.44+0-(51.05+0)=-28.61$ kJ/mol .

Free energy changes are determined on water and carbon dioxide gas zero $G_{\text{H}_2\text{O}}=G_{\text{CO}_2\text{gas}}=G_{\text{e}^-}=0$ kJ/mol reference scale. Iterative found on absolute scale hydrogen standard potential is: $E^{\circ}_{\text{H}}=-0.29654$ V. Equilibrium free energy minimum is exoergic: $\Delta G_{\text{eq}}=E^{\circ}_{\text{H}}\cdot F\cdot 1=-0.29654\cdot 96485\cdot 1=-28.61$ kJ/mol coinciding with Alberty data. Absolute potential scale slips by $\Delta E=-0.29654-0.10166=-0.3982$ Volts down. Nernst's hydrogen equilibrium constant is grater as one: $K_{\text{H(Pt)_Red}}=[\text{H}_3\text{O}^+]\cdot[\text{e}^-]/[\text{H}_2\text{O}]/[\text{H(Pt)}]=\text{EXP}(-\Delta G_{\text{Alberty}}/R/T)=\text{EXP}(28612/8.3144/298.15)=102954$.

I type electrode Metal interface **H(Pt)** / on its cation H_3O^+ solution application.

High rate protolysis attractors $[\text{H}_3\text{O}^+]=10^{-7.36}$ M , $\text{pH}=7.36$ and water mass $[\text{H}_2\text{O}]=997/18=55.3$ M account in liter shows metal hydrogen strong reducing potential: $E_{\text{pH}=7.36}=-0.29654+0.0591\cdot\log(10^{-7.36}/55.3)=-0.8345$ V and free energy change minimum $\Delta G_{\text{eqpH}_7.36}=E^{\circ}_{\text{H}}\cdot F\cdot 1=-0.8345\cdot 96485\cdot 1/1000=-80.5$ kJ/mol .

Nernst's half reaction metal reduction potential $E^{\circ}_{\text{H}}=-0.29654$ V energy $\Delta G_{\text{eq}}=-28.6$ kJ/mol.

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

Ratio $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]=1/52.5=X_{\text{H}_3\text{O}^+}/X_{\text{H}_2\text{O}}$ give classic zero **0** insted thermodynamic

standard potential: $E^{\circ}_{\text{H}}=0.10166$ V and from Alberty data on absolute scale

absolute standard potential is $E^{\circ}_{\text{H}}=-0.29654$ Volts.

absolute $E^{\circ}_{\text{H}}=-0.29654$ V

classic zero $E^{\circ}_{\text{H}}=0$ V

0.10166 V E, V

$$E_{(\text{Pt})\text{H}/\text{H}^+}=E^{\circ}_{\text{H}}+0.0591\cdot\log\left(\frac{X_{\text{H}_3\text{O}^+}}{X_{\text{H}_2\text{O}}}\right) \quad E_{\text{H_classic}}=E^{\circ}_{\text{H}}+0.0591\cdot\log([\text{H}_3\text{O}^+]) \quad \text{thermodynamic } E^{\circ}_{\text{H}}$$

Absolute standard potential $E^{\circ}_{\text{H}}=-0.29654$ V based on Alberty data $G_{\text{H}_2\text{gas}}=85.64$ kJ/mol and $G_{\text{H}_2\text{aq}}=103,24$ kJ/mol for hydrogen, which was detected on water and carbon dioxide gas zero scale $G_{\text{H}_2\text{O}}=G_{\text{CO}_2\text{gas}}=G_{\text{e}^-}=0$ kJ/mol. Reducing agent at $\text{pH}=7,36$, $[\text{H}_3\text{O}^+]=10^{-7,36}$ M with

potential $E=-0,2965+0,0591\cdot\log(10^{(-7.36)}/55,3)=-0,8345$ V is strong reductant. Free energy content in one mol metal hydrogen is: $G_{\text{H(Pt)}}=51.05$ kJ/mol .

$$\text{Ag}+2\text{NH}_3(\text{aq})=\text{Ag}(\text{NH}_3)_2^++\text{e}^-; E_{\text{Ag}/\text{Ag}(\text{NH}_3)_2^+}=E^{\circ}_{\text{Ag}/\text{Ag}(\text{NH}_3)_2^+}+0.0591/1\cdot\log\frac{[\text{Ag}]\cdot[\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]^2} \\ =-0.0765+0.0591\cdot\log(0.1/1/(0.3-2\cdot 0.1)^2)=0.1351\text{ V;}$$

$$2\text{Ag}+2\text{OH}^-=\text{Ag}_2\text{O}(\text{s})+\text{H}_2\text{O}+2\text{e}^-; E_{2\text{Ag}/\text{Ag}_2\text{O}}=E^{\circ}_{2\text{Ag}/\text{Ag}_2\text{O}}+0.0591/2\cdot\log\frac{[\text{Ag}_2\text{O}]\cdot[\text{H}_2\text{O}]}{[\text{Ag}]^2\cdot[\text{OH}]^2} \\ =-0.003+0.0591/2\cdot\log(1\cdot 55.3/10^{(-7\cdot 2)});$$

Substance	$\Delta H^{\circ}_{\text{H}}$ kJ/mol	$\Delta S^{\circ}_{\text{H}}$ J/mol/K	$\Delta G^{\circ}_{\text{H}}$, kJ/mol
Ag	-	-	18.64
Ag ⁺	105.6	72.7	77.1
AgCl(s)	-127.01	96.25	-155.71
Cl ⁻	-167.08	56.6	-183.955

$$G_{\text{Ag}}=G_{\text{Ag}^+}-(\Delta G_{\text{eq_Ag}}+G_{\text{H}_2\text{O}})=77.1-(58.46+0)=18.64\text{ kJ/mol}$$

$$G_{\text{Ag}}=G_{\text{AgCl}}+G_{\text{H}_2\text{O}}-(\Delta G_{\text{eq_Ag}}+G_{\text{Cl}^-})=45.342\text{ kJ/mol}$$

$$\Delta G_{\text{AgCl}}=\Delta H_{\text{H}}-T\cdot\Delta S_{\text{H}}=-127.01-298.15\cdot 0.09625=-155.71\text{ kJ/mol;}$$

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

Table 1. Nernst's half reactions Standard Electrodes Potentials classic, Thermodynamic, Absolute in V.

	Reduced form = Oxidized form + n e ⁻ ;	H ₂ O disaccount classic zero E _o	Thermodynamic scale on H ₂ O account	Absolute scale -0,37238 (-0.3982) V
H	H (Pt) + H ₂ O = H ₃ O ⁺ + (Pt) + e ⁻ ; general reference CRC [1]	classic zero 0	0,10166	-0,27072
	H (Pt) + OH ⁻ = H ₂ O + (Pt) + e ⁻ ; classic CRC [1]	-0.8277	-0,8282	-1,2006
	H (Pt) + OH ⁻ = H ₂ O + (Pt) + e ⁻ ; corrected -0.104495 by Alberty	-0.95801	-0,95850	-1,33088
	H₂aq + 2H₂O = 2H₃O⁺ + 2e⁻ ; g raphite electrode	-	-	0.302
O	5H ₂ O = O _{2aq} + 4H ₃ O ⁺ + 4e ⁻ ;	1,2288	1,4592	1,0610
	H ₂ O ₂ + 2H ₂ O = O ₂ + 2H ₃ O ⁺ + e ⁻	1.2764	+1.58416	1.0829
	4H ₂ O = H ₂ O ₂ + 2 H ₃ O ⁺ + 2e ⁻ ; Suchotina [17]	1.776	+2.08366	1.6855
	H₂O₂ + 2H₂O = O₂ + 2H₃O⁺ + 2e⁻; University Alberta [19]	0.6945	0.8477	0.4495
	HOO⁻ + H₂O = O₂ + H₃O⁺ + 2e⁻; Kaksis	-	-	0.07587
N	NO₂⁻ + 2OH⁻ = NO₃⁻ + H₂O + 2e⁻; pH > 3.15 Suchotina [17]	0.01	0.0602	-0.3380
	HNO₂ + 4H₂O = NO₃⁻ + 3H₃O⁺ + 2e⁻; pH < 3.15 Kortly, Shucha	0.94	1.2477	0.8495
	NO_{aq} + 6H₂O = NO₃⁻ + 4H₃O⁺ + 3e⁻; pH > 3.15 Kortly, Shucha	0.96	1.2677	0.8695
	NH₄⁺ + 13H₂O = NO₃⁻ + 10H₃O⁺ + 8e⁻; Suchotina [17]	0.87	1.4180	1.0198
Br	2Br ⁻ = Br ₂ (aq) + 2e ⁻ ; CRC	1.0873	1.18896	0.79076
Bi	BiO ⁺ + 6H ₂ O = BiO ₃ ⁻ + 4H ₃ O ⁺ + 2e ⁻ ; 1 < pH < 7 Suchotina [17]	1.80	2.210645	1.812445
Mn H⁺	Mn ²⁺ + 12H ₂ O = MnO ₄ ⁻ + 8H ₃ O ⁺ + 5e ⁻ ; Kortly, Shucha [18]	1.51	1.8588	1.4506
H₂O	MnO₂ + 4OH⁻ = MnO₄⁻ + 2H₂O + 3e⁻; Suchotina	0.603	0.6360	0.2378
OH⁻	MnO₄²⁻ = MnO₄⁻ + e⁻; Suchotina	0.558	0.6597	0.2615
Pb	Pb ²⁺ + 6H ₂ O = PbO ₂ (s) + 4H ₃ O ⁺ + 2e ⁻ ; Kortly, Shucha	1.455	1.8656	1.4674
	Pb + H ₂ O = Pb ²⁺ + 2e ⁻ ; pH < 7 Kortly, Shucha	-0.126	0.0272	-0.3710
S	H ₂ SO ₃ + 4H ₂ O = HSO ₄ ⁻ + 3H ₃ O ⁺ + 2e ⁻ ; Suchotina pH < 1.9	0.172	0.47965	0.08145
	HSO ₃ ⁻ + 4H ₂ O = SO ₄ ²⁻ + 3H ₃ O ⁺ + 2e ⁻ ; Suchotina 2 = < pH < 7	0.172	0.47965	0.08145
	SO ₃ ²⁻ + 2OH ⁻ = SO ₄ ²⁻ + H ₂ O + 2e ⁻ ; Suchotina pH > 7	-0.93	-0.87984	-1.27804
	S²⁻ = S_{rombic} + H₂O + 2 e⁻; CRC2010	-0.4763	-0.4261	-0.8243
	HS⁻ + OH⁻ = S_{rombic} + 2H₂O + 2e⁻; CRC 2010	-0.478	-0.4793	-0.8775
	H₂S_{aq} + 2H₂O = S_{rombic} + 2H₃O⁺ + 2e⁻; CRC 2010:Kortly,Shucha	0.142	0.3467	-0.0515
	2S ₂ O ₃ ²⁻ = S ₄ O ₆ ²⁻ + 2e ⁻ ; Suchotina	0.08	0.18166	-0.2165
Fe	Fe ²⁺ = Fe ³⁺ + e ⁻ ; Suchotina [17]	0.769	0.8717	0.4735
	Fe(s) + H ₂ O = Fe ²⁺ + 2e ⁻ ; Suchotina	-0.4402	-0.2870	-0.6852
Ag	Ag + H ₂ O = Ag ⁺ + e ⁻ ; Kortly, Shucha [18]	0.7994	1.0041	0.6059
	Ag(s) + Cl ⁻ = AgCl(s) + H ₂ O + e ⁻ ; Kortly, Shucha	0.2223	0.2210	-0.1772
	Ag + 2NH _{3(aq)} = Ag(NH ₃) ₂ ⁺ + e ⁻ ; Suchotina	0.373	0.4747	0.0765
	2Ag + 2OH ⁻ = Ag ₂ O(s) + H ₂ O + 2e ⁻ ; Suchotina	0.345	0.3952	-0.0030
Hg	2Hg + H ₂ O = Hg ₂ ²⁺ + 2e ⁻ ; Kortly, Shucha [18]	0.907	1.0602	0.6620
	2Hg + 2Cl ⁻ = Hg ₂ Cl ₂ (s) + 2H ₂ O + 2e ⁻ ; Suchotina ; [17]	0.2676	0.2663	-0.1319
	2Hg + SO ₄ ²⁻ = Hg ₂ SO ₄ (s) + 2e ⁻ ; Kortly, Shucha ; [18]	0.614	0.7157	0.3175
	Hg + 2OH ⁻ = HgO + 2H ₂ O + 2e ⁻ ; Suchotina ; [17]	0.098	0.0967	-0.3015
I	3I ⁻ = I ₃ ⁻ + 2e ⁻ ; Kortly, Shucha	0.6276	0.72926	0.33106
Cu	Cu(Hg) + H ₂ O = Cu ²⁺ + (Hg) + 2e ⁻ ; Kortly, Shucha	0.3435	0.4967	0.0985
F	2F ⁻ = F ₂ (g) + 2e ⁻ ; Kortly, Shucha	2.87	2.97166	2.5735
Cl	2Cl ⁻ = Cl ₂ (g) + 2e ⁻ ; Kortly, Shucha	1.358	1.45966	1.06146
Cl	Cl ₂ (g) + 4H ₂ O = 2HOCl + 2H ₃ O ⁺ + 2e ⁻ ; Kortly, Shucha	1.63	1.93765	1.53945
Cr	2Cr ³⁺ + 21H ₂ O = Cr ₂ O ₇ ²⁻ + 14H ₃ O ⁺ + 6e ⁻ ; 1 < pH < 7 [18]	1.33	1.7921	1.3939
	Cr ³⁺ + 11H ₂ O = HCrO ₄ ⁻ + 7H ₃ O ⁺ + 3e ⁻ ; pH > 7 Kortly, Shucha	1.20	1.6793	1.2811
	Cr(OH) ₃ + 5OH ⁻ = CrO ₄ ²⁻ + 4H ₂ O + 3e ⁻ ; pH > 9 ; Suchotina	-0.13	-0.1657	-0.5639
C	H ₂ C ₂ O ₄ + 2H ₂ O = 2CO ₂ + 2H ₃ O ⁺ + 2e ⁻ ; pH < 1,25 Suchotina [17]	-0.49	-0.28534	-0.6835
	HC ₂ O ₄ ⁻ + H ₂ O = 2CO ₂ + H ₃ O ⁺ + 2e ⁻ ; 1,25 < pH Suchotina [17]	-0.49	-0.3368	-0.7350
	C ₂ O ₄ ²⁻ = 2CO ₂ + 2e ⁻ ; 4,14 < pH Suchotina [17]	-0.49	-0.3883	-0.7865
Cr	Cr + H ₂ O = Cr ³⁺ + 3e ⁻ ; Suchotina	-0.744	-0.6080	-1.0062
Zn	Zn + H ₂ O = Zn ²⁺ + 2e ⁻ ; Kortly, Shucha	-0.7628	-0.6096	-1.0078
Al	Al + H ₂ O = Al ³⁺ + 3e ⁻ ; CRC	-1.662	-1.5260	-1.9242
	Al + 4OH ⁻ = H ₂ AlO ₃ ⁻ + H ₂ O + 3e ⁻ ; CRC	-2.33	-2.2627	-2.6609

E^o_{Hg} = -1.2264 V; **H**(Pt) + OH⁻ = H₂O + (Pt) + e⁻; Nernst's absolute standard potential corrected E^o_{Hg} = -1.33088 V [1]

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} = -0.8277 V:

E^o_{H_H_OH} = E^o - 0.0591/1 * lg([H₂O]¹) + 0.10166 - 0.3982 = -0.8277 - 0.0591/1 * lg(53.5¹) + 0.10166 - 0.3982 = -1.2264 V;

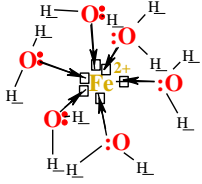
ΔG_{eq_H_OH} = E^o_{H_H_OH} * F * 1 = -1.2264 * 96485 * 1 = -118.33 kJ/mol;

ΔG_{eq_H_OH} = G_{H₂O} - (G_{H(Pt)} + G_{OH⁻}) = 0 - (51.05 + 77.36) = -128.41 kJ/mol;

Corrected ΔG_{eq_H_OH} = E^o_{H_H_OH} * F * 1 = -1.33088 * 96485 * 1 = -128.41 kJ/mol;

Metal immersed in its ions solution by Nernst's oxidation half reaction forms Electrode potential in Volts.
 Coordination of metal ions in solution bind water with donor-acceptor bonds.

Reaction $\text{Fe}_{(s)} + \text{H}_2\text{O} = \text{Fe}^{2+} + 2\text{e}^-$; $[\text{Fe}^{2+}] = 0.1 \text{ M}$; density 1.03 g/mL ; $0.1 \text{ Molar mass FeSO}_4 = 15.191 \text{ g/mol}$;
 $E_{\text{Fe}} = E^\circ_{\text{Fe}} + 0.0591/2 \cdot \log([\text{Fe}^{2+}]/[\text{Fe}]/([\text{H}_2\text{O}])) = -0.6852 + 0.0591/2 \cdot \log(0.1/1/(55.3)) = -0.76625 \text{ V}$;
 Distinguish on number -0.76625 V in the fourth sign -0.7663 V



$$E_{\text{Fe}} = E^\circ_{\text{Fe}} + 0.0591/2 \cdot \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}] \cdot ([\text{H}_2\text{O}] - 6[\text{Fe}^{2+}])} = -0.7663 \text{ V};$$

$E_{\text{Fe}} = E^\circ_{\text{Fe}} + 0.0591/2 \cdot \log([\text{Fe}^{2+}]/[\text{Fe}]/([\text{H}_2\text{O}] - 6[\text{Fe}^{2+}])) = -0.6852 + 0.0591/2 \cdot \log(0.1/1/(56.38 - 0.6)) = -0.7663 \text{ V}$;
 $\frac{996 \text{ g/L}}{18 \text{ g/mol}}$;
 $m_{\text{H}_2\text{O}} = m_{\text{L}} - m_{\text{FeSO}_4} = 1030 - 15.191 = 1284.8 \text{ g}$; $[\text{H}_2\text{O}] = 1014.8 \text{ g}/18 \text{ g/mol} = 56.38 \text{ M}$.

$\Delta G_{\text{eqFe}} = E^\circ_{\text{Fe}} \cdot F \cdot 2 = -0.6852 \cdot 96485 \cdot 2 = -132.223 \text{ kJ/mol}$, $\Delta G_{\text{eqFe}} = G_{\text{Fe}^{2+}} - (G_{\text{Fe}} + G_{\text{H}_2\text{O}}) = -82.14 - (50.08 + 0) = -132.223 \text{ kJ/mol}$;
 $G_{\text{Fe}} = G_{\text{Fe}^{2+}} - (\Delta G_{\text{eqFe}} + G_{\text{H}_2\text{O}}) = -82.14 - (-132.223 + 0) = 50.08 \text{ kJ/mol}$;

Substance	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol
Fe	$E^\circ_{\text{Fe}} =$	-0.6852 V	50.08
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	$E^\circ_{\text{Cu}} =$	0.0985 V	113.03
Cu ²⁺	64.8	-98	94.0187
Zn	$E^\circ_{\text{Zn}} =$	-1.0078 V	73.82
Zn ²⁺	-153.39	-109.8	-120.653
Ag ⁺	-	-	77.1
AgCl	-	-	-155.71
Cl ⁻	-	-	-183.955
Ag	$E^\circ_{\text{Ag}/\text{AgCl}} =$	-0.1772 V	45.342
Ag	$E^\circ_{\text{Ag}} =$	0.6059 V	18.64

$$G_{\text{Fe}} = G_{\text{Fe}^{2+}} - (\Delta G_{\text{eqFe}} + G_{\text{H}_2\text{O}}) = 50.08 \text{ kJ/mol};$$

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$$G_{\text{Cu}} = G_{\text{Cu}^{2+}} - (\Delta G_{\text{eqCu}} + G_{\text{H}_2\text{O}}) = 113.03 \text{ kJ/mol};$$

$$\Delta G_{\text{Cu}^{2+}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = 64.8 - 298.15 \cdot (-0.098) = 94.0187 \text{ kJ/mol};$$

$$G_{\text{Zn}} = G_{\text{Zn}^{2+}} - (\Delta G_{\text{eqZn}} + G_{\text{H}_2\text{O}}) = -120.653 - (-194.475 + 0) = 73.82 \text{ kJ/mol};$$

$$\Delta G_{\text{Zn}^{2+}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -153.39 - 298.15 \cdot (-0.1098) = -120.65 \text{ kJ/mol};$$

CRC;

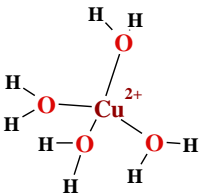
BioThermodynamic 2006

BioThermodynamic 2006

$$G_{\text{Ag}} = G_{\text{AgCl}} + G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqAg}} + G_{\text{Cl}^-}) = 45.342 \text{ kJ/mol};$$

$$G_{\text{Ag}} = G_{\text{Ag}^+} - (\Delta G_{\text{eqAg}} + G_{\text{H}_2\text{O}}) = 77.1 - (58.46 + 0) = 18.64 \text{ kJ/mol};$$

Reaction $\text{Cu}(\text{Hg}) + \text{H}_2\text{O} = \text{Cu}^{2+} + (\text{Hg}) + 2\text{e}^-$; $[\text{Cu}^{2+}] = 1 \text{ M}$ density 1.19 g/mL ; $1 \text{ Molar mass } \text{M}_{\text{CuSO}_4} = 159.602 \text{ g/mol}$;
 $E_{\text{Cu}} = E^\circ_{\text{Cu}} + 0.0591/2 \cdot \log([\text{Cu}^{2+}]/[\text{Cu}]/([\text{H}_2\text{O}])) = 0.0985 + 0.0591/2 \cdot \log(1/1/(55.3)) = 0.047002 \text{ V}$;
 Distinguish on number 0.047002 V in the fourth sign 0.04696 V



$$E_{\text{Cu}} = E^\circ_{\text{Cu}} + 0.0591/2 \cdot \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}] \cdot ([\text{H}_2\text{O}] - 4 \cdot [\text{Cu}^{2+}])} = 0.04696 \text{ V};$$

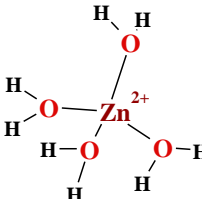
$m_{\text{H}_2\text{O}} = (m_{\text{L}} - m_{\text{CuSO}_4})/18 = 1190 - 159.602 = 1030.4/18 = 57.24 - 4 = 53.24 \text{ mol}$;

$E_{\text{Cu}} = E^\circ_{\text{Cu}} + 0.0591/2 \cdot \log([\text{Cu}^{2+}]/[\text{Cu}]/([\text{H}_2\text{O}] - 4[\text{Cu}^{2+}])) = 0.0985 + 0.0591/2 \cdot \log(1 \text{ M}/1/(57.24 - 4)) = 0.04696 \text{ V}$;

$\Delta G_{\text{eqCu}} = E^\circ_{\text{Cu}} \cdot F \cdot 2 = -0.0985 \cdot 96485 \cdot 2 = -19.01 \text{ kJ/mol}$, $\Delta G_{\text{eqCu}} = G_{\text{Cu}^{2+}} - (G_{\text{Cu}} + G_{\text{H}_2\text{O}}) = 94.0187 - (G_{\text{Cu}} + 0) = -19.01 \text{ kJ/mol}$;

$$G_{\text{Cu}} = G_{\text{Cu}^{2+}} - (\Delta G_{\text{eqCu}} + G_{\text{H}_2\text{O}}) = 94.0187 - (-19.01 + 0) = 113.03 \text{ kJ/mol};$$

$\text{Zn} + \text{H}_2\text{O} = \text{Zn}^{2+} + 2\text{e}^-$; $\text{ZnSO}_4 = 161.44 \text{ g/mol}$ $[\text{Zn}^{2+}] = \text{C}_{\text{ZnSO}_4} = 2 \text{ M}$ density 1.31 g/mL ; $m_{\text{ZnSO}_4} = 2 \cdot 161.44 = 322.88 \text{ g}$;



$$E_{\text{Zn}} = E^\circ_{\text{Zn}} + 0.0591/2 \cdot \log([\text{Zn}^{2+}]/[\text{Zn}]/([\text{H}_2\text{O}])) = -1.0078 + 0.0591/2 \cdot \log(2/1/(55.3)) = -1.0504 \text{ V};$$

Distinguish on number -1.0504 V in the fourth sign -1.04827 V 2M ;

$$E_{\text{Zn}} = E^\circ_{\text{Zn}} + 0.0591/2 \cdot \log \frac{[\text{Zn}^{2+}]}{[\text{Zn}] \cdot ([\text{H}_2\text{O}] - 4 \cdot [\text{Zn}^{2+}])} = -1.04827 \text{ V};$$

Solubility $57.7 \text{ g}/100\text{g}$ in hundreds grams of water; $w\% = 57.7/157.7 \cdot 100 = 36.6\%$;

$m_{\text{H}_2\text{O}} = m_{\text{L}} - m_{\text{ZnSO}_4} = 1310 - 161.44 \cdot 2 = 987.12 \text{ g}$; $m_{\text{ZnSO}_4} = 2 \cdot 161.44 = 322.88 \text{ g}$; $[\text{H}_2\text{O}] = 987.12 \text{ g}/18 \text{ g/mol} = 54.84 \text{ M}$.

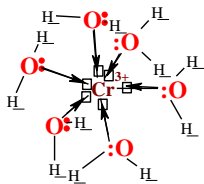
$$E_{\text{Zn}} = E^\circ_{\text{Zn}} + 0.0591/2 \cdot \log \frac{[\text{Zn}^{2+}]}{[\text{Zn}] \cdot ([\text{H}_2\text{O}] - 4 \cdot [\text{Zn}^{2+}])} = -1.0078 + 0.0591/2 \cdot \log(2/1/(54.84 - 4 \cdot 2)) = -1.04827 \text{ V};$$

$\Delta G_{\text{eqZn}} = E^\circ_{\text{Zn}} \cdot F \cdot 2 = -1.0078 \cdot 96485 \cdot 2 = -194.475 \text{ kJ/mol}$,

$$\Delta G_{\text{eqZn}} = G_{\text{Zn}^{2+}} - (G_{\text{Zn}} + G_{\text{H}_2\text{O}}) = -120.653 - (G_{\text{Zn}} + 0) = -194.475 \text{ kJ/mol};$$

$$G_{\text{Zn}} = G_{\text{Zn}^{2+}} - (\Delta G_{\text{eqZn}} + G_{\text{H}_2\text{O}}) = -120.653 - (-194.475 + 0) = 73.82 \text{ kJ/mol};$$

$\text{Cr} + \text{H}_2\text{O} = \text{Cr}^{3+} + 3\text{e}^-$; $\text{Cr}_2(\text{SO}_4)_2 = 159.602 \text{ g/mol}$; $C_{\text{Cr}_2(\text{SO}_4)_2} = 0.5 \text{ M}$ $[\text{Cr}^{3+}] = 2 * C_{\text{Cr}_2(\text{SO}_4)_2} = 1 \text{ M}$ density 1.172 g/mL ;
 $E_{\text{Cr}} = E^\circ_{\text{Cr}} + 0.0591/3 * \log([\text{Cr}^{3+}]/[\text{Cr}]/([\text{H}_2\text{O}])) = -1.0062 + 0.0591/3 * \log(1/(1/(55.3))) = -1.04053 \text{ V}$;
 Distinguish on number -1.04053 V in the fourth sign -1.03936 V 1M; 2.32 M -1.027 V



$$E_{\text{Cu}} = E^\circ_{\text{Cu}} + 0.0591/2 * \log \frac{[\text{Cr}^{3+}]}{[\text{Cr}] \cdot ([\text{H}_2\text{O}] - 6 \cdot [\text{Cr}^{3+}])} = -1.03936 \text{ V};$$

$m_{\text{H}_2\text{O}} = m_{\text{L}} - m_{\text{Cr}_2(\text{SO}_4)_2} = 1172 - 196.08 = 975.92 \text{ g}$; $m_{\text{Cr}_2(\text{SO}_4)_3} = 392.16/2 = 196.08$;
 $[\text{Cr}^{3+}] = 2 * C_{\text{Cr}_2(\text{SO}_4)_2} = 1 \text{ M}$ density 1.172 g/mL ; $m_{\text{Cr}_2(\text{SO}_4)_3} = 196.08 \text{ g}$; $[\text{H}_2\text{O}] = 975.92 \text{ g}/18 \text{ g/mol} = 54.21778 \text{ M}$

$$E_{\text{Cr}} = E^\circ_{\text{Cr}} + 0.0591/3 * \log \frac{[\text{Cr}^{3+}]}{[\text{Cr}] \cdot ([\text{H}_2\text{O}] - 6 \cdot [\text{Cr}^{3+}])} = -1.0062 + 0.0591/3 * \log(1/(54.21778 - 6 * 1)) = -1.03936 \text{ V};$$

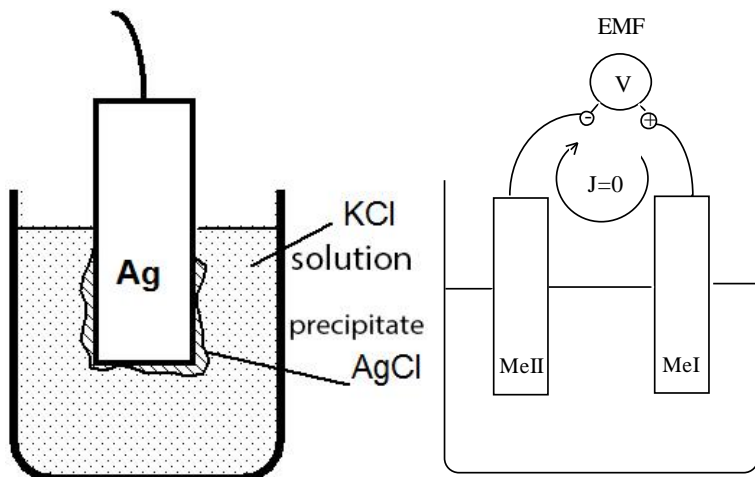
Solubility 64 g/100g in hundred grams of water; $w\% = 64/164 * 100 = 39\%$;
 $39/100 \text{ g} = X/1172 \text{ g/L}$; $39/100 * 1172 = 457.07 = X \text{ g/L}$; $C_{\text{Cr}_2(\text{SO}_4)_2} = 457.07/392.16 = 1.1655 \text{ M}$ $\text{Cr}_2(\text{SO}_4)_3$;
 $m_{\text{H}_2\text{O}} = m_{\text{L}} - m_{\text{Cr}_2(\text{SO}_4)_2} = 1172 - 457.07 = 714.93 \text{ g}$; $m_{\text{Cr}_2(\text{SO}_4)_2} = 457.07 \text{ g}$; $[\text{H}_2\text{O}] = 714.93 \text{ g}/18 \text{ g/mol} = 39.718 \text{ M}$

$$[\text{H}_2\text{O}] = 714.93 \text{ g}/18 \text{ g/mol} = 39.718 \text{ M}; E_{\text{Cr}} = E^\circ_{\text{Cr}} + 0.0591/3 * \log \frac{[\text{Cr}^{3+}]}{[\text{Cr}] \cdot ([\text{H}_2\text{O}] - 6 \cdot [\text{Cr}^{3+}])} =$$

$$= -1.0062 + 0.0591/3 * \log(2 * 1.1655/1/(39.718 - 6 * 2 * 1.1655)) = -1.027 \text{ V};$$

Metal/insoluble salt/ion II-type electrode

Silver/silver chloride/chloride ion consists of silver metal, AgCl precipitate insoluble salt and



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 :
 $\text{EI} = \text{EMF} + \text{EII}$
 Indicator electrode EI –has reactivity with solution that electrode of investigations, Standard reference electrode EII =constant , because chloride concentration is constant.

$\text{Ag}(\text{s}) + \text{H}_2\text{O} = \text{Ag}^+ + \text{e}^-$; absolute standard potential $E^\circ_{\text{Ag}} = 0.6059 \text{ V}$; Kortly, Shucha ; [18]

$$E_{\text{Ag}} = E^\circ_{\text{Ag}} + 0.0591 \cdot \log([\text{Ag}^+]/[\text{Ag}(\text{s})]/[\text{H}_2\text{O}]) = 0.6059 + 0.0591 \cdot \log([\text{Ag}^+]/55.3);$$

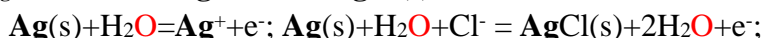
$$\Delta G_{\text{eq_Ag}} = E^\circ_{\text{Ag}} \cdot F \cdot 2 = 0.6059 * 96485 * 1 = \mathbf{58.46} \text{ kJ/mol},$$

$$\Delta G_{\text{eq_As}} = G_{\text{Ag}^+} - (G_{\text{Ag}} + G_{\text{H}_2\text{O}}) = 77.1 - (G_{\text{Ag}} + 0) = \mathbf{58.46} \text{ kJ/mol};$$

$$G_{\text{Ag}} = G_{\text{Ag}^+} - (\Delta G_{\text{eq_Ag}} + G_{\text{H}_2\text{O}}) = 77.1 - (58.46 + 0) = \mathbf{18.64} \text{ kJ/mol};$$

Solubility equilibrium $\text{AgCl}(\text{s}) + 2\text{H}_2\text{O} = \text{Ag}^+ + \text{Cl}^-$; $\text{AgCl}(\text{s}) + 2\text{H}_2\text{O} - \text{Cl}^- = \text{Ag}^+$ and absolute constant :

$$K_{\text{AbsoluteAgCl}} = K_{\text{spAgCl}}/[\text{H}_2\text{O}]^2 = [\text{Ag}^+] * [\text{Cl}^-]/[\text{AgCl}(\text{s})]/[\text{H}_2\text{O}]^2 = 1.77 * 10^{(-10)}/55.3^2 = 5.79 * 10^{-14};$$



$\text{Ag}(\text{s}) + \text{Cl}^- = \text{AgCl}(\text{s}) + \text{H}_2\text{O} + \text{e}^-$; $E^\circ_{\text{AgCl}} = -0.1772 \text{ V}$ [18]; $[\text{Cl}^-] = 0.1 \text{ M} = [\text{K}^+\text{Cl}^-]$ potassium chloride 0.1 M solution;

$$E_{\text{ag/AgCl}} = E^\circ_{\text{AgCl}} + 0.0591 \cdot \log([\text{AgCl}(\text{s})] * [\text{H}_2\text{O}]/[\text{Ag}(\text{s})]/[\text{Cl}^-]) = -0.1772 + 0.0591 \cdot \log(1 * 55.3/1/[\text{Cl}^-]) =$$

$$= -0.1772 + 0.074205 - 0.0591 \cdot \log([\text{Cl}^-]) = -0.102995 = -0.0591 \cdot \log([\text{Cl}^-]) = -0.102995 - 0.0591 \cdot \log(0.1) = -0.043895 \text{ V};$$

$$E_{\text{ag/AgCl}} = E^\circ_{\text{AgCl}} + 0.0591 \cdot \log([\text{AgCl}(\text{s})] * [\text{H}_2\text{O}]/[\text{Ag}(\text{s})]/[\text{Cl}^-]) = -0.102995 - 0.0591 \cdot \log([\text{Cl}^-]);$$

$$\Delta G_{\text{eq_Ag}} = E^\circ_{\text{Ag}} \cdot F \cdot 2 = -0.1772 * 96485 * 1 = \mathbf{-17.097} \text{ kJ/mol},$$

$$\Delta G_{\text{eq_As}} = G_{\text{AgCl}} + G_{\text{H}_2\text{O}} - (G_{\text{Ag}} + G_{\text{Cl}}) = -155.71 + 0 - (G_{\text{Ag}} - 183.955) = \mathbf{-17.097} \text{ kJ/mol};$$

$$G_{\text{Ag}} = G_{\text{AgCl}} + G_{\text{H}_2\text{O}} - (\Delta G_{\text{eq_Ag}} + G_{\text{Cl}}) = -155.71 + 0 - (-17.097 - 183.955) = \mathbf{45.342} \text{ kJ/mol};$$

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

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
Hg	-	75.9	40.67
Hg_2^{2+}	-166.87	66.74	-146.8
Hg_2^{2+}	$E^\circ_{\text{Hg}/\text{Hg}_2^{2+}}$	-0.6620 V	209.09
Hg^{2+}	-170.21	-36.19	-
$\text{Hg}_2\text{SO}_4(\text{s})$	-743.1	200.7	-625.8
$\text{Hg}_2\text{SO}_4(\text{s})$	$K_{\text{AbsoluteHg}_2\text{SO}_4}$	$10^{(-9.673)}$	-593.87
SO_4^{2-}	-907.62	-536.2	-747.75
SO_4^{2-}	$E^\circ_{\text{Hg}_2\text{SO}_4}$	0.3175 V	-736.48
SO_4^{2-}	-909.3	20.1	-744.5
$\text{Hg}_2\text{Cl}_2(\text{s})$	-265.37	191.6	-210.7
$\text{Hg}_2\text{Cl}_2(\text{s})$	$K_{\text{AbsoluteHg}_2\text{Cl}_2}$	$10^{(-23.1)}$	-210.7
$\text{HgCl}_2(\text{s})$	-224.3	146	-178.6
Cl^-	-167.08	56.6	-183.955
Cl^-	$E^\circ_{\text{HgCl}_2}$	-0.1319 V	33.975
$\text{HgO}(\text{s})$	-99.79	70.25	-
$\text{HgO}(\text{s})$	-90.8	70.3	-58.5

$$(E^\circ_{\text{H}_2\text{O}_2\text{aqRed}} - E^\circ_{\text{HgO}}) = (0.4495 + 0.3015) \text{ V}$$

$$G_{\text{Hg}} = G_{\text{eqRedOx}_2\text{H}_2\text{O}_2} - G_{\text{O}_2\text{aqua}} + (G_{\text{HO}} + G_{\text{H}_2\text{O}_2}) = 40.67 \text{ kJ/mol};$$

$$G_{\text{Hg}_2^{2+}} = \Delta G_{\text{eq}_\text{Hg}} + (2G_{\text{Hg}} + G_{\text{H}_2\text{O}}) = 127.75 + (2 \cdot 40.67 + 0) = 209.09 \text{ kJ/mol};$$

$$G_{\text{Hg}_2\text{SO}_4} = G_{\text{Hg}_2^{2+}} + G_{\text{SO}_4^{2-}} - (\Delta G_{\text{eqHg}_2\text{SO}_4} + 2G_{\text{H}_2\text{O}}) = -593.87 \text{ kJ/mol};$$

$$G_{\text{SO}_4} = G_{\text{Hg}_2\text{SO}_4} - (2G_{\text{Hg}} + \Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4}) = -736.48 \text{ kJ/mol};$$

$$G_{\text{Hg}_2\text{Cl}_2} = G_{\text{Hg}_2^{2+}} + 2G_{\text{Cl}^-} - (\Delta G_{\text{eqHg}_2\text{Cl}_2} + 3G_{\text{H}_2\text{O}}) = -210.7 \text{ kJ/mol};$$

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

$$G_{\text{Cl}^-} = (-G_{\text{Hg}_2^{2+}} + \Delta G_{\text{eqHg}_2\text{Cl}_2} + (G_{\text{Hg}_2\text{Cl}_2} + 3G_{\text{H}_2\text{O}})) / 2 = 33.975 \text{ kJ/mol};$$

$2\underline{\text{Hg}} + \text{H}_2\text{O} = \text{Hg}_2^{2+} + 2e^-$; absolute standard potential $E^\circ_{\text{Hg}} = 0.6620 \text{ V}$; Kortly, Shucha ; [18]

$$E^\circ_{\text{Hg}} = E^\circ - 0.0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^1) + 0.10166 - 0.3982 = 0.907 - 0.0591/2 \cdot \lg(1/55.3^1) + 0.10166 - 0.3982 = -0.6620 \text{ V};$$

$$\Delta G_{\text{eq}_\text{Hg}} = E^\circ_{\text{Hg}} \cdot F \cdot 2 = 0.6620 \cdot 96485 \cdot 2 = 127.75 \text{ kJ/mol},$$

$$\Delta G_{\text{eq}_\text{Hg}} = G_{\text{Hg}_2^{2+}} - (2G_{\text{Hg}} + G_{\text{H}_2\text{O}}) = G_{\text{Hg}_2^{2+}} - (2 \cdot 40.67 + 0) = 127.75 \text{ kJ/mol};$$

$$G_{\text{Hg}_2^{2+}} = \Delta G_{\text{eq}_\text{Hg}} + (2G_{\text{Hg}} + G_{\text{H}_2\text{O}}) = 127.75 + (2 \cdot 40.67 + 0) = 209.09 \text{ kJ/mol};$$

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 constant :

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

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

$$\Delta G_{\text{eqHg}_2\text{Cl}_2} = G_{\text{Hg}_2^{2+}} + 2G_{\text{Cl}^-} - (G_{\text{Hg}_2\text{Cl}_2} + 3G_{\text{H}_2\text{O}}) = -146.8 + 2G_{\text{Cl}^-} - (-210.7 + 3 \cdot 0) = 131.85 \text{ kJ/mol};$$

$$G_{\text{Cl}^-} = (-G_{\text{Hg}_2^{2+}} + \Delta G_{\text{eqHg}_2\text{Cl}_2} + (G_{\text{Hg}_2\text{Cl}_2} + 3G_{\text{H}_2\text{O}})) / 2 = (-209.09 + 131.85 + (-210.7 + 3 \cdot 0)) / 2 = 33.975 \text{ kJ/mol};$$

$$\Delta G_{\text{eqHg}_2\text{Cl}_2} = G_{\text{Hg}_2^{2+}} + 2G_{\text{Cl}^-} - (G_{\text{Hg}_2\text{Cl}_2} + 3G_{\text{H}_2\text{O}}) = 209.09 + 2 \cdot -143.945 - (-210.7 + 3 \cdot 0) = 131.85 \text{ kJ/mol};$$

$$G_{\text{Hg}_2\text{Cl}_2} = G_{\text{Hg}_2^{2+}} + 2G_{\text{Cl}^-} - (\Delta G_{\text{eqHg}_2\text{Cl}_2} + 3G_{\text{H}_2\text{O}}) = 209.09 + 2 \cdot -143.945 - (131.85 + 3 \cdot 0) = -210.7 \text{ kJ/mol};$$

$2\underline{\text{Hg}} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{H}_2\text{O} + 2e^-$; absolute standard potential $E^\circ_{\text{HgCl}_2} = -0.1319 \text{ V}$; Suchotina ; [17]

$$E^\circ_{\text{HgCl}_2} = E^\circ - 0.0591/2 \cdot \lg([\text{H}_2\text{O}]^2) + 0.10166 - 0.3982 = 0.2678 - 0.0591/2 \cdot \lg(55.3^2) + 0.10166 - 0.3982 = -0.1319 \text{ V};$$

$$\Delta G_{\text{eq}_\text{HgCl}_2} = E^\circ_{\text{HgCl}_2} \cdot F \cdot 2 = -0.1319 \cdot 96485 \cdot 2 = -25.45 \text{ kJ/mol},$$

$$\Delta G_{\text{eq}_\text{HgCl}_2} = G_{\text{Hg}_2\text{Cl}_2} + 2G_{\text{H}_2\text{O}} + 2G_{\text{Cl}^-} - (2G_{\text{Hg}}) = G_{\text{Hg}_2\text{Cl}_2} + 2 \cdot 0 + 2 \cdot 34 - (2 \cdot 40.67) = -25.45 \text{ kJ/mol};$$

$$????? G_{\text{Hg}_2\text{Cl}_2} = \Delta G_{\text{eq}_\text{HgCl}_2} - 2G_{\text{H}_2\text{O}} - 2G_{\text{Cl}^-} + (2G_{\text{Hg}}) = -25.45 - 2 \cdot 0 - 2 \cdot 34 + (2 \cdot 40.67) = -12.11 \text{ kJ/mol};$$

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 constant:

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

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

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

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



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

$2\underline{\text{Hg}} + \text{SO}_4^{2-} = \text{Hg}_2\text{SO}_4(\text{s}) + 2e^-$; absolute standard potential $E^\circ_{\text{Ag}} = 0.3175 \text{ V}$; Kortly, Shucha ; [18]

$$E^\circ_{\text{Hg}_2\text{SO}_4} = E^\circ - 0.0591/2 \cdot \lg([\text{H}_2\text{O}]^0) + 0.10166 - 0.3982 = 0.614 - 0.0591/2 \cdot \lg(55.3^0) + 0.10166 - 0.3982 = 0.3175 \text{ V};$$

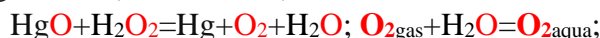
$$\Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4} = E^\circ_{\text{Hg}_2\text{SO}_4} \cdot F \cdot 2 = 0.3175 \cdot 96485 \cdot 2 = 61.27 \text{ kJ/mol},$$

$$\Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4} = G_{\text{Hg}_2\text{SO}_4} - (2G_{\text{Hg}} + G_{\text{SO}_4}) = -593.87 - (2 \cdot 40.67 + G_{\text{SO}_4}) = 61.27 \text{ kJ/mol};$$

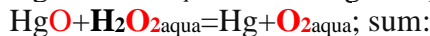
$$G_{\text{SO}_4} = G_{\text{Hg}_2\text{SO}_4} - (2G_{\text{Hg}} + \Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4}) = -593.87 - (2 \cdot 40.67 + 61.27) = -736.48 \text{ kJ/mol};$$

$\text{Hg}+2\text{OH}^- = \text{HgO}+2\text{H}_2\text{O}+2\text{e}^-$ absolute standard potential $E^\circ_{\text{Hg}} = -0.3015$ V; Kortly, Shucha ; [18]
 $E^\circ_{\text{HgO}} = E^\circ - 0.0591/2 * \lg([\text{H}_2\text{O}]^2) + 0.10166 - 0.3982 = 0.098 - 0.0591/2 * \lg(55.3^2) + 0.10166 - 0.3982 = -0.3015$ V;
Ox $\text{HgO}+2\text{H}_2\text{O}+2\text{e}^- = \text{Hg}+2\text{OH}^-$, inverse standard potential $-E^\circ_{\text{HgO}} = 0.3015$ V Suchotina [17].

chlorine, hydrogen peroxide, magnesium (when heated), disulfur dichloride and hydrogen trisulfide



Red $\text{H}_2\text{O}_{2\text{aqua}}+2\text{H}_2\text{O} = \text{O}_{2\text{aqua}}+2\text{H}_3\text{O}^++2\text{e}^-$ $E^\circ_{\text{RedH}_2\text{O}_2} = 0.4495$ V absolute potential Alberta University [19]



$$\Delta G_{\text{eqRedOx}_2\text{H}_2\text{O}_2} = (E^\circ_{\text{H}_2\text{O}_2\text{aqRed}} - E^\circ_{\text{HgO}}) * \mathbf{F} * \mathbf{n} = (0.4495 + 0.3015) * 96485 * 2 = (0.7510) * 96485 * 2 = 144.92 \text{ kJ/mol};$$

$$\Delta G_{\text{eqRedOx}_2\text{H}_2\text{O}_2} = G_{\text{Hg}} + G_{\text{O}_{2\text{aqua}}} - (G_{\text{HgO}} + G_{\text{H}_2\text{O}_2}) = G_{\text{Hg}} + 330 - (-58.5 + 284.25) = 144.92 \text{ kJ/mol};$$

$$G_{\text{Hg}} = G_{\text{eqRedOx}_2\text{H}_2\text{O}_2} - G_{\text{O}_{2\text{aqua}}} + (G_{\text{HgO}} + G_{\text{H}_2\text{O}_2}) = 144.92 - 330 + (-58.5 + 284.25) = 40.67 \text{ kJ/mol};$$

Substance	$\Delta H^\circ_{\text{H}}$, kJ/mol	$\Delta S^\circ_{\text{H}}$, J/mol/K	$\Delta G^\circ_{\text{H}}$, kJ/mol
H₃O⁺	-285.81	-3.854	-213.275
O_{2aqua}	-11.715	110.876	16.4
O_{2aqua}	-11.70	-94.2	16.40
H₂O	-285.85	69.9565	-237.191
H₂O	-286.65	-453.188	-151.549
H₂O_{2(aq)}	-191.99	-481.688	-48.39
H₂O_{2(aq)}	-191.17	143.9	-134.03
H₂O_{2l}	-237.129	69.91	-237.129

$$G_{\text{H}_2\text{O}_2} = 284.25 \text{ kJ/mol};$$

Miščenko 1968, Himia, Leningrad

CRC 2010;

$$G_{\text{O}_{2\text{aqua}}} = 330 \text{ kJ/mol}; G_{\text{H}_2\text{O}} = 0 \text{ kJ/mol};$$

BiochemThermodynamic 2006 Masachusetts Technology institute
 University Alberta 1997.

Nernst's potential studies $5(\text{Pt})\text{H} + \text{MnO}_4^-$ on hydroxonium H_3O^+ and water H_2O account

Oxidant reduction inverse Nernst's potential: $\text{MnO}_4^- + 7\text{H}_3\text{O}^+ + 5e^- \leftrightarrow \text{Mn}^{2+} + 12\text{H}_2\text{O}$; $-E^\circ_{\text{MnO}_4^-} = -1.46065\text{V}$.

Reductant oxidation Nernst's: $5(\text{Pt})\text{H} + 5\text{H}_2\text{O} \leftrightarrow 5\text{H}_3\text{O}^+ + 5e^-$; standard potential $E^\circ_{\text{H}} = -0.2965\text{V}$.

Electrons balancing $+ne^- = 5e^- = -ne^-$ summary Red-Ox reaction: $5(\text{Pt})\text{H} + \text{MnO}_4^- + 3\text{H}_3\text{O}^+ \leftrightarrow \text{Mn}^{2+} + 7\text{H}_2\text{O}$.

$$-E_{\text{MnO}_4^-} = -E^\circ + \frac{0.0591}{4} \cdot \lg \frac{[\text{H}_2\text{O}]^{12} \cdot [\text{Mn}^{2+}]}{[\text{MnO}_4^-] \cdot [\text{H}_3\text{O}^+]^8} = -1.46065\text{V} + \frac{0.0591}{4} \cdot \lg \frac{[\text{H}_2\text{O}]^{12} \cdot [\text{Mn}^{2+}]}{[\text{MnO}_4^-] \cdot [\text{H}_3\text{O}^+]^8}; [\text{H}_2\text{O}] = 55.3\text{M} = \frac{996\text{ g/L}}{18\text{ g/mol}}$$

$$E_{\text{H}} = E^\circ_{\text{H}} + 0.0591 \cdot \lg \frac{[\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]} = -0.2965\text{V} + 0.0591 \cdot \lg \frac{[\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]} ;$$

Substan	$\Delta H^\circ_{\text{H}}$, kJ/mol	$\Delta S^\circ_{\text{H}}$, J/mol/K	$\Delta G^\circ_{\text{H}}$, 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
$\text{H}_2(\text{aq})$	23.4	-130	99.13
$\text{H}_2(\text{aq})$	-5.02	-363.92	103.24
$\text{H}(\text{Pt})(\text{aq})$	-	-	51.05
MnO_4^-	-541.4	-191.2	-447.2
Mn^{2+}	-220.8	-73.6	-228.1
$\text{O}_{2\text{aqua}}$	-11.7	-94.2	16.4

$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{Mn}^{2+}} + 7\Delta G^\circ_{\text{H}_2\text{O}} - 3\Delta G^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{\text{MnO}_4^-} - 5\Delta G^\circ_{\text{H}(\text{Pt})} = -1056.7\text{ kJ/mol}$
 $-228.1 + 7 \cdot (-237.191) - (3 \cdot (-213.2746) - 447.2 + 5 \cdot 51.05) = -1056.7\text{ kJ/mol}$
 Biochem. Thermodyn, Alberty, 2006, Massachusetts Technology Inst.
 CRC Handbook of Chemistry and Physics, 2010. D. Lide
 $= -228.1 + 7 \cdot (-237.191) - (3 \cdot (-213.2746) - 447.2 + 5 \cdot 99.13/2) = -1049\text{ kJ/mol}$
 Alberty 2006 Biochem. Thermodyn Massachusetts Technology Inst.
 $\Delta G_{\text{eq}} = -847.7\text{ kJ/mol}$; $\Delta G_{\text{Hess}} = -1056.7\text{ kJ/mol}$
 for $5(\text{Pt})\text{H} + \text{MnO}_4^- + 8\text{H}_3\text{O}^+ \rightleftharpoons \text{Mn}^{2+} + 8\text{H}_2\text{O}$ as absolute value
 $|\Delta G_{\text{eq}} = -847.7\text{ kJ/mol}| < |\Delta G_{\text{Hess}} = -1056.7\text{ kJ/mol}|$;

Concentration $[\text{H}_2\text{O}]^{12}$ exponent 12 included in classic standard potential $E_0 = 1.51\text{V}$ as logarithm:

$$E^\circ_{\text{MnO}_4^-} = E_0 - 0.0591/5 \cdot \log(1/[\text{H}_2\text{O}]^{12}) = 1.51 + 0.10166 - 0.0591/5 \cdot \log(1/55.3^{12}) + 0.10166 = 1.858848 - 0.3982 = 1.460648\text{V};$$

$$\Delta G_{\text{eq}} = (E^\circ_{\text{H}} - E^\circ_{\text{MnO}_4^-}) \cdot F \cdot 1 \cdot 5 = (-0.2965 - 1.460648) \cdot 96485 \cdot 5 = -1.757 \cdot 96485 \cdot 5 = -847.7\text{ kJ/mol}$$

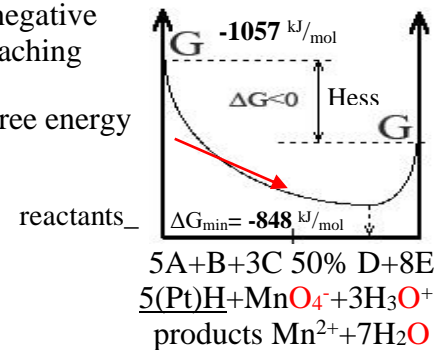
$$K_{\text{eq}} = \exp(-\Delta G_{\text{eq}} / (R \cdot T)) = \exp(847692 / (8.3144 / 298.15)) = \exp(341.96) = 10^{148.5};$$

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

$\Delta G_{\text{Hess}} = \Delta G_{\text{OxRed}} = -1056.7\text{ kJ/mol}$, but minimizes $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -847.7\text{ kJ/mol}$ reaching

$$\text{equilibrium mixture } 10^{148.5} = K_{\text{eq}} = \frac{[\text{H}_2\text{O}]^{12} \cdot [\text{Mn}^{2+}]}{[(\text{Pt})\text{H}]^5 \cdot [\text{MnO}_4^-] \cdot [\text{H}_3\text{O}^+]^8}; \text{Prigogine attractor is free energy}$$

change minimum ΔG_{min} reaching. Free energy change minimum reaching establishes equilibrium.

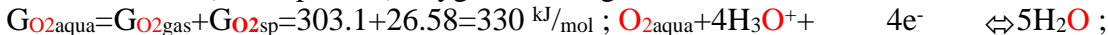


Nernst's potential $\text{O}_{2\text{aqua}}/\text{H}_2\text{O}$ red-ox system biochemical mechanism of acidosis and oxidative stress

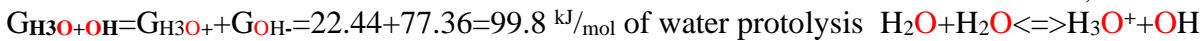
(forced oxidizing agent power by potential E increase)

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

Water medium (blood plasma) oxygen is strong oxidant **1.0610 V** reaction $E_{\text{O}_2} = 1.0610\text{V}$:



oxidized form free electrons reduced form;



Biochemistry oxygen $\text{O}_{2\text{aqua}}$ decreases free energy content $\Delta G_{\text{O}_2\text{aqua}} = 329.7 - 241.75 = 87.95\text{ kJ/mol}$ to

$\text{G}_{\text{O}_2\text{Biochemistry}} = 87.95\text{ kJ/mol}$. Concentration arterial $[\text{O}_{2\text{aqua}}] = 6 \cdot 10^{-5}\text{M}$ and $\text{pH} = 7.36$ concentration $[\text{H}_3\text{O}^+] = 10^{-7.36}\text{M}$.

$$E_{\text{O}_2} = E^\circ + 0.0591/4 \cdot \log([\text{O}_{2\text{aqua}}] \cdot [\text{H}_3\text{O}^+]^4 / [\text{H}_2\text{O}]^5) = 1.0610 + 0.0591/4 \cdot \log(6 \cdot 10^{-5} \cdot 10^{-7.36 \cdot 4} / 55.346^{12}) = 0.4349\text{ Volts}$$

$$\text{decrease } \Delta E_{\text{arterial}} = -(E_{\text{O}_2} - E_{\text{O}_2}) = -(1.0610 - 0.4346) = -0.6264\text{V};$$

$$\Delta G_{\text{arterial}} = \Delta E_{\text{H}_2\text{O}} \cdot F \cdot n = 0.6264 \cdot 96485 \cdot 4 / 1000 = -241.75\text{ kJ/mol}.$$

Solubility product constant $\text{O}_{2\text{gas}} + \text{H}_2\text{O} \xrightarrow{\text{Aquaporins}} \text{O}_{2\text{Blood}}$ increases to level $\text{G}_{\text{O}_2\text{sp}} = 26.58\text{ kJ/mol}$:

$$\frac{[\text{O}_{2\text{aqua}}]}{[\text{O}_{2\text{gas}}] \cdot [\text{H}_2\text{O}]} = K_{\text{sp}} = 2.205 \cdot 10^{-5}. \text{G}_{\text{O}_2\text{sp}} = -R \cdot T \cdot \ln(K_{\text{sp}}) = -8.3144 \cdot 298.15 \cdot \ln(2.205 \cdot 10^{-5}) = 26.58\text{ kJ/mol}.$$

Free energy protolysis decreases $\text{G}_{\text{O}_2\text{Biochem}_\text{arterial}} = \text{G}_{\text{O}_2\text{aqua}} + \text{G}_{\text{O}_2\text{sp}} + \Delta G_{\text{arterial}} = 303.1 + 26.58 - 241.75 = 87.95\text{ kJ/mol}$ and oxygen becomes fire safe biochemical oxidant, forming **arterial concentration** $[\text{O}_{2\text{aqua}}] = 6 \cdot 10^{-5}\text{M}$ as safe Bioenergetic sustaining normal isooxia. [3];

1) Water 55.346 M decreases potential from **1.0610 V** about **-0.155 V** $=\Delta E_{H_2O}$.

$$E_{O_2} = E^{\circ}_{O_2} + 0.0591/4 \cdot \log(1/[H_2O]^5) = 1.0610 + 0.01478 \cdot \log(1/55.346^5) = 0.9322 \text{ V};$$

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

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

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

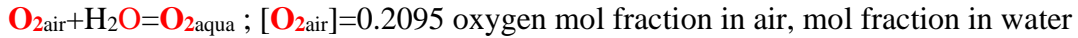
$$\Delta E_{O_2 100\%} = 0.01478 \cdot \lg(100\% [O_{2\text{aqua}}]) = 0.01478 \cdot \lg(5) = +0.0103 \text{ V}. \text{ Free energy content for}$$

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

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

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

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



$$K_{sp}[O_{2\text{gais}}] = [O_{2\text{aqua}}]/[H_2O] = 2.205 \cdot 10^{(-5)} \cdot 0.2095 = 4.61948 \cdot 10^{-6} = 10^{(-5.335)}.$$

$$\Delta G_H = \Delta G^{\circ}_{H_2O} + \Delta G^{\circ}_{O_{2\text{aqua}}} - \Delta G^{\circ}_{H_2O} - \Delta G^{\circ}_{O_{2\text{gas}}} = 16.4 - (-151.549) = 168 \text{ kJ/mol endoergic};$$

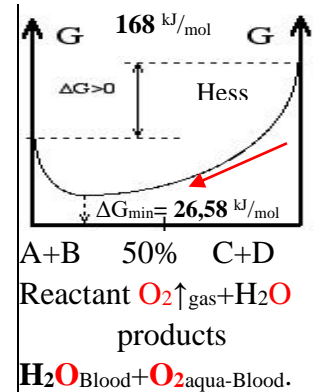
$$\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = -8.3144 \cdot 298.15 \cdot \ln(2.205 \cdot 10^{-5}) = -8.3144 \cdot 298.15 \cdot 6.414 = 26.58 \text{ kJ/mol}$$

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

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

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

Equilibrium reaching is Prigogine attractor free energy change minimum ΔG_{\min} .



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

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

$$[O_{2\text{water}}] = K_{eq} \cdot [O_{2\text{air}}] \cdot [H_2O] = 2.205 \cdot 10^{-5} \cdot 0.2095 \cdot 55.3 = 0.00025546 = 2.5546 \cdot 10^{-4} = 10^{-3.593} \text{ M}.$$

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

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

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

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

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

by osmosis oxygen molecules crossing through aquaporins membranes against gradient.

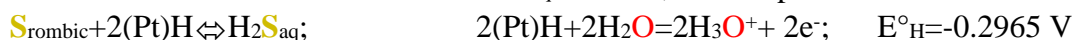
Inverse: $O_{2\text{aqua}} + 4H_3O^+ + 4e^- \leftrightarrow 6H_2O$; $-E^{\circ}_{O_2} = -1.0610 \text{ V}$; Nernst's half: $4(Pt)H + 4H_2O \leftrightarrow 4H_3O^+ + 4e^-$; $E^{\circ}_H = -0.2965 \text{ V}$

$$O_{2\text{aqua}} + 4(Pt)H = 2H_2O; \Delta G_{eq} = (E^{\circ}_H - E^{\circ}_{O_2}) \cdot F \cdot 1 \cdot 4 = (-0.2965 - 1.0610) \cdot 96485 \cdot 4 = -1.358 \cdot 96485 \cdot 4/1000 = -523.9 \text{ kJ/mol};$$

Knowing equilibrium value $\Delta G_{eq 2H_2O} = 2G_{H_2O} - 4G_{(Pt)H} - G_{O_{2\text{aqua}}} = 2 \cdot 0 - (4 \cdot G_{(Pt)H} + 329.68) = -523.9 \text{ kJ/mol}$, hydrogen

metal free energy is $G_{H(Pt)} = (2G_{H_2O} - \Delta G_{eq 2H_2O} - G_{O_{2\text{aqua}}})/4 = (2 \cdot 0 + 523.914 - 329.68)/4 = 204.2/4 = 48.56 (51.05) \text{ kJ/mol}$;

Sulfur reduction: $S_{\text{rhom}} + 2H_3O^+ + 2e^- = H_2S_{\text{aq}} + 2H_2O$; inverse potential $-E^{\circ}_S = 0.05254 \text{ V}$;



$$\Delta G_{eq} = (E^{\circ}_H - E^{\circ}_S) \cdot F \cdot 1 \cdot 2 = (-0.2965 + 0.05254) \cdot 96485 \cdot 2 = -0.245 \cdot 96485 \cdot 2/1000 = -47.077 \text{ kJ/mol};$$

$$G_{H_2S_{\text{aq}}} = \Delta G_{\text{Hess } H_2S} + (2G_{H(Pt)} + G_{S_{\text{rhom}}}) = -47.077 + (2 \cdot 51.05 - 85.64) = -30.617 \text{ kJ/mol}. \text{ [2nd page](#) .}$$

Nernst's half: $H_2S_{\text{aq}} + 2H_2O = S_{\text{rhom}} + 2H_3O^+ + 2e^-$ has absolute standard potential $E^{\circ}_{H_2S} = -0.0515 \text{ V}$

for free energy change: $\Delta G_{eq H_2S} = E^{\circ}_{H_2S} \cdot F \cdot n = -0.0515 \cdot 96485 \cdot 2 = -9.938 \text{ kJ/mol}$.

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

$\Delta G_{\text{Hess } H_2S_{\text{aq}}} = G_{S_{\text{rhom}}} + 2G_{H_3O^+} - (G_{H_2S_{\text{aq}}} + 2G_{H_2O}) = -85.64 + 2 \cdot 22.44 - (G_{H_2S_{\text{aq}}} + 2 \cdot 0) = -9.938 \text{ kJ/mol}$ than absolute value

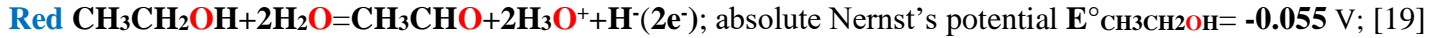
is: $G_{H_2S_{\text{aq}}} = G_{S_{\text{rhom}}} + 2G_{H_3O^+} - (\Delta G_{\text{Hess } H_2S_{\text{aq}}} + 2G_{H_2O}) = -85.64 + 2 \cdot 22.44 - (-9.938 + 2 \cdot 0) = -30.82 \text{ kJ/mol}$.

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



ΔG_{Hess}=ΔG°_{H₃O}+ΔG°_{CH₃CHO}+ΔG°_{NADH}-ΔG°_{CH₃CH₂OH}-ΔG°_{H₂O}-ΔG°_{NAD⁺}=159.1 kJ/mol;

ΔG_{Hess}=32.2824+1175.5732-151.549-(75.2864+1059.11-237.191)=159.1 kJ/mol endoergic. Anaerobic:



Sum: E°_{CH₃CH₂OH}-E°_{NAD⁺}=-0.055+0.4095=0.3545 V. n=2; ΔG_{eq}=ΔE°•F•n=0.3545*96485*2=68.4 kJ/mol;

By convention balanced n=2=m number of electrons 2e⁻ donors E°_{NADH}= -0.4095 V plus acceptors of electrons



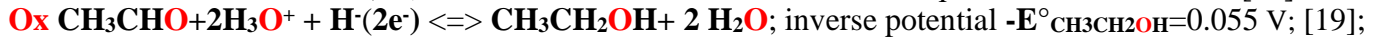
E°_{H₂O}=0.190-0.0591/2*log(1/[H₂O])=0.190-0.02955*log(1/55.3333)+0.10166-0.3982=-0.05503 V=E°_{CH₃CH₂OH};

ΔG_{eq}=-R•T•ln(K_{eq}); K_{eq}= $\frac{[NADH] \cdot [CH_3CHO] \cdot [H_3O^+]}{[NAD^+] \cdot [CH_3CH_2OH] \cdot [H_2O]}$ = e^{-ΔG_{eq}/R•T} = e^{-68408 / (8.314•298.15)}} = 1.036•10⁻¹²=10^{-11.985}



ΔG_{Hess}=ΔG°_{CH₃CH₂OH}+ΔG°_{H₂O}+ΔG°_{NAD⁺} -ΔG°_{H₃O}-ΔG°_{CH₃CHO}-ΔG°_{NADH} = -159.1 kJ/mol;

ΔG_{Hess}=75.2864+1059.11-237.191-(32.2824+1175.5732-151.549)= -159.1 kJ/mol endoergiska;



Sum:

ΔE°=E°_{NADH}-E°_{CH₃CHO}=-0.4095+0.055=-0.3545 V, ΔG_{eq}=ΔE°•F•n=-0.3545 V•2 mol•96485 C/mol= -68.4 kJ/mol ;

By convention balanced n=2=m number of electrons 2e⁻ ΔE° donors E°_{NADH}=-0.4095 V plus electrons acceptor



ΔG_{eq}=-R•T•ln(K_{eq})=- 68.408 kJ/mol; K_{eq}= $\frac{[NAD^+] \cdot [CH_3CH_2OH] \cdot [H_2O]}{[NADH] \cdot [CH_3CHO] \cdot [H_3O^+]}$ = e^{ΔG_{eq}/R•T} = e^{-68408 / (8.314•298.15)}} = 9.65•10¹¹=10^{11.985}.

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

ΔG_{Homeostasis}=68.408+ R•T•ln(10⁶*1/1*10^{-7.36}/55.3)=68.408-86.2=-17.8.....kJ/mol.

[NAD⁺]/[NADH]=10³; ΔG_{Homeostasis}=68.408-69.08=-0.676.....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 ethanol

oxidation Hess law free energy change positive ΔG_{Hess}=159.....kJ/mol and inverse

ethanal anaerobic reduction negative ΔG_{Hess}=-159.....kJ/mol , but minimises reaching

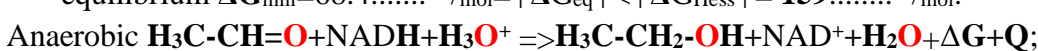
equilibrium aerobic ΔG_{min}=ΔG_{eq}=68.4..... kJ/mol and anaerobic

ΔG_{min}=ΔG_{eq}=-68.4..... kJ/mol reaching equilibrium mixture

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.



Anaerobic ΔG_{eq}=ΔE°•F•n=-0.3545 V•2 mol•96485 C/mol=-68.408..... kJ/mol 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

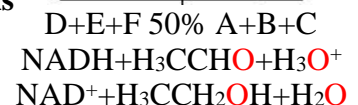
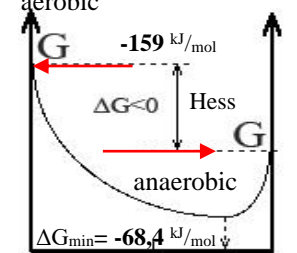
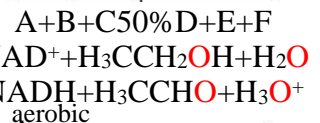
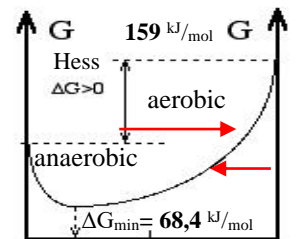
ΔG_{Homeostasis}=-27.86.....kJ/mol

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

ΔG_{Homeostasis}=-68.41+8.3144*298.15*ln(K_{Homeostasis})=-68.41+40.54 =-27.86..... kJ/mol

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

[NADH]/[NAD⁺]=1/770; ΔG_{Homeostasis}=68.408+8.3144*298.15*ln(700/1*1/1*55.3457/10^{-7.36})=0.028 kJ/mol.



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

Ox inverse half reaction $-E_{O_2} = -1.0865$ V: $O_{2(aq)} + 4H_3O^+ + 4e^- \rightleftharpoons 6H_2O$;

Red Nernst's half reaction: $4(Pt)H + 4H_2O \rightleftharpoons 4H_3O^+ + 4e^-$; metal hydrogen $G_{H(Pt)} = 51.05$ kJ/mol >

$O_{2(aq)} + 4(Pt)H \rightleftharpoons 2H_2O$; $\Delta G_{Hess, 2H_2O} = 2G_{H_2O} - 4G_{H(Pt)} - G_{O_{2(aq)}} = 2 \cdot (-237.191) - (4 \cdot 51.05 + 330) = -1008.6 = 2 \cdot -504.3$ kJ/mol;

$\Delta G_{eq} = (E_{H^+} - E_{O_2}) \cdot F \cdot 4 = (-0.2965 - 1.0868) \cdot 96485 \cdot 4 = -1.38334 \cdot 96485 \cdot 4 / 1000 = -533.9 = 2 \cdot -266.9$ kJ/mol;

$\Delta G_{eq, 2H_2O} = 2G_{H_2O} - 4G_{H(Pt)} - G_{O_{2(aq)}} = 2 \cdot 0 - (4 \cdot 51.05 + 329.68) = -533.9 = 2 \cdot -266.9$ kJ/mol;

$G_{H(Pt)} = (2G_{H_2O} - \Delta G_{eq, 2H_2O} - G_{O_{2(aq)}}) / 4 = (2 \cdot 0 + 533.886 - 329.68) / 4 = 51.05$ kJ/mol .

Gas $O_{2(gas)} + 2H_{2(gas)} = 2H_2O$; $\Delta G_{Hess, 2H_2O} = 2\Delta G^{\circ}_{H_2O} - (2\Delta G^{\circ}_{H_2(gas)} + \Delta G^{\circ}_{O_{2(gas)}}) = 2 \cdot (-273.19) - (2 \cdot 0 + 0) = 2 \cdot -273.19 = -546.4$ kJ/mol

$O_{2(aq)} + 2H_{2(aq)} = 2H_2O$; $\Delta G_{Alberty, 2H_2O} = 2G_{H_2O} - 2G_{H_{2(aq)}} - G_{O_{2(aq)}} = 2 \cdot 0 - (2 \cdot 103.24 + 329.68) = -536.16$ kJ/mol;

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

Substance	ΔH°_H , kJ/mol	ΔS°_H , J/mol/K	ΔG°_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
H₂(aq)	-5.02	-363.92	103.24
O₂(aq)	-11.70	-94.2	16.4
O₂(aq)	-11.715	110.876	16.4

$\Delta G_{Hess} = 2\Delta G^{\circ}_{H_2O} - 4\Delta G^{\circ}_{(Pt)H} - \Delta G^{\circ}_{O_{2(aq)}} = -689 = 2 \cdot -344.521$ kJ/mol;
 $= 2 \cdot -237.191 - (4 \cdot 99.13 / 2 + 16.4) = -689 = 2 \cdot -344.5$ kJ/mol. CRC 2010

$\Delta G_{eq} = -266.9$ kJ/mol ; $\Delta G_{Hess} = -344.5$ kJ/mol

in reaction $4(Pt)H + O_{2(aq)} \rightleftharpoons 2H_2O$; absolute free energy change

$|\Delta G_{eq} = -266.9$ kJ/mol | < | $\Delta G_{Hess} = -344.5$ kJ/mol | ;

Alberty 2006 Biochem. Thermodyn Massachusetts Technology Inst.

Water concentration $[H_2O]^6$ as logarithm extracted of $E^{\circ}_{classic} = 1.229$ V to hydrogen absolute reference $E^{\circ} = 1.383 + 0.10166 - 0.3982 = 1.0865$ V

$K_{eq, 2H_2O} = K_{OxRed} = \exp(-\Delta G_{OxRed} / R/T) = \exp(533886 / 8.3144 / 298.15) = \exp(215.4) = 3.42 \cdot 10^{93}$;

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

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

$\Delta G_{Hess, 2H_2O} = -546$ kJ/mol , $\Delta G_{Hess, H_2O_2} = -480$ kJ/mol, but minimized

reaching equilibrium $\Delta G_{eq, 2H_2O} = -534$ kJ/mol and $\Delta G_{eq, Standart, H_2O_2} = -228.6$ kJ/mol

mixture constants $K_{eq, 2H_2O} = 3.42 \cdot 10^{93}$ and $K_{eq, Standart, H_2O_2} = 6.104 \cdot 10^{41}$

The minimum ΔG_{min} is Prigogine attractor. Free energy change minimum reaching establish equilibrium state.

Red $H_2O_2 + 2H_2O = O_{2(aq)} + 2H_3O^+ + 2e^-$; $E^{\circ}_{H_2O_2} = 0.4495$ V Alberta University ;

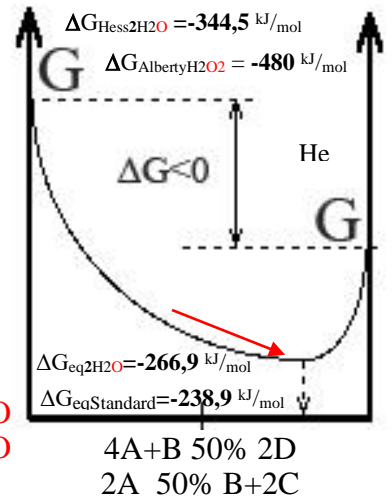
$[H_2O_2] = 1$ M concentration environment has pH=7.36. .

Ox inverse $H_2O_2 + 2H_3O^+ + 2e^- = 4H_2O$ potential $-E^{\circ}_{Ox} = -1.6855$ V Suhotina

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

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

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



$\Delta G_{eq, Standart, H_2O_2} = (E_{Red} - E_{Ox}) \cdot F \cdot n = (0.4495 - 1.6855) \cdot 96485 \cdot 2 = (-1.236) \cdot 96485 \cdot 2 = -238.5$ kJ/mol ;

$K_{eq, Standart, H_2O_2} = \frac{[O_2]_{aq} \cdot [H_2O]^2}{[H_2O_2]_{aq}^2} = K_{H_2O_2} = \exp(-\Delta G_{eq} / R/T) = \exp(2385510.9 / 8.3144 / 298.15) = 6.104 \cdot 10^{41}$

$E_{O_{H_2O_2}} = E^{\circ}_{H_2O_2} + 0.0591 / 2 \cdot \lg([O_{2(aq)}}] \cdot [H_3O^+]^2 / [H_2O_2] / [H_2O]^2) = 0.4495 + 0.0591 / 2 \cdot \lg(6 \cdot 10^{(-5)} \cdot 10^{(-7.36 \cdot 2)} / 1 / 55.3^2) = 0.2132$ V

$E_{O_{Ox}} = E^{\circ}_{H_2O_2, Ox} + 0.0591 / 2 \cdot \lg([H_2O]^4 / [H_2O_2] / [H_3O^+]^2) = -1.6855 + 0.0591 / 2 \cdot \lg(55.3^4 / 1 / 10^{(-7.36 \cdot 2)}) = -1.0445$ V

Sum Nernst+inverse $\Delta G_{eq, BioChem} = (E_{Red} - E_{Ox}) \cdot F \cdot n = (0.2132 - 1.0443) \cdot 96485 \cdot 2 = (-0.831) \cdot 96485 \cdot 2 = -160.4$ kJ/mol

Biochem $\Delta G_{Alberty} = G_{O_2, BioChem, arteriaj} + 2 \cdot G_{H_2O, BioChemistry} - 2 \cdot G_{H_2O_2} = 78.08 + 2 \cdot 85.64 - 2 \cdot 364.79 = -480.22$ kJ/mol; [Alberty](#)

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

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

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

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

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

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

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

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

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



$$\Delta G_{\text{eqStandarta}_2\text{H}_2\text{O}_2} = (E^\circ_{\text{H}_2\text{O}_2\text{aqRed}} - E^\circ_{\text{H}_2\text{O}_2\text{aqOx}}) * F * n = (0.4495 - 1.6855) * 96485 * 2 = (-1.236) * 96485 * 2 = -238.5 \text{ kJ/mol};$$

$$\Delta G_{\text{Alberty}_2\text{H}_2\text{O}_2} = G_{\text{O}_2\text{aq}} + 2 * G_{\text{H}_2\text{O}} - 2 * G_{\text{H}_2\text{O}_2} = 330 + 2 * 0 - 2 * G_{\text{H}_2\text{O}_2} = -238.5 \text{ kJ/mol}; \text{ exoergic}$$

$$G_{\text{H}_2\text{O}_2} = (G_{\text{O}_2\text{aq}} + 2 * G_{\text{H}_2\text{O}} + \Delta G_{\text{Alberty}_2\text{H}_2\text{O}_2}) / 2 = (330 + 2 * 0 + 238.5) / 2 = 568.5 / 2 = 284.25 \text{ kJ/mol};$$

Substance	$\Delta H^\circ_{\text{H}}$, kJ/mol	$\Delta S^\circ_{\text{H}}$, J/mol/K	$\Delta G^\circ_{\text{H}}$, 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
$\text{H}_2\text{O}_2\text{l}$	-237.129	69.91	-237.129

Miščenko 1968, Himia, Leningrad

CRC 2010;

$$G_{\text{O}_2\text{aq}} = 330 \text{ kJ/mol}; G_{\text{H}_2\text{O}} = 0 \text{ kJ/mol};$$

$$\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{O}_2} + 2\Delta H^\circ_{\text{H}_2\text{O}} - 2\Delta H^\circ_{\text{H}_2\text{O}_2} = -201.02 \dots = -201.06 \dots \text{ kJ/mol}$$

$$= -11.7 - 2 * 286.65 - (2 * -191.99) = -201.02 \dots \text{ kJ/mol} \text{ eksotermiska..}$$

$$= -11.7 - 2 * 285.85 - (2 * -191.17) = -201.06 \dots \text{ kJ/mol}$$

BiochemThermodynamic 2006 Masachusetts Technology institute

University Alberta 1997.

$$\Delta S_{\text{kopēja}} = \Delta S_{\text{H}} + \Delta S_{\text{izkļiedēta}} = -37.2 + 679.725 = 642.525 \dots \text{ J/mol/K}$$

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

$$\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{O}_2} + 2\Delta S^\circ_{\text{H}_2\text{O}} - 2\Delta S^\circ_{\text{H}_2\text{O}_2} = -94.2 + 2 * -453.188 - (2 * -481.688) = -37.2 \dots \text{ J/mol/K};$$

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

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

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

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

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

Red: $\text{H}_2\text{O}_2 + 2\text{H}_2\text{O} = \text{O}_2 + 2\text{H}_3\text{O}^+ + 2e^-$; $E^\circ_{\text{Red}} = E^\circ_{\text{RedH}_2\text{O}_2} = 0.4495 \text{ V}$ Nernst's absolute potential Alberta University;

Ox: $\text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2e^- = 4\text{H}_2\text{O}$; $-E^\circ_{\text{OxH}_2\text{O}_2} = -1.6855 \text{ V}$ inverse standard potential Suhotina;

$2\text{H}_2\text{O}_2(\text{aq}) = \text{O}_{2\text{aq}} + 2\text{H}_2\text{O} + \text{Q} + \Delta G$; For activate homeostasis products, hydroxonium and peroxide anions:

$$G_{\text{H}_2\text{O}_2} = 364.8 \text{ kJ/mol}; G_{\text{H}_3\text{O}^+} + G_{\text{HOO}^-} = 22.44 + 418.32 = 440.76 \text{ kJ/mol}$$

free energy referring to water and CO_2gas zero

$G_{\text{H}_2\text{O}} = G_{\text{CO}_2\text{gas}} = 0 \text{ kJ/mol}$ appreciate values : Summary **Red:** + **Ox** reaction :

$$\Delta G_{\text{min}} = \Delta G_{\text{eqStandart}} = (E^\circ_{\text{RedH}_2\text{O}_2} - E^\circ_{\text{OxH}_2\text{O}_2}) * F * n = (0.4495 - 1.6855) * 96485 * 2 = (-1.236) * 96485 * 2 = -238.5 \text{ kJ/mol};$$

$$K_{\text{eqStandart}} = \frac{[\text{O}_2]_{\text{aq}} * [\text{H}_2\text{O}]^2}{[\text{H}_2\text{O}_2]_{\text{aq}}^2} = K_{\text{H}_2\text{O}_2} = \exp(-\Delta G_{\text{eq}} / R / T) = \exp(238511 / 8.3144 / 298.15) = 6.104 * 10^{41} \dots$$

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

$$E_{\text{Red}} = E^\circ_{\text{H}_2\text{O}_2} + 0.0591 / 2 * \lg([\text{O}_{2\text{aq}}] * [\text{H}_3\text{O}^+]^2 / [\text{H}_2\text{O}_2] / [\text{H}_2\text{O}]^2) = 0.4495 + 0.0591 / 2 * \lg(6 * 10^{-5} * 10^{-(7.36 * 2)} / 1 / 55.3^2) = 0.2132 \text{ V}$$

$$E_{\text{Ox}} = -E^\circ_{\text{H}_2\text{O}_2\text{Ox}} + 0.0591 / 2 * \lg([\text{H}_2\text{O}_2] * [\text{H}_3\text{O}^+]^2 / [\text{H}_2\text{O}]^4) = -1.6855 + 0.0591 / 2 * \lg(1 * 10^{-(7.36 * 2)} / 55.3^4) = -1.443 \text{ V}$$

Homeostasis sum $\Delta G_{\text{eqBioChem}} = (E_{\text{Red}} - E_{\text{Ox}}) * F * n = (0.2132 - 1.0445) * 96485 * 2 = (-0.831) * 96485 * 2 = -160.4 \dots \text{ kJ/mol};$

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

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

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

$\Delta G_{\text{eqStandart}} = -238.5 \dots \text{ kJ/mol}$ reaching equilibrium mixture constant $K_{\text{eq}} = 6.1 * 10^{41} \dots$

Le Chatelier principle is Prigogine attractor free energy change minimum ΔG_{min}

reaching. High rate protolysis attractors $\text{pH} = 7.36$, oxygen 20.95% in air stay at

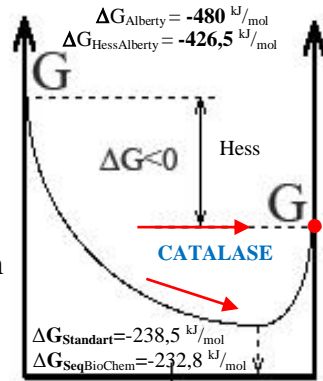
equilibrium, while homeostasis irreversibly continues, as are non equilibrium state.

Prigogine attractors Nobel Prize Chemistry 1977th. CATALASE erase peroxide

molecules H_2O_2 to 100% $\omega=6, \omega=3$ fatty acids C20:4 efficiency elongation synthesis in

peroxisomes. CATALASE reactivity is indispensable irreversible homeostasis

Brownian molecular engine for evolution and survival.



A+A 50% B+2C
reactants $2\text{H}_2\text{O}_2(\text{aq})$
products $\text{O}_{2\text{aq}} + 2\text{H}_2\text{O}$

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 silicon acid reaction:

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

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

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



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

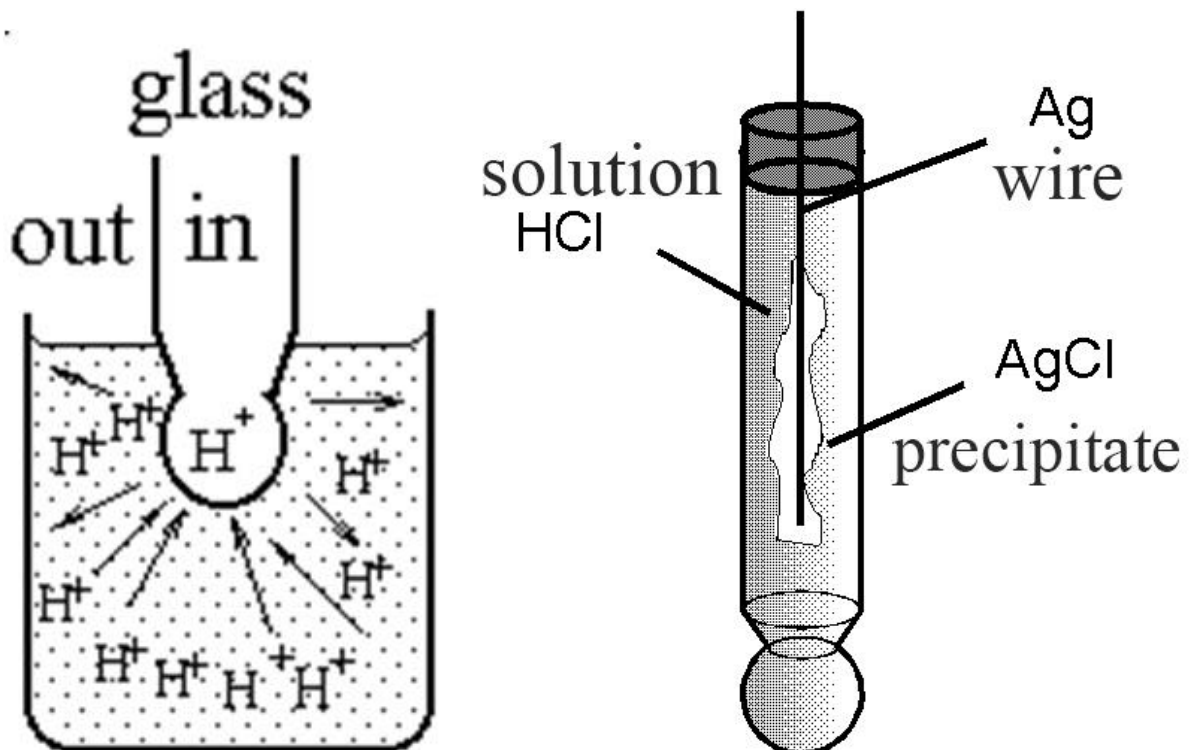
$$K_{\text{inner}} = \frac{[\text{H}_2\text{O}]}{[\text{H}_3\text{O}^+]_{\text{inner}}}; \quad K_{\text{outer}} = \frac{[\text{H}_3\text{O}^+]_{\text{outer}}}{[\text{H}_2\text{O}]}; \quad K_{\text{inner}} \cdot K_{\text{outer}} = K_{\text{membr}} = \frac{[\text{H}_3\text{O}^+]_{\text{outer}}}{[\text{H}_3\text{O}^+]_{\text{inner}}};$$

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

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

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

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



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

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

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

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

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

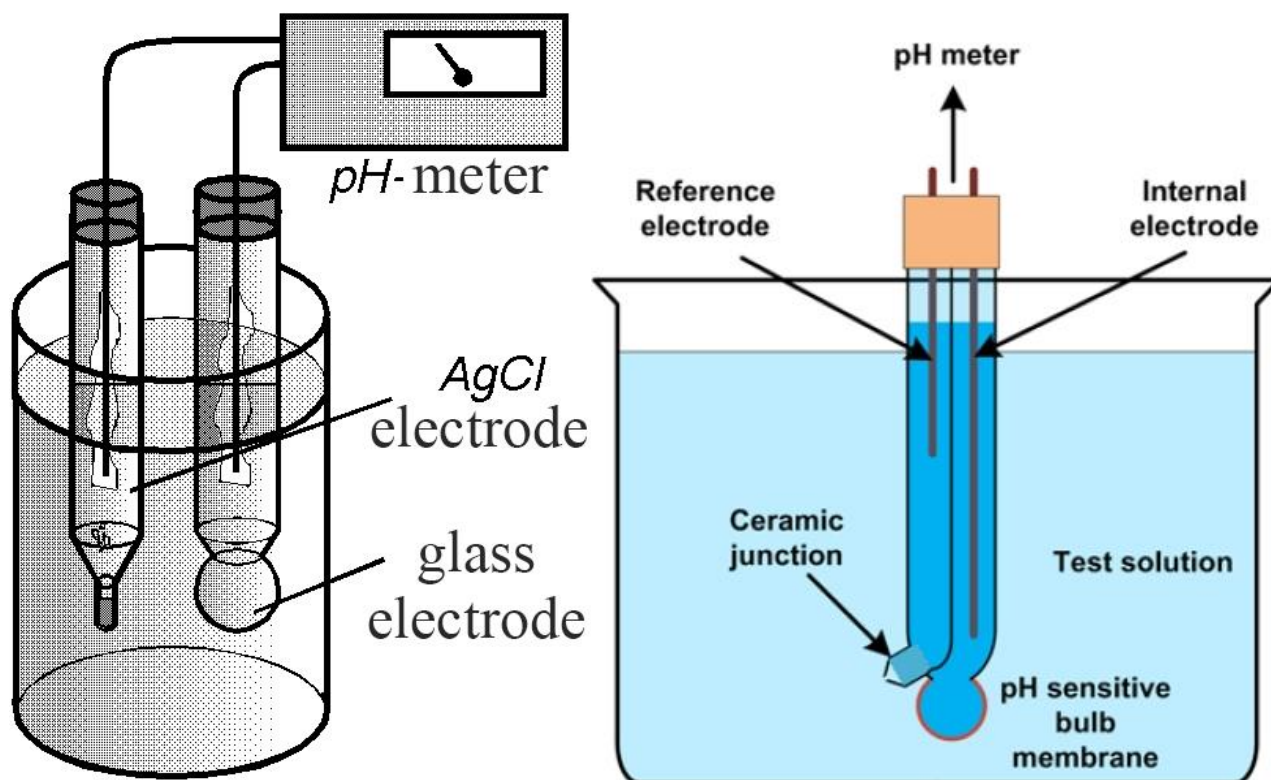
$$E_{\text{DS}} = E_{\text{AgCl}} + E_{\text{membr.}} + E_{\text{AgCl inner}} = (E_{\text{AgCl}} + E_{\text{AgCl inner}} + E_{\text{const.}}) + 0.0591 \cdot \lg [\text{H}_3\text{O}^+_{\text{inner}}] = E'_{\text{const.}} - 0.0591 \cdot \text{pH} \quad (25)$$

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

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

pH measurement by glass electrode has opportunities :

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



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

Nernst's potential $\text{SO}_4^{2-}/\text{SO}_3^{2-}$ red-ox system behaving in acidic H_3O^+ water and basic OH^- medium
Nernst's absolute standard potential. $[\text{H}_2\text{O}]=55.3 \text{ M}$;

Substance	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol	
H_2SO_4	-814.0	156.9	-690.0	CRC; $\text{GH}_2\text{SO}_4=\text{GHSO}_4+\text{GH}_3\text{O}-(\Delta G_{\text{eqH}_2\text{SO}_4}+\text{GH}_2\text{O})=-718.17 \text{ kJ/mol}$;
H_2SO_4			-718.17	$\text{GH}_2\text{SO}_4=-746.64+22.44-(-6.035+0)=-718.17 \text{ kJ/mol}$
H_2SO_4		formation	-84.04	$\text{GH}_2\text{SO}_4=\Delta G_{\text{Form}}=\Delta G^\circ_{\text{H}_2\text{SO}_4}+\text{G}_{\text{Srombic}}+2\Delta G_{\text{O}_2}+\text{GH}_2\text{gas}=-84.04 \text{ kJ/mol}$;
H_2SO_4		$\text{pK}_{\text{a}1}=-2.8$	-164.3	$\text{GH}_2\text{SO}_{4\text{aq}}=-192.74+22.44-(-6.035+0)=-164.3 \text{ kJ/mol}$;
HSO_4^-	-887.3	131.8	-755.9	CRC
HSO_4^-	-	-	-746.62	$\text{GHSO}_4=\text{GSO}_4+\text{GH}_3\text{O}-(21.307+\text{GH}_2\text{O})=-746.62 \text{ kJ/mol}$;
HSO_4^-	-	formation	-192.74	$\text{GHSO}_4=\Delta G_{\text{Form}}=\Delta G^\circ_{\text{HSO}_4}+\text{G}_{\text{Srombic}}+2\Delta G_{\text{O}_2}+\text{GH}_2\text{gas}/2=-192.74 \text{ kJ/mol}$;
HSO_4^-	-	$\text{pK}_{\text{a}2}=1.99$	-226.3	$\text{GHSO}_4=-227.39+22.44-(21.307+0)=-226.3 \text{ kJ/mol}$;
HSO_4^-	$E^\circ_{\text{HSO}_4^-}$	0.08145	-192.7	$\text{GHSO}_4=\Delta G_{\text{eqHSO}_4}-3\text{GH}_3\text{O}+(\text{GH}_2\text{SO}_3+4\text{GH}_2\text{O})=-192.7 \text{ kJ/mol}$;
SO_4^{2-}	-907.62	-536.2	-747.75	BioTherm2006; $\Delta G_{\text{SO}_4}=\Delta H-T\Delta S=-907.62-298.15\cdot 0.5362=-747.75 \text{ kJ/mol}$;
SO_4^{2-}	-	formation	-227.39	$\text{GSO}_4=\Delta G_{\text{Form}}=\Delta G^\circ_{\text{SO}_4}+\text{G}_{\text{Srombic}}+2\Delta G_{\text{O}_2}=-747.75-85.64+2\cdot 303=-227.39 \text{ kJ/mol}$;
SO_4^{2-}	$E^\circ_{\text{SO}_4^{2-}}$	0.08145	-202.3	$\text{GSO}_4=\Delta G_{\text{eqSO}_4}-3\text{GH}_3\text{O}+(\text{GHSO}_3+4\text{GH}_2\text{O})=-202.3 \text{ kJ/mol}$;
SO_4^{2-}	$E^\circ_{\text{SO}_3^{2-}}$	-1.278	-213.4	$\text{GSO}_4=\Delta G_{\text{eqSO}_3\text{-OH}}-\text{GH}_2\text{O}+(\text{GSO}_3+2\text{GOH})=-213.4 \text{ kJ/mol}$;
SO_4^{2-}	-909.3	20.1	-744.5	CRC
H_2SO_3	-	formation	-381.23	$\text{GH}_2\text{SO}_3=\Delta G_{\text{Form}}=\Delta G^\circ_{\text{H}_2\text{SO}_3}+\text{G}_{\text{Srombic}}+1.5\Delta G_{\text{O}_2}+\text{GH}_2\text{gas}=-381.23 \text{ kJ/mol}$;
H_2SO_3	-	$\text{pK}_{\text{a}1}=1.85$	-72.9075	$\text{GH}_2\text{SO}_{3\text{aq}}=-74.84+22.44-(20.5075+0)=-72.9075 \text{ kJ/mol}$;
H_2SO_3	$E^\circ_{\text{HSO}_4^-}$	0.08145	-141.1	$\text{GH}_2\text{SO}_3=\text{GHSO}_4+3\text{GH}_3\text{O}-(\Delta G_{\text{eqHSO}_4}+4\text{GH}_2\text{O})=-141.1 \text{ kJ/mol}$;
HSO_3^-		formation;	-74.84	$\text{GHSO}_3=\Delta G_{\text{Form}}=\Delta G^\circ_{\text{HSO}_3}+\text{G}_{\text{Srombic}}+1.5\Delta G_{\text{O}_2}+\text{GH}_2\text{gas}/2=-74.84 \text{ kJ/mol}$;
HSO_3^-		$\text{pK}_{\text{a}2}=7.21$	-150.2	$\text{GHSO}_{3\text{-aq}}=-121.52+22.44-(51.1+0)=-150.2 \text{ kJ/mol}$;
HSO_3^-	$E^\circ_{\text{SO}_4^{2-}}$	0.08145	-150.7	$\text{GHSO}_3=\text{GSO}_4+3\text{GH}_3\text{O}-(\Delta G_{\text{eqSO}_4}+4\text{GH}_2\text{O})=-150.7 \text{ kJ/mol}$;
HSO_3^-	-635.5	-29	-486.5	CRC
SO_3^{2-}	-632.1888	-474.0502	-490.38	BioTherm2006 $\text{DG}_{\text{H}_2\text{SO}_3}=\text{DH}_2\text{SO}_3-T\Delta S_{\text{H}_2\text{SO}_3}=-632.1888-298.15\cdot 0.47405=-490.85 \text{ kJ/mol}$;
SO_3^{2-}	-	formation	-121.52	$\text{GSO}_3=\Delta G_{\text{Form}}=\Delta G^\circ_{\text{SO}_3}+\text{G}_{\text{Srombic}}+1.5\Delta G_{\text{O}_2}=-121.52 \text{ kJ/mol}$;
SO_3^{2-}	$E^\circ_{\text{SO}_3^{2-}}$	-1.278	-135.5	$\text{GSO}_3=\text{GSO}_4+\text{GH}_2\text{O}-(\Delta G_{\text{eqSO}_3\text{-OH}}+2\text{GOH})=-135.5 \text{ kJ/mol}$;

Formation solubility $\text{S}_{\text{rombic}}+2\text{O}_2\text{gas}+\text{H}_2\text{gas}+\text{H}_2\text{O}=\text{H}_2\text{SO}_{4\text{aq}}$; $\text{G}_{\text{Srombic}}=-85.64 \text{ kJ/mol}$; $\text{GH}_2\text{gas}=85.6 \text{ kJ/mol}$ [Alberty](#) ;

$\text{GO}_2\text{gas}=303 \text{ kJ/mol}$; $\text{GH}_2\text{SO}_4=\Delta G_{\text{Form}}=\Delta G^\circ_{\text{H}_2\text{SO}_4}+\text{G}_{\text{Srombic}}+2\Delta G_{\text{O}_2}+\text{GH}_2\text{gas}=-690.0-85.64+2\cdot 303+85.6=-84.04 \text{ kJ/mol}$;

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

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

$\text{H}_2\text{SO}_4+\text{H}_2\text{O}=\text{HSO}_4^-+\text{H}_3\text{O}^+$; $\text{pK}_{\text{a}1}=-2.8$; $\text{K}_{\text{eq}1}=\text{K}_{\text{a}1}/[\text{H}_2\text{O}]=10^{(2.8)}/55.3=11.41$;

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

$\text{GH}_2\text{SO}_{4\text{aq}}=\text{GHSO}_4+\text{GH}_3\text{O}-(\Delta G_{\text{eqH}_2\text{SO}_4}+\text{GH}_2\text{O})=-192.74+22.44-(-6.035+0)=-164.3 \text{ kJ/mol}$;

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

$\Delta G_{\text{eqHSO}_4}=-R\cdot T\cdot \ln(\text{K}_{\text{eq}2})=-8.3144\cdot 298.15\cdot \ln(0.0001850)=\text{GSO}_4+\text{GH}_3\text{O}-(\text{GHSO}_4+\text{GH}_2\text{O})=21.307 \text{ kJ/mol}$;

$\text{GHSO}_4=\text{GSO}_4+\text{GH}_3\text{O}-(\Delta G_{\text{eqHSO}_4}+\text{GH}_2\text{O})=-227.39+22.44-(21.307+0)=-226.3 \text{ kJ/mol}$;

Formation solubility $\text{S}_{\text{rombic}}+1.5\text{O}_2\text{gas}+\text{H}_2\text{gas}+\text{H}_2\text{O}=\text{H}_2\text{SO}_{3\text{aq}}$; $\text{G}_{\text{Srombic}}=-85.64 \text{ kJ/mol}$; $\text{GH}_2\text{gas}=85.6 \text{ kJ/mol}$ [Alberty](#) ;

$\text{GO}_2\text{gas}=303 \text{ kJ/mol}$; $\text{GH}_2\text{SO}_3=\Delta G_{\text{Form}}=\Delta G^\circ_{\text{H}_2\text{SO}_3}+\text{G}_{\text{Srombic}}+1.5\Delta G_{\text{O}_2}+\text{GH}_2\text{gas}=-835.69-85.64+1.5\cdot 303+85.6=-381.23 \text{ kJ/mol}$;

$\text{GHSO}_3=\Delta G_{\text{Form}}=\Delta G^\circ_{\text{HSO}_3}+\text{G}_{\text{Srombic}}+1.5\Delta G_{\text{O}_2}+0.5\text{GH}_2\text{gas}=-486.5-85.64+1.5\cdot 303+85.6/2=-74.84 \text{ kJ/mol}$;

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

$\text{H}_2\text{SO}_3+\text{H}_2\text{O}=\text{HSO}_3^-+\text{H}_3\text{O}^+$; $\text{pK}_{\text{a}1}=1.85$; $\text{K}_{\text{eq}1}=\text{K}_{\text{a}1}/[\text{H}_2\text{O}]=10^{(-1.85)}/55.3=0.0002554$

$\Delta G_{\text{eqH}_2\text{SO}_3}=-R\cdot T\cdot \ln(\text{K}_{\text{eq}1})=-8.3144\cdot 298.15\cdot \ln(0.0002554)=\text{GHSO}_3+\text{GH}_3\text{O}-(\text{GH}_2\text{SO}_3+\text{GH}_2\text{O})=20.5075 \text{ kJ/mol}$;

$\text{GH}_2\text{SO}_{3\text{aq}}=\text{GHSO}_3+\text{GH}_3\text{O}-(\Delta G_{\text{eqH}_2\text{SO}_3}+\text{GH}_2\text{O})=-74.84+22.44-(20.5075+0)=-72.9075 \text{ kJ/mol}$;

$\text{HSO}_3^-+\text{H}_2\text{O}=\text{SO}_3^{2-}+\text{H}_3\text{O}^+$; $\text{pK}_{\text{a}2}=7.21$; $\text{K}_{\text{eq}2}=\text{K}_{\text{a}2}/[\text{H}_2\text{O}]=10^{(-7.21)}/55.3=0.000000001115$

$\Delta G_{\text{eqHSO}_3}=-R\cdot T\cdot \ln(\text{K}_{\text{eq}2})=-8.3144\cdot 298.15\cdot \ln(0.000000001115)=\text{GSO}_3+\text{GH}_3\text{O}-(\text{GHSO}_3+\text{GH}_2\text{O})=51.1 \text{ kJ/mol}$;

$\text{GHSO}_{3\text{-aq}}=\text{GSO}_3+\text{GH}_3\text{O}-(\Delta G_{\text{eqHSO}_3}+\text{GH}_2\text{O})=-121.52+22.44-(51.1+0)=-150.18 \text{ kJ/mol}$;

$\text{H}_2\text{SO}_3 + 4\text{H}_2\text{O} = \text{HSO}_4^- + 3\text{H}_3\text{O}^+ + 2\text{e}^-$; $\text{pH} < 1.9$ $E^\circ_{\text{SO}_4^{2-}} = \mathbf{0.08145}$ V Suchotina.

$$E^\circ_{\text{SO}_4^{2-}} = E^\circ + 0.10166 - 0.0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^4) - 0.3982 = 0.172 + 0.10166 - 0.02955 \cdot \lg(1/55.3^4) - 0.3982 = \mathbf{0.08145}$$
 V;

$$E_{\text{HSO}_4^-} = E^\circ_{\text{HSO}_4^-} + \frac{0.0591}{2} \cdot \lg \frac{[\text{HSO}_4^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{H}_2\text{SO}_3] \cdot [\text{H}_2\text{O}]^5} = \mathbf{0.08145}$$
 V + $\frac{0.0591}{2} \cdot \lg \frac{[\text{HSO}_4^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{H}_2\text{SO}_3] \cdot [\text{H}_2\text{O}]^5}$

$$\Delta G_{\text{eqHSO}_4^-} = E^\circ_{\text{HSO}_4^-} \cdot F \cdot 2 = \mathbf{0.08145} \cdot 96485 \cdot 2 = \mathbf{15.717}$$
 kJ/mol, \Leftrightarrow $\mathbf{15.68}$ kJ/mol;

$$\Delta G_{\text{eqHSO}_4^-} = G_{\text{HSO}_4^-} + 3G_{\text{H}_3\text{O}^+} - (G_{\text{H}_2\text{SO}_3} + 4G_{\text{H}_2\text{O}}) = \mathbf{-192.74} + 3 \cdot 22.44 - (\mathbf{-141.1} + 4 \cdot 0) = \mathbf{15.68}$$
 kJ/mol;

$$G_{\text{H}_2\text{SO}_3} = G_{\text{HSO}_4^-} + 3G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqHSO}_4^-} + 4G_{\text{H}_2\text{O}}) = \mathbf{-192.74} + 3 \cdot 22.44 - (\mathbf{15.717} + 4 \cdot 0) = \mathbf{-141.1}$$
 kJ/mol

$$G_{\text{HSO}_4^-} = \Delta G_{\text{eqHSO}_4^-} - 3G_{\text{H}_3\text{O}^+} + (G_{\text{H}_2\text{SO}_3} + 4G_{\text{H}_2\text{O}}) = \mathbf{15.717} - 3 \cdot 22.44 + (\mathbf{-141.1} + 4 \cdot 0) = \mathbf{-192.7}$$
 kJ/mol;

$\text{HSO}_3^- + 4\text{H}_2\text{O} = \text{SO}_4^{2-} + 3\text{H}_3\text{O}^+ + 2\text{e}^-$; $2 < \text{pH} < 7$, Suchotina $E^\circ_{\text{SO}_4^{2-}} = \mathbf{0.08145}$ V;

$$E^\circ_{\text{SO}_4^{2-}} = E^\circ + 0.10166 - 0.0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^4) - 0.3982 = 0.172 + 0.10166 - 0.02955 \cdot \lg(1/55.3^4) - 0.3982 = \mathbf{0.08145}$$
 V;

$$E_{\text{SO}_4^{2-}} = E^\circ_{\text{SO}_4^{2-}} + \frac{0.0591}{2} \cdot \lg \frac{[\text{SO}_4^{2-}] \cdot [\text{H}_3\text{O}^+]^3}{[\text{HSO}_3^-] \cdot [\text{H}_2\text{O}]^4} = \mathbf{0.08145}$$
 V + $\frac{0.0591}{2} \cdot \lg \frac{[\text{SO}_4^{2-}] \cdot [\text{H}_3\text{O}^+]^3}{[\text{HSO}_3^-] \cdot [\text{H}_2\text{O}]^4}$

$$\Delta G_{\text{eqSO}_4^{2-}} = E^\circ_{\text{SO}_4^{2-}} \cdot F \cdot 2 = \mathbf{0.08145} \cdot 96485 \cdot 2 = \mathbf{15.717}$$
 kJ/mol, \Leftrightarrow $\mathbf{15.72}$ kJ/mol;

$$\Delta G_{\text{eqSO}_4^{2-}} = G_{\text{SO}_4^{2-}} + 3G_{\text{H}_3\text{O}^+} - (G_{\text{HSO}_3^-} + 4G_{\text{H}_2\text{O}}) = \mathbf{-202.3} + 3 \cdot 22.44 - (\mathbf{-150.7} + 4 \cdot 0) = \mathbf{15.72}$$
 kJ/mol;

$$G_{\text{HSO}_3^-} = G_{\text{SO}_4^{2-}} + 3G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqSO}_4^{2-}} + 4G_{\text{H}_2\text{O}}) = \mathbf{-202.3} + 3 \cdot 22.44 - (\mathbf{15.717} + 4 \cdot 0) = \mathbf{-150.7}$$
 kJ/mol;

$$G_{\text{SO}_4^{2-}} = \Delta G_{\text{eqSO}_4^{2-}} - 3G_{\text{H}_3\text{O}^+} + (G_{\text{HSO}_3^-} + 4G_{\text{H}_2\text{O}}) = \mathbf{15.717} - 3 \cdot 22.44 + (\mathbf{-150.7} + 4 \cdot 0) = \mathbf{-202.3}$$
 kJ/mol;

$\text{SO}_3^{2-} + 2\text{OH}^- = \text{SO}_4^{2-} + \text{H}_2\text{O} + 2\text{e}^-$; $\text{pH} > 7$; $E^\circ_{\text{SO}_4^{2-}} = \mathbf{-1.278}$ V Suchotina

$$E^\circ_{\text{SO}_3^{2-}\text{-OH}^-} = E^\circ + 0.10166 - 0.0591/2 \cdot \lg([\text{H}_2\text{O}]) = -0.93 + 0.10166 - 0.02955 \cdot \lg(55.3) - 0.3982 = \mathbf{-1.278}$$
 V;

$$E_{\text{SO}_3^{2-}\text{-OH}^-} = E^\circ_{\text{SO}_3^{2-}\text{-OH}^-} + \frac{0.0591}{2} \cdot \lg \frac{[\text{SO}_4^{2-}] \cdot [\text{H}_2\text{O}]}{[\text{SO}_3^{2-}] \cdot [\text{OH}^-]^2} = \mathbf{-1.278}$$
 V + $\frac{0.0591}{2} \cdot \lg \frac{[\text{SO}_4^{2-}] \cdot [\text{H}_2\text{O}]}{[\text{SO}_3^{2-}] \cdot [\text{OH}^-]^2}$

$$\Delta G_{\text{eqSO}_3^{2-}\text{-OH}^-} = E^\circ_{\text{SO}_3^{2-}\text{-OH}^-} \cdot F \cdot 2 = \mathbf{-1.278} \cdot 96485 \cdot 2 = \mathbf{-246.62}$$
 kJ/mol, \Leftrightarrow $\mathbf{-246.6}$;

$$\Delta G_{\text{eqSO}_3^{2-}\text{-OH}^-} = G_{\text{SO}_4^{2-}} + G_{\text{H}_2\text{O}} - (G_{\text{SO}_3^{2-}} + 2G_{\text{OH}^-}) = \mathbf{-213.4} + 0 - (\mathbf{-121.52} + 2 \cdot 77.36) = \mathbf{-246.6}$$
 kJ/mol;

$$G_{\text{SO}_3^{2-}} = G_{\text{SO}_4^{2-}} + G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqSO}_3^{2-}\text{-OH}^-} + 2G_{\text{OH}^-}) = \mathbf{-213.4} + 0 - (\mathbf{-246.62} + 2 \cdot 77.36) = \mathbf{-121.5}$$
 kJ/mol;

$$G_{\text{SO}_4^{2-}} = \Delta G_{\text{eqSO}_3^{2-}\text{-OH}^-} - G_{\text{H}_2\text{O}} + (G_{\text{SO}_3^{2-}} + 2G_{\text{OH}^-}) = \mathbf{-246.62} - 0 + (\mathbf{-121.52} + 2 \cdot 77.36) = \mathbf{-213.4}$$
 kJ/mol;

**Nernst's potential NO₃⁻/NO₂⁻ red-ox system behaving in acidic H₃O⁺ water and basic OH⁻ medium
Nernst's absolute standard potential.**

Formation $\Delta G^{\circ}_{\text{HNO}_2\text{gas}} + 0.5\text{N}_2\text{gas} + \text{O}_2\text{gas} + 0.5\text{H}_2\text{gas} = G_{\text{HNO}_2\text{gas}} = -46 + (0.5 \cdot -9.55 + 303 + 0.5 \cdot 85.6) = 295.025 \text{ kJ/mol}$;
 $G_{\text{N}_2\text{gas}} = G_{\text{N}_2\text{aq}} - (\Delta G_{\text{Hess_sk_N}_2\text{aq}} + G_{\text{H}_2\text{O}}) = 18.7 - (28.25 + 0) = -9.55 \text{ kJ/mol}$; $G_{\text{H}_2\text{gas}} = 85.6 \text{ kJ/mol}$ [Alberty](#) ; $G_{\text{O}_2\text{gas}} = 303 \text{ kJ/mol}$;
 $G_{\text{NO}_2\text{Form}} = \Delta G^{\circ}_{\text{NO}_2\text{aq}} + 0.5G_{\text{N}_2\text{gas}} + G_{\text{O}_2\text{gas}} + G_{\text{H}_2\text{O}} = -33.01 + 0.5 \cdot -9.55 + 1 \cdot 303 + 0 = 265.2 \text{ kJ/mol}$;
 $\text{HNO}_2 + \text{H}_2\text{O} = \text{NO}_2^- + \text{H}_3\text{O}^+$; $pK_a = 3.15$; $K_{\text{eq}} = K_a / [\text{H}_2\text{O}] = 10^{-(3.15)} / 55.3 = 0.00001280$;
 $\Delta G_{\text{eqHNO}_2} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8.3144 \cdot 298.15 \cdot \ln(0.0000128) = G_{\text{NO}_2^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{HNO}_2} + G_{\text{H}_2\text{O}}) = 27.927 \text{ kJ/mol}$;
 $\Delta G_{\text{eqHNO}_2} = G_{\text{NO}_2^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{HNO}_2} + G_{\text{H}_2\text{O}}) = 265.2 + 22.44 - (259.713 + 0) = 27.927 \text{ kJ/mol}$;
 $G_{\text{NO}_2^-} = \Delta G_{\text{eqHNO}_2} - G_{\text{H}_3\text{O}^+} + (G_{\text{HNO}_2} + G_{\text{H}_2\text{O}}) = 27.927 + 22.44 - (259.713 + 0) = 265.2 \text{ kJ/mol}$;
 $G_{\text{HNO}_2} = G_{\text{NO}_2^-} + G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqHNO}_2} + G_{\text{H}_2\text{O}}) = 265.2 + 22.44 - (27.927 + 0) = 259.713 \text{ kJ/mol}$;

$G_{\text{NO}_3\text{Form}} = \Delta G^{\circ}_{\text{NO}_3\text{aq}} + (0.5G_{\text{N}_2\text{gas}} + 1.5G_{\text{O}_2\text{gas}} + 0.5G_{\text{H}_2\text{gas}} + G_{\text{H}_2\text{O}}) = -109.55 + (0.5 \cdot -9.55 + 1.5 \cdot 303 + 0) = 340.2 \text{ kJ/mol}$;
 $\text{HNO}_3 + \text{H}_2\text{O} = \text{NO}_3^- + \text{H}_3\text{O}^+$; $pK_a = -1.4$; $K_{\text{eq}} = K_a / [\text{H}_2\text{O}] = 10^{-(1.4)} / 55.3 = 0.4542$;
 $\Delta G_{\text{eqHNO}_3} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8.3144 \cdot 298.15 \cdot \ln(0.4542) = G_{\text{NO}_3^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{HNO}_3} + G_{\text{H}_2\text{O}}) = 1.956 \text{ kJ/mol}$;
 $\Delta G_{\text{eqHNO}_3} = G_{\text{NO}_3^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{HNO}_3} + G_{\text{H}_2\text{O}}) = 340.2 + 22.44 - (360.684 + 0) = 1.956 \text{ kJ/mol}$;
 $G_{\text{HNO}_3} = G_{\text{NO}_3^-} + G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqHNO}_3} + G_{\text{H}_2\text{O}}) = 340.2 + 22.44 - (1.956 + 0) = 360.7 \text{ kJ/mol}$;
 $G_{\text{NO}_3^-} = \Delta G_{\text{eqHNO}_3} - G_{\text{H}_3\text{O}^+} + (G_{\text{HNO}_3} + G_{\text{H}_2\text{O}}) = 1.956 - 22.44 + (360.684 + 0) = 340.2 \text{ kJ/mol}$;

Substance	$\Delta H^{\circ}_{\text{H}}$ kJ/mol	$\Delta S^{\circ}_{\text{H}}$ J/mol/K	$\Delta G^{\circ}_{\text{H}}$ kJ/mol
HNO ₂	$E^{\circ}_{\text{NO}_3-\text{H}_3\text{O}^+} = 0.8495 \text{ V}$	0.8495 V	243.592
HNO ₂	-	$pK_a = 3.15$	259.713
HNO _{2gas}	-79.5	254.1	-46.0
HNO _{2gas}	-	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	-	-	592.29
HNO ₃	-	$pK_a = -1.4$	360.7
NO ₃ ⁻	$E^{\circ}_{\text{NH}_4+\text{H}_2\text{O}} = 1.0198 \text{ V}$	1.0198 V	795.66
NO ₃ ⁻	-206.85	146.7	-250.5886
NO ₃ ⁻	-	formation	340.2
NO ₃ ⁻	-	$pK_a = -1.4$	340.2
NO ₃ ⁻	$E^{\circ}_{\text{NO}_3-\text{O}_\text{H}} = -0.3380 \text{ V}$	-0.3380 V	354.696
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}	$E^{\circ}_{\text{NO(g)H}_3\text{O}^+} = 0.8695$	0.8695	178.28
NH ₄ ⁺	On data of Alberty	Alberty	232.9
NH ₄ ⁺ +OH ⁻	-361.2	165.6	-254

$\text{HNO}_2 + 4\text{H}_2\text{O} = \text{NO}_3^- + 3\text{H}_3\text{O}^+ + 2\text{e}^-$;
 $G_{\text{HNO}_2} = G_{\text{NO}_2^-} - G_{\text{H}_3\text{O}^+} + (\Delta G_{\text{eqHNO}_2} + G_{\text{H}_2\text{O}}) = 259.713 \text{ kJ/mol}$;
 CRC
 $G_{\text{HNO}_2\text{gas}} = \Delta G^{\circ}_{\text{HNO}_2\text{gas}} + 0.5\text{N}_2\text{gas} + \text{O}_2\text{gas} + 0.5\text{H}_2\text{gas} = 295.025 \text{ kJ/mol}$
 $G_{\text{NO}_2\text{form}} = \Delta G^{\circ}_{\text{NO}_2\text{aq}} + 0.5G_{\text{N}_2\text{gas}} + G_{\text{O}_2\text{gas}} + G_{\text{H}_2\text{O}} = 265.2 \text{ kJ/mol}$;
 $G_{\text{NO}_2^-} = \Delta G_{\text{eqHNO}_2} - G_{\text{H}_3\text{O}^+} + (G_{\text{HNO}_2} + G_{\text{H}_2\text{O}}) = 265.2 \text{ kJ/mol}$;
BioTherm2006
 $G_{\text{NO}_3^-} = \Delta G_{\text{eqNH}_4+\text{H}_2\text{O}} - 10G_{\text{H}_3\text{O}^+} + (G_{\text{NH}_4^+} - 13G_{\text{H}_2\text{O}}) = 580.31 \text{ kJ/mol}$
 Wikiped $G^{\circ}_{\text{NO}_3^-} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -207 - 298.15 \cdot 0.146 = -250.5886 \text{ kJ/mol}$;
 $G_{\text{HNO}_3} = G_{\text{NO}_3^-} + G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqHNO}_3} + G_{\text{H}_2\text{O}}) = 360.7 \text{ kJ/mol}$;
 $G_{\text{NO}_3^-} = \Delta G_{\text{eqNH}_4+\text{H}_2\text{O}} - 10G_{\text{H}_3\text{O}^+} + (G_{\text{NH}_4^+} - 13G_{\text{H}_2\text{O}}) = 795.66 \text{ kJ/mol}$;
 $\Delta G^{\circ}_{\text{NO}_3^-} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -206.85 - 298.15 \cdot 0.1467 = -250.5886 \text{ kJ/mol}$;
 $G_{\text{NO}_3\text{Form}} = \Delta G^{\circ}_{\text{HNO}_3\text{aq}} + (0.5G_{\text{N}_2\text{gas}} + 1.5G_{\text{O}_2\text{gas}} + G_{\text{H}_2\text{O}}) = 340.2 \text{ kJ/mol}$;
 $G_{\text{NO}_3^-} = \Delta G_{\text{eqHNO}_3} - G_{\text{H}_3\text{O}^+} + (G_{\text{HNO}_3} + G_{\text{H}_2\text{O}}) = 340.2 \text{ kJ/mol}$;
 $\text{NO}_2^- + 2\text{OH}^- = \text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^-$; $E^{\circ}_{\text{NO}_3-\text{H}_2\text{O}} = -0.3380 \text{ V}$
BioTherm2006
 CRC
 $G_{\text{NO}_\text{gas}} = G_{\text{NO}_\text{aq}} - (G_{\text{H}_2\text{O}} + \Delta G_{\text{sp}}) = 86.55 - (0 + 25.526) = 61.024 \text{ kJ/mol}$;

$\text{HNO}_2 + 4\text{H}_2\text{O} = \text{NO}_3^- + 3\text{H}_3\text{O}^+ + 2\text{e}^-$; $E^{\circ}_{\text{NO}_3-\text{H}_3\text{O}^+} = 0.8495 \text{ V}$ Kortly, Shucha pH<3.15;

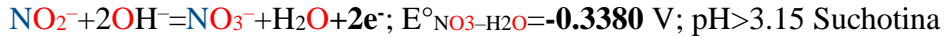
$E^{\circ}_{\text{NO}_3-\text{H}_3\text{O}^+} = E^{\circ} + 0.10166 - 0.0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^4) - 0.3982 = 0.94 + 0.10166 - 0.02955 \cdot \lg(1/55.3^4) - 0.3982 = 0.8495 \text{ V}$;

$E_{\text{NO}_3-\text{H}_3\text{O}^+} = E^{\circ}_{\text{NO}_3-\text{H}_3\text{O}^+} + \frac{0.0591}{2} \cdot \log \frac{[\text{NO}_3^-][\text{H}_3\text{O}^+]^3}{[\text{HNO}_2][\text{H}_2\text{O}]^4} = 0.8495 \text{ V} + \frac{0.0591}{2} \cdot \log \frac{[\text{NO}_3^-][\text{H}_3\text{O}^+]^3}{[\text{HNO}_2][\text{H}_2\text{O}]^4}$

$\Delta G_{\text{eqNO}_3-\text{H}_3\text{O}^+} = E^{\circ}_{\text{NO}_3-\text{H}_3\text{O}^+} \cdot F \cdot 2 = 0.8495 \cdot 96485 \cdot 2 = 163.928 \text{ kJ/mol}$. $\Leftrightarrow 163.928 \text{ kJ/mol}$,

$\Delta G_{\text{eqNO}_3-\text{H}_3\text{O}^+} = G_{\text{NO}_3^-} + 3G_{\text{H}_3\text{O}^+} - (G_{\text{HNO}_2} + 4G_{\text{H}_2\text{O}}) = 340.2 + 3 \cdot 22.44 - (243.592 + 4 \cdot 0) = 163.928 \text{ kJ/mol}$,

$G_{\text{HNO}_2} = G_{\text{NO}_3^-} + 3G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqNO}_3-\text{H}_3\text{O}^+} + 4G_{\text{H}_2\text{O}}) = 340.2 + 3 \cdot 22.44 - (163.928 + 4 \cdot 0) = 243.592 \text{ kJ/mol}$;



$$E^\circ_{\text{NO}_3^-/\text{OH}^-} = E^\circ + 0.10166 - 0.0591/2 \cdot \lg([\text{H}_2\text{O}]) - 0.3982 = 0.94 + 0.10166 - 0.02955 \cdot \lg(55.3^{11}) - 0.3982 = -0.3380 \text{ V};$$

$$E_{\text{NO}_3^-/\text{OH}^-} = E^\circ_{\text{NO}_3^-/\text{OH}^-} + \frac{0.0591}{2} \cdot \lg \frac{[\text{NO}_3^-] \cdot [\text{H}_2\text{O}]}{[\text{NO}_2^-] \cdot [\text{OH}^-]^2} = -0.3380 \text{ V} + \frac{0.0591}{2} \cdot \lg \frac{[\text{NO}_3^-] \cdot [\text{H}_2\text{O}]}{[\text{NO}_2^-] \cdot [\text{OH}^-]^2}$$

$$\Delta G_{\text{eqNO}_3^-/\text{OH}^-} = E^\circ_{\text{NO}_3^-/\text{OH}^-} \cdot F \cdot 2 = -0.3380 \cdot 96485 \cdot 2 = -65.224 \text{ kJ/mol},$$

$$\Delta G_{\text{eqNO}_3^-/\text{OH}^-} = G_{\text{NO}_3^-} + G_{\text{H}_2\text{O}} - (G_{\text{NO}_2^-} + 2G_{\text{OH}^-}) = 340.2 + 0 - (265.2 + 2 \cdot 77.36) = -79.72 \text{ kJ/mol},$$

$$\Delta G_{\text{eqNO}_3^-/\text{OH}^-} = G_{\text{NO}_3^-} + G_{\text{H}_2\text{O}} - (G_{\text{NO}_2^-} + 2G_{\text{OH}^-}) = 354.696 + 0 - (265.2 + 2 \cdot 77.36) = -65.224 \text{ kJ/mol},$$

$$G_{\text{NO}_3^-} = \Delta G_{\text{eqNO}_3^-/\text{OH}^-} - G_{\text{H}_2\text{O}} + (G_{\text{NO}_2^-} + 2G_{\text{OH}^-}) = -65.224 - 0 + (265.2 + 2 \cdot 77.36) = 354.696 \text{ kJ/mol},$$

$$G_{\text{NO}_2^-} = 354.696 + 0 - 2 \cdot 77.36 + 65.224 = 256.2 \text{ kJ/mol};$$

Solubility $\text{NO}^{(\text{g})}$ 0.00562 g/99.6g (20 C); w% = 0.0056/(0.00562+99.6) * 100 = 0.00562%;

$$M_{\text{NO}} = 30.006 \text{ g/mol}; [\text{NO}_{\text{aq}}] = (0.00562/100 \cdot 996)/30.006 = 0.001865 \text{ M}, \text{ if pure gas mol fraction is one } [\text{NO}^{(\text{g})}] = 1;$$

Solubility product $\text{NO}^{(\text{g})} + \text{H}_2\text{O} = \text{NO}_{\text{aq}}$; if $[\text{NO}^{(\text{g})}] = 1$ mol fraction of pure gas

$$K_{\text{sp}} = [\text{NO}_{\text{aq}}]/[\text{NO}^{(\text{g})}]/[\text{H}_2\text{O}] = 0.001865/1/55.3 = 10^{(-4.472)}.$$

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

$$\Delta G_{\text{sp}} = G_{\text{H}_2\text{O}} + G_{\text{NO}_{\text{gas}}} - (G_{\text{NO}_{\text{aq}}}) = 0 + (\text{data Alberty } 86.55) - (\text{data CRC } 87.6) - (61.024 \text{ Solubility product}) = 25.526 \text{ kJ/mol};$$

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



$$E^\circ_{\text{NO}^{(\text{g})}/\text{H}_3\text{O}^+} = E^\circ + 0.10166 - 0.0591/3 \cdot \lg(1/[\text{H}_2\text{O}]^6) - 0.3982 = 0.96 + 0.10166 - 0.0197 \cdot \lg(1/55.3^{16}) - 0.3982 = 0.8695 \text{ V};$$

$$E_{\text{NO}^{(\text{g})}/\text{H}_3\text{O}^+} = E^\circ_{\text{NO}^{(\text{g})}/\text{H}_3\text{O}^+} + 0.0591/3 \cdot \lg \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{NO}_{\text{aq}}] \cdot [\text{H}_2\text{O}]^6} = 0.8695 \text{ V} + 0.0197 \cdot \lg \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{NO}_{\text{aq}}] \cdot [\text{H}_2\text{O}]^6}$$

$$\Delta G_{\text{eqNO}^{(\text{g})}/\text{H}_3\text{O}^+} = E^\circ_{\text{NO}^{(\text{g})}/\text{H}_3\text{O}^+} \cdot F \cdot 3 = 0.8695 \cdot 96485 \cdot 3 = 251.68 \text{ kJ/mol},$$

$$\Delta G_{\text{eqNO}^{(\text{g})}/\text{H}_3\text{O}^+} = G_{\text{NO}_3^-} + 4G_{\text{H}_3\text{O}^+} - (G_{\text{NO}_{\text{aq}}} + 6G_{\text{H}_2\text{O}}) = 340.2 + 4 \cdot 22.44 - (178.28 + 6 \cdot 0) = 251.68 \text{ kJ/mol},$$

$$G_{\text{NO}_{\text{aq}}} = G_{\text{NO}_3^-} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqNO}^{(\text{g})}/\text{H}_3\text{O}^+} + 6G_{\text{H}_2\text{O}}) = 340.2 + 4 \cdot 22.44 - (251.68 + 6 \cdot 0) = 178.28 \text{ kJ/mol}.$$



$$E^\circ_{\text{NH}_4^+/\text{H}_2\text{O}} = E^\circ + 0.10166 - 0.0591/8 \cdot \lg(1/[\text{H}_2\text{O}]^{13}) - 0.3982 = 0.87 + 0.10166 - 0.00739 \cdot \lg(1/55.3^{13}) - 0.3982 = 1.0198 \text{ V};$$

$$E_{\text{NH}_4^+/\text{H}_2\text{O}} = E^\circ_{\text{NH}_4^+/\text{H}_2\text{O}} + 0.0591/8 \cdot \lg \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^{10}}{[\text{NH}_4^+] \cdot [\text{H}_2\text{O}]^{13}} = 1.0198 \text{ V} + 0.00739 \cdot \lg \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^{10}}{[\text{NH}_4^+] \cdot [\text{H}_2\text{O}]^{13}}$$

$$\Delta G_{\text{eqNH}_4^+/\text{H}_2\text{O}} = E^\circ_{\text{NH}_4^+/\text{H}_2\text{O}} \cdot F \cdot 8 = 1.0198 \cdot 96485 \cdot 8 = 787.16 \text{ kJ/mol},$$

$$\Delta G_{\text{eqNH}_4^+/\text{H}_2\text{O}} = G_{\text{NO}_3^-} + 10G_{\text{H}_3\text{O}^+} - (G_{\text{NH}_4^+} + 13G_{\text{H}_2\text{O}}) = G_{\text{NO}_3^-} + 10 \cdot 22.44 - (232.9 - 13 \cdot 0) = 787.16 \text{ kJ/mol},$$

$$G_{\text{NO}_3^-} = \Delta G_{\text{eqNH}_4^+/\text{H}_2\text{O}} - 10G_{\text{H}_3\text{O}^+} + (G_{\text{NH}_4^+} + 13G_{\text{H}_2\text{O}}) = 787.16 - 10 \cdot 22.44 + (232.9 - 13 \cdot 0) = 795.66 \text{ kJ/mol};$$

Nernst's potential 2CO₂ / H₂C₂O₄ red-ox system behaving in acidic H₃O⁺, water medium
Nernst's absolute standard potential. H₂C₂O₄ pK_{a1}=1.25; pK_{a2}=4.14;

Substance	ΔH ^o _H /kJ/mol	ΔS ^o _H /J/mol/K	ΔG ^o _H , kJ/mol
H ₂ C ₂ O _{4cr}	-829.9	-109.8	-797.16
H ₂ C ₂ O _{4cr}	-	pK _{a1} =1.25	-602.329
H ₂ C ₂ O ₄	E ^o _{H₂C₂O₄} =	-0.6835 V	-595.18
HC ₂ O ₄ ⁻	-	pK _{a2} =4.14	-607.687
HC ₂ O ₄ ⁻	-	pK _{a2} =1.25	-600.538
HC ₂ O ₄ ⁻	E ^o _{HC₂O₄} =	-0.7350 V	-607.687
C ₂ O ₄ ²⁻	-	-	-677.14
C ₂ O ₄ ²⁻	-	pK _{a2} =4.14	-596.549
C ₂ O ₄ ²⁻	E ^o _{C₂O₄} =	-0.7865 V	-620.19
CO _{2aq}	-413.798	117.5704	-385.98

$$\Delta G_{H_2C_2O_4} = \Delta H_H - T \cdot \Delta S_H = -829.9 - 298.15 \cdot (-0.1098) = \mathbf{-747.75 \text{ kJ/mol}}$$

$$G_{H_2C_2O_4} = G_{HC_2O_4} + G_{H_3O} - (\Delta G_{eq1H_2C_2O_4} + \Delta G_{H_2O}) = \mathbf{-602.329 \text{ kJ/mol}}$$

$$G_{H_2C_2O_4} = 2G_{CO_2} + 2G_{H_3O} - (\Delta G_{eqH_2C_2O_4} + 2G_{H_2O}) = \mathbf{-595.18 \text{ kJ/mol}}$$

$$G_{HC_2O_4} = G_{C_2O_4} + G_{H_3O} - (\Delta G_{eq2HC_2O_4} + G_{H_2O}) = \mathbf{-607.687 \text{ kJ/mol}}$$

$$G_{HC_2O_4} = \Delta G_{eq1H_2C_2O_4} - G_{H_3O} + (G_{H_2C_2O_4} + \Delta G_{H_2O}) = \mathbf{-600.538 \text{ kJ/mol}}$$

$$G_{H_2C_2O_4} = 2G_{CO_2} + G_{H_3O} - (\Delta G_{eqH_2C_2O_4} + G_{H_2O}) = \mathbf{-607.687 \text{ kJ/mol}}$$

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$$G_{C_2O_4} = \Delta G_{eq2HC_2O_4} - G_{H_3O} + (G_{HC_2O_4} + G_{H_2O}) = \mathbf{-596.549 \text{ kJ/mol}}$$

$$G_{C_2O_4} = 2G_{CO_2} - (\Delta G_{eqHC_2O_4}) = 2 \cdot (-385.98) - (-151.77) = \mathbf{-620.19 \text{ kJ/mol}}$$

$$HC_2O_4^- + H_2O = C_2O_4^{2-} + H_3O^+; pK_{a2}=4.14; K_{eq2} = K_{a2}/[H_2O] = 10^{-(4.14)}/55.3 = 0.000001310;$$

$$\Delta G_{eq2HC_2O_4} = -R \cdot T \cdot \ln(K_{eq2}) = -8.3144 \cdot 298.15 \cdot \ln(0.000001310) = \Delta G_{C_2O_4} + \Delta G_{H_3O} - (\Delta G_{HC_2O_4} + \Delta G_{H_2O}) = \mathbf{33.578 \text{ kJ/mol}}$$

$$\Delta G_{eq2HC_2O_4} = G_{C_2O_4} + G_{H_3O} - (G_{HC_2O_4} + G_{H_2O}) = \mathbf{-596.549 + 22.44 - (-607.687 + 0) = 33.578 \text{ kJ/mol}}$$

$$G_{HC_2O_4} = G_{C_2O_4} + G_{H_3O} - (\Delta G_{eq2HC_2O_4} + G_{H_2O}) = \mathbf{-596.549 + 22.44 - (33.578 + 0) = -607.687 \text{ kJ/mol}}$$

$$G_{C_2O_4} = \Delta G_{eq2HC_2O_4} - G_{H_3O} + (G_{HC_2O_4} + G_{H_2O}) = \mathbf{33.578 - 22.44 + (-607.687 + 0) = -596.549 \text{ kJ/mol}}$$

$$H_2C_2O_4 + H_2O = HC_2O_4^- + H_3O^+; pK_{a1}=1.25; K_{eq1} = K_{a1}/[H_2O] = 10^{-(1.25)}/55.3 = 0.0010169;$$

$$\Delta G_{eq1H_2C_2O_4} = -R \cdot T \cdot \ln(K_{eq1}) = -8.3144 \cdot 298.15 \cdot \ln(0.0010169) = \Delta G_{HC_2O_4} + \Delta G_{H_3O} - (\Delta G_{H_2C_2O_4} + \Delta G_{H_2O}) = \mathbf{17.08 \text{ kJ/mol}}$$

$$\Delta G_{eq1H_2C_2O_4} = G_{HC_2O_4} + G_{H_3O} - (G_{H_2C_2O_4} + \Delta G_{H_2O}) = \mathbf{-600.538 + 22.44 - (-595.18 + 0) = 17.082 \text{ kJ/mol}}$$

$$G_{H_2C_2O_4} = G_{HC_2O_4} + G_{H_3O} - (\Delta G_{eq1H_2C_2O_4} + \Delta G_{H_2O}) = \mathbf{-600.538 + 22.44 - (17.082 + 0) = -595.18 \text{ kJ/mol}}$$

$$G_{HC_2O_4} = \Delta G_{eq1H_2C_2O_4} - G_{H_3O} + (G_{H_2C_2O_4} + \Delta G_{H_2O}) = \mathbf{17.082 - 22.44 + (-595.18 + 0) = -600.538 \text{ kJ/mol}}$$

$$\Delta G_{eq1H_2C_2O_4} = -R \cdot T \cdot \ln(K_{eq1}) = -8.3144 \cdot 298.15 \cdot \ln(0.0010169) = \Delta G_{HC_2O_4} + \Delta G_{H_3O} - (\Delta G_{H_2C_2O_4} + \Delta G_{H_2O}) = \mathbf{17.08 \text{ kJ/mol}}$$

$$\Delta G_{eq1H_2C_2O_4} = G_{HC_2O_4} + G_{H_3O} - (G_{H_2C_2O_4} + \Delta G_{H_2O}) = \mathbf{-607.687 + 22.44 - (-602.329 + 0) = 17.082 \text{ kJ/mol}}$$

$$G_{H_2C_2O_4} = G_{HC_2O_4} + G_{H_3O} - (\Delta G_{eq1H_2C_2O_4} + \Delta G_{H_2O}) = \mathbf{-607.687 + 22.44 - (17.082 + 0) = -602.329 \text{ kJ/mol}}$$

$$G_{HC_2O_4} = \Delta G_{eq1H_2C_2O_4} - G_{H_3O} + (G_{H_2C_2O_4} + \Delta G_{H_2O}) = \mathbf{17.082 - 22.44 + (-602.329 + 0) = -607.687 \text{ kJ/mol}}$$

$$pH \leq 1.25 \quad H_2C_2O_4 + 2H_2O = 2CO_2 + 2H_3O^+ + 2e^-; E^o_{H_2C_2O_4} = \mathbf{-0.6835 \text{ V}} \text{ Suchotina [17]}$$

$$E^o_{H_2C_2O_4} = E^o + 0.10166 + 0.0591/2 \cdot \lg([H_2O]^2) - 0.3982 = -0.49 + 0.10166 - 0.02955 \cdot \lg(1/55.3^2) - 0.3982 = \mathbf{-0.6835 \text{ V}}$$

$$\text{Absolute Nernst's Standard potential } E^o_{H_2C_2O_4} = \mathbf{-0.6835 \text{ V}}; \text{ Suchotina [17]}$$

$$E_{H_2C_2O_4} = E^o_{H_2C_2O_4} + \frac{0.0591}{2} \cdot \lg \frac{[CO_2]^2 \cdot [H_3O^+]^2}{[H_2C_2O_4] \cdot [H_2O]^2} = \mathbf{-0.6835 \text{ V}} + \frac{0.0591}{2} \cdot \lg \frac{[CO_2]^2 \cdot [H_3O^+]^2}{[H_2C_2O_4] \cdot [H_2O]^2}$$

$$\Delta G_{eqH_2C_2O_4} = E^o_{H_2C_2O_4} \cdot F \cdot 2 = \mathbf{-0.6835 \cdot 96485 \cdot 2 = -131.895 \text{ kJ/mol}}$$

$$\Delta G_{eqH_2C_2O_4} = 2G_{CO_2} + 2G_{H_3O} - (G_{H_2C_2O_4} + 2G_{H_2O}) = 2 \cdot (-385.98) + 2 \cdot 22.44 - (-595.185 + 2 \cdot 0) = \mathbf{-131.9 \text{ kJ/mol}}$$

$$G_{H_2C_2O_4} = 2G_{CO_2} + 2G_{H_3O} - (\Delta G_{eqH_2C_2O_4} + 2G_{H_2O}) = 2 \cdot (-385.98) + 2 \cdot 22.44 - (-131.9 + 2 \cdot 0) = \mathbf{-595.18 \text{ kJ/mol}}$$

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

$$\text{Absolute Nernst's Standard potential } E^o_{HC_2O_4} = \mathbf{-0.7350 \text{ V}} \text{ Suchotina [17]}$$

$$E^o_{HC_2O_4} = E^o + 0.10166 - 0.0591/2 \cdot \lg(1/[H_2O]) - 0.3982 = -0.49 + 0.10166 - 0.0591/2 \cdot \lg(1/55.3^{1}) - 0.3982 = \mathbf{-0.7350 \text{ V}}$$

$$\Delta G_{eqHC_2O_4} = E^o_{HC_2O_4} \cdot F \cdot 2 = \mathbf{-0.7350 \cdot 96485 \cdot 2 = -141.833 \text{ kJ/mol}}$$

$$\Delta G_{eqHC_2O_4} = 2G_{CO_2} + G_{H_3O} - (G_{HC_2O_4} + G_{H_2O}) = 2 \cdot (-385.98) + 22.44 - (-607.687 + 0) = \mathbf{-141.833 \text{ kJ/mol}}$$

$$G_{HC_2O_4} = 2G_{CO_2} + G_{H_3O} - (\Delta G_{eqHC_2O_4} + G_{H_2O}) = 2 \cdot (-385.98) + 22.44 - (-141.833 + 0) = \mathbf{-607.687 \text{ kJ/mol}}$$

$$4.14 < pH; C_2O_4^{2-} = 2CO_2 + 2e^-; \text{ Absolute Nernst's Standard potential } E^o_{C_2O_4} = \mathbf{-0.7865 \text{ V}}; \text{ Suchotina [17]}$$

$$E^o_{C_2O_4} = E^o + 0.10166 - 0.0591/2 \cdot \lg([1/H_2O]^0) - 0.3982 = -0.49 + 0.10166 - 0.0591/2 \cdot \lg(1/55.3^0) - 0.3982 = \mathbf{-0.6835 \text{ V}}$$

$$\Delta G_{eqC_2O_4} = E^o_{C_2O_4} \cdot F \cdot 2 = \mathbf{-0.7865 \cdot 96485 \cdot 2 = -151.77 \text{ kJ/mol}}$$

$$\Delta G_{eqC_2O_4} = 2G_{CO_2} - (G_{C_2O_4}) = 2 \cdot (-385.98) - (-620.19) = \mathbf{-151.77 \text{ kJ/mol}}$$

$$G_{C_2O_4} = 2G_{CO_2} - (\Delta G_{eqC_2O_4}) = 2 \cdot (-385.98) - (-151.77) = \mathbf{-620.19 \text{ kJ/mol}}$$

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. $\log K_D=2.05$; $K_D=10^{2.05}$; $2\text{HCrO}_4^- = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$;

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$2\text{Cr}^{3+} + 21\text{H}_2\text{O} = \text{Cr}_2\text{O}_7^{2-} + 14\text{H}_3\text{O}^+ + 6e^-; 1 < \text{pH} < 7; \text{Standard potential } E^\circ_{\text{Cr}_2\text{O}_7} = \mathbf{1.3939} \text{ V Kortly, Shucha [18]}$$

$$E^\circ_{\text{Cr}_2\text{O}_7} = E^\circ + 0.10166 - 0.0591/6 \cdot \lg(1/[\text{H}_2\text{O}]^{21}) - 0.3982 = 1.33 + 0.10166 - 0.0591/6 \cdot \lg(1/55.3^{21}) - 0.3982 = \mathbf{1.3939} \text{ V};$$

$$E_{\text{Cr}_2\text{O}_7 / 2\text{Cr}^{3+}} = E^\circ_{\text{Cr}_2\text{O}_7 / 2\text{Cr}^{3+}} + \frac{0.0591}{6} \cdot \lg \frac{[\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{H}_3\text{O}^+]^{14}}{[\text{Cr}^{3+}]^2 \cdot [\text{H}_2\text{O}]^{21}} = \mathbf{1.3939} \text{ V} + \frac{0.0591}{6} \cdot \lg \frac{[\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{H}_3\text{O}^+]^{14}}{[\text{Cr}^{3+}]^2 \cdot [\text{H}_2\text{O}]^{21}}$$

$$\Delta G_{eq\text{Cr}_2\text{O}_7 / 2\text{Cr}^{3+}} = E^\circ_{\text{Cr}_2\text{O}_7 / 2\text{Cr}^{3+}} \cdot F \cdot 6 = \mathbf{1.3939} \cdot 96485 \cdot 6 = \mathbf{806.9} \text{ kJ/mol};$$

$$\Delta G_{eq\text{Cr}_2\text{O}_7 / 2\text{Cr}^{3+}} = G_{\text{Cr}_2\text{O}_7} + 14G_{\text{H}_3\text{O}} - (2G_{2\text{Cr}^{3+}} + 21G_{\text{H}_2\text{O}}) = G_{\text{Cr}_2\text{O}_7} + 14 \cdot \mathbf{22.44} - (2G_{2\text{Cr}^{3+}} + 21 \cdot 0) = \mathbf{806.9} \text{ kJ/mol};$$

$$2G_{2\text{Cr}^{3+}} = G_{\text{Cr}_2\text{O}_7} + 14 \cdot \mathbf{22.44} - (\mathbf{806.9} + 21 \cdot 0) = ??? \text{ kJ/mol};$$

$$\text{Cr}^{3+} + 11\text{H}_2\text{O} = \text{HCrO}_4^- + 7\text{H}_3\text{O}^+ + 3e^-; \text{pH} > 7; \text{Standard potential } E^\circ_{\text{Cr}_2\text{O}_7} = \mathbf{1.2811} \text{ V Kortly, Shucha [18]}$$

$$E^\circ_{\text{CrO}_4} = E^\circ + 0.10166 - 0.0591/3 \cdot \lg(1/[\text{H}_2\text{O}]^{11}) - 0.3982 = 1.2 + 0.10166 - 0.0591/3 \cdot \lg(1/55.3^{11}) - 0.3982 = \mathbf{1.2811} \text{ V};$$

$$\Delta G_{eq\text{CrO}_4 / \text{Cr}^{3+}} = E^\circ_{\text{CrO}_4 / \text{Cr}^{3+}} \cdot F \cdot 3 = \mathbf{1.2811} \cdot 96485 \cdot 3 = \mathbf{370.8} \text{ kJ/mol};$$

$$\Delta G_{eq\text{H}_2\text{CrO}_4} = G_{\text{CrO}_4} + 14G_{\text{H}_3\text{O}} - (2G_{2\text{Cr}^{3+}} + 21G_{\text{H}_2\text{O}}) = G_{\text{CrO}_4} + 14 \cdot \mathbf{22.44} - (2G_{2\text{Cr}^{3+}} + 21 \cdot 0) = \mathbf{370.8} \text{ kJ/mol};$$

$$2G_{2\text{Cr}^{3+}} = G_{\text{CrO}_4} + 14 \cdot \mathbf{22.44} - (\mathbf{370.8} + 21 \cdot 0) = ??? \text{ kJ/mol};$$

$$\text{Cr}(\text{OH})_3 \downarrow + 5\text{OH}^- = \text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3e^-; \text{pH} > 9; E^\circ_{\text{CrO}_4 / \text{OH}} = \mathbf{-0.5639} \text{ V Suchotina [17]}$$

$$E^\circ_{\text{CrO}_4 / \text{OH}} = E^\circ - 0.0591/3 \cdot \lg([\text{H}_2\text{O}]^4) + 0.10166 - 0.3982 = -0.13 - 0.0591/3 \cdot \lg(55.3^4) + 0.10166 - 0.3982 = \mathbf{-0.5639} \text{ V};$$

$$\Delta G_{eq\text{CrO}_4 / \text{OH}} = E^\circ_{\text{CrO}_4 / \text{OH}} \cdot F \cdot 3 = \mathbf{-0.5639} \cdot 96485 \cdot 3 = \mathbf{163.2} \text{ kJ/mol};$$

$$\Delta G_{eq\text{CrO}_4 / \text{OH}} = G_{\text{CrO}_4} + 4G_{\text{H}_3\text{O}} - (G_{\text{Cr}(\text{OH})_3} + 5G_{\text{OH}}) = G_{\text{CrO}_4} + 4 \cdot \mathbf{22.44} - (2G_{2\text{Cr}^{3+}} + 5 \cdot 77.36) = \mathbf{163.2} \text{ kJ/mol};$$

$$G_{\text{Cr}(\text{OH})_3} = G_{\text{CrO}_4} + 14 \cdot \mathbf{22.44} - (\mathbf{163.2} + 21 \cdot 0) = ??? \text{ kJ/mol};$$

$$E_{\text{CrO}_4 / \text{Cr}(\text{OH})_3 \downarrow} = E^\circ_{\text{CrO}_4 / \text{Cr}(\text{OH})_3 \downarrow} + \frac{0.0591}{3} \cdot \lg \frac{[\text{CrO}_4^{2-}] \cdot [\text{H}_2\text{O}]^4}{[\text{Cr}(\text{OH})_3] \cdot [\text{OH}]^5} = \mathbf{-0.5639} \text{ V} + \frac{0.0591}{3} \cdot \lg \frac{[\text{CrO}_4^{2-}] \cdot [\text{H}_2\text{O}]^4}{[\text{Cr}(\text{OH})_3] \cdot [\text{OH}]^5} \text{ V};$$

$$\text{Solubility product } \text{Cr}(\text{OH})_3 + 4\text{H}_2\text{O} = \text{Cr}^{3+} + 3\text{OH}^-; K_{sp} = 6.7 \cdot 10^{-(31)}; K_{eq} = K_{sp} / [\text{H}_2\text{O}]^4 = 6.7 \cdot 10^{-(31)} / 55.3^4 = 10^{-(37.14)};$$

$$\Delta G_{eqsp} = -R \cdot T \cdot \ln(K_{eqsp}) = -8.3144 \cdot 298.15 \cdot \ln(10^{-(37.14)}) = G_{\text{Cr}^{3+}} + 3G_{\text{OH}} - (G_{\text{Cr}(\text{OH})_3} + 4G_{\text{H}_2\text{O}}) = \mathbf{211.99} \text{ kJ/mol};$$

$$G_{\text{Cr}(\text{OH})_3} = G_{\text{Cr}^{3+}} + 3G_{\text{OH}} - (\Delta G_{eqsp} + 4G_{\text{H}_2\text{O}}) = G_{\text{Cr}^{3+}} + 3 \cdot 77.36 - (\mathbf{211.99} + 4 \cdot 0) = ??? \text{ kJ/mol};$$

Substance	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol
CrCl ₂ (cr)	-395.4	115.3	-356
CrCl ₃ (cr)	-556.5	123	-486.1
Cr	-	23.8	-
CrO ₃ (l)	-292.9	266.2	-
Cr ₂ O ₃ (cr)	-1139.7	81.2	1058.1

$$2G_{2\text{Cr}^{3+}} = G_{\text{CrO}_4} + 14 \cdot \mathbf{22.44} - (\mathbf{370.8} + 21 \cdot 0) = ??? \text{ kJ/mol};$$

$$G_{\text{Cr}(\text{OH})_3} = G_{\text{CrO}_4} + 14 \cdot \mathbf{22.44} - (\mathbf{163.2} + 21 \cdot 0) = ??? \text{ kJ/mol};$$

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

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

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

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

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

$$2G_{2\text{Cr}^{3+}} = G_{\text{Cr}_2\text{O}_7} + 14 \cdot \mathbf{22.44} - (\mathbf{806.9} + 21 \cdot 0) = ??? \text{ kJ/mol};$$

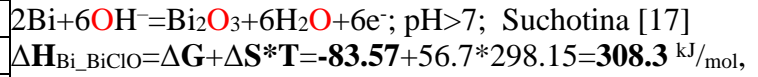
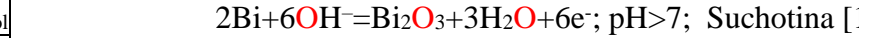
$$G_{\text{Cr}(\text{OH})_3} = G_{\text{Cr}^{3+}} + 3 \cdot 77.36 - (\mathbf{211.99} + 4 \cdot 0) = ??? \text{ kJ/mol};$$

Nernst's potential $\text{BiO}_3^- / \text{Bi}^{3+}$ red-ox system behaving in acidic H_3O^+ , water medium
Nernst's absolute standard potential.

$$E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}} = E^\circ - 0.0591/6 \cdot \lg([\text{H}_2\text{O}]^3) + 0.10166 - 0.3982 = -0.46 - 0.0591/6 \cdot \lg(55.3^3) + 0.10166 - 0.3982 = \mathbf{-0.808 \text{ V}} ;$$

$$E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}} = E^\circ - 0.0591/6 \cdot \lg([\text{H}_2\text{O}]^6) + 0.10166 - 0.3982 = -0.46 - 0.0591/6 \cdot \lg(55.3^6) + 0.10166 - 0.3982 = \mathbf{-0.8595 \text{ V}} ;$$

Substance	$\Delta H^\circ_{\text{H}} \text{ kJ/mol}$	$\Delta S^\circ_{\text{H}} \text{ J/mol/K}$	$\Delta G^\circ_{\text{H}} \text{ kJ/mol}$
Bi^{3+}	-	82.8	-
Bi	308.3	56.7	-83.57
Bi_2	219.7	-	-
Bi(OH)^{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	-	-



$$E_{\text{Bi}_2\text{O}_3/\text{Bi}} = E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}} + \frac{0.0591}{6} \cdot \lg \frac{[\text{Bi}_2\text{O}_3] \cdot [\text{H}_2\text{O}]^3}{[\text{Bi}]^2 \cdot [\text{OH}]^6} =$$

$$= \mathbf{-0.808} + 0.0591/6 \cdot \lg([\text{Bi}_2\text{O}_3] \cdot [\text{H}_2\text{O}]^3 / [\text{Bi}]^2 \cdot [\text{OH}]^6)$$

$$G_{\text{Bi}} = G_{\text{BiCl}} + 3G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqBiCl}_3/\text{Bi}} + 3G_{\text{Cl}}) = \mathbf{306.2 \text{ kJ/mol}},$$

$$G_{\text{Bi}} = G_{\text{BiClO}} + 2G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqBiClO}/\text{Bi}} + 3G_{\text{H}_2\text{O}} + G_{\text{Cl}}) = \mathbf{291.44 \text{ kJ/mol}},$$

$$= \mathbf{-0.8595} + 0.0591/6 \cdot \lg([\text{Bi}_2\text{O}_3] \cdot [\text{H}_2\text{O}]^6 / [\text{Bi}]^2 \cdot [\text{OH}]^6)$$

$$E_{\text{Bi}_2\text{O}_3/\text{Bi}} = E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}} + \frac{0.0591}{6} \cdot \lg \frac{[\text{Bi}_2\text{O}_3] \cdot [\text{H}_2\text{O}]^6}{[\text{Bi}]^2 \cdot [\text{OH}]^6} =$$

$$\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}} = E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}} \cdot F \cdot 6 = \mathbf{-0.808} \cdot 96485 \cdot 6 = \mathbf{-467.76 \text{ kJ/mol}},$$

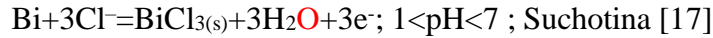
$$\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}} = G_{\text{Bi}_2\text{O}_3} + 3G_{\text{H}_2\text{O}} - (2G_{\text{Bi}} + 6G_{\text{OH}}) = -493.7 + 3 \cdot 0 - (2 \cdot G_{\text{Bi}} + 6 \cdot 77.36) = \mathbf{-467.76 \text{ kJ/mol}},$$

$$G_{\text{Bi}} = (G_{\text{Bi}_2\text{O}_3} + 3G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}} + 6G_{\text{OH}})) / 2 = (-493.7 + 3 \cdot 0 - (-467.76 + 6 \cdot 77.36)) / 2 = \mathbf{-245.05 \text{ kJ/mol}},$$

$$\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}} = E^\circ_{\text{Bi}_2\text{O}_3/\text{Bi}} \cdot F \cdot 6 = \mathbf{-0.8595} \cdot 96485 \cdot 6 = \mathbf{-497.57 \text{ kJ/mol}},$$

$$\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}} = G_{\text{Bi}_2\text{O}_3} + 6G_{\text{H}_2\text{O}} - (2G_{\text{Bi}} + 6G_{\text{OH}}) = -493.7 + 3 \cdot 0 - (2 \cdot G_{\text{Bi}} + 6 \cdot 77.36) = \mathbf{-497.57 \text{ kJ/mol}},$$

$$G_{\text{Bi}} = (G_{\text{Bi}_2\text{O}_3} + 6G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}} + 6G_{\text{OH}})) / 2 = (-493.7 + 6 \cdot 0 - (-497.57 + 6 \cdot 77.36)) / 2 = \mathbf{-246.985 \text{ kJ/mol}},$$

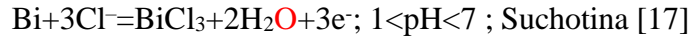


$$E^\circ_{\text{BiCl}_3/\text{Bi}} = E^\circ - 0.0591/3 \cdot \lg([\text{H}_2\text{O}]^3) + 0.10166 - 0.3982 = 0.16 - 0.0591/3 \cdot \lg(55.3^3) + 0.10166 - 0.3982 = \mathbf{-0.2395 \text{ V}} ;$$

$$\Delta G_{\text{eqBiCl}_3/\text{Bi}} = E^\circ_{\text{BiCl}_3/\text{Bi}} \cdot F \cdot 3 = \mathbf{-0.2395} \cdot 96485 \cdot 3 = \mathbf{-69.32 \text{ kJ/mol}},$$

$$\Delta G_{\text{eqBiCl}_3/\text{Bi}} = G_{\text{BiCl}} + 3G_{\text{H}_2\text{O}} - (G_{\text{Bi}} + 3G_{\text{Cl}}) = -315 + 3 \cdot 0 - (G_{\text{Bi}} + 3 \cdot -183.955) = \mathbf{-69.32 \text{ kJ/mol}},$$

$$G_{\text{Bi}} = G_{\text{BiCl}_3} + 3G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqBiCl}_3/\text{Bi}} + 3G_{\text{Cl}}) = -315 + 3 \cdot 0 - (-69.32 + 3 \cdot -183.955) = \mathbf{306.2 \text{ kJ/mol}},$$

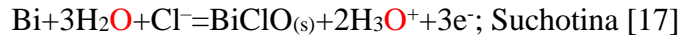


$$E^\circ_{\text{BiCl}_3/\text{Bi}} = E^\circ - 0.0591/3 \cdot \lg([\text{H}_2\text{O}]^2) + 0.10166 - 0.3982 = 0.16 - 0.0591/3 \cdot \lg(55.3^2) + 0.10166 - 0.3982 = \mathbf{-0.2052 \text{ V}} ;$$

$$\Delta G_{\text{eqBiCl}_3/\text{Bi}} = E^\circ_{\text{BiCl}_3/\text{Bi}} \cdot F \cdot 3 = \mathbf{-0.2052} \cdot 96485 \cdot 3 = \mathbf{-59.40 \text{ kJ/mol}},$$

$$\Delta G_{\text{eqBiCl}_3/\text{Bi}} = G_{\text{BiCl}} + 2G_{\text{H}_2\text{O}} - (G_{\text{Bi}} + 3G_{\text{Cl}}) = -315 + 3 \cdot 0 - (G_{\text{Bi}} + 3 \cdot -183.955) = \mathbf{-59.40 \text{ kJ/mol}},$$

$$G_{\text{Bi}} = G_{\text{BiCl}_3} + 2G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqBiCl}_3/\text{Bi}} + 3G_{\text{Cl}}) = -315 + 3 \cdot 0 - (-59.40 + 3 \cdot -183.955) = \mathbf{296.3 \text{ kJ/mol}},$$

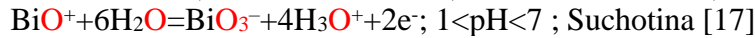


$$E^\circ_{\text{BiClO}/\text{Bi}} = E^\circ - 0.0591/3 \cdot \lg(1/[\text{H}_2\text{O}]^3) + 0.10166 - 0.3982 = 0.16 - 0.0591/3 \cdot \lg(1/55.3^3) + 0.10166 - 0.3982 = \mathbf{-0.0335 \text{ V}} ;$$

$$\Delta G_{\text{eqBiClO}/\text{Bi}} = E^\circ_{\text{BiClO}/\text{Bi}} \cdot F \cdot 3 = \mathbf{-0.0335} \cdot 96485 \cdot 3 = \mathbf{-9.697 \text{ kJ/mol}},$$

$$\Delta G_{\text{eqBiClO}/\text{Bi}} = G_{\text{BiClO}} + 2G_{\text{H}_3\text{O}^+} - (G_{\text{Bi}} + 3G_{\text{H}_2\text{O}} + G_{\text{Cl}}) = -322.1 + 2 \cdot 22.44 - (G_{\text{Bi}} + 3 \cdot 0 - 183.955) = \mathbf{-9.697 \text{ kJ/mol}},$$

$$G_{\text{Bi}} = G_{\text{BiClO}} + 2G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqBiClO}/\text{Bi}} + 3G_{\text{H}_2\text{O}} + G_{\text{Cl}}) = -322.1 + 2 \cdot 22.44 - (-9.697 + 3 \cdot 0 - 183.955) = \mathbf{-83.57 \text{ kJ/mol}},$$



$$E^\circ_{\text{BiO}_3^-/\text{BiO}^+} = E^\circ - 0.0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^6) + 0.10166 - 0.3982 = 1.80 - 0.0591/2 \cdot \lg(1/55.3^6) + 0.10166 - 0.3982 = \mathbf{1.812 \text{ V}} ;$$

$$E_{\text{BiO}_3^-/\text{BiO}^+} = E^\circ_{\text{BiO}_3^-/\text{BiO}^+} + \frac{0.0591}{2} \cdot \lg \frac{[\text{BiO}_3^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{BiO}^+] \cdot [\text{H}_2\text{O}]^6} = \mathbf{1.812 \text{ V}} + \frac{0.0591}{2} \cdot \lg \frac{[\text{BiO}_3^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{BiO}^+] \cdot [\text{H}_2\text{O}]^6}$$

$$\Delta G_{\text{eqBiO}_3^-/\text{BiO}^+} = E^\circ_{\text{BiO}_3^-/\text{BiO}^+} \cdot F \cdot 3 = \mathbf{1.812} \cdot 96485 \cdot 2 = \mathbf{349.7 \text{ kJ/mol}},$$

$$\Delta G_{\text{eqBiO}_3^-/\text{BiO}^+} = G_{\text{BiO}_3^-} + 4G_{\text{H}_3\text{O}^+} - (G_{\text{BiO}^+} + 6G_{\text{H}_2\text{O}}) = G_{\text{BiO}_3^-} + 4 \cdot 22.44 - (G_{\text{BiO}^+} + 6 \cdot 0) = \mathbf{349.7 \text{ kJ/mol}},$$

$$G_{\text{BiO}^+} = G_{\text{BiO}_3^-} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqBiO}_3^-/\text{BiO}^+} + 6G_{\text{H}_2\text{O}}) = G_{\text{BiO}_3^-} + 4 \cdot 22.44 - (349.7 + 6 \cdot 0) = \mathbf{??? \text{ kJ/mol}},$$

$$G_{\text{Bi}} = \mathbf{-245.05 \text{ kJ/mol}}, G_{\text{Bi}} = \mathbf{-246.985 \text{ kJ/mol}}, G_{\text{Bi}} = \mathbf{306.2 \text{ kJ/mol}}, G_{\text{Bi}} = \mathbf{296.3 \text{ kJ/mol}}, G_{\text{Bi}} = \mathbf{-83.57 \text{ kJ/mol}},$$

$$G_{\text{Bi}} = (G_{\text{Bi}_2\text{O}_3} + 3G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}} + 6G_{\text{OH}})) / 2 = (-493.7 + 3 \cdot 0 - (-467.76 + 6 \cdot 77.36)) / 2 = \mathbf{-245.05 \text{ kJ/mol}},$$

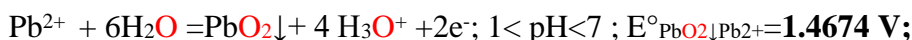
$$G_{\text{Bi}} = (G_{\text{Bi}_2\text{O}_3} + 6G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqBi}_2\text{O}_3/\text{Bi}} + 6G_{\text{OH}})) / 2 = (-493.7 + 6 \cdot 0 - (-497.57 + 6 \cdot 77.36)) / 2 = \mathbf{-246.985 \text{ kJ/mol}},$$

$$G_{\text{Bi}} = G_{\text{BiCl}_3(\text{s})} + 3G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqBiCl}_3/\text{Bi}} + 3G_{\text{Cl}}) = -315 + 3 \cdot 0 - (-69.32 + 3 \cdot -183.955) = \mathbf{306.2 \text{ kJ/mol}},$$

$$G_{\text{Bi}} = G_{\text{BiCl}_3} + 2G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqBiCl}_3/\text{Bi}} + 3G_{\text{Cl}}) = -315 + 3 \cdot 0 - (-59.40 + 3 \cdot -183.955) = \mathbf{296.3 \text{ kJ/mol}},$$

$$G_{\text{Bi}} = G_{\text{BiClO}} + 2G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqBiClO}/\text{Bi}} + 3G_{\text{H}_2\text{O}} + G_{\text{Cl}}) = -322.1 + 2 \cdot 22.44 - (-9.697 + 3 \cdot 0 - 183.955) = \mathbf{-83.57 \text{ kJ/mol}}.$$

Nernst's absolute standard potential $\text{PbO}_2\downarrow/\text{Pb}^{2+}$ red-ox system behaving in acidic H_3O^+ , water medium



$$E^\circ_{\text{PbO}_2\downarrow/\text{Pb}^{2+}} = E^\circ + 0.10166 - 0.0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^6) = 1.8 + 0.10166 - 0.02955 \cdot \lg(1/55.3^6) - 0.3982 = 1.4674 \text{ V};$$

$$\Delta G_{\text{eqPbO}_2\downarrow/\text{Pb}^{2+}} = E^\circ_{\text{PbO}_2\downarrow/\text{Pb}^{2+}} \cdot F \cdot 2 = 1.4674 \cdot 96485 \cdot 2 = 284.48 \text{ kJ/mol},$$

$$\Delta G_{\text{eqPbO}_2\downarrow/\text{Pb}^{2+}} = G_{\text{PbO}_2\downarrow} + 4G_{\text{H}_3\text{O}^+} - (G_{\text{Pb}^{2+}} + 6G_{\text{H}_2\text{O}}) = -217.3 + 4 \cdot 22.44 - (G_{\text{Pb}^{2+}} + 6 \cdot 0) = 424.746 \text{ kJ/mol},$$

$$G_{\text{Pb}^{2+}} = G_{\text{PbO}_2\downarrow} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqPbO}_2\downarrow/\text{Pb}^{2+}} + 6G_{\text{H}_2\text{O}}) = -217.3 + 4 \cdot 22.44 - (424.746 + 6 \cdot 0) = -552.286 \text{ kJ/mol},$$

Substance	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol
Pb	$E^\circ_{\text{Pb}\downarrow/\text{Pb}^{2+}}$	0.3710 V	-480.696
Pb	-	64.8	-
Pb^{2+}	$E^\circ_{\text{PbO}_2\downarrow/\text{Pb}^{2+}}$	1.4674 V	-552.286
Pb^{2+}	0.92	18.5	-4.596
$\text{PbO}_2\downarrow$	-277.4	68.6	-217.3
Al	-	28.3	-
Al	$E^\circ_{\text{Al}/\text{Al}^{3+}}$	-1.9242 V	115.469
Al^{3+}	-538.4	-325	-441.5
H_2AlO_3^-	$E^\circ_{\text{H}_2\text{AlO}_3\text{Al}}$	-2.6609 V	-345.3
$\text{NaAlO}_2\downarrow$	-1133.2	70.4	-
H_2S	-38.6	126	-76.167
HS^-	-16.3	67	-36.276
HS^-	$E^\circ_{\text{S}\downarrow/\text{HS}^-}$	-0.8775 V	6.33
HS^-	$\text{pK}_{\text{a}1}=7.05$	$\text{pK}_{\text{a}1}=7.05$	-3.072
H_2S	$E^\circ_{\text{S}\downarrow/\text{H}_2\text{S}}$	-0.9290 V	-61.09
H_2S	$E^\circ_{\text{S}\downarrow/\text{H}_2\text{S}}$	-0.6715 V	88.82
H_2S	$E^\circ_{\text{S}\downarrow/\text{H}_2\text{S}}$	-0.0515 V	-30.82
S^{2-}	$E^\circ_{\text{S}\downarrow/\text{S}^{2-}}$	-0.8243 V	64.43
S^{2-}	$\text{pK}_{\text{a}2}=19$	$\text{pK}_{\text{a}2}=19$	92.868

$$G_{\text{Pb}} = G_{\text{Pb}^{2+}} - (\Delta G_{\text{eqPb}\downarrow/\text{Pb}^{2+}} + G_{\text{H}_2\text{O}}) = -552.286 - (-71.59 + 0) = -480.696 \text{ kJ/mol},$$

$$G_{\text{Pb}^{2+}} = G_{\text{PbO}_2\downarrow} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqPbO}_2\downarrow/\text{Pb}^{2+}} + 6G_{\text{H}_2\text{O}}) = -552.286 \text{ kJ/mol};$$

$$\Delta G_{\text{Pb}^{2+}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = 0.92 - 298.15 \cdot 0.0185 = -4.596 \text{ kJ/mol};$$

$$G_{\text{Al}} = G_{\text{Al}^{3+}} - (\Delta G_{\text{eqAl}/\text{Al}^{3+}} + G_{\text{H}_2\text{O}}) = 115.469 \text{ kJ/mol},$$

$$\Delta G_{\text{Al}^{3+}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -538.4 - 298.15 \cdot (-0.325) = -441.5 \text{ kJ/mol};$$

$$G_{\text{H}_2\text{AlO}_3^-} = \Delta G_{\text{eqH}_2\text{AlO}_3\text{Al}} - G_{\text{H}_2\text{O}} + (G_{\text{Al}} + 4G_{\text{OH}}) = -345.3 \text{ kJ/mol},$$

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

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

$$G_{\text{HS}^-} = G_{\text{S}^{2-}} + 2G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqS}^{2-}/\text{HS}^-} + G_{\text{OH}}) = 6.33 \text{ kJ/mol};$$

$$G_{\text{HS}^-} = \Delta G_{\text{eq}} - G_{\text{H}_3\text{O}^+} + (G_{\text{H}_2\text{S}} + G_{\text{H}_2\text{O}}) = 50.188 - 22.44 + (-30.82 + 0) = -3.072 \text{ kJ/mol};$$

$$G_{\text{H}_2\text{S}} = G_{\text{S}^{2-}} + 3G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqH}_2\text{S}/\text{S}^{2-}} + 2G_{\text{OH}}) = -61.09 \text{ kJ/mol};$$

$$G_{\text{H}_2\text{S}} = G_{\text{S}^{2-}} + 2G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{Hess}_\text{H}_2\text{S}/\text{aq}} + 2G_{\text{H}_2\text{O}}) = 88.82 \text{ kJ/mol};$$

$$G_{\text{H}_2\text{S}} = G_{\text{S}^{2-}} + 2G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{Hess}_\text{H}_2\text{S}/\text{aq}} + 2G_{\text{H}_2\text{O}}) = -30.822 \text{ kJ/mol}.$$

$$G_{\text{S}^{2-}} = G_{\text{S}^{2-}} + G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqS}^{2-}/\text{aq}}) = -85.64 + 0 - (-150.07) = 64.43 \text{ kJ/mol};$$

$$G_{\text{S}^{2-}} = \Delta G_{\text{eq}} - G_{\text{H}_3\text{O}^+} + (G_{\text{HS}^-} + G_{\text{H}_2\text{O}}) = 118.38 - 22.44 + (-3.072 + 0) = 92.868 \text{ kJ/mol};$$

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



$$E^\circ_{\text{Pb}\downarrow/\text{Pb}^{2+}} = E^\circ - 0.0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^1) + 0.10166 - 0.3982 = -0.126 - 0.02955 \cdot \lg(1/55.3^1) + 0.10166 - 0.3982 = -0.3710 \text{ V};$$

$$\Delta G_{\text{eqPb}\downarrow/\text{Pb}^{2+}} = E^\circ_{\text{Pb}\downarrow/\text{Pb}^{2+}} \cdot F \cdot 2 = -0.371 \cdot 96485 \cdot 2 = -71.59 \text{ kJ/mol},$$

$$\Delta G_{\text{eqPb}\downarrow/\text{Pb}^{2+}} = G_{\text{Pb}\downarrow} - (G_{\text{Pb}} + G_{\text{H}_2\text{O}}) = -552.286 - (-480.696 + 0) = -71.59 \text{ kJ/mol},$$

$$G_{\text{Pb}} = G_{\text{Pb}^{2+}} - (\Delta G_{\text{eqPb}\downarrow/\text{Pb}^{2+}} + G_{\text{H}_2\text{O}}) = -552.286 - (-71.59 + 0) = -480.696 \text{ kJ/mol},$$

Nernst's absolute standard potential $\text{H}_2\text{AlO}_3^-/\text{Al}\downarrow$ red-ox system behaving in acidic H_3O^+ , water medium

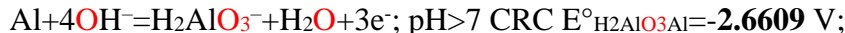


$$E^\circ_{\text{Al}/\text{Al}^{3+}} = E^\circ - 0.0591/3 \cdot \lg(1/[\text{H}_2\text{O}]^1) + 0.10166 - 0.3982 = -1.662 - 0.0591/3 \cdot \lg(1/55.3^1) + 0.10166 - 0.3982 = -1.9242 \text{ V};$$

$$\Delta G_{\text{eqAl}/\text{Al}^{3+}} = E^\circ_{\text{Al}/\text{Al}^{3+}} \cdot F \cdot 3 = -1.9242 \cdot 96485 \cdot 3 = -556.969 \text{ kJ/mol},$$

$$\Delta G_{\text{eqAl}/\text{Al}^{3+}} = G_{\text{Al}^{3+}} - (G_{\text{Al}} + G_{\text{H}_2\text{O}}) = -441.5 - (115.469 + 0) = -556.969 \text{ kJ/mol},$$

$$G_{\text{Al}} = G_{\text{Al}^{3+}} - (\Delta G_{\text{eqAl}/\text{Al}^{3+}} + G_{\text{H}_2\text{O}}) = -441.5 - (-556.969 + 0) = 115.469 \text{ kJ/mol},$$



$$E^\circ_{\text{H}_2\text{AlO}_3\text{Al}} = E^\circ - 0.0591/3 \cdot \lg([\text{H}_2\text{O}]^1) + 0.10166 - 0.3982 = -2.33 - 0.0591/3 \cdot \lg(55.3^1) + 0.10166 - 0.3982 = -2.6609 \text{ V};$$

$$\Delta G_{\text{eqH}_2\text{AlO}_3\text{Al}} = E^\circ_{\text{H}_2\text{AlO}_3\text{Al}} \cdot F \cdot 3 = -2.6609 \cdot 96485 \cdot 3 = -770.21 \text{ kJ/mol},$$

$$\Delta G_{\text{eqH}_2\text{AlO}_3\text{Al}} = G_{\text{H}_2\text{AlO}_3^-} + G_{\text{H}_2\text{O}} - (G_{\text{Al}} + 4G_{\text{OH}}) = -345.3 + 0 - (115.469 + 4 \cdot 77.36) = -770.21 \text{ kJ/mol},$$

$$G_{\text{H}_2\text{AlO}_3^-} = \Delta G_{\text{eqH}_2\text{AlO}_3\text{Al}} - G_{\text{H}_2\text{O}} + (G_{\text{Al}} + 4G_{\text{OH}}) = -770.21 - 0 + (115.469 + 4 \cdot 77.36) = -345.3 \text{ kJ/mol},$$

$$E_{\text{AlO}_2^-/\text{Al}\downarrow} = E^\circ_{\text{AlO}_2^-/\text{Al}\downarrow} + \frac{0.0591}{3} \cdot \lg \frac{[\text{H}_2\text{AlO}_3^-][\text{H}_2\text{O}]}{[\text{Al}] \cdot [\text{OH}^-]^4} = -2.6609 \text{ V} + \frac{0.0591}{3} \cdot \lg \frac{[\text{H}_2\text{AlO}_3^-][\text{H}_2\text{O}]}{[\text{Al}] \cdot [\text{OH}^-]^4}$$

Nernst's absolute standard potential $S_{\text{rombic}} \downarrow / \text{H}_2\text{S}_{\text{aq}}$ red-ox system behaving in acidic H_3O^+ , water medium

$$\text{S}^{2-} = \text{S}_{\text{rombic}} + \text{H}_2\text{O} + 2\text{e}^-; E^\circ_{\text{S}^{2-}/\text{S}} = -0.8243 \text{ V Kortly, Shucha};$$

$$E^\circ_{\text{S}^{2-}/\text{S}} = E^\circ - 0.0591/2 * \lg([\text{H}_2\text{O}]^1) + 0.10166 - 0.3982 = -0.4763 - 0.02955 * \lg(55.3^1) + 0.10166 - 0.3982 = -0.8243 \text{ V};$$

$$\Delta G_{\text{eqS}^{2-}} = E^\circ_{\text{S}^{2-}/\text{S}} * F * n = -0.8243 * 96485 * 2 = -150.07 \text{ kJ/mol}; G_{\text{S}_{\text{rombic}}} = -85.64 \text{ kJ/mol};$$

$$\Delta G_{\text{eqS}^{2-\text{aq}}} = G_{\text{S}_{\text{rombic}}} + G_{\text{H}_2\text{O}} - (G_{\text{S}^{2-\text{aq}}}) = -85.64 + 0 - (64.43) = -150.07 \text{ kJ/mol};$$

$$G_{\text{S}^{2-\text{aq}}} = G_{\text{S}_{\text{rombic}}} + G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqS}^{2-\text{aq}}}) = -85.64 + 0 - (-150.07) = 64.43 \text{ kJ/mol};$$

$$\text{HS}^- + \text{OH}^- = \text{S}_{\text{rombic}} + 2\text{H}_2\text{O} + 2\text{e}^-; \text{CRC 2010}$$

$$E^\circ_{\text{HS}^-/\text{S}} = E^\circ - 0.0591/2 * \lg([\text{H}_2\text{O}]^2) + 0.10166 - 0.3982 = -0.4763 - 0.02955 * \lg(55.3^2) + 0.10166 - 0.3982 = -0.8775 \text{ V};$$

$$\Delta G_{\text{eqHS}^-} = E_{\text{HS}^-/\text{S}} * F * n = -0.8775 * 96485 * 2 = -169.33 \text{ kJ/mol};$$

$$\Delta G_{\text{eqHS}^- \text{aq}} = G_{\text{S}_{\text{rombic}}} + 2G_{\text{H}_2\text{O}} - (G_{\text{HS}^- \text{aq}} + G_{\text{OH}^-}) = -85.64 + 2 * 0 - (6.33 + 77.36) = -169.33 \text{ kJ/mol};$$

$$G_{\text{HS}^- \text{aq}} = G_{\text{S}_{\text{rombic}}} + 2G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqHS}^- \text{aq}} + G_{\text{OH}^-}) = -85.64 + 2 * 0 - (-169.33 + 77.36) = 6.33 \text{ kJ/mol};$$

$$\text{H}_2\text{S}_{\text{aq}} + 2\text{H}_2\text{O} = \text{S}_{\text{rombic}} + 2\text{H}_3\text{O}^+ + 2\text{e}^-; \text{Kortly, Shucha } 1 < \text{pH} < 7;$$

$$E^\circ_{\text{H}_2\text{S}/\text{S}} = E^\circ - 0.0591/2 * \lg(1/[\text{H}_2\text{O}]^2) + 0.10166 - 0.3982 = 0.142 - 0.02955 * \lg(1/55.3^2) + 0.10166 - 0.3982 = -0.0515 \text{ V};$$

$$\Delta G_{\text{eqH}_2\text{S}} = E^\circ_{\text{H}_2\text{S}/\text{S}} * F * n = -0.0515 * 96485 * 2 = -9.938 \text{ kJ/mol};$$

$$\Delta G_{\text{eqH}_2\text{S}_{\text{aq}}} = G_{\text{S}_{\text{rombic}}} + 2G_{\text{H}_3\text{O}^+} - (G_{\text{H}_2\text{S}_{\text{aq}}} + 2G_{\text{H}_2\text{O}}) = -85.64 + 2 * 22.44 - (-30.82 + 2 * 0) = -9.938 \text{ kJ/mol};$$

$$G_{\text{H}_2\text{S}_{\text{aq}}} = G_{\text{S}_{\text{rombic}}} + 2G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqH}_2\text{S}_{\text{aq}}} + 2G_{\text{H}_2\text{O}}) = -85.64 + 2 * 22.44 - (-9.938 + 2 * 0) = -30.822 \text{ kJ/mol};$$

pKa=7.0 Wikipedia; CRC2010 pKa1=7.05; pKa2=19

$$pK_{a1} = 7.05 \text{ H}_2\text{S} + \text{H}_2\text{O} = \text{HS}^- + \text{H}_3\text{O}^+; K_{\text{eq}1} = K_{a1}/[\text{H}_2\text{O}] = 10^{-(7.05)}/55.3 = 0.000000001612;$$

$$\Delta G_{\text{eq}} = -R * T * \ln(K_{\text{eq}}) = -8.3144 * 298.15 * \ln(0.000000001612) = G_{\text{HS}^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{H}_2\text{S}} + G_{\text{H}_2\text{O}}) = 50.188 \text{ kJ/mol};$$

$$\Delta G_{\text{eq}} = G_{\text{HS}^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{H}_2\text{S}} + G_{\text{H}_2\text{O}}) = -3.072 + 22.44 - (-30.82 + 0) = 50.188 \text{ kJ/mol};$$

$$G_{\text{HS}^-} = \Delta G_{\text{eq}} - G_{\text{H}_3\text{O}^+} + (G_{\text{H}_2\text{S}} + G_{\text{H}_2\text{O}}) = 50.188 - 22.44 + (-30.82 + 0) = -3.072 \text{ kJ/mol};$$

$$pK_{a2} = 19 \text{ HS}^- + \text{H}_2\text{O} = \text{S}^{2-} + \text{H}_3\text{O}^+; K_{\text{eq}2} = K_{a2}/[\text{H}_2\text{O}] = 10^{-(19)}/55.3 = 10^{-(20.74)};$$

$$\Delta G_{\text{eq}} = -R * T * \ln(K_{\text{eq}}) = -8.3144 * 298.15 * \ln(10^{-(20.74)}) = G_{\text{S}^{2-}} + G_{\text{H}_3\text{O}^+} - (G_{\text{HS}^-} + G_{\text{H}_2\text{O}}) = 118.38 \text{ kJ/mol};$$

$$\Delta G_{\text{eq}} = G_{\text{S}^{2-}} + G_{\text{H}_3\text{O}^+} - (G_{\text{HS}^-} + G_{\text{H}_2\text{O}}) = 92.868 + 22.44 - (-3.072 + 0) = 118.38 \text{ kJ/mol};$$

$$G_{\text{S}^{2-}} = \Delta G_{\text{eq}} - G_{\text{H}_3\text{O}^+} + (G_{\text{HS}^-} + G_{\text{H}_2\text{O}}) = 118.38 - 22.44 + (-3.072 + 0) = 92.868 \text{ kJ/mol};$$

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