Nernsta Oks-Red potenciāls un membrānas potenciāls voltos
Oksidēšanās-reducēšanās balansēšana ar Nernsta pus reakcijām

Nernsts saņem Nobeļa Prēmiju ķīmijā 1920. gadā:

Metāls kontaktā ar šķīdumu, reducētāju un oksidētāju rada **elektroda** potenciālu voltos

Elektroķīmisko potenciālu abpus šūnu membrānai veido jonu koncentrācijas gradients $C_{labā\_puse}/C_{kreisā\_puse}$.

Elektroķīmiskas reakcijas šķērsojot membrānu virza E7 klases transporta enzīmi.

Metāla brīvo elektronu gāze atdod elektronus reducēšanās un paņem no oksidēšanās pus reakcijas

Metāla elektrods ir brīvo elektronu avots rezervuārs RedOks pus reakcijām.

Klasificē šādus **elektrodu** veidus:

I veida: lādētu **jonu** un **elektronu** pārnesē cauri fāzu **robežvirsmai**;

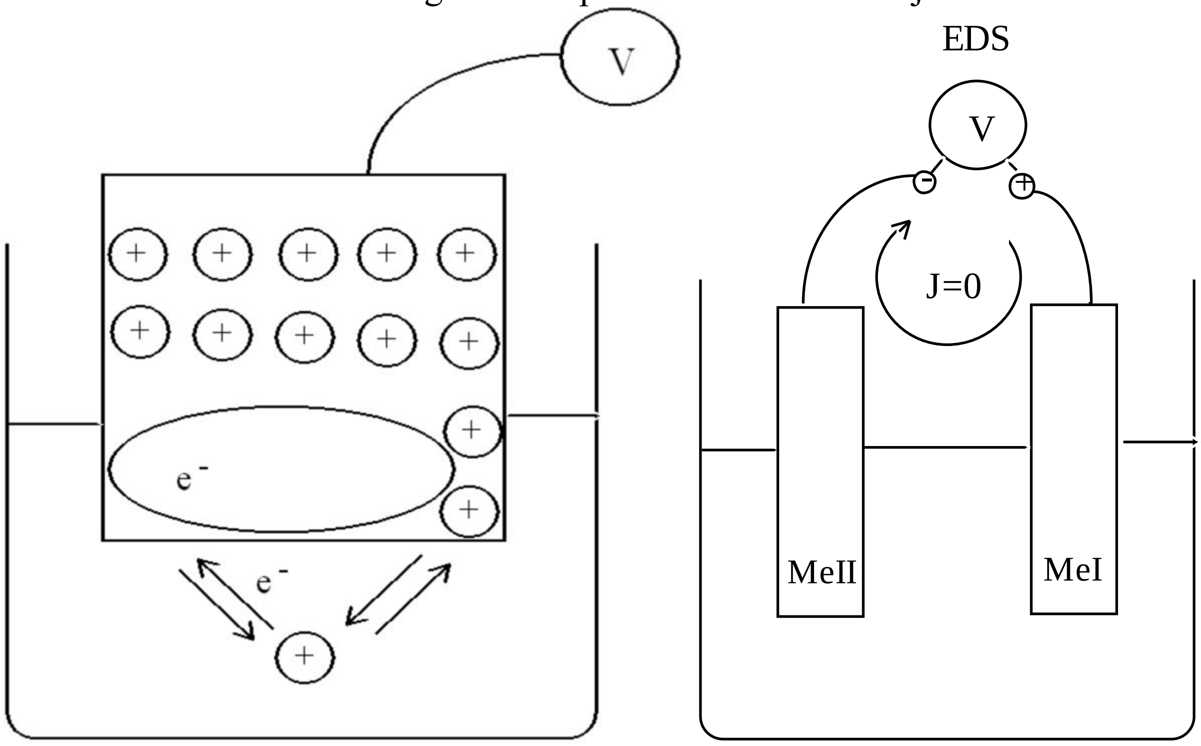
II veida : lādētu **jonu** un **elektronu** pārnesē cauri fāzu **robežvirsmai**;

Red-Oks elektrodi: lādētu **jonu** un **elektronu** pārnesē cauri fāzu **robežvirsmai**;

Membrānas elektrods: : lādētu **jonu** pārnesē cauri šūnu **membrānām** bez **elektroniem**.

Elektroķīmiskajā reakcijā lādētu jonu virzīts gradients cauri **membrānas** kanāliem: veido **membrānas potenciālu E_M.**

Metāla sastāvā ir elektronu **e^-** gāze un + pozitīvi metāla atomu jonu kristāliskais režģis.



Voltmetrs ar mīnus "-" un plus "+" spailēm mēra potenciāla starpību jeb **EDS** (Elektro Dzinēj Spēks) elektriskā ķēdē starp diviem savienotiem elektrodiem **MeI** (**Indikatora**) un **MeII** (**Standarta**):

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

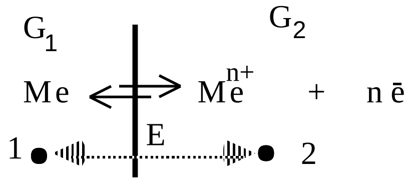
Indikatora elektrods ar **E_I** – ir mijiedarbība ar šķīdumu ,

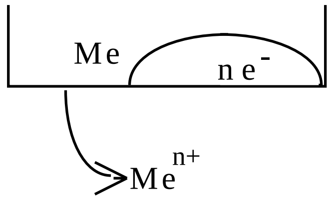
Standarta elektrods ar **E_{II}** = constant – mijiedarbības ar apkārtējo vidi nav.

Pirmā (vienkāršotā) pieeja Nernsta vienādojuma izvedumam.

(Pirmā veida elektrods)

$\Delta G = G_2 - G_1$





$$Red \Longleftrightarrow Ox^{\Delta n+} + n e^-$$

Darbs W viena mola jonu Me^{n+} pārvietošanai no punkta 1 metālā uz punktu 2 šķīdumā ir vienāds ar Hesa likuma brīvās enerģijas izmaiņas negatīvo lielumu $-\Delta G^\circ$ viena mola lādiņam $q = nF$ pārvarot elektrisko potenciālu E ir, $W = qE = nFE$; $W_{darbs} = nFE = -\Delta G^\circ = RT\ln K_{l\bar{\imath}dzsv}$.

Red–Ox līdzsvara konstante ir $K_{l\bar{\imath}dzsv} = \frac{[Ox]\bullet[e^-]^n}{[Red]}$ tātad

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

$$E^\circ = \frac{RT}{F}\bullet\ln([e^-]) \text{ ; } \ln([e^-]) = \frac{E^\circ F}{RT} \text{ ; } [e^-] = e^{\frac{E^\circ F}{RT}} = \text{const un } E^\circ = \text{const.}$$

Nernsta vienādojums naturālā (skaitļa **e=2,7**) logaritma ln un decimālā (skaitļa 10) logaritma lg formā $\ln(a) = \ln(10) \bullet \lg(a) = 2{,}3 \bullet \lg(a)$ un temperatūra ir T=298,15 K gradu:

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

Otrā termodinamiskā pieeja Nernsta vienādojuma izvedumam.

Kad ir iestājies līdzsvars tad izejvielu un produktu ķīmisko potenciālu summa ir vienāda $\mu_{Red}+EnF=\mu_{Ox}+n\mu_{e^-}$ bet katras ķīmiskās vielas ķīmiskais potenciāls ir: $\mu = \Delta G^\circ + RT\ln(N_A)$,

kur N_A ir A vielas koncentrācija molu daļās. ΔG° ir dotās vielas A veidošanās no elementiem brīvā enerģija. Tīru vielu veidošanās no elementiem brīvās enerģijas izmaiņa Hesa likumā ir ΔG°_{Ox} , $\Delta G^\circ_{e^-}$ un ΔG°_{Red} .

Ķīmiskā līdzsvara maisījumā $\Delta G^\circ_{Red} + RT\ln(N_{Red}) + \mathbf{EnF} = \Delta G^\circ_{Ox} + RT\ln(N_{Ox}) + n\Delta G^\circ_{e^-} + RT\ln(N_{e^-})$

No šejienes var izteikt elektroda potenciāla lielumu E:

$$E = \frac{\Delta G^\circ_{Ox} + n\bullet\Delta G^\circ_{e^-} - \Delta G^\circ_{Red}}{nF} + \frac{RT}{nF}\bullet\ln\left(\frac{N_{Ox}\bullet N^n_{e^-}}{N_{Red}}\right).$$

Elektroni savā atsevišķajā fāzē (tā saucamajā elektronu gāzē) metālā tieši arī ir tīra viela $N_{e^-}=1$ tā pēc tīras vielas

$\ln(N_{e^-}{}^{n})=0$ elektronu gāzei un $E=\frac{\Delta G^\circ_{Ox} + n\bullet\Delta G^\circ_{e^-} - \Delta G^\circ_{Red}}{nF} + \frac{RT}{nF}\bullet\ln\left(\frac{N_{Ox}}{N_{Red}}\right)$.

Standarta potenciāls $E^\circ = \frac{\Delta G^\circ_{Ox} + n\bullet\Delta G^\circ_{e^-} - \Delta G^\circ_{Red}}{nF}$ veido Prigožina atraktoru brīvās enerģijas izmaiņas minimumu līdzsvarā $\Delta G_{eq}=E^\circ nF=\Delta G_{eq}=\Delta G^\circ_{Ox}+n\Delta G^\circ_{e^-} - \Delta G^\circ_{Red}$.

Pārejot uz decimāliem logaritmiem un termodinamisko standartu T=298,15 K iegūst Nernsta vienādojums reakcijai : izejvielas **<u>Red</u>**ucētā forma<=>$\mathbf{Ox}^{\Delta n^+}$**+ne⁻** Oksidēto forma produkti; $E=E^\circ+\frac{0{,}0591}{n}\bullet\lg\left(\frac{[Ox]}{[Red]}\right)$.

Reakcijā zaudē $\mathbf{ne^-}$ elektronus tātad šķīduma virzienā tiek pārvietoti $\Delta\mathbf{n^+}$ pozitīvi lādēti papildus joni. Elektroni $\mathbf{ne^-}$ paliek metālā elektronu gāzē. $\Delta\mathbf{n^+}$ lādiņa pārvietošanās sistēmā produktos oksidētajā formā $\mathbf{Ox}^{\Delta n^+}$ienes ķīmiskā potenciāla elektrisko elektrona $\mathbf{ne^-}$ daļu $\mathbf{n\mu_{elektr}=n\Delta G^\circ_{e^-}=-nFE}$, kur $\mathbf{\mu_{elektr} = -FE}$.

I veida elektrods ūdeņraža metāla **H**(**Pt**) robežvirsma / ar tā katjona H_3O^+ šķīdumu pielietojums

Atraktoram pH=7,36 līdzsvara stāvoklī ir patiesa pOH=6.64 vērtība, jo pK_w=14= pH+pOH =7,36 +6.64. Ūdens daudzuma atlaide [H_2O]=963/18=53.5 M litrā sērskābes [H_2SO_4]=[H_3O^+]=1 M šķīduma ar 1.061 $^g/_{mL}$ blīvumu **ūdeņraža elektrodam** Nernsta izteiksmē ir klasiska standarta potenciāla $E_{o\_classic}$=0 V atskaites vērtība:

H(**Pt**)=H^++e^-; $E_{classic}=E_{o\_classic}$+0.0591•log$K°_{classicH(Pt)}$=0+0.0591•log[$H^+$]=0+0.0591•log(1 M)=0 Volti. [11]

Termodinamiska hidroksonija jonu uzskaite pieprasa ūdeni: **H**(**Pt**)+H_2O<=>H_3O^++e^- un $E°_H$=0,10166 V. Attiecība [H_3O^+]/[H_2O]=1 M/52,5 M=X_{H3O+}/X_{H2O} ir mol daļa aizstājot molaritāti [H^+]=1 M klasiskajā potenciāla izteiksmē. Ūdens uzskaite dod termodinamisko standartu $E°_H$=0,10166 V potenciālu skalā.

Nernsta izteiksme ar klasisko mērījumu nulle pieprasa termodinamisko standarta potenciālu $E°_H$=0,10166 V :

$$\mathbf{E}=E°_H+\frac{\ln(10)\bullet R\bullet T}{F\bullet 1}\bullet\log\frac{X_{H_3O^+}}{X_{H_2O}}=E_o+E°_H+0.0591*\log(1/52.5)=0.10166-0.10166=0\ V.$$

Ja attiecība ir viens **1**=$K_{H(Pt)}=X_{H3O+}/X_{H2O}$, tad potenciāls $E°_H$=0,10166 V ir termodinamiskais standarts:

$$\mathbf{E}=E°_H+\frac{\ln(10)\bullet R\bullet T}{F\bullet 1}\bullet\log\frac{X_{H_3O^+}}{X_{H_2O}}=0.10166+0.0591*\log(1)=0.10166\ V.$$

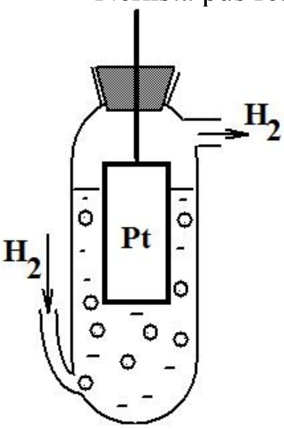
Metāla oksidēšanas brīvās enerģijas izmaiņa ir atšķirīga endoerģiska $\Delta G_{eq}=E°_H$•F•1•1=0.10166*96485*1=9.81 $^{kJ}/_{mol}$ pretstatā Alberty eksoerģiskai. Alberty Hesa vērtība ir eksoerģiska: $\Delta G_{Hess\_eq}=G_{H3O+}+G_{e-}-(G_{H(Pt)}+G_{H2O})$=22,44+0-(**51,05**+0)=**-28,61** $^{kJ}/_{mol}$. Brīvās enerģijas izmaiņa ir noteikta nulles atskaites skalā $G_{H2O}=G_{CO2gas}=G_{e-}$=0 $^{kJ}/_{mol}$. Iteratīvi izskaitļotais absolūtajā skalā ūdeņraža standarta potenciāls ir: $E°_H$= -0,29654 Volti. Līdzsvara brīvās enerģijas minimums ir eksoerģisks: $\Delta G_{eq}=E°_H$•F•1•1=-0,29654*96485*1=**-28,61** $^{kJ}/_{mol}$ sakrītot ar Alberty datiem. Absolūtā potenciālu skala noslīd par ΔE=-0,29654-0,10166= -0,3982 Voltiem zemāk. Nernsta līdzsvara konstante ir lielāka par vienu:

$K_{H(Pt)\_Red}$=[H_3O^+]*[e^-]/[H_2O]/[H(Pt)]=EXP(-$\Delta G_{Alberty}$/R/T)=EXP(**28612**/8.3144/298.15)=102954 .

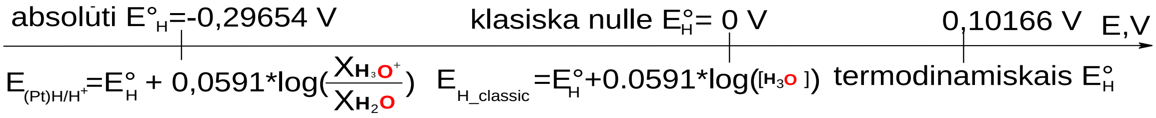
I veida elektrods metāls **H(Pt)** / iegremdēts tā katjonu H_3O^+ šķīdumā pielietojums.

Liela ātruma protolīzes atraktori [H_3O^+]=$10^{-7.36}$ M , pH=7.36 un ūdens masas [H_2O]=997/18=55.3 M uzskaite litrā rāda metāla ūdeņraža stipru reducējošu potenciālu: $E_{pH=7,36}$=-0,29654+0,0591*log($10^{-7,36}$/55,3)= -0,8345 V un brīvās enerģijas izmaiņas minimumu $\Delta G_{eqpH\_7,36}=E°_H$•F•1=-0,8345*96485*1/1000=-80,5 $^{kJ}/_{mol}$.

Nernsta pus reakcijas metāla reducēšanas potenciāla $E°_H$=-0,29654 V enerģija ir ΔG_{eq}=**-28,6** $^{kJ}/_{mol}$.



Platīna plāksnīte iemērkta hidroksonija jonu [H^+]=[H_3O^+]=[H_2SO_4]=1 M sērskābes šķīdumā **H**(**Pt**)=H^++e^-: **E**=**E**°+0.0591•log[H^+]=**0.0**+0.0591•log(1 M)=**0** V ir klasika. Attiecība [H_3O^+]/[H_2O]=1/52.5=X_{H3O+}/X_{H2O} dod klasiskās nulles **0** vietā termodinamisko standarta potenciālu: $E°_H$=0.10166 V un no Alberty datiem absolūtajā skalā absolūto standarta potenciālu $E°_H$=-0,29654 Volti.



Absolūtais standarta potenciāls $E°_H$=-0,29654 V pamatojas uz Alberty ūdeņraža datiem G_{H2gas}=**85,64** $^{kJ}/_{mol}$ un G_{H2aq}=**103,24** $^{kJ}/_{mol}$, kuri ir noteikti ūdens un oglekļa dioksīda gāzes nulles skalā $G_{H2O}=G_{CO2gas}=G_{e-}$=0 $^{kJ}/_{mol}$. Pie pH=7,36 , [H_3O^+]=$10^{-7,36}$ M ir stiprs reducētājs metāls **H(Pt)** ar potenciālu **E**=-0,2965+0,0591*log(10^(-7,36)/55,3)=-0,8345 V. Brīvās enerģijas saturs ir: $G_{H(Pt)}$=**51.05** $^{kJ}/_{mol}$.

Ag+2$NH_{3(aq)}$=Ag$(NH_3)_2^+$+e^-; $E_{Ag/Ag(NH3)2+}=E°_{Ag/Ag(NH3)2+}$+0,0591/1*log $\frac{[Ag(NH_3)_2^+]}{[Ag]\cdot([NH_3]-2\cdot[Ag(NH_3)_2^+])^2}$=

=0,0765+0,0591*log(0,1/1/(0,3-2*0,1)^2)=0,1351 V;

2Ag+2OH^-=Ag_2O(s)+H_2O+2e^-; $E_{2Ag/Ag2O}=E°_{2Ag/Ag2O}$+0,0591/2*log $\frac{[Ag_2O]\cdot[H_2O]}{[Ag]^2\cdot[OH]^2}$ =

=-0,003+0,0591/2*log(1*55,3/1^2/10^(-7*2));

Viela	$\Delta H°_H$ $^{kJ}/_{mol}$	$\Delta S°_H$ $^{J}/_{mol/K}$	$\Delta G°_H$, $^{kJ}/_{mol}$
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**

$G_{Ag}=G_{Ag+}-(\Delta G_{eq\_Ag}+G_{H2O})$= 77,1-(**58,46**+0)=**18,64** $^{kJ}/_{mol}$

$G_{Ag}=G_{AgCl}+G_{H2O}-(\Delta G_{eq\_Ag}+G_{Cl-})$=**45,342** $^{kJ}/_{mol}$

$\Delta G_{AgCl}=\Delta H_H-T*\Delta S_H$=-127,01-298,15*0,09625=**-155,71** $^{kJ}/_{mol}$;

$\Delta G_{Cl-}=\Delta H_H-T*\Delta S_H$=-167,08-298,15*0,0566=**-183,955** $^{kJ}/_{mol}$;

Tabula 1. Nernsta pus reakciju Standarta Electrodu Potenciāli klsikais, termodinamiskais, absolūtais V.

	Reducētā forma = Oksidētā forma + n e^-;	H_2O atlaide klasika nulle E_o	Termodinamiskā. skala 0.10166 V	Absolūtā skala -0.3982 V
H	$H(Pt) + H_2O = H_3O^+ + (Pt) + e^-$; general reference CRC [1]	klasika nulle **0**	**0.10166**	-0,2965
	$H(Pt) + OH^- = H_2O + (Pt) + e^-$; klassika CRC [1]	-0,828	-0,8282	-1,2264
	$H(Pt) + OH^- = H_2O + (Pt) + e^-$; corrected -0,104495	-0.932195	-0,93268	-1,33088
	$H_{2aq} + 2H_2O = 2H_3O^+ + 2e^-$; **grafīta** elektrods	-	-	0,302
O	$6H_2O = O_2^{(g)} + 4 H_3O^+ + 4e^-$	1,2288	+1,48466	1,0865
	$H_2O_2 + 2H_2O = O^-_{2aqua} + 2H_3O^+ + e^-$	1,2764	+1,58416	1,0829
	$4H_2O = H_2O_2 + 2 H_3O^+ + 2e^-$; Suchotina [17]	1,776	+2,08366	1,6855
	$H_2O_{2aqua} + 2H_2O = O_{2aqua} + 2H_3O^+ + 2e^-$ University Alberta	0,6945	0,8477	0,4495
	$HOO^- + H_2O = O_{2aqua} + H_3O^+ + 2e^-$; Kaksis	-	-	0,07587
N	$NO_2^- + 2OH^- = NO_3^- + H_2O + 2e^-$; pH>3,15 Suchotina [17]	0.01	0,0602	-0,3380
	$HNO_2 + 4H_2O = NO_3^- + 3H_3O^+ + 2e^-$; pH<3,15 Kortly, Shucha	0.94	1,2477	0,8495
	$NO_{aq} + 6H_2O = NO_3^- + 4H_3O^+ + 3e^-$; pH>3,15 Kortly, Shucha	0.96	1,2677	0,8695
	$NH_4^+ + 13H_2O = NO_3^- + 10H_3O^+ + 8e^-$; Suchotina	0,87	1,4180	1,0198
Br	$2Br^- = Br_2(aq) + 2e^-$; CRC [1]	1,0873	1,18896	0,79076
Bi	$BiO^+ + 6H_2O = BiO_3^- + 4H_3O^+ + 2e^-$; Suchotina	1,80	2,210645	1,812445
Mn H^+	$Mn^{2+} + 12H_2O = MnO_4^- + 8H_3O^+ + 5e^-$; Kortly, Shucha [18]	1,51	1,858848	1,460648
H_2O	$MnO_2\downarrow + 4OH^- = MnO_4^- + 2H_2O + 3e^-$; Suchotina	0,603	0,635997	0,237797
OH^-	$MnO_4^{2-} = MnO_4^- + e^-$; Suchotina [17]	0,558	0,65966	0,26146
Pb	$Pb^{2+} + 6H_2O = PbO_2(s) + 4H_3O^+ + 2e^-$; Kortly, Shucha	1.455	1,8656	1,4674
	$Pb + H_2O = Pb^{2+} + 2e^-$; pH<7 Kortly, Shucha	-0,126	0,0272	-0,3710
S	$H_2SO_3 + 4H_2O = HSO_4^- + 3H_3O^+ + 2e^-$; Suchotina pH<1,9	0,172	0,47965	0,08145
S	$HSO_3^- + 4H_2O = SO_4^{2-} + 3H_3O^+ + 2e^-$; Suchotina 2=<pH<7	0,172	0,47965	0,08145
	$SO_3^{2-} + 2OH^- = SO_4^{2-} + H_2O + 2e^-$; Suchotina pH > 7	-0,93	-0,87984	-1,27804
	$S^{2-} = S_{rombisks} + H_2O + 2 e^-$; CRC 2010	-0,4763	-0,3746	-0,7728
	$HS^- + OH^- = S_{rombisks} + 2H_2O + 2e^-$; CRC 2010	-0,478	-0,4793	-0,8775
	$H_2S_{aq} + 2H_2O = S_{rombisks} + 2H_3O^+ + 2e^-$; CRC 2010:Kortly,Shucha	0,142	0,3467	-0,0515
	$2S_2O_3^{2-} = S_4O_6^{2-} + 2e^-$; Suchotina	0,08	0,18166	-0,2165
Fe	$Fe^{2+} = Fe^{3+} + e^-$; Suchotina	0,769	0,8717	0,4735
	$Fe_{(s)} + H_2O = Fe^{2+} + 2e^-$; Suchotina	-0,4402	-0,2870	-0,6852
Ag	$Ag + H_2O = Ag^+ + e^-$; Kortly, Shucha [18]	0,7994	1,0041	0,6059
	$Ag(s) + Cl^- = AgCl(s) + H_2O + e^-$; Kortly, Shucha	0,2223	0,2210	-0,1772
	$Ag + 2NH_{3(aq)} = Ag(NH_3)_2^+ + e^-$; Suchotina	0,373	0,4747	0,0765
	$2Ag + 2OH^- = Ag_2O(s) + H_2O + 2e^-$; Suchotina	0,345	0,3952	-0,0030
Hg	$2Hg + H_2O = Hg_2^{2+} + 2e^-$; Kortly, Shucha [18]	0,907	1,0602	0,6620
	$2Hg + 2Cl^- = Hg_2Cl_{2(s)} + 2H_2O + 2e^-$; Suchotina ; [17]	0,2676	0,2663	-0,1319
	$2Hg + SO_4^{2-} = Hg_2SO_{4(s)} + 2e^-$; Kortly, Shucha ; [18]	0,614	0,7157	0,3175
	$Hg + 2OH^- = HgO + 2H_2O + 2e^-$, Suchotina ; [17]	0,098	0,0967	-0,3015
I	$3I^- = I_3^- + 2e^-$; Kortly, Shucha	0,6276	0,72926	0,33106
Cu	$Cu(Hg) + H_2O = Cu^{2+} + (Hg) + 2e^-$; 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	$Cl_2(g) + 4H_2O = 2HOCl + 2H_3O^+ + 2e^-$; Kortly, Shucha	1,63	1,93765	1,53945
Cr	$2Cr^{3+} + 21H_2O = Cr_2O_7^{2-} + 14H_3O^+ + 6e^-$; Kortly, Shucha	1,33	1,7921	1,3939
	$Cr^{3+} + 11H_2O = HCrO_4^- + 7H_3O^+ + 3e^-$; Kortly, Shucha	1,20	1,6793	1,2811
	$Cr(OH)_3\downarrow + 5OH^- = CrO_4^{2-} + 4H_2O + 3e^-$; pH>9 ; Suchotina	-0,13	-0,1657	-0,5639
C	$H_2C_2O_4 + 2H_2O = 2CO_2 + 2H_3O^+ + 2e^-$; Suchotina	-0,49	-0,28534	-0,6835
Cr	$Cr + H_2O = Cr^{3+} + 3e^-$; Suchotina	-0,744	-0,6080	-1,0062
Zn	$Zn + H_2O = Zn^{2+} + 2e^-$; Kortly, Shucha	-0,7628	-0,6096	-1,0078
Al	$Al + H_2O = Al^{3+} + 3e^-$; CRC	-1,662	-1,5260	-1,9242
	$Al + 4OH^- = H_2AlO_3^- + H_2O + 3e^-$; CRC	-2,33	-2,2627	-2,6609

$E°_{Hg}$=**-1,2264** V; $H(Pt) + OH^- = H_2O + (Pt) + e^-$; Nernsta absolūtais standarta potenciāls koriģēts $E°_{Hg}$=**-1,33088** V [1]
Ūdens daudzuma atlaide [H_2O]=963/18=53.5 M litrā sērskābes [H_2SO_4]=[H_3O^+]=1 M šķīduma ar 1.061 g/mL blīvumu **ūdeņraža elektrodam** Nernsta izteiksmē ir klasiska standarta potenciāla $E_{o\_classic}$=-0,8277 V:

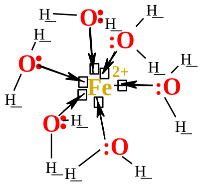
$E°_{H\_H\_OH^-}$=E°-0,0591/1*lg([H_2O]^1) +0,10166-0,3982=-0,8277-0,0591/1*lg(53,5^1) +0,10166-0,3982=**-1,2264** V;

$\Delta G_{eq\_H\_OH^-}$=$E°_{H\_H\_OH^-}$•F•1=**-1,2264***96485*1=**-118,33** kJ/mol,

$\Delta G_{eq\_H\_OH^-}$=G_{H_2O}-($G_{H(Pt)}$+G_{OH^-})=**0-(51,05+77,36)=-128,41** kJ/mol;

Koriģēts $\Delta G_{eq\_H\_OH^-}$=$E°_{H\_H\_OH^-}$•F•1=**-1,33088***96485*1=**-128,41** kJ/mol, Metāls iegremdēts savu jonu šķīdumā Nernsta oksidēšanas pus reakcijā veido Elektroda potenciālu Voltos. Metālu joni koordinējas šķīdumā. piesaistot ūdeni ar donoru akceptoru saitēm .

Reakcijā $Fe_{(s)}+H_2O=Fe^{2+}+\mathbf{2e^-}$. $[Fe^{2+}]$=0,1 M; blīvums 1,03 g/mL; 0,1 Mola masa $FeSO_4$=15,191 g/mol;



$E_{Fe}=E°_{Fe}+0,0591/2*\log([Fe^{2+}]/[Fe]/([H_2O]))=-0,6852+0,0591/2*\log(0,1/1/(55,3))=-0,76625$ V;

Atšķirības skaitlī -0,76625 V ir ceturtajā zīmē -0,7663 V

$$E_{Fe}=E°_{Fe}+0,0591/2*\log\frac{[Fe^{2+}]}{[Fe]\cdot([H_2O]-6[Fe^{2+}])} = -0,7663 \text{ V};$$

$E_{Fe}=E°_{Fe}+0,0591/2*\log([Fe^{2+}]/[Fe]/([H_2O]-6[Fe^{2+}]))=-0,6852+0,0591/2*\log(0,1/1/(56,38-0,6))=-0,7663$ V;

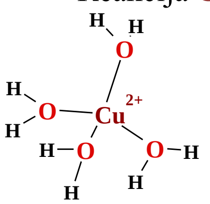
$[H_2O]=55,3\text{ M}=\frac{996\_g/L}{18\_g/mol}$; $m_{H_2O}=m_L-m_{FeSO_4}$=1030-15,191=1284,8 g; $[H_2O]$=1014,8 g/18 g/mol=56,38 M.

$\Delta \mathbf{G_{eq}}{}_{\_Fe}=E°_{Fe}•F•2=\mathbf{-0,6852}*96485*2=\mathbf{-132,223}$ kJ/mol, $\Delta \mathbf{G_{eq}}{}_{\_Fe}=G_{Fe^{2+}}-(G_{Fe}+\mathbf{G_{H_2O}})=\mathbf{-82,14}-(G_{Fe}+0)=\mathbf{-132,223}$ kJ/mol ;

$G_{Fe}=G_{Fe^{2+}}-(\Delta \mathbf{G_{eq}}{}_{\_Fe}+\mathbf{G_{H_2O}})=\mathbf{-82,14}-(\mathbf{-132,223}+0)=\mathbf{50,08}$ kJ/mol ;

Viela	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$, kJ/mol	
Fe	-	-	**50,08**	$G_{Fe}=G_{Fe^{2+}}-(\Delta \mathbf{G_{eq}}{}_{\_Fe}+\mathbf{G_{H_2O}})=\mathbf{-82,14}-(\mathbf{-132,223}+0)=\mathbf{50,08}$ kJ/mol;
Fe^{2+}	**-87,45**	**-17,8**	**-82,14**	**BioThermodynamic 2006**
Fe^{2+}	-89,1	-137,7	-78,9	
Fe^{3+}	**-44,79**	**-110**	**-11,99**	
Fe^{3+}	-48,5	-315,9	-4,7	**CRC 2010**
Cu	-	-	**113,03**	$G_{Cu}=G_{Cu^{2+}}-(\Delta \mathbf{G_{eq}}{}_{\_Cu}+\mathbf{G_{H_2O}})=\mathbf{113,03}$ kJ/mol ;
Cu^{2+}	64,8	-98	**94,0187**	$\Delta G_{Cu^{2+}}=\Delta H_H-T*\Delta S_H$=64,8-298,15*-0,098=**94,0187** kJ/mol;
Zn	-	-	**73,82**	$G_{Zn}=G_{Zn^{2+}}-(\Delta \mathbf{G_{eq}}{}_{\_Zn}+\mathbf{G_{H_2O}})=\mathbf{-120,653}-(\mathbf{-194,475}+0)=\mathbf{73,82}$ kJ/mol;
Zn^{2+}	-153,39	-109,8	**-120,653**	$\Delta G_{Zn^{2+}}=\Delta H_H-T*\Delta S_H$=-153,39-298,15*-0,1098=**-120,65** kJ/mol;
Ag+	-	-	77,1	CRC;
AgCl	-	-	**-155,71**	**BioThermodynamic 2006**
Cl-	-	-	**-183,955**	**BioThermodynamic 2006**
Ag	$E°_{Ag/AgCl}$=	**-0,1772 V**	**45,342**	$G_{Ag}=G_{AgCl}+\mathbf{G_{H_2O}}-(\Delta \mathbf{G_{eq}}{}_{\_Ag}+G_{Cl^-})=\mathbf{45,342}$ kJ/mol;
Ag	$E°_{Ag}$=	0,6059 V	**18,64**	$G_{Ag}=G_{Ag^+}-(\Delta \mathbf{G_{eq}}{}_{\_Ag}+\mathbf{G_{H_2O}})$= 77,1-(**58,46**+0)=**18,64** kJ/mol ;

Reakcijā $Cu(Hg)+H_2O=Cu^{2+}+(Hg)+\mathbf{2e^-}$; $[Cu^{2+}]$=1 M blīvums 1,19 g/mL; 1 Mola masa M_{CuSO_4}=159,602 g/mol;



$E_{Cu}=E°_{Cu}+0,0591/2*\log([Cu^{2+}]/[Cu]/([H_2O]))=0,0985+0,0591/2*\log(1/1/(55,3))=0,047002$ V;

Atšķirības skaitlī 0,047002 V ir otrajā zīmē 0,04696 V

$$E_{Cu}=E°_{Cu}+0,0591/2*\log\frac{[Cu^{2+}]}{[Cu]\cdot([H_2O]-4\cdot[Cu^{2+}])}=0,04696 \text{ V};$$

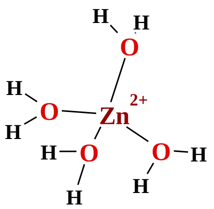
$m_{H_2O}=(m_L-m_{CuSO_4})/18$=1190-159,602=1030,4/18=57,24-4=53,24 mol;

$E_{Cu}=E°_{Cu}+0,0591/2*\log([Cu^{2+}]/[Cu]/([H_2O]-4[Cu^{2+}]))=0,0985+0,0591/2*\log(1\text{ M}/1/(57,24-4))=0,04696$ V;

$\Delta \mathbf{G_{eq}}{}_{\_Cu}=E°_{Cu}•F•2=\mathbf{-0,0985}*96485*2=\mathbf{-19,01}$ kJ/mol, $\Delta \mathbf{G_{eq}}{}_{\_Cu}=G_{Cu^{2+}}-(G_{Fe}+\mathbf{G_{H_2O}})=\mathbf{94,0187}-(G_{Cu}+0)=\mathbf{-19,01}$ kJ/mol ;

$G_{Cu}=G_{Cu^{2+}}-(\Delta \mathbf{G_{eq}}{}_{\_Cu}+\mathbf{G_{H_2O}})=\mathbf{94,0187}-(\mathbf{-19,01}+0)=\mathbf{113,03}$ kJ/mol ;

$Zn+H_2O=Zn^{2+}+\mathbf{2e^-}$; $ZnSO_4$=161,44 g/mol $[Zn^{2+}]=C_{ZnSO_4}$=2 M density 1,31 g/mL ; m_{ZnSO_4}=2*161,44=322,88 g;



$E_{Zn}=E°_{Zn}+0,0591/2*\log([Zn^{2+}]/[Zn]/([H_2O]))=-1,0078+0,0591/2*\log(2/1/(55,3))=-1,0504$ V;

Atšķirības skaitlī -1,0504 V ir trešajā zīmē -1,04827 V 2M;

$$E_{Zn}=E°_{Zn}+0,0591/2*\log\frac{[Zn^{2+}]}{[Zn]\cdot([H_2O]-4\cdot[Zn^{2+}])} = -1,04827 \text{ V};$$

Šķīdība 57,7 g/100g simts gramos ūdens; w%=57,7/157,7*100=36,6%;

$m_{H_2O}=m_L-m_{ZnSO_4}$=1310-161,44*2=987,12 g; m_{ZnSO_4}=2*161,44=g; $[H_2O]$=987,12 g/18 g/mol=54,84 M.

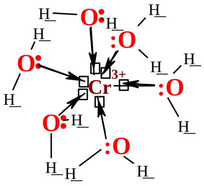
$E_{Zn}=E°_{Zn}+0,0591/2*\log\frac{[Zn^{2+}]}{[Zn]\cdot([H_2O]-4\cdot[Zn^{2+}])}=\mathbf{-1,0078}+0,0591/2*\log(2/1/(54,84-4*2))=-1,04827$ V;

$\Delta \mathbf{G_{eq}}{}_{\_Zn}=E°_{Zn}•F•2=\mathbf{-1,0078}*96485*2=\mathbf{-194,475}$ kJ/mol,

$\Delta \mathbf{G_{eq}}{}_{\_Zn}=G_{Zn^{2+}}-(G_{Fe}+\mathbf{G_{H_2O}})=\mathbf{-120,653}-(G_{Cu}+0)=\mathbf{-194,475}$ kJ/mol ;

$G_{Zn}=G_{Zn2+}$**-(**Δ**G_{eq_Zn}+G_{H2O}**)=**-120,653-(-194,475**+0)=**73,82** $^{kJ}/_{mol}$;

$Cr+H_2O=Cr^{3+}+3e^-$; $Cr_2(SO_4)_2$=159,602 g/mol; $C_{Cr2(SO4)2}$=0,5 M$[Cr^{3+}]=2*C_{Cr2(SO4)2}$=1 M density 1,172 g/mL ;



$E_{Cr}=E°_{Cr}+0{,}0591/3*\log([Cr^{3+}]/[Cr]/([H_2O]))=-1{,}0062+0{,}0591/3*\log(1/1/(55{,}3))=-1{,}04053$ V;

Atšķirības skaitlī -1,04053 V ir trešajā zīmē -1,03936 V 1M; 2,32 M -1,027 V

$$E_{Cu}=E°_{Cu}+0{,}0591/2*\log\frac{[Cr^{3+}]}{[Cr]\cdot([H_2O]-6\cdot[Cr^{3+}])}=-1{,}03936\ V;$$

$m_{H2O}=m_L-m_{Cr2(SO4)2}$=1172-196,08=975,92 g; $m_{Cr2(SO4)3}$=392,16/2=196,08;

$[Cr^{3+}]=2*C_{Cr2(SO4)2}$=1 M density 1,172 g/mL ; $m_{Cr2(SO4)3}$=196,08g; $[H_2O]$=975,92 g/18 g/mol=54,21778 M

$$E_{Cr}=E°_{Cr}+0{,}0591/3*\log\frac{[Cr^{3+}]}{[Cr]\cdot([H_2O]-6\cdot[Cr^{3+}])}=-1{,}0062+0{,}0591/3*\log(1/1/(54{,}21778-6*1))=-1{,}03936\ V;$$

Šķīdība 64 g/100g simts gramos ūdens; w%=64/164*100=39%

39/100g=X/??1172//g/L; 39/100*1172=457,07=X/g/L; $C_{Cr2(SO4)2}$=457,07/392,16=1,1655 M $Cr_2(SO_4)_3$;

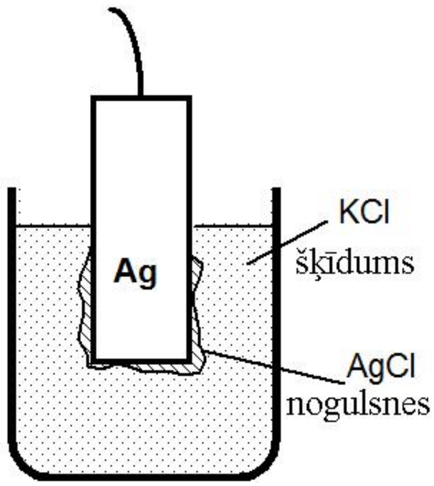
$m_{H2O}=m_L-m_{Cr2(SO4)2}$=??1172??-457,07=714,93 g; $m_{Cr2(SO4)2}$=457,07g; $[H_2O]$=714,93 g/18 g/mol=39,718 M

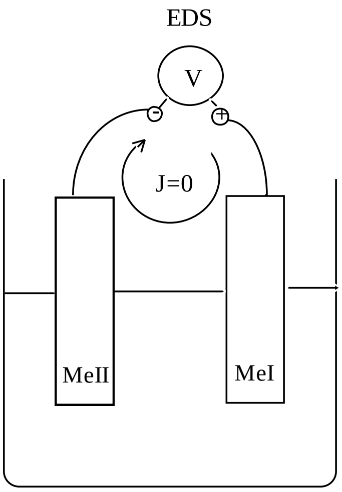
$$[H_2O]=714{,}93\ g/18\ g/mol=39{,}718\ M;\ E_{Cr}=E°_{Cr}+0{,}0591/3*\log\frac{[Cr^{3+}]}{[Cr]\cdot([H_2O]-6\cdot[Cr^{3+}])}=$$

$$=-1{,}0062+0{,}0591/3*\log(2*1{,}1655/1/(39{,}718-6*2*1{,}1655))=-1{,}027\ V;$$

Metāls/tā nešķīstošā sāls/jons II-tipa elektrods

Sudraba /sudraba hlorīds/hlorīda jons būvēts no sudraba metāla, AgCl nešķīstošās sāls nogulsnēm .





K^+Cl^- šķīduma ar AgCl pret joniem Cl^- nešķīstošajā sālī. Nernsta pus reakcijas sudraba metālam Ag. Elektriskā potenciala mērījumi voltos ar elektrodu pāri ir **E**lektro **D**zinēja **S**pēks EDS volti. Starp diviem elektrodiem MeI (indikatora elektrodu) un un MeII (salīdzināšanas elektrodu) savienotiem noslēgtā elektriskā ķēdē aprēķina MeI indikatora elektroda potenciālu EI kā summu:

EI = EDS + EII.

Indikatora elektrodu EI – ietekmē šķīduma reaktivitāte - pētāmais elektrods. Standarta salīdzināšanas elektrods ir EII= konstants , jo hlorīda koncentrācija konstanta.

Ag(s)+H_2O=**Ag**$^+$+e$^-$; absolūtais standarta potenciāls $E°_{Ag}$=0,6059 V; Kortly, Shucha ; [18]

$E_{Ag}=E°_{Ag}+0{,}0591\bullet\log([Ag^+]/[Ag(s)]/[H_2O])=0{,}6059+0{,}0591*\log([Ag^+]/55{,}3)$;

$\Delta G_{eq\_Ag}=E°_{Ag}\bullet F\bullet 2=0{,}6059*96485*1=$ **58,46** kJ/mol,

$\Delta G_{eq\_As}=G_{Ag+}-(G_{Ag}+G_{H2O})=77{,}1-(G_{Ag}+0)=$ **58,46** kJ/mol ;

$G_{Ag}=G_{Ag+}-(\Delta G_{eq\_Ag}+G_{H2O})=77{,}1-(58{,}46+0)=$ **18,64** kJ/mol ;

Šķīdības līdzsvars **Ag**Cl(s)+2H_2O=**Ag**$^+$+Cl$^-$; **Ag**Cl(s)+2H_2O-Cl$^-$=**Ag**$^+$; un absolūtā konstante :

$K_{AbsoluteAgCl}=K_{spAgCl}/[H_2O]^{\wedge 2}=[Ag^+]*[Cl^-]/[AgCl(s)]/[H_2O]^{\wedge 2}=1{,}77*10^{\wedge(-10)}/55{,}3^{\wedge}2=5{,}79*10^{-14}$;

Ag(s)+H_2O=**Ag**$^+$+e$^-$; **Ag**(s)+H_2O+Cl$^-$ = **Ag**Cl(s)+2H_2O+e$^-$;

Ag(s)+Cl$^-$ =**Ag**Cl(s)+H_2O+e$^-$; $E°_{AgCl}$=-0,1772 V [18]; $[Cl^-]$=0,1 M=$[K^+Cl^-]$ kālija hlorīda 0,1 M šķīdums;

$E_{ag/AgCl}=E°_{AgCl}+0{,}0591\bullet\log([AgCl(s)]*[H_2O]/[Ag(s)]/[Cl^-])=-0{,}1772+0{,}0591*\log(1*55{,}3/1/[Cl^-])=$

$=-0{,}1772+0{,}074205-0{,}0591*\log([Cl^-])=-0{,}102995=-0{,}0591*\log([Cl^-])=-0{,}102995-0{,}0591*\log(0{,}1)=-0{,}043895$ V;

$E_{ag/AgCl}=E_{oAgCl}+0{,}0591\bullet\log([AgCl(s)]*[H_2O]/[Ag(s)]/[Cl^-])=-0{,}102995-0{,}0591*\log([Cl^-])$;

$\Delta G_{eq\_Ag}=E°_{Ag}\bullet F\bullet 2=-0{,}1772*96485*1=$ **-17,097** kJ/mol,

$\Delta G_{eq\_As}=G_{AgCl}+G_{H2O}-(G_{Ag}+G_{Cl})=$ **-155,71**+0-(G_{Ag}**-183,955**)=**-17,097** kJ/mol ;

$G_{Ag}=G_{AgCl}+G_{H2O}-(\Delta G_{eq\_Ag}+G_{Cl-})=$ **-155,71**+0-(**-17,097-183,955**)=**45,342** kJ/mol ;

Praksē II-tipa elektrodi ir salīdzināšanas elektrodi, jo potenciāla lielumu nosaka vienīgi hlorīda jonu koncentrācija. Hlorīda koncentrācija ir precīzi kontrolēta instrumentālo pielietojumu tehnoloģijās.

Nernsta potenciāla studijas $\underline{Hg}/Hg_2^{2+}/Hg^{2+}$, Hg_2Cl_2, $Hg_2SO_{4(s)}$, HgO uzskaitot hidroksoniju H_3O^+ un ūdeni H_2O.

Viela	$\Delta H°_H$, kJ/mol	$\Delta S°_H$, J/mol/K	$\Delta G°_H$, kJ/mol
$\underline{Hg}$	-	75,9	**40,67**
Hg_2^{2+}	-166,87	66,74	-146,8
Hg_2^{2+}	$E°_{Hg/Hg22+}$=	**-0,6620** V	**209,09**
Hg^{2+}	-170,21	-36,19	-
$Hg_2SO_{4(s)}$	-743,1	200,7	-625,8
$Hg_2SO_{4(s)}$	$K_{Absolute\mathbf{Hg2}SO4}$=	$10^{\wedge(-9,673)}$	**-593,87**
SO_4^{2-}	**-907,62**	**-536,2**	**-747,75**
SO_4^{2-}	$E°_{Hg2SO4}$=	**0,3175** V	**-736,48**
SO_4^{2-}	-909,3	20,1	-744,5
$Hg_2Cl_{2(s)}$	-265,37	191.6	-210,7
$Hg_2Cl_{2(s)}$	$K_{Absolute\mathbf{Hg2}Cl2}$=	$10^{\wedge(-23,1)}$	**-210,7**
$HgCl_{2(s)}$	-224,3	146	-178,6
Cl-	-167,08	56,6	**-183.955**
Cl-	$E°_{HgCl2}$=	**-0,1319** V	**33,975**
$HgO_{(s)}$	-99,79	70,25	-
$HgO_{(s)}$	-90,8	70,3	-58,5

$(E°_{H2O2aqRed}-E°_{HgO})=(0.4495+\mathbf{0.3015})$ V

$G_{\mathbf{Hg}}=G_{eqRedOx\_2H2O2}-\mathbf{G}_{O2aqua}+(G_{HO}+\mathbf{G}_{H2O2})=\mathbf{40.67}$ kJ/mol;

$G_{Hg22+}=\Delta\mathbf{G}_{eq\_Hg}+(2G_{Hg}+\mathbf{G}_{H2O})=\mathbf{127.75}+(2*\mathbf{40.67}+\mathbf{0})=\mathbf{209.09}$ kJ/mol;

$G_{Hg2SO4}=G_{\mathbf{Hg22+}}+G_{SO42-}-(\Delta\mathbf{G}_{eq Hg2SO4}+\mathbf{2G}_{H2O})=\mathbf{-593.87}$ kJ/mol;

$G_{SO4}=G_{Hg2SO4}-(2G_{Hg}+\Delta\mathbf{G}_{eq\_Hg2SO4})=\mathbf{-736.48}$ kJ/mol ;

$G_{Hg2Cl2}=G_{\mathbf{Hg22+}}+\mathbf{2G}_{Cl-}-(\Delta\mathbf{G}_{eq Hg2Cl2}+\mathbf{3G}_{H2O})=\mathbf{-210.7}$ kJ/mol;

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

$G_{Cl-}=(-G_{\mathbf{Hg22+}}+\Delta\mathbf{G}_{eq Hg2Cl2}+(G_{Hg2Cl2}+\mathbf{3G}_{H2O}))/2=\mathbf{33.975}$ kJ/mol;

$2\underline{Hg}+H_2O=Hg_2^{2+}+2e^-$; absolūtais standarta potenciāls $E°_{Hg}=\mathbf{0,6620}$ V; Kortly, Shucha ; [18]

$E°_{Hg}=E°-0,0591/2*\lg(1/[H_2O]^1)+0,10166-0,3982=0,907-0,0591/2*\lg(1/55,3^{\wedge1})+0,10166-0,3982=\mathbf{-0,6620}$ V;

$\Delta\mathbf{G}_{eq\_Hg}=E°_{Hg}\bullet F\bullet 2=\mathbf{0,6620}*96485*2=\mathbf{127,75}$ kJ/mol,

$\Delta\mathbf{G}_{eq\_Hg}=G_{Hg22+}-(2G_{Hg}+\mathbf{G}_{H2O})=G_{Hg22+}-(2*\mathbf{40,67}+\mathbf{0})=\mathbf{127,75}$ kJ/mol ;

$G_{Hg22+}=\Delta\mathbf{G}_{eq\_Hg}+(2G_{Hg}+\mathbf{G}_{H2O})=\mathbf{127,75}+(2*\mathbf{40,67}+\mathbf{0})=\mathbf{209,09}$ kJ/mol ;

Šķīdības līdzsvara $Hg_2Cl_{2(s)}+3H_2O=\mathbf{Hg_2}^{2+}+2Cl^-$; $2\underline{Hg}+H_2O=Hg_2^{2+}+2e^-$; absolūtā konstante :

$K_{Absolute\mathbf{Hg2}Cl2}=K_{sp\mathbf{Hg2}Cl2}/[H_2O]^{\wedge3}=[\mathbf{Hg_2}^{2+}]*[Cl^-]^2/[Hg_2Cl_{2(s)}]/[H_2O]^{\wedge3}=1,43*10^{\wedge(-18)}/55,3^{\wedge}3=10^{-23,1}$;

$\Delta\mathbf{G}_{eq\mathbf{Hg2}Cl2}=\mathbf{-R\bullet T\bullet ln}(K_{Absolute\mathbf{Hg2}Cl2})=\mathbf{-8,314*298,15*ln}(10^{\wedge(-23,1)})=\mathbf{131,85}$ kJ/mol;

$\Delta\mathbf{G}_{eq Hg2Cl2}=G_{\mathbf{Hg22+}}+\mathbf{2G}_{Cl-}-(G_{Hg2Cl2}+\mathbf{3G}_{H2O})=\mathbf{-146,8+2G}_{Cl-}-(-210,7+3*\mathbf{0})=\mathbf{131,85}$ kJ/mol;

$\mathbf{G}_{Cl-}=(-G_{\mathbf{Hg22+}}+\Delta\mathbf{G}_{eq Hg2Cl2}+(G_{Hg2Cl2}+\mathbf{3G}_{H2O}))/2=(\mathbf{--146,8+131,9}+(-210,7+3*\mathbf{0}))/2=\mathbf{33,975}$ kJ/mol;

$\Delta\mathbf{G}_{eq Hg2Cl2}=G_{\mathbf{Hg22+}}+\mathbf{2G}_{Cl-}-(G_{Hg2Cl2}+\mathbf{3G}_{H2O})=\mathbf{209,09+2*-143,945}-(G_{Hg2Cl2}+3*\mathbf{0})=\mathbf{131,85}$ kJ/mol;

$G_{Hg2Cl2}=G_{\mathbf{Hg22+}}+\mathbf{2G}_{Cl-}-(\Delta\mathbf{G}_{eq Hg2Cl2}+\mathbf{3G}_{H2O})=\mathbf{209,09+2*-143,945-(131,9}+3*\mathbf{0})=\mathbf{-210,7}$ kJ/mol;

$2\underline{Hg}+2Cl^-=Hg_2Cl_{2(s)}+2H_2O+2e^-$; absolūtais standarta potenciāls $E°_{HgCl2}=\mathbf{-0,1319}$ V; Suchotina ; [18]

$E°_{HgCl2}=E°-0,0591/2*\lg([H_2O]^2)+0,10166-0,3982=0,2678-0,0591/2*\lg(55,3^{\wedge2})+0,10166-0,3982=\mathbf{-0,1319}$V;

$\Delta\mathbf{G}_{eq\_Hg2Cl2}=E°_{Hg2Cl2}\bullet F\bullet 2=\mathbf{-0,1319}*96485*2=\mathbf{-25,45}$ kJ/mol,

$\Delta\mathbf{G}_{eq\_Hg2Cl2}=G_{Hg2Cl2}+\mathbf{2G}_{H2O}+\mathbf{2G}_{Cl-}-(2G_{Hg})=G_{Hg2Cl2}+\mathbf{2*0+2*34}-(2*\mathbf{40,67})=\mathbf{-25,45}$ kJ/mol ;

????? $G_{Hg2Cl2}=\Delta\mathbf{G}_{eq\_Hg2Cl2}-\mathbf{2G}_{H2O}-\mathbf{2G}_{Cl-}+(2G_{Hg})=\mathbf{-25,45-2*0-2*34}+(2*\mathbf{40,67})=\mathbf{-12,11}$ kJ/mol ;

Šķīdības līdzsvars $Hg_2SO_{4(s)}+2H_2O=\mathbf{Hg_2}^{2+}+SO_4^{2-}$; $2\underline{Hg}+2H_2O=Hg_2^{2+}+2e^-$; un absolūtā konstante :

$K_{Absolute\mathbf{Hg2}SO4}=K_{sp\mathbf{Hg2}SO4}/[H_2O]^{\wedge2}=[\mathbf{Hg_2}^{2+}]*[SO_4^{2-}]/[Hg_2SO_{4(s)}]/[H_2O]^{\wedge2}=6,5*10^{\wedge(-7)}/1/55,3^{\wedge}2=10^{--9,673}$;

$\Delta\mathbf{G}_{eq\mathbf{Hg2}SO4}=\mathbf{-R\bullet T\bullet ln}(K_{Absolute\mathbf{Hg2}SO4})=\mathbf{-8,314*298,15*ln}(10^{\wedge(-9,673)})=\mathbf{55,21}$ kJ/mol;

$\Delta\mathbf{G}_{eq Hg2SO4}=G_{\mathbf{Hg22+}}+\mathbf{G}_{SO42-}-(G_{Hg2SO4}+\mathbf{2G}_{H2O})=\mathbf{209,09-747,75}-(G_{Hg2SO4}+2*\mathbf{0})=\mathbf{55,21}$ kJ/mol;

$G_{Hg2SO4}=G_{\mathbf{Hg22+}}+\mathbf{G}_{SO42-}-(\Delta\mathbf{G}_{eq Hg2SO4}+\mathbf{2G}_{H2O})=\mathbf{209,09-747,75-(55,21}+2*\mathbf{0})=\mathbf{-593,87}$ kJ/mol;

$Hg_2SO_{4(s)}+2H_2O=\mathbf{Hg_2}^{2+}+SO_4^{2-}$; $2\underline{Hg}+2H_2O=\mathbf{Hg_2^{2+}}+2e^-$;

$Hg_2SO_{4(s)}+2H_2O-SO_4^{2-}=\mathbf{Hg_2}^{2+}$; $2\underline{Hg}+2H_2O=\mathbf{Hg_2^{2+}}+2e^-$;

$Hg_2SO_{4(s)}+2H_2O-SO_4^{2-}=\mathbf{Hg_2}^{2+}$; $2\underline{Hg}+2H_2O=\mathbf{Hg_2^{2+}}+2e^-$; $2\underline{Hg}+2H_2O=Hg_2SO_{4(s)}+2H_2O-SO_4^{2-}+2e^-$;

$2\underline{Hg}+SO_4^{2-}=Hg_2SO_{4(s)}+2e^-$; absolute standard potential $E°_{Ag}=\mathbf{0,3175}$ V; Kortly, Shucha ; [18]

$E°_{HgSO4}=E°-0,0591/2*\lg([H_2O]^0)+0,10166-0,3982=0,614-0,0591/2*\lg(55,3^{\wedge0})+0,10166-0,3982=\mathbf{0,3175}$ V;

$\Delta\mathbf{G}_{eq\_HgSO4}=E°_{HgSO4}\bullet F\bullet 2=\mathbf{0,3175}*96485*2=\mathbf{61,27}$ kJ/mol,

$\Delta\mathbf{G}_{eq\_Hg2SO4}=G_{Hg2SO4}-(2G_{Hg}+\mathbf{G}_{SO4})=\mathbf{-593,87}-(2*\mathbf{40,67}+\mathbf{G}_{SO4})=\mathbf{61,27}$ kJ/mol ;

$\mathbf{G}_{SO4}=G_{Hg2SO4}-(2G_{Hg}+\Delta\mathbf{G}_{eq\_Hg2SO4})=\mathbf{-593,87}-(2*\mathbf{40,67+61,27})=\mathbf{-736,48}$ kJ/mol ;

$Hg+2OH^- = HgO+2H_2O+2e^-$, absolūtais standarta potenciāls $E°_{Hg}$=**-0,3015** V; Kortly, Shucha ; [18]
Ox $HgO+2H_2O+2e^-=Hg+2OH^-$, inversais standarta potenciāls $-E°_{HgO}$=**0,3015** V Suchotina [17].

$E°_{HgO}=E°-0{,}0591/2*\lg([H_2O]^2) +0{,}10166-0{,}3982=0{,}098-0{,}0591/2*\lg(55{,}3^{\wedge 2}) +0{,}10166-0{,}3982=$**-0,3015** V;
chlorine, hydrogen peroxide, magnesium (when heated), disulfur dichloride and hydrogen trisulfide

$HgO+H_2O_2=Hg+O_2+H_2O$; $O_{2gas}+H_2O=O_{2aqua}$;

Red $H_2O_{2aqua}+2H_2O=O_{2aqua}+2H_3O^++2e^-$ $E°_{RedH2O2}$=0,4495 V absolūtais potenciāls Alberta University [19]

$HgO+2H_2O+\cancel{2e^-}+H_2O_{2aqua}+2H_2O = Hg+2OH^-+O_{2aqua}+2H_3O^+$; $H_2O_{2aqua}+2H_2O=O_{2aqua}+2H_3O^++\cancel{2e^-}$;
$HgO+H_2O_{2aqua}+4H_2O=Hg+O_{2aqua}+(2OH^-+2H_3O^+)$; $HgO+H_2O_{2aqua}+4H_2O=Hg+O_{2aqua}+(4H_2O)$;
$HgO+H_2O_{2aqua}=Hg+O_{2aqua}$; sum:

$\Delta G_{eqRedOx\_2H2O2}=(E°_{H2O2aqRed}-E°_{HgO})*F*n$=(0,4495+**0,3015**)*96485*2=(**0,7510**)*96485*2=**144,92** kJ/mol ;
$\Delta G_{eqRedOx\_2H2O2}=G_{Hg}+G_{O2aqua}-(G_{HO}+G_{H2O2})=G_{Hg}$**+330-**(-58,5**+284,25**)=**144,92** kJ/mol ;
$G_{Hg}=G_{eqRedOx\_2H2O2}-G_{O2aqua}+(G_{HO}+G_{H2O2})$=**144,92-330+**(-58,5**+284,25**)= **40,67** kJ/mol ;

Substance	$\Delta H°_H$, kJ/mol	$\Delta S°_H$, J/mol/K	$\Delta G°_H$, kJ/mol
H_3O^+	-285.81	-3.854	-213.275
O_{2aqua}	-11.715	110.876	16.4
O_{2aqua}	**-11.70**	**-94.2**	**16.40**
H_2O	-285.85	69.9565	-237.191
H_2O	**-286.65**	**-453.188**	**-151.549**
$H_2O_{2\ (aq)}$	**-191.99**	**-481.688**	**-48.39**
$H_2O_{2(aq)}$	-191.17	143.9	-134.03
$H_2O_{2\ l}$	-237.129	69.91	-237.129

G_{H2O2}=**284,25** kJ/mol;

Miščenko 1968, Himia, Leningrad

CRC 2010; G_{O2aqua}=**330** kJ/mol ; G_{H2O}=**0** kJ/mol;

BiochemThermodynamic 2006 Masachusets Technology institute

University Alberta 1997.

Nernsta potenciāla studijas 5(Pt)H $+MnO_4^-$ uzskaitot hidroksoniju H_3O^+ un ūdeni H_2O.

Oksidētāja reducēšanas inversais Nernsta potenciāls: $MnO_4^- + 8H_3O^+ + 5e^- = Mn^{2+} + 12H_2O$; $-E°_{MnO4} = -1.46065$ V.

Reducētāja oksidēšanas Nernsta standarta potenciāls:_________ 5(Pt)H$+5H_2O=5H_3O^+ + 5e^-$; $E°_H=-0,2965$ V

Elektronu balansēšana $+ne^-=5e^-=-ne^-$ summārajā Red-Ox reakcijā: 5 H(Pt) $+MnO_4^- + 3H_3O^+ \Leftrightarrow Mn^{2+} + 7H_2O$.

$$-E_{MnO4}=-E°+\frac{0.0591}{4}\bullet\lg\frac{[H_2O]^{12}\cdot[Mn^{2+}]}{[MnO_4^-]\cdot[H_3O^+]^8}=-1.46065\ V+\frac{0.0591}{4}\bullet\lg\frac{[H_2O]^{12}\cdot[Mn^{2+}]}{[MnO_4^-]\cdot[H_3O^+]^8};\ [H_2O]=55,3\ M=\frac{996\_g/L}{18\_g/mol}$$

$$E_H = E°_H + 0,0591\bullet\lg\frac{[H_3O^+]}{[H_2O]} = -0,2965\ V + 0,0591\bullet\lg\frac{[H_3O^+]}{[H_2O]}\ ;$$

Viela	$\Delta H°_H$, kJ/mol	$\Delta S°_H$, J/mol/K	$\Delta G°_H$, kJ/mol	$\Delta G_{Hess}=\Delta G°_{Mn2}+7\Delta G°_{H2O}-3\Delta G°_{H3O}-\Delta G°_{MnO4}-5\Delta G°_{(Pt)H}=-1056,7$ kJ/mol
H_2O	-285,85	69,9565	-237,191	$=-228,1+7*-237,191-(3*-213,2746-447,2+5*$**51,05**$)=-1056,7$ kJ/mol
H_2O	**-286,65**	**-453,188**	**-151,549**	Biochem.Thermodyn,Alberty,2006, Massachusets Technology Inst.
H_3O^+	-285,81	-3,854	-213,2746	CRC Handbook of Chemistry.and Physics, 2010, D.Lide
$H_{2(aq)}$	23,4	-130	99,13	$=-228,1+7*-237,191-(3*-213,2746-447,2+5*99,13/2)=-1049$ kJ/mol
$H_{2(aq)}$	**-5,02**	**-363,92**	**103.24**	**Alberty 2006** Biochem.Thermodyn Massachusets Technology Inst.
H(Pt)$_{(aq)}$	-	-	**51,05**	$\Delta G_{eq}=-847,7$ kJ/mol ; $\Delta G_{Hess}=-1056,7$ kJ/mol
MnO_4^-	-541,4	-191,2	-447,2	izteiksmē 5(Pt)H $+MnO_4^- + 3H_3O^+ <=> Mn^{2+}+7H_2O$ kā absolūti
Mn^{2+}	–220,8	-73,6	-228,1	lielumi $\lvert\Delta G_{eq}=-847,7$ kJ/mol$\rvert<\lvert\Delta G_{Hess}=-1056,7$ kJ/mol$\rvert$;
O_{2aqua}	**-11,7**	**-94,2**	**16,4**	

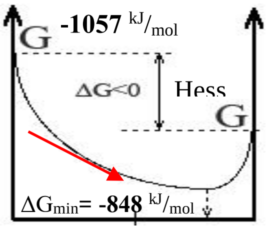
Ūdens koncentrācija $[H_2O]^{12}$ pakāpē 12 ir iekļauta standarta potenciāla vērtībā E °=1,46065 V kā logaritms:

$E°_{MnO4-}=E_o$ 0,0591/5*log(1/$[H_2O]^{12}$)=1,46065+0,10166-0,0591/5*log(1/55,3^12)+0,10166=1,858848-0,3982=1,460648 V;

$\Delta G_{eq}=(E°_H-E°_{MnO4-})\bullet F\bullet 1\bullet 5=(-0,2965-1,460648)*96485*5=-1,757*96485*5=-847,7$ kJ/mol

K_{eq}=**exp(-$\Delta G_{eqOxRed}$/R/T)**=exp(847692/8,3144/298,15)=exp(341,96)=$10^{148,5}$;

Eksotermiska un eksoerģiskas MnO_4^- reducēšanas ar metālisku 5(Pt)H Hesa brīvās enerģijas izmaiņa negatīva $\Delta G_{Hess}=\Delta G_{OxRed}=-1056,7$ kJ/mol , bet minimizējas sasniedzot līdzsvara maisījumu $\Delta G_{min}=\Delta G_{eq}=-847,7$ kJ/mol;



$$10^{148,5}=K_{eq}=\frac{[H_2O]^7\cdot[Mn^{2+}]}{[(Pt)H]^5[MnO_4^-]\cdot[H_3O^+]^3};$$

Brīvās enerģijas izmaiņas minimums ΔG_{min} ir Prigožina atraktors. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

izejvielas_ 5A+B+3C 50% D+8E
5(Pt)H$+MnO_4^-+3H_3O^+$
produkti $Mn^{2+}+7H_2O$

Nernsta potenciāla O_{2aqua}/ H_2O red-oks sistēmas acidozes oksidatīvā stresa bioķīmiskais mehānisms (pastiprinoties oksidētāja spēkam potenciāla E vērtība)

Piezīme: Oksidatīvā stresā norisinās **ne enzimātiskas** oksidēšanās reakcijas daudzveidīgos ķēdes reakciju un paralēlos produktos, sagraujot organismu! Iznīcinoši bīstami dzīvībai!

Ūdens vidē (asins plazmā) skābeklis ir stiprs oksidētājs **-1,0865** V inversajā pus reakcijā $-E_{oO2}$=**-1,0865 V**:

$G_{O2aqua}=G_{O2gas}+G_{O2šķ}=303.1+26.58=330$ kJ/mol ; $O_{2aqua} + 4H_3O^+$ + $4e^-$ $\Leftrightarrow$ $6\ H_2O$

oksidētā forma   brīvie elektroni   reducētā forma

$G_{H3O+OH}=G_{H3O+}+G_{OH-}=22.44+77.36=99.8$ kJ/mol protolīzes reakcijā $H_2O+H_2O<=>H_3O^++OH$;

Bioķīmija skābekļa **O_{2aqua}** brīvo enerģijas saturu $G_{O2aqua}=329,7$ kJ/mol samazina līdz $G_{O2Bio}=78.08$ kJ/mol.

Arteriālo asiņu koncentrācija $[O_{2aqua}]=6*10^{-5}$ M un pH=7,36 koncentrācija $[H_3O^+]=10^{-7,36}$ M.

$E_{O2}=E°+{}^{0,0591}/_4\bullet\log([O_{2aqua}]\bullet[H_3O^+]^4/_{[H2O]}{}^6)$=**1,0865**+${}^{0,0591}/_4$*log(6*10^(-5)*10^(-7,36*4))/$_{55,346}$^6)=0.4346 Volti.

Samazināts $\Delta E_{arterial}=-(E_{oO2}-E_{O2})=-($**1,0865**-0,4346)=-0.6519 V;

$\Delta G_{arterial}=\Delta E_{H2O}$*F*n=0.6519*96485*4/1000=-251.6 kJ/mol.

Šķīdība konstantes vērtība **$O_{2gas\ AIR}$+H_2O**$\overset{\text{Aquaporins}}{=>}$**$O_{2Blood}$** palielina produktu līmenī $G_{O2šķ}=26.58$ kJ/mol:

$$\frac{[O_{2\ aqua}]}{[O_{2\ gas}]\cdot[H_2O]}=K_{šķ}=2.205*10^{-5}.\ G_{O2šķ}=-R\bullet T\bullet\ln(K_{šķ})=-8.3144*298.15*\ln(2.205*10^{-5})=26.58\ kJ/mol.$$

Brīvo enerģiju protolīze samazina $G_{O2arteriāla}=G_{O2aqua}+G_{O2šķ}+\Delta G_{arteriāla}=303,1+26,58-251,6=78,08$ kJ/mol un skābeklis kļūst uguns drošs bioķīmisks oksidants, veidojot arteriālo koncentrāciju [**O_{2aqua}**]=6*10^{-5} M kā bioenerģētiski drošu uzturētu izooksijas normu. [3];

1) Ūdens 55,346 M samazina potenciālu no **1,0865 V** par **-0,155** V=ΔE_{H2O}.

$E_{oO2}=E°_{O2}+^{0,0591}/_4*\log(^1/_{[H2O]}{}^6)=$**1,0865**$+0,01478*\log(^1/_{55,346}{}^{\wedge 6})=$**0,9319** V ;

2) Paskābināšana H_3O^+ 10 reizes potenciālu un brīvās enerģijas saturu palielina par $\Delta E_{H3O+}=$**0,05912** V;

$\Delta E_{H3O}=0,01478\bullet\lg([H^+]^4)=$**0,05912** V un $\Delta G_{max}=\Delta E_{H3O}*F*n=0,05912*96485*4/1000=$ **22,817** $^{kJ}/_{mol}$;

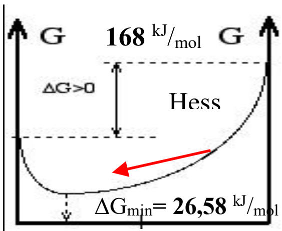
3) Gaisa 20.95% aizvietojot ar 100% skābekļa [O_{2aqua}] koncentrācija 5 reizes lielāka palielina potenciālu par $\Delta E_{O2100\%}=0,01478\bullet\lg(100\%\ [O_{2aqua}])=0,01478*\log(5)=$ **+0,0103** V. Brīvās enerģijas saturs palielinās par $\Delta G_{max}=\Delta E_{H3O}*F*n=0,01033*96485*4/1000=$**3,987** $^{kJ}/_{mol}$. 6. lapas puse: Lielā oksidatīvā stresa un tehnoloģisko briesmu dēļ 1972. gadā slēdza NASA Apollo projektu.

Kuras koncentrācijas ūdens [H_2O], oksidētāja [Ox], reducētāja [Red], skābes [H^+] izmaiņas samazina brīvās enrģijas saturu vai palielina brīvās enerģijas saturu oksidētājam? Kā potenciāla E_o izmaiņas ietekmē brīvās enerģijas saturu oksidētājos un reducētājos! Kad saturs palielinās un kad saturs samazinās?

Skābekļa šķīdības Prigožina atraktors brīvās enerģijas izmaiņa Hesa likumā **ir** eksotermiska, endoerģiska

$O_{2gaiss}+H_2O=O_{2aqua}$; [$O_{2gaiss}$]=0,2095 skābekļa mol daļa gaisā, mol daļa ūdenī

$K_{šķ}[O_{2gaiss}]=[O_{2aqua}]/[H_2O]=2,205*10^{\wedge(-5)}*0,2095=4,61948*10^{-6}=10^{\wedge(-5,335)}$.



A+B 50% C+D

izejvielas $O_2\uparrow_{gas}+H_2O$

produkti

$H_2O_{Asinis}+O_{2aqua\text{-}Asinis}$.

$\Delta G_H=\Delta G°_{O2aqua}-\Delta G°_{H2O}-\Delta G°_{O2gas}=$**16.4-(0-151,549)=168** $^{kJ}/_{mol}$ **endoerģiska;**

$\Delta G_{šķ}=-R\bullet T\bullet\ln(K_{šķ})=-8,3144*298,15*\ln(2,205*10^{-5})=-8,3144\bullet298,15\bullet6,414=$**26,58** $^{kJ}/_{mol}$

[O_2] šķīdības Hesa brīvās enerģijas izmaiņa ir pozitīva $\Delta G_{Hess}=\Delta G_{šķīdība}=$**168** $^{kJ}/_{mol}$, bet minimizējas sasniedzot šķīdības līdzsvara maisījumu $\Delta G_{min}=\Delta G_{šķ}=$**26,58** $^{kJ}/_{mol}$

$$K_{šķ}=\frac{[O_{2\ aqua}]}{[O_{2\ gaiss}]\cdot[H_2O]}=2,205*10^{-5}=10^{-4,66}$$

Brīvās enerģijas izmaiņas minimums ΔG_{min} ir Prigožina atraktors.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars. 53. lapas puses:

Nulles osmolārā C_{osm}=0 M un jonu spēka **I**=0 M destilētā ūdenī no gaisa 20,95% šķīdība ir:

$[O_{2ūdens}]=K_{šķ}*[O_{2gas}]*[H_2O]=2,205*10^{\wedge(-5)}*0,2095*55,3=0,00025546=2,5546*10^{-4}=10^{-3,593}$ M.

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

1. WeiXinga, MinYinb, QingLvb, YangHub, ChangpengLiub, JiujunZhangc. Tīra 1atm mol daļa ir [O_{2gas}] =1. Osmolārā C_{osm}=0,305 M, jonu spēka **I**=0,25 M, gaisa skābekļa 20,95% apstākļos izšķīst [O_{2aqua}]=$9,768\cdot10^{-5}$ M. Tā pēc fizioloģiskā līdzsvara konstante ir $K_{O2asinis}=[O_{2aqua}]/[O_{2gaiss}]=9,768\cdot10^{-5}/0,2095=4,663*10^{-4}=10^{-3,3314}$.

Arteriālo [O_{2aqua}] = $6\cdot10^{-5}$ M un venozo [O_{2aqua}]=$0,426*10^{-5}$ M koncentrāciju nodrošina $pK_{O2asinis}$=3,3314 skābekļa molekulām osmozē pretēji koncentrācijas gradientam šķērsojot akvaporīnu kanalus membrānās.

Inversa: $O_{2aqua}+4H_3O^++4e^-\Leftrightarrow6H_2O$; $-E°_{O2}=$**-1,0865** Volts; Nernsta pus: $4(Pt)H+4H_2O\Leftrightarrow4H_3O^++4e^-$; $E°_H=-0,2965$ V

$O_{2aqua}+4(Pt)H=2H_2O$; $\Delta G_{eq}=(E°_H-E°_{O2})\bullet F\bullet1\bullet4=(-0,2965-$**1,0865**$)*96485*4=-1,28*96485*4/1000=-533,9$ $^{kJ}/_{mol}$;

Zinot līdzsvara vērtību $\Delta G_{eq2H2O}=2G_{H2O}-4G_{(Pt)H}-G_{O2aqua}=2*0-(4*G_{(Pt)H}+329.68)=-533,9$ $^{kJ}/_{mol}$, ūdeņrsža metāla brīvā enerģija ir $G_{H(Pt)}=(2G_{H2O}-\Delta G_{eq2H2O}-G_{O2aqua})/4=(2*0+533,886-329,68)/4=$**204,2**/4=**51,05** $^{kJ}/_{mol}$;

Sēra reducēšana inversais potenciāls: $S_{rombic}+2\ H_3O^++2e^-=H_2S_{aq}+2\ H_2O$; $-E°_S=0.05254$ V;

$S_{rombic}+2(Pt)H\Leftrightarrow H_2S_{aq}$; $2(Pt)H+2H_2O=2H_3O^++2e^-$; $E°_H=-0,2965$ V

$\Delta G_{eq}=(E°_H-E°_S)\bullet F\bullet1\bullet2=(-0,2965+0.05254)*96485*2=-0,245*96485*2=-47,077$ $^{kJ}/_{mol}$;

$G_{H2Saquq}=\Delta G_{HessH2S}+(2G_{H(Pt)}+G_{Srombic})=-47,077+(2*$**51,05-85,64**$)=$**-30**,617 $^{kJ}/_{mol}$. 2. lapas puse.

Nernsta pus reakcijai: $H_2S_{aq}+2H_2O=S_{rhombic}+2H_3O^++2e^-$ absolūtais standarta potenciāls $E°^1_{H2S}$=-0.0515 V brīvās enerģijas izmaiņai: $\Delta G_{eqH2S}=E°^1_{H2S}Fn=-0.0515*96485*2=$**-9.938** $^{kJ}/_{mol}$.

Ūdeņraža sulfīda šķīduma pus reakcijā Hesa likuma brīvās enerģijas izmaiņas vērtība izteiksmē ir:

$\Delta G_{Hess\_H2Saq}=G_{Srhombic}+2G_{H3O+}-(G_{H2Saq}+2G_{H2O})=$**-85.64**+2*22.44-($G_{H2Saq}$+2*0)=**-9.938** $^{kJ}/_{mol}$ tad absolūtā vērtība ir: $G_{H2Saq}=G_{Srhombic}+2G_{H3O+}-(\Delta G_{Hess\_H2Saq}+2G_{H2O})=$**-85.64**+2*22.44-(**-9.938**+2*0)=**-30.82** $^{kJ}/_{mol}$.

Nernsta potenciāla studijas reducējot ar vitamīnu B3 etanālu $H_3CCH{=}O$ un oksidējot H_3CCH_2OH etanolu

Aerobi [**NAD**$^+$]/[**NADH**]=10^6; **H_3C-CH_2-OH**+NAD^+**+H_2O**+ΔG**+Q=>H_3C-CH=O**+NADH**+H_3O^+**

$\Delta G_{Hess}=\Delta G°_{H3O}+\Delta G°_{CH3CHO}+\Delta G°_{NADH}-\Delta G°_{CH3CH2OH}-\Delta G°_{H2O}-\Delta G°_{NAD+}$=159,1 kJ/mol;

ΔG_{Hess}=**32,2824+1175,5732-151,549**-(**75,2864**+1059,11-237,191)=159,1 kJ/mol endoerģiska;

Ox **NAD^+ + H^-(H^++$2e^-$)= NADH**; inversais -**E°$_{NAD+}$=0,4095** V; absolute David Harris; [22]

Red **CH_3CH_2OH+2H_2O=CH_3CHO+2H_3O^++H^-($2e^-$)**; absolūtais Nernsta potenciāls **E°$_{CH3CH2OH}$= -0,055** V; [19]

Summa: **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;

Novērtētajā balansā **n=2=m ar** elektronu skaitu **2e$^-$ donors E°$_{CH3CH2OH}$= -0,055** V plus electronu **akceptors -E°$_{NAD+}$=0,4095** V, jo -E°$_{NAD+}$=0,4095 V **akceptē** elektronus no **etanola E°$_{CH3CH2OH}$= -0,055** V:

E°$^2_{H2O}$=0,190-0,0591/2*log(1/[H_2O])=**0,190**-0,02955*log(1/55,3333)+0,10166-0,3982=**-0,05503 V**=**E°$_{CH3CH2OH}$;**

$$\Delta G_{eq}=-R\bullet T\bullet\ln(K_{eq})=68{,}4\ {}^{kJ}/_{mol};\ K_{eq}=\frac{[NADH]\cdot[CH_3CHO]\cdot[H_3O^+]}{[NAD^+]\cdot[CH_3CH_2OH]\cdot[H_2O]}=e^{-\frac{\Delta Geq}{R\bullet T}}=e^{-\frac{68408}{8.314\bullet 298.15}}=1{,}036\bullet 10^{-12}=10^{-11{,}985};$$

Anaerobi [**NADH**]/[**NAD**$^+$]=10 **H_3C-CH=O**+NADH**+H_3O^+**+ΔG**+Q =>H_3C-CH_2-OH**+NAD^+**+H_2O**;

$\Delta G_{Hess}=\Delta G°_{CH3CH2OH}+\Delta G°_{H2O}+\Delta G°_{NAD+}-\Delta G°_{H3O}-\Delta G°_{CH3CHO}-\Delta G°_{NADH}$ = -159,1 kJ/mol;

ΔG_{Hess}=**75,2864**+1059,11-237,191-(**32,2824+1175,5732-151,549**)= -159,1 kJ/mol endoerģiska;

Red **NADH** = **NAD^+ + H^-($2e^-$)**; **E°$_{NADH}$= -0,4095** V; absolūtais Nernsta potenciāls David Harris; [22]

Ox **CH_3CHO+2H_3O^+ + H^-($2e^-$)** <=> **CH_3CH_2OH+ 2 H_2O**; inversais potenciāls **-E°$_{CH3CH2OH}$**=0,055 V; [19];

Summa:

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 ;

Novērtētajā balansā **n=2=m ar** elektronu skaitu **2e$^-$ donors E°$_{NADH}$**=-0,4095 V plus electronu **akceptors -E°$_{CH3CHO}$**=0,055 V, jo **-E°$_{CH3CHO}$**=0,055 V **akceptē** elektronus no B3 vitamīna **E°$_{NADH}$= -0,4095** V .

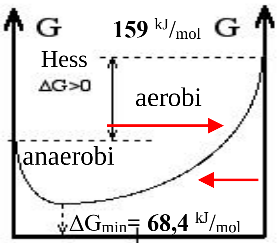
$$\Delta G_{eq}=-R\bullet T\bullet\ln(K_{eq})=-68{,}408\ {}^{kJ}/_{mol};\ K_{eq}=\frac{[NAD^+]\cdot[CH_3CH_2OH]\cdot[H_2O]}{[NADH]\cdot[CH_3CHO]\cdot[H_3O^+]}=e^{-\frac{\Delta Geq}{R\bullet T}}=e^{-\frac{-68408}{8.314\bullet 298.15}}=10^{11{,}985}.$$

Aerobā organismā **O_{2aqua}** NADH oksidāze reda attiecību [**NAD**$^+$]/[**NADH**]=10^6;

$\Delta G_{Homeostāze}$=68,408+ **R•T•ln**(10^6*1/1*$10^{-7,36}$/55,3)=**68,408**-86,2= -17,8..........kJ/mol.

[**NAD**$^+$]/[**NADH**]=10^3; $\Delta G_{Homeostāze}$=**68,408**-69,08= -0,676..........kJ/mol.

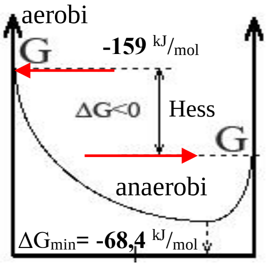
Līdzsvars novirzīts **izejvielās** kā aerobā konstante **K_{eq}** =$10^{-11,985}$ un ir inversa anaerobi produktos konstantē **K_{eq}**=$10^{11,985}$. Aerobā endotermiskā un endoerģiskā etanola oksidēšanā Hesa likuma brīvās enerģijas izmaiņa ir pozitīva **ΔG_{Hess}**=159........kJ/mol un asimetriski negatīva etanāla anaerobai reducēšanai **ΔG_{Hess}**=-159........kJ/mol , bet minimizējas sasniedzot līdzsvaru **ΔG_{min}**=**ΔG_{eq}**=68,4....... kJ/mol aerobi un asimetriski anaerobi **ΔG_{min}**=**ΔG_{eq}**=-68,4...... kJ/mol sasniedzot līdzsvara maisījumu ar asimetriskām konstantēm **$10^{-11,985}$=K_{eq}** un **$10^{11,985}$=K_{eq}** .



A+B+C50%D+E+F

izejvielas_ NAD^++H_3CCH_2OH+H_2O

produkti_ NADH+H_3CCHO+H_3O^+



D+E+F 50% A+B+C

NADH+H_3CCHO+H_3O^+

NAD^++H_3CCH_2OH+H_2O

Prigožina atraktors ir brīvās enerģijas izmaiņas absolūts minimums **ΔG_{min}** sasniedzot līdzsvaru: **ΔG_{min}**=68,4....... kJ/mol=│ΔG_{eq}│<│**ΔG_{Hess}**│**=159**........kJ/mol.

Anaerobi **H_3C-CH=O**+NADH**+H_3O^+** =>**H_3C-CH_2-OH**+NAD^+**+H_2O**+ΔG**+Q**;

reducēšana labvēlīgi ΔG_{eq}=**ΔE°**•**F**•**n**=-0.3545 V•2 mol•96485 C/mol=-68,408.........kJ/mol.

Anaerobā etanola oksidēšana nelabvēlīga zemās **O_{2aqua}** koncentrācijas hipoksijā, bet etanāla reducēšana par etanolu labvēlīga [**H_3CCH_2OH**]/[**H_3CCH=O**]=1/10 **homeostāzē** ar NADH reduktāzes enzīmu kā negatīva brīvās enerģijas izmaiņa **$\Delta G_{Homeostāze}$**=-27,86........kJ/mol

Anaerobā attiecība homeostāzē virs c labvēlīga reducēšanai:

$\Delta G_{Homeostāze}$=-68,41+8,3144*298.15***ln**(**$K_{Homeostāze}$**)**=-68,41+40,54 = -27,86**........ **kJ/mol**

$$\Delta G_{Homeostāze}=-68{,}41+8{,}3144*298{,}15*\ln\left(\frac{1}{10}\ \frac{1}{10}\ \frac{55.333}{10^{-7.36}}\right)=-27{,}86\ {}^{kJ}/_{mol};\ K_{Homeostāz}=\frac{[NAD^+]\cdot[CH_3CH_2OH]\cdot[H_2O]}{[NADH]\cdot[CH_3CHO]\cdot[H_3O^+]}$$

[**NADH**]/[**NAD**$^+$]=1/770; **$\Delta G_{Homeostāze}$=68,408+8,3144*298,15*ln**(700/1*1/1*55,3457/$10^{-7,36}$)=0,028 kJ/mol.

Nernsta potenciāla O_{2aqua} / H_2O | $\underline{(Pt)H}$ / H_3O^+ un H_2O_2 / H_2O | H_2O_2 / O_2 studijas

Ox inversā pus reakcija $-E_{oO2}$=**-1,0865 V**: O_{2aqua} + $4H_3O^+$ + $4e^-$ <=> 6 H_2O ;

Red Nernsta pus reakcija: $\underline{4(Pt)H}$ + $4H_2O$ ⇔ 4 H_3O^+ + $4e^-$; metāls ūdeņradis $G_{H(Pt)}$=**51,05** kJ/mol;

O_{2aqua}+$\underline{4(Pt)H}$⇔$2H_2O$; $\Delta G_{Hes2H2O}$=$2G_{H2O}$-$4G_{H(Pt)}$-G_{O2aqua}=2*-237,191-(4*51,05+**330**)= -1008,6=2*-**504,3** kJ/mol;

Δ**G_{eq}**=(E°$_H$-E°$_{O2}$)•F•4=(**-0,2965-1,0868**)*96485*4=-1,38334*96485*4/1000=-533,9=2*-**266,9** kJ/mol

ΔG_{eq2H2O}=$2G_{H2O}$-$4G_{H(Pt)}$-G_{O2aqua}=2*0-(4*$G_{H(Pt)}$+**329,68**)=-533,9=2*-**266,9** kJ/mol

$G_{H(Pt)}$=($2G_{H2O}$-Δ**G_{eq2H2O}**-G_{O2aqua})/4=(2*0+533,886-**329,68**)/4=**51,05** kJ/mol .

Gas O_{2gas}+$\underline{2H_{2gas}}$=$2H_2O$; $\Delta G_{Hess2H2O}$=2ΔG°$_{H2O}$-(2ΔG°$_{H2gas}$+ΔG°$_{O2gas}$)=2*-273,19-(2*0+0)=2*-273,19=-546,4 kJ/mol

O_{2aqua}+$\underline{2H_{2aqua}}$=$2H_2O$; $\Delta G_{Alberty2H2O}$=$2G_{H2O}$-$2G_{H2aqua}$-G_{O2aqua}=2*0-(2***103,24**+329,68)=-536,2 kJ/mol;

Ūdeņraža brīvā enerģija G_{H2aqua}=**103** kJ/mol of Alberty R.A. Biochemical Thermodynamic's 1-463. (2006).

Viela	ΔH°$_H$, kJ/mol	ΔS°$_H$, J/mol/K	ΔG°$_H$, 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
$H_{2(aq)}$	23,4	-130	99,13
$H_{2(aq)}$	**-5,02**	**-363,92**	**103,24**
O_{2aqua}	**-11,70**	**-94,2**	**16,4**
O_{2aqua}	-11,715	110,876	16,4

ΔG_{Hess}=2ΔG°$_{H2O}$-4ΔG°$_{(Pt)H}$ -ΔG°$_{O2aqua}$=-689=2*--344,521 kJ/mol;
=2*-237,191-(4*99,13/2+**16,4**)=-689=2*344,5 kJ/mol. CRC 2010

ΔG_{eq}= **-266,9** kJ/mol ; ΔG_{Hess}= -344,5 kJ/mol

reakcijā $\underline{4(Pt)H}$ + O_{2aqua} ⇔ 2 H_2O ; absolūtā brīvā enerģijas izmaiņa

|ΔG_{eq}=**-266,9** kJ/mol| < |ΔG_{Hess}= -344,5 kJ/mol| ;

Alberty 2006 Biochem.Thermodyn Massachusets Technology Inst.

Ūdens koncentrācijas $[H_2O]^6$ logaritms ekstraģēts no E°$_{classic}$=1,229 V

līdz ūdeņraža absolūtam potenciālam E°=$_{1,383+0,10166-0.3982}$=**1,0865** V

K_{eq2H2O}=K_{OxRed}=exp(-ΔG_{OxRed}/R/T)=exp(**533886**/8,3144/298,15)=exp(215,4)= 3,42*10^{93} ;

Eksotermiska un eksoerģiska O_{2aqua} reducēšana ar metālu ūdeņradi
$\underline{4(Pt)H}$ un H_2O_2 dismutēšanas Hesa brīvās enerģijas izmaiņa negatīva
$\Delta G_{Hess2H2O}$=**-504,3**....... kJ/mol , ΔG_{Hess_H2O2}=**-480**........ kJ/mol, bet minimizējas
sasniedzot līdzsvaru Δ**G_{eq2H2O}**=**-266,9** kJ/mol un Δ**$G_{eqStandart\_H2O2}$**=**-238,5**........kJ/mol
konstantes **K_{eq2H2O}**=3,42*10^{93}......... and **$K_{eqStandard\_H2O2}$**=6,104*10^{41}........
Minimums ΔG_{min} ir Prigožina atraktors. Brīvās enerģijas izmaiņas minimuma
sasniegšanā iestājas līdzsvara stāvoklis.

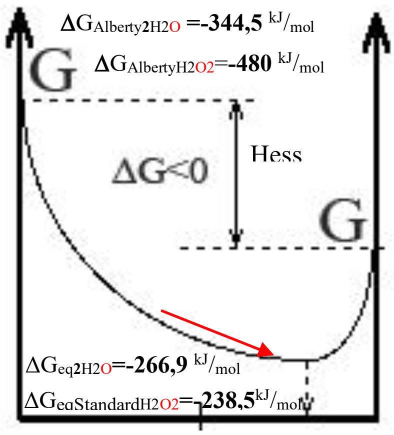
Red H_2O_2+$2H_2O$=O_{2aqua}+$2H_3O^+$+$2e^-$; **E°$_{H2O2}$**=0,4495 V Alberta University ;
$[H_2O_2]$=1 M koncentrācijas vidē ir pH=7,36. .

Oks inversais H_2O_2+$2H_3O^+$+2e =$4H_2O$ potenciāls **-E °$_{Ox}$**=-1,6855 V Suhotina ;

Summārā dismutācija **$2H_2O_{2aq}$=>O_{2aqua}+$2H_2O$+Q+ΔG**;

Reaktanti $\underline{4(Pt)H}$+ O_{2aqua} un produkti $2H_2O$

Reactanti **$2H_2O_{2aq}$** un produkti O_{2aqua}+$2H_2O$



4A+B 50% 2D

2A 50% B+2C

$\Delta G_{eqStandart\_H2O2}$=($E_{Red}$-$E_{oOx}$)***F*n**=(0,4495-1,6855)*96485*2=(-1,236)*96485*2= **-238,5**....kJ/mol ;

$$K_{eqStandart\_H2O2}=\frac{[O_2]_{aqua}\cdot[H_2O]^2}{[H_2O_2]^2_{aqua}}$$ =**K_{H2O2}=exp(-ΔG_{eq}/R/T)**=exp(2385510,9/8,3144/298,15)=6,104*10^{41}........

E_{oH2O2}=E °$_{H2O2}$+0,0591/2•lg(O_{2aqua}]*$[H_3O^+]^2$/$[H_2O_2]$/$[H_2O]^2$)=0,4495+0,0591/2*lg(6*10^(-5)*10^(-7,36*2)/1/55,3^2)=0,2132 V

E_{oOx}=E°$_{H2O2Ox}$+0,0591/2•log($[H_2O]^4$/$[H_2O_2]$/$[H_3O^+]^2$)=-1,6855+0,0591/2*lg(55,3^4/1/10^(-7,36*2))=-1,0445 V

Sum Nernst+inverse Δ**G_{eq}**$_{BioChem}$=(E_{Red}-E_{oOx})***F*n**=(0,2132-1,0443)*96485*2=(-0,831)*96485*2= **-160,4**....kJ/mol

Biochem $\Delta G_{Alberty}$=$G_{O2Biochem\_arteriaj}$+2*$G_{H2OBioChemistry}$-2*G_{H2O2}=**78.08+2*85.64-2*364.79=-480.22** kJ/mol; **Alberty**

1.ΔH_{Hess}=ΔH°$_{O2}$+2ΔH°$_{H2O}$-2ΔH°$_{H2O2}$=**-11.7**-2***286.65**-(2*-**191.99**)=**-201.02** kJ/mol =-11.7-2*285.85-(2*-191.17)=-201.06 kJ/mol

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

ΔS_{Hess}=ΔS°$_{O2}$+2ΔS°$_{H2O}$-2ΔS°$_{H2O2}$=**-94.2**+2*-**453.188**-(2*-**481.688**)=**-37.2** J/mol/K;

ΔS_{Hess}=ΔS°$_{O2}$+2ΔS°$_{H2O}$-2ΔS°$_{H2O2}$=110.876+2*69.9565-(2*143.9)=-37 J/mol/K;

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

4. ΔG_{Hess}=ΔH_H-T*ΔS_H=**-201.02**-298.15*-**0.0372**=**-189.9** kJ/mol **exoergic spontaneous**.

ΔG_{Hess}=ΔH_H-T*ΔS_H=-201.06-298.15*-0.037=-190 kJ/mol ;

T•ΔS_{total}=**0.637***298.15=**189.9** kJ/mol ; T•ΔS_{total}=0.63735*298.15=190 kJ/mol;

Liela ātruma protolīzes peroksīda jonu sadursmē **HOO⁻><⁻OOH** ir liela **Ea**=79000 $^{J}/_{mol}$ aktivācijas enerģija, bet jonu **HOO⁻=>Fe^{3+}** sadursmē aktivācijas enerģija ir maza E_a=29 $^{J}/_{mol}$. Producējot ω=6, ω=3 taukskābes, skābekli, ūdeni un siltumu: **$2H_2O_{2(aq)}$<=>O_{2aqua}+2H_2O+Q+ΔG_H** ;

$ΔG_{eqStandarta\_2H2O2}$=($E°_{H2O2aqRed}$-$E°_{H2O2aqOx}$)***F*n**=(0,4495-1,6855)*96485*2=(-1,236)*96485*2= **-238,5** $^{kJ}/_{mol}$;

$ΔG_{Alberty\_2H2O2}$=G_{O2aqua}+2*G_{H2O}-2*G_{H2O2}=**330+2*0**-2*G_{H2O2}=**-238,5** $^{kJ}/_{mol}$; **exoergic**

G_{H2O2}=(G_{O2aqua}+2*G_{H2O}+$ΔG_{Alberty\_2H2O2}$)/2=(**330+2*0+238,5**)/2=**568,5**/2=**284,25** $^{kJ}/_{mol}$;

G_{H2O2}=**284,25** $^{kJ}/_{mol}$;

Viela	$ΔH°_H$, $^{kJ}/_{m}$	$ΔS°_H$, $^{J}/_{mol/}$	$ΔG°_H$, $^{kJ}/_{mo}$
H_3O^+	-285,81	-3,854	-213,275
O_{2aqua}	-11.715	110,876	16,4
O_{2aqua}	**-11.70**	**-94,2**	**16,40**
H_2O	-285,85	69,9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**
H_2O_2 (a	**-191,99**	**-481,688**	**-48,39**
H_2O_2(a	-191,17	143,9	-134,03
H_2O_2 l	-237,129	69,91	-237,129

Miščenko 1968, Himia, Leningrad

CRC 2010; G_{O2aqua}=**330** $^{kJ}/_{mol}$; G_{H2O}=**0** $^{kJ}/_{mol}$;

$ΔH_{Hess}$=ΔH°$_{O2}$+2ΔH°$_{H2O}$-2ΔH°$_{H2O2}$=**-201.02**.....=-201.06......$^{kJ}/_{mol}$

=**-11.7**-2***286.65**-(2*-**191.99**)=**-201.02**......$^{kJ}/_{mol}$ **eksotermiska**..

=-11.7-2*285.85-(2*-191.17)=-201.06......$^{kJ}/_{mol}$

BiochemThermodynamic 2006 Masachusets Technology institute

University Alberta 1997.

$ΔS_{kopēja}$= $ΔS_H$+ $ΔS_{izkliedēta}$=**-37,2+679,725= 642,525**.......... $^{J}/_{mol/K}$

2.ΔS=-$ΔH_H$/T=-(**-201,02**)/298,15=**674,2**....$^{J}/_{mol/K}$; $ΔS_{izkliede}$=-$ΔH_H$/T=-(-201,06)/298,15=674,36....$^{J}/_{mol/K}$;

$ΔS_{Hess}$=ΔS°$_{O2}$+2ΔS°$_{H2O}$-2ΔS°$_{H2O2}$=**-94,2**+2***-453,188**-(2***-481,688**)=**-37,2**....$^{J}/_{mol/K}$**;**

$ΔS_{Hess}$=ΔS°$_{O2}$+2ΔS°$_{H2O}$-2ΔS°$_{H2O2}$=110,876+2*69,9565-(2*143,9)=-37....$^{J}/_{mol/K}$**;**

2. $ΔS_{kopējā}$=$ΔS_H$+$ΔS_{izkliede}$=**-37,2+674,2=637**.....$^{J}/_{mol/K}$ $ΔS_{kopējā}$=-37,011+674,36=637,35......$^{J}/_{mol/K}$**;**

4. **ΔG_{Hess}**=ΔH_H-T*ΔS_H=**-201,02**-298,15*-**0,0372**=**-189,9**........ $^{kJ}/_{mol}$ **eksoerģiska**........... **patvaļīga**...........

ΔG_{Hess}=ΔH_H-T*ΔS_H=-201,06-298,15*-0,037=-190........ $^{kJ}/_{mol}$;

T•$ΔS_{kopējā}$=**0,637***298,15=**189,9**.........$^{kJ}/_{mol}$; T•$ΔS_{kopējā}$=0,63735*298,15=190.........$^{kJ}/_{mol}$;

Red: H_2O_2+2H_2O=O_2+2H_3O^++2e⁻ ; **E°$_{Red}$**=E°$_{RedH2O2}$=0,4495 V Nernsta absolūtais potenciāls Alberta University;

Ox: H_2O_2+2H_3O^++2e⁻=4H_2O ; -E° $_{OxH2O2}$=-1,6855 V inversais standarta potenciāls Suhotina ;

$2H_2O_{2(aq)}$ =O_{2aqua}+2H_2O+Q+ΔG; Aktivētiem peroksīda homeostāzes produktiem: hidroksonijam un peroksīda: anjonam: G_{H2O2}=364.8 $^{kJ}/_{mol}$; G_{H3O+}+G_{HOO-}=22.44+418.32=440.76 $^{kJ}/_{mol}$ brīvā enerģija novērtēta attiecībā pret nulli ūdenim un oglekļa dioksīdam **CO_{2gas}** : G_{H2O}=G_{CO2gas}=0 $^{kJ}/_{mol}$;

ΔG_{min}=**Δ$G_{eqStandart}$**=(**E°$_{Red H2O2}$**-**E°$_{Ox H2O2}$**)***F*n**=(0,4495-1,6855)*96485*2=(-1.236)*96485*2=**-238.5** $^{kJ}/_{mo}$;

$$K_{eqStandart}=\frac{[O_2]_{aqua}\cdot[H_2O]^2}{[H_2O_2]^2_{aqua}}$$ =**K_{H2O2}=exp(-ΔG_{eq}/R/T)**=exp(238511/8.3144/298.15)=6.104*10^{41}........

Pus reakciju RedOx Nernsta reducēšanas un oksidēšanas elektronu balanss 2 e⁻ pie pH=7,36, [O_{aq}]=6*10^{-5} M

E_{Red}=E°$_{H2O2}$+0.0591/2•lg([O_{2aqua}]*[H_3O^+]^2/[H_2O_2]/[H_2O]^2)=0,4495+0.0591/2*lg(6*10^(-5)*10^(-7.36*2)/1/55.3^2)=0.2132 V

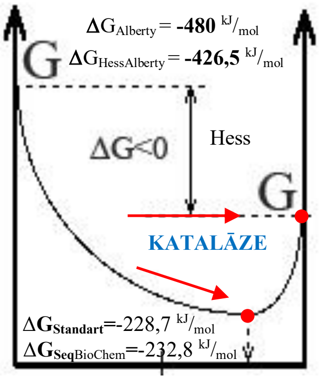
E_{Ox}=-E°$_{H2O2Ox}$+0.0591/2•log([H_2O_2]*[H_3O^+]^2/[H_2O]^4)=-1,6855+0.0591/2*lg(1*10^(-7.36*2)/55.3^4)=-1.443 V

Homeostāzē summā Δ$G_{eqBioChem}$=(E_{Red}-E_{oOx})***F*n**=(0.2132-1.0445)*96485*2=(-0,831)*96485*2= **-160,4**....$^{kJ}/_{mol}$;

Δ$G_{Alberty}$=$G_{O2Biochem}$+2*$G_{H2OBioChemistry}$-2*G_{H2O2}=**78,08+2*85,64-2*364,79=-480,22** $^{kJ}/_{mol}$; **Alberty**

Eksotermiska, eksoerģiska **H_2O_2** (aq) dismutēšanas Hesa brīvā enerģijas izmaiņa Δ$G_{Alberty}$ Δ$G_{HessAlberty}$ un bioķīmijas vidē ir negatīva **-480**........ $^{kJ}/_{mol}$, **-426,5**........ $^{kJ}/_{mol}$, bet minimizējas Δ$G_{eqStandart}$=**-238,5**........$^{kJ}/_{mol}$ sasniedzot līdzsvaru maisījuma konstanti **K_{eq}**=6,1*10^{41}.......

Lešateljē princips ir Prigožina atraktors brīvās enerģijas izmaiņas minimums ΔG_{min} līdzsvarā. Liela ātruma protolīzes atraktori pH=7,36, skābeklis 20,95% gaisā atrodas līdzsvara stāvoklī, kamēr neatgriezeniskā homeostāze turpinās, jo ir nelīdzsvara stāvokl Prigožina atraktors Nobela prēmija ķīmijā 1977. gadā. KATALĀZE izdzēš peroksīda molekulas **H_2O_2** līdz 100% ω=6, ω=3 taukskābju C20:4 iznākumam elongācijas sintēz peroksisomās. KATALĀZES reaktivitāte ir nepieciešams neatgriezeniskas homeostāzes Brauna molekulārs dzinējs evolūcijai un izdzīvošanai.



A+A 50% B+2C

izejvielas 2**$H_2O_{2(aq)}$**

produkti_**O_{2aqua}+2H**

Stikla $\underline{SiO_2}\downarrow$ /////SiO_2//// $\downarrow\underline{SiO_2}$ membrānas elektrods un pH mērīšana

Stikla elektrods ir parasti lietotais elektrods šķīduma pH noteikšanai. Tas pieskaitāms membrānu elektrodiem, bet tā potenciāls veidojas uz silīcija dioksīda (SiO_2) kristaliskās virsmas silīcijskābes protolīzes reakcijā $\underline{SiO_2{-}SiO_3H}+H_2O \rightleftarrows \downarrow\underline{SiO_2{-}SiO_3}^{-}+H_3O^{+}$. Stikla elektroda potenciāla rašanās izskaidrojama sekojoši.

Uz stikla virsmas atrodas silīcijskābes anjonu funkcionālās grupas $\downarrow\underline{SiO_2{-}SiO_3}^{-}$. Uz plāna kristaliska stikla membrānas virsmas protonē ūdeni (piemēram, sālsskābē HCl) iestājas protolītiskais līdzsvars starp kristālisku silīcijskābi $\underline{SiO_2{-}SiO_3H}$ un silikāta anjonu grupas $\underline{SiO_2{-}SiO_3}^{-}$. Silīcijskābe ir ūdenī nešķīstoša skābe un ļoti vājš elektrolīts: $\underline{SiO_2{-}SiO_3H}+H_2O \rightleftarrows \downarrow\underline{SiO_2{-}SiO_3}^{-}+H_3O^{+}$.

Tā kā kristāliskai membrānai ir iekšējās virsmas līdzsvars un uz ārējās membrānas virsmas ir ārējais līdzsvars , kurš ir mainīgs no mērāmās vides H^{+} koncentrācijas testa eksperimentos.

$$H_3O^{+}{}_{iekš}+\underline{SiO_3^{-}{-}SiO_2}\downarrow \rightleftarrows H_2O+\underline{HSiO_3{-}SiO_2}\downarrow/////SiO_2////\ \underline{SiO_2{-}SiO_3H}+H_2O \rightleftarrows \downarrow\underline{SiO_2{-}SiO_3}^{-}+H_3O^{+}{}_{ārēj.}$$

Virknē saslēgtu līdzsvaru konstanšu reizinājums veido membrānas līdzsvara konstanti $K_{iekš}\bullet K_{ārēj.}=K_{membr}$:

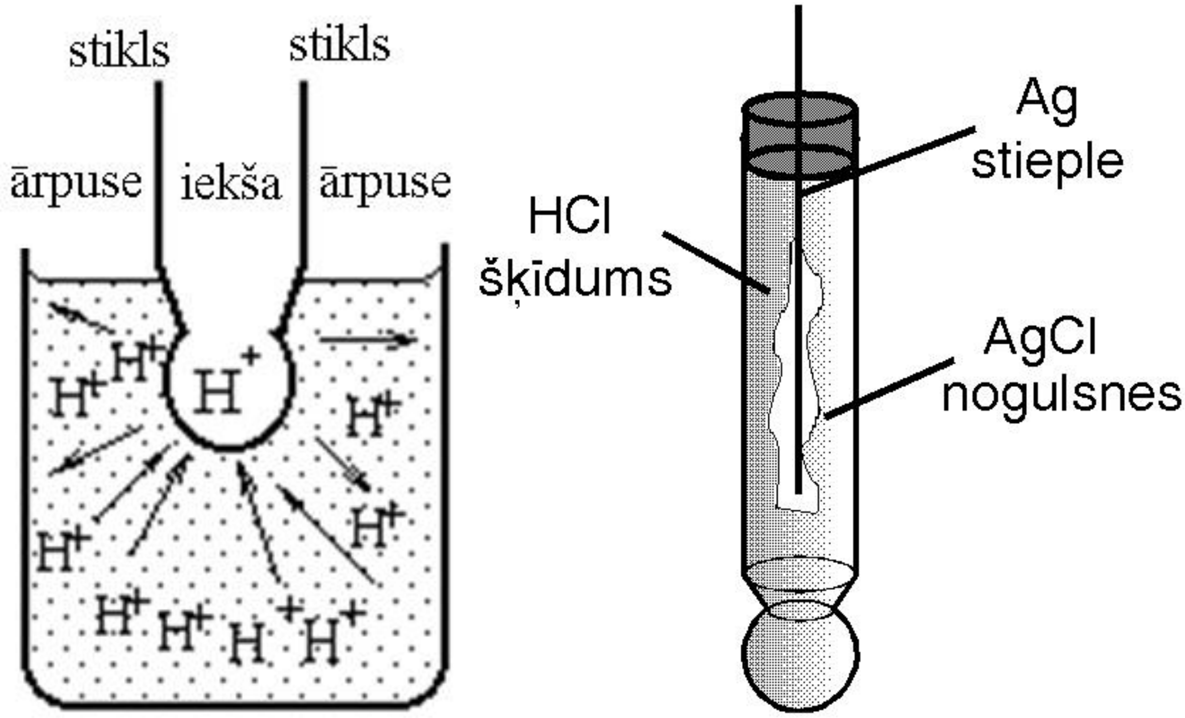
$$K_{iekš.}=\frac{[H_2O]}{[H_3O^{+}]_{iekš}}\ ;\qquad K_{ārēj.}=\frac{[H_3O^{+}]_{ārējs}}{[H_2O]}\ ;\qquad K_{iekš}\bullet K_{ārēj.}=K_{membr}=\frac{[H_3O^{+}]_{ārējs}}{[H_3O^{+}]_{iekš}}\ ;$$

$$E_{membr}=\frac{0{,}0591}{n}\log\frac{[H_3O^{+}]_{ārējs}}{[H_3O^{+}]_{iekš}}=0{,}0591(\log[H_3O^{+}{}_{ārēj}]-\log[H_3O^{+}{}_{iekš}])=E_{const}-0{,}0591\bullet pH \qquad (24)$$

kur n=+1 ūdeņraža jona lādiņš H^{+}, bet logaritms no koncentrāciju attiecības ir logaritmu no koncentrācijām starpība. Jonu koncentrācija membrānas iekšpusē mainās un ir konstanta $E_{const.}=-0{,}0591\bullet\log[H_3O^{+}{}_{iekš}]$. Membrānas potenciāls ir atkarīgs tikai no šķīduma ūdeņraža joniem $H_3O^{+}{}_{ārēj}$ vai $pH=-\log[H_3O^{+}{}_{ārēj}]$.

$$E_{membr}=E_{const.}+0{,}0591\bullet\log[H_3O^{+}{}_{outer.}] \qquad (24)$$

Praktiski lietojama stikla elektroda uzbūves shēma parādīta attēlā. Stikla caurulītes galā ir izveidots plāns stikla pūslītis, kas kalpo par stikla membrānu. Stikla elektroda iekšpusē ieliets HC1 šķīdums ar zināmu koncentrāciju. Ārpusi iegremdē pētāmajā šķīdumā nomēra šķīduma pH.



Stikla membrāna $\underline{HSiO_3{-}SiO_2}\downarrow$ /////SiO_2//// $\downarrow\underline{SiO_2{-}SiO_3H}$ un elektroda komplekts ar sudraba stiepli.

Elektrisko kontaktu ar stikla membrānu iekšējā šķīdumā iegremdē sudraba stiepli, kas izveido otrā veida elektroda potenciālu $E_{AgCl\ iekš}$ virknē ar membrānas potenciālu $E_{membr.}+ E_{AgCl\ iekš}$. Potenciāls ir atkarīgs tikai no ārējā – pētāmā šķīduma pH, jo sālsskābes koncentrācija ir konstanta. EDS (elektro dzinēja spēku) mēra noslēgtai elektriskai ķēdei. To panāk ārējā šķīdumā iemērcot salīdzināšanas elektrodu ar standarta potencialu E_{AgCl}. Elektriskā ķēde noslēdzas pie pH-metra kontakta spailēm:

Kopējais EDS potenciāls sastāv no 3 virknē saslēgtiem elektrodiem no 3 daļām:

1) stikla elektroda iekšpusē izveidotā AgCl elektroda potenciāla $E_{AgCl\ iekš.}$;
2) stikla membrānas elektrods $E_{membr}= E_{const.}+0{,}0591\bullet \log[H_3O^+_{outer}]=E_{const.}-0{,}0591\bullet pH$ (24).;
3) alīdzināšanas elektrods ar standarta potenciālu E_{AgCl}.

Saskaitot nemainīgo saskaitāmo daļas summā iegūst jaunu konstanti : $E'_{const}= (E_{AgCl}+E_{AgCl\ iekš}\ E_{const.})$

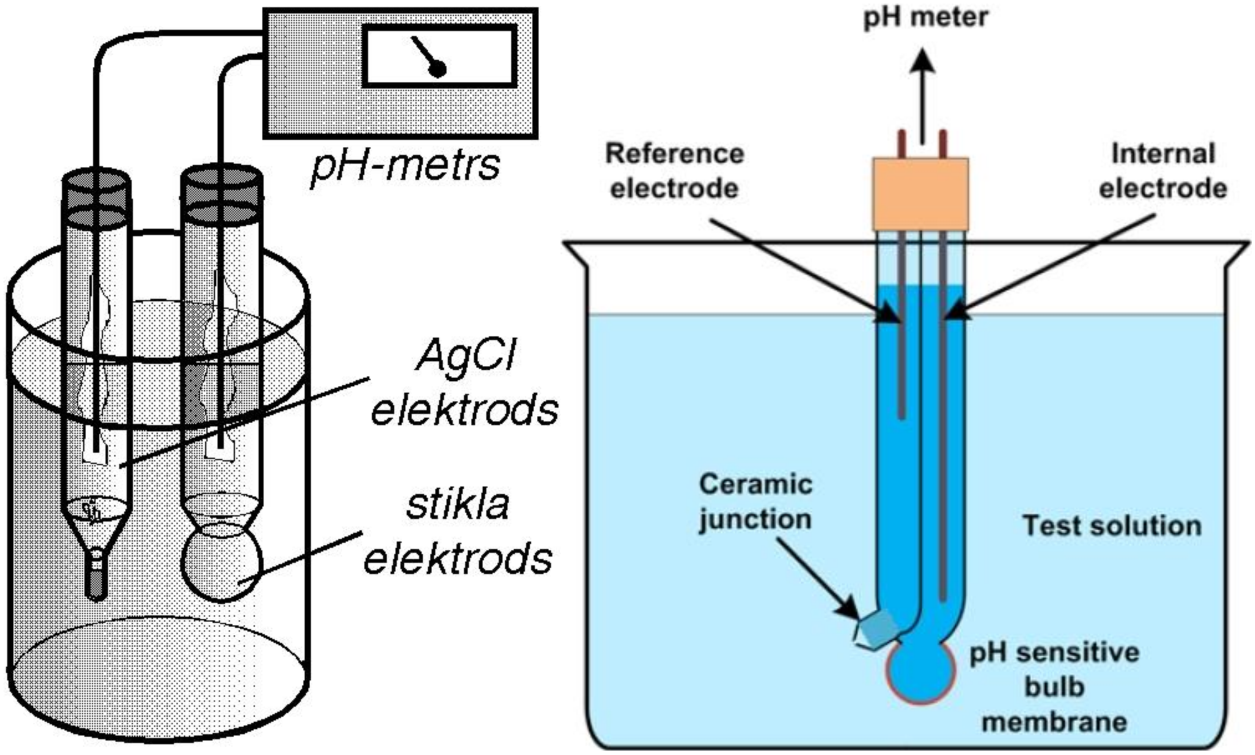
$$EDS=E_{AgCl}+E_{membr}+E_{AgCl\ iekš.}= (E_{AgCl}+E_{AgCl\ iekš}\ E_{const.})+0{,}0591\cdot \lg\ [H_3O^+_{ārēj.}] = E'_{const}-0{,}0591\bullet pH \quad (25)$$

$$EDS = E'_{const}-0{,}0591\bullet pH \quad (26)$$

Nomērītais elektro dzinēja spēks (EDS) ir proporcionāls ārējā šķīduma pH vērtībai.

pH mērīšanai ar stikla elektrodu ir vairākas priekšrocības:

1) stikla elektrods ir lietojams visā nepieciešamajā pH intervālā (no pH = 0 līdz pH = 14);
2) mērījumi ir ļoti precīzi (līdz 0,01 pH vienībai);
3) mērījumi nav atkarīgi no oksidētāju, reducētāju un olbaltumvielu klātbūtnes šķīdumā;
4) pieslēdzot pH-metru pašrakstītājam, var nepārtraukti kontrolēt pH izmaiņas pētāmajā sistēmā.



Šķīduma pH mērīšana ar kombinēto stikla un sudraba hlorīda elektrodu EDS pāri

Nernsta SO_4^{2-}/ SO_3^{2-} pus reakcija skābā $[H_3O^+]$>=0,1 M vidē pH=1 un baziskā OH^- vidē pH>7.

Nernsta absolūtais standarta potenciāls. $[H_2O]$=55,3 M ;

Viela	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$, kJ/mol	
H_2SO_4	-814,0	156,9	-690,0	CRC; $G_{H2SO4}=G_{HSO4-}+G_{H3O}-(\Delta G_{eqH2SO4}+G_{H2O})$=**-718,17** kJ/mol;
H_2SO_4			**-718,17**	G_{H2SO4}=**-746,64+22,44-(-6,035+0)=-718,17** kJ/mol
H_2SO_4		formation	**-84,04**	$G_{H2SO4}=\Delta G°_{H2SO4}+G_{Srombisks}+2\Delta G_{O2}+G_{H2gas}$=**-84,04** kJ/mol;
H_2SO_4		pK_{a1}=-2,8	**-164,3**	$G_{H2SO4aq}$=**-192,74+22,44-(-6,035+0)=-164,3** kJ/mol;
HSO_4^-	-887,3	131,8	-755,9	CRC
HSO_4^-	-	-	**-746,62**	$G_{HSO4-}=G_{SO42-}+G_{H3O}-(21,307+G_{H2O})$=**-746,62** kJ/mol;
HSO_4^-		formation	**-192,74**	$G_{HSO4}=\Delta G°_{HSO4}+G_{Srombisks}+2\Delta G_{O2}+G_{H2gas}/2$=**-192,74** kJ/mol;
HSO_4^-		pK_{a2}=1,99	**-226,3**	G_{HSO4-}=**-227,39+22,44-(21,307+0)=-226,3** kJ/mol;;
HSO_4^-	$E°_{HSO4-}$=	**0,08145**	**-192,7**	$G_{HSO4-}=\Delta G_{eqHSO4-}-3G_{H3O}+(G_{H2SO3}+4G_{H2O})$=**-192,7** kJ/mol ;
SO_4^{2-}	**-907,62**	**-536,2**	**-747,75**	**BioTherm2006**; $\Delta G_{\_SO42-}=\Delta H–T*\Delta S$=**-907,62**-298,15*-0,**5362**=**-747,75** kJ/mol;
SO_4^{2-}	-	formation	**-227,39**	$G_{SO4}=\Delta G_{Form}=\Delta G°_{SO4}+G_{Srombisks}+2\Delta G_{O2}$=**-747,75-85,64**+2*303=**-227,39** kJ/mol;
SO_4^{2-}	$E°_{SO42-}$=	**0,08145**	**-202,3**	$G_{SO42-}=\Delta G_{eqSO42-}-3G_{H3O}+(G_{HSO3}+4G_{H2O})$=**-202,3** kJ/mol ;
SO_4^{2-}	$E°_{SO32-}$=	**-1,278**	**-213,4**	$G_{SO42-}=\Delta G_{eqSO32-OH}-G_{H2O}+(G_{SO32-}+2G_{OH})$=**-213,4** kJ/mol ;
SO_4^{2-}	-909,3	20,1	-744,5	CRC
H_2SO_3		formation	**-381,23**	$G_{H2SO3}=\Delta G°_{H2SO3}+G_{Srombisks}+1,5\Delta G_{O2}+G_{H2gas}$=**-381,23** kJ/mol;
H_2SO_3		pK_{a1}=1,85	**-72,9075**	$G_{H2SO3aq}$=**-74,84+22,44-(20,5075+0)=-72,9075** kJ/mol;
H_2SO_3	$E°_{HSO4-}$=	**0,08145**	**-141,1**	$G_{H2SO3}=G_{HSO4-}+3G_{H3O}-(\Delta G_{eqHSO4-}+4G_{H2O})$=**-141,1** kJ/mol;
HSO_3^-		formation	**-74,84**	$G_{HSO3}=\Delta G°_{HSO3}+G_{Srombisks}+1,5\Delta G_{O2}+G_{H2gas}/2$=**-74,84** kJ/mol;
HSO_3^-		pK_{a2}=7,21	**-150,2**	$G_{HSO3-aq}$=**-121,52+22,44-(51,1+0)=-150,2** kJ/mol;
HSO_3^-	$E°_{SO42-}$=	**0,08145**	**-150,7**	$G_{HSO3}=G_{SO42-}+3G_{H3O}-(\Delta G_{eqSO42-}+4G_{H2O})$=**-150,7** kJ/mol ;
HSO_3^-	-635,5	-29	-486,5	CRC
SO_3^{2-}	**-632,1888**	**-474,0502**	**-490,38**	**BioTherm2006** $DG_{H\_SO32-}=DH_H–T*DS_H$=**-632,1888**-298,15*-0,**47405**=**-490,85** kJ/mol;
SO_3^{2-}	-	formation	**-121,52**	$G_{SO3}=\Delta G_{Form}=\Delta G°_{SO3}+G_{Srombisks}+1,5\Delta G_{O2}$= **-121,52** kJ/mol;
SO_3^{2-}	$E°_{SO32-}$=	**-1,278**	**-135,5**	$G_{SO32-}=G_{SO42-}+G_{H2O}-(\Delta G_{eqSO32-OH}+2G_{OH})$=**-135,5** kJ/mol ;

Veidošanās šķīdība $S_{rombisks}+2O_{2gas}+H_{2gas}+H_2O=H_2SO_{4aq}$; $G_{Srombisks}$=**-85,64** kJ/mol; G_{H2gas}=**85,6** kJ/mol Alberty ;

G_{O2gas}=**303** kJ/mol; $G_{H2SO4}=\Delta G_{Form}=\Delta G°_{H2SO4}+G_{Srombisks}+2\Delta G_{O2}+G_{H2gas}$=-690,0-**85,64**+2*303+85,6= **-84,04** kJ/mol;

$G_{HSO4}=\Delta G_{Form}=\Delta G°_{HSO4}+G_{Srombisks}+2\Delta G_{O2}+0,5G_{H2gas}$=-755,9-**85,64**+2*303+85,6/2=**-192,74** kJ/mol;

$G_{SO4}=\Delta G_{Form}=\Delta G°_{SO4}+G_{Srombisks}+2\Delta G_{O2}$=**-747,75-85,64**+2*303=**-227,39** kJ/mol;

$H_2SO_4+H_2O=HSO_4^-+H_3O^+$; pK_{a1}=-2,8; $K_{eq1}=K_{a1}/[H_2O]=10^{(2,8)}/55,3$=11,41;

$\Delta G_{eqH2SO4}=-R•T•\ln(K_{eq})$=-8,3144*298,15*ln(11,41)=$G_{HSO4-}+G_{H3O}-(G_{H2SO4}+G_{H2O})$=**-6,035** kJ/mol;

$G_{H2SO4aq}=G_{HSO4-}+G_{H3O}-(\Delta G_{eqH2SO4}+G_{H2O})$=**-192,74+22,44-(-6,035+0)=-164,3** kJ/mol;

$HSO_4^-+H_2O=SO_4^{2-}+H_3O^+$; pK_{a2}=1,99; $K_{eq2}=K_{a2}/[H_2O]=10^{(-1,99)}/55,3$=0,0001850;

$\Delta G_{eqHSO4}=-R•T•\ln(K_{eq2})$=-8,3144*298,15*ln(0,0001850)=$G_{SO42-}+G_{H3O}-(G_{HSO4-}+G_{H2O})$=**21,307** kJ/mol;

$G_{HSO4-}=G_{SO42-}+G_{H3O}-(\Delta G_{eqHSO4}+G_{H2O})$= **-227,39+22,44-(21,307+0)=-226,3** kJ/mol;

Veidošanās šķīdība $S_{rombisks}+1,5O_{2gas}+H_{2gas}+H_2O=H_2SO_{3aq}$; $G_{Srombisks}$=**-85,64** kJ/mol; G_{H2gas}=**85,6** kJ/mol Alberty ;

G_{O2gas}=**303** kJ/mol; $G_{H2SO3}=\Delta G_{Form}=\Delta G°_{H2SO3}+G_{Srombisks}+1,5\Delta G_{O2}+G_{H2gas}$=**-835,69-85,64**+1,5*303+85,6=**-381,23** kJ/mol;

$G_{HSO3}=\Delta G_{Form}=\Delta G°_{HSO3}+G_{Srombisks}+1,5\Delta G_{O2}+0,5G_{H2gas}$=-486,5-**85,64**+1,5*303+85,6/2=**-74,84** kJ/mol;

$G_{SO3}=\Delta G_{Form}=\Delta G°_{SO3}+G_{Srombisks}+1,5\Delta G_{O2}$=**-490,38-85,64**+1,5*303=**-121,52** kJ/mol;

$H_2SO_3+H_2O=HSO_3^-+H_3O^+$;$pK_{a1}$=1,85;$K_{eq1}=K_{a1}/[H_2O]=10^{(-1,85)}/55,3$=0,0002554

$\Delta G_{eqH2SO3}=-R•T•\ln(K_{eq1})$=-8,3144*298,15*ln(0,0002554)=$G_{HSO3-}+G_{H3O}-(G_{H2SO3}+G_{H2O})$=**20,5075** kJ/mol;

$G_{H2SO3aq}=G_{HSO3-}+G_{H3O}-(\Delta G_{eqH2SO3}+G_{H2O})$=**-74,84+22,44-(20,5075+0)=-72,9075** kJ/mol;

$HSO_3+H_2O=SO_3^{2-}+H_3O^+$;$pK_{a2}$=7,21;$K_{eq2}=K_{a2}/[H_2O]=10^{(-7,21)}/55,3$= 0,000000001115

$\Delta G_{eqHSO3}=-R•T•\ln(K_{eq2})$=-8,3144*298,15*ln(0,000000001115)=$G_{SO32-}+G_{H3O}-(G_{HSO3-}+G_{H2O})$=**51,1** kJ/mol;

$G_{HSO3-aq}=G_{SO32-}+G_{H3O}-(\Delta G_{eqHSO3}+G_{H2O})$=**-121,52+22,44-(51,1+0)=-150,2** kJ/mol;

$H_2SO_3+4H_2O=HSO_4^-+3H_3O^+$**$+2e^-$**; pH<1,9 $E°_{HSO42-}$=**0,08145** V Suchotina.

$E°_{SO42-}$=E°+0,10166-0,0591/2*lg(1/[H_2O]^4) -0,3982=0,172+0,10166-0,02955*lg(1/55,3^^{4}) -0,3982 =**0,08145** V;

$$E_{HSO4-}=E°_{HSO4-}+\frac{0.0591}{2}\bullet\log\frac{[HSO_4^-]\cdot[H_3O^+]^4}{[H_2SO_3]\cdot[H_2O]^5}=\mathbf{0,08145}\ V+\frac{0.0591}{2}\bullet\log\frac{[HSO_4^-]\cdot[H_3O^+]^4}{[H_2SO_3]\cdot[H_2O]^5}$$

Δ**G**$_{eqHSO4-}$=$E°_{HSO4-}$•F•2=**0,08145***96485*2=**15,717** kJ/mol, <=> **15,68** kJ/mol;

Δ**G**$_{eqHSO4-}$=G_{HSO4-}+3**G**$_{H3O}$**-**(G_{H2SO3}+4**G**$_{H2O}$)=**-192,74**+3*22,44-(**-141,1**+4*0)=**15,68** kJ/mol ;

G_{H2SO3}=G_{HSO4-}+3**G**$_{H3O}$**-**(Δ**G**$_{eqHSO4-}$+4**G**$_{H2O}$)=**-192,74**+3*22,44-(**15,717**+4*0)= **-141,1** kJ/mol

G_{HSO4-}=Δ**G**$_{eqHSO4-}$-3**G**$_{H3O}$+(G_{H2SO3}+4**G**$_{H2O}$)=**15,717**-3*22,44+(**-141,1**+4*0)= **-192,7** kJ/mol ;

$HSO_3^-+4H_2O=SO_4^{2-}+3H_3O^+$**$+2e^-$** ; 2=<pH<7, Suchotina $E°_{SO42-}$=**0,08145** V;

$E°_{SO42-}$=E°+0,10166-0,0591/2*lg(1/[H_2O]^4) -0,3982=0,172+0,10166-0,02955*lg(1/55,3^^{4}) -0,3982 =**0,08145** V;

$$E_{SO42-}=E°_{SO42-}+\frac{0.0591}{2}\bullet\log\frac{[SO_4^{2-}]\cdot[H_3O^+]^3}{[HSO_3^-]\cdot[H_2O]^4}=\mathbf{0,08145}\ V+\frac{0.0591}{2}\bullet\log\frac{[SO_4^{2-}]\cdot[H_3O^+]^3}{[HSO_3^-]\cdot[H_2O]^4}$$

Δ**G**$_{eqSO42-}$=$E°_{SO42-}$•F•2=**0,08145***96485*2=**15,717** kJ/mol, <=> **15,72** kJ/mol ;

Δ**G**$_{eqSO42-}$=G_{SO42-}+3**G**$_{H3O}$**-**(G_{HSO3}+4**G**$_{H2O}$)=**-202,3**+3***22,44-**(**-150,7**+4*0)=**15,72** kJ/mol ;

G_{HSO3}=G_{SO42-}+3**G**$_{H3O}$**-**(Δ**G**$_{eqSO42-}$+4**G**$_{H2O}$)=**-202,3**+3***22,44-**(**15,717**+4*0)= **-150,7** kJ/mol ;

G_{SO42-}=Δ**G**$_{eqSO42-}$-3**G**$_{H3O}$+(G_{HSO3}+4**G**$_{H2O}$)=**15,717**-3***22,44**+(**-150,7**+4*0)=**-202,3** kJ/mol ;

$SO_3^{2-}+2OH^-=SO_4^{2-}+H_2O+2e^-$; pH > 7 ; $E°_{SO42-}$=**-1,278** V Suchotina

$E°_{SO32-OH}$=E°+0.10166-0.0591/2*lg([H_2O])=-0.93+0.10166-0.02955*lg(55.3)-0,3982= **-1,278** V;

$$E_{SO32-OH}=E°_{SO32-OH}+\frac{0.0591}{2}\bullet\log\frac{[SO_4^{2-}]\cdot[H_2O]}{[SO_3^{2-}]\cdot[OH^-]^2}=\mathbf{-1,278}\ V+\frac{0.0591}{2}\bullet\log\frac{[SO_4^{2-}]\cdot[H_2O]}{[SO_3^{2-}]\cdot[OH^-]^2}$$

Δ**G**$_{eqSO42-OH}$=$E°_{SO32-OH}$•F•2=**-1,278***96485*2=**-246,62** kJ/mol, <=> **-246,6**;

Δ**G**$_{eqSO32-OH}$=G_{SO42-}+**G**$_{H2O}$**-**(G_{SO32-}+2**G**$_{OH}$)=**-213,4+0-**(**-121,52**+2*77,36)=**-246,6** kJ/mol ;

G_{SO32-}=G_{SO42-}+**G**$_{H2O}$**-**(Δ**G**$_{eqSO32-OH}$ +2**G**$_{OH}$)=**-213,4+0-**(**-246,62**+2*77,36)= **-121,5** kJ/mol ;

G_{SO42-}=Δ**G**$_{eqSO32-OH}$-**G**$_{H2O}$+(G_{SO32-}+2**G**$_{OH}$)=**-246,62-0+**(**-121,52**+2*77,36)= **-213,4** kJ/mol ;

Nernsta potenciāla NO_3^-/NO_2^- red-oks sistēmas īpašības skābā H_3O^+ ūdens un baziskā OH^- vidē
Nernsta absolūtais standarta potenciāls.

Formation $\Delta G°_{HNO2gas}+0,5N_{2gas}+O_{2gas}+0,5H_{2gas}=G_{HNO2gas}$=-46+(0,5*-**9,55**+**303**+0,5*85,6)= **295,025** kJ/mol ;
$G_{N2gas}=G_{N2aqua}-(\Delta G_{Hess\_šķ\_N2aqua}+G_{H2O})$=**18,7**-(**28,25**+0)=**-9,55** kJ/mol; G_{H2gas}=**85,6** kJ/mol Alberty ; G_{O2gas}=**303** kJ/mol;
$G_{NO2Form}=\Delta G°_{NO2aq}+0,5G_{N2gas}+G_{O2gas}+G_{H2O}$=**-33,01**+0,5*-9,55+1*303+0=**265,2** kJ/mol;
$HNO_2+H_2O=NO_2^-+H_3O^+$;pKa=3,15; $K_{eq}=K_a/[H_2O]=10^{(-3,15)}/55,3$= 0,00001280;
ΔG_{eqHNO2}=-R•T•ln(K_{eq})=-8,3144*298,15*ln(0,0000128)=$G_{NO2-}+G_{H3O}-(G_{HNO2}+G_{H2O})$=**27,927** kJ/mol;
$\Delta G_{eqHNO2}=G_{NO2-}+G_{H3O}-(G_{HNO2}+G_{H2O})$=**265,2**+**22,44**-(**259,713** +0)=**27,927** kJ/mol;
$G_{NO2-}=\Delta G_{eqHNO2}-G_{H3O}+(G_{HNO2}+G_{H2O})$=**27,927**+**22,44**-(**259,713** +0)=**265,2** kJ/mol;
$G_{HNO2}=G_{NO2-}+G_{H3O}-(\Delta G_{eqHNO2}+G_{H2O})$=**265,2**+**22,44**-(**27,927**+0)=**259,713** kJ/mol;

$G_{NO3Form}=\Delta G°_{NO3aq}+(0,5G_{N2gas}+1,5G_{O2gas}+0,5G_{H2gas}+G_{H2O})$=**-109,55**+(0,5*-9,55+1,5*303+0)=**340,2** kJ/mol;
$HNO_3+H_2O=NO_3^-+H_3O^+$;pKa=-1,4; $K_{eq}=K_a/[H_2O]=10^{(1,4)}/55,3$=0,4542;
ΔG_{eqHNO3}=-R•T•ln(K_{eq})=-8,3144*298,15*ln(0,4542)=$G_{NO3-}+G_{H3O}-(G_{HNO3}+G_{H2O})$=**1,956** kJ/mol;
$\Delta G_{eqHNO3}=G_{NO3-}+G_{H3O}-(G_{HNO3}+G_{H2O})$=**340,2**+**22,44**-(**360,684**+0)=**1,956** kJ/mol;
$G_{HNO3}=G_{NO3-}+G_{H3O}-(\Delta G_{eqHNO3}+G_{H2O})$=**340,2**+**22,44**-(**1,956**+0)=**360,7** kJ/mol;
$G_{NO3-}=\Delta G_{eqHNO3}-G_{H3O}+(G_{HNO3}+G_{H2O})$=**1,956**-**22,44**+(**360,684**+0)=**340,2** kJ/mol;

Viela	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$, kJ/mol	
HNO_2	$E°_{NO3-H3O+}$	=**0,8495 V**	**243,592**	$HNO_2+4H_2O=NO_3^-+3H_3O^+$+**2e**$^-$;
HNO_2	-	pKa=3,15	**259,713**	$G_{HNO2}=G_{NO2-}-G_{H3O}+(\Delta G_{eqHNO2}+G_{H2O})$=**259,713** kJ/mol;
HNO_{2gas}	-79,5	254,1	-46,0	
HNO_{2gas}	-	formation	**295,025**	$G_{HNO2gas}=\Delta G°_{HNO2gas}+0,5N_{2gas}+O_{2gas}+0,5H_{2gas}$=**295,025** kJ/mol
NO_2^-	-	formation	**265,2**	$G_{NO2form}=\Delta G°_{NO2aq}+0,5G_{N2gas}+G_{O2gas}+G_{H2O}$=**265,2** kJ/mol;
NO_2^-		pKa=3,15	**265,2**	$G_{NO2-}=\Delta G_{eqHNO2}-G_{H3O}+(G_{HNO2}+G_{H2O})$=**265,2** kJ/mol;
NO_2^-	**-104,19**	**-238,7**	**-33,01**	**BioTherm2006**
NO_2^-			**482,3**	$G_{NO3-}=\Delta G_{eqNH4+H2O}-10G_{H3O}+(G_{NH4+}-13G_{H2O})$=**580,31** kJ/mol
HNO_3	-207	146	-250,53	Wiki $G°_{NO3-}=\Delta H_H-T*\Delta S_H$=-207-298,15*0,146=-250,5886 kJ/mol;
HNO_3	-	-	**592,29**	
HNO_3	-	pKa=-1,4	**360,7**	$G_{HNO3}=G_{NO3-}+G_{H3O}-(\Delta G_{eqHNO3}+G_{H2O})$=**360,7** kJ/mol;
NO_3^-	$E°_{NH4+H2O}$=	**1,0198** V	**795,66**	$G_{NO3-}=\Delta G_{eqNH4+H2O}-10G_{H3O}+(G_{NH4+}-13G_{H2O})$=**795,66** kJ/mol;
NO_3^-	-206,85	146,7	-250,5886	$\Delta G°_{NO3-}=\Delta H_H-T*\Delta S_H$=-206,85-298,15*0,1467=-250,5886 kJ/mol;
NO_3^-	-	formation	**340,2**	$G_{NO3Form}=\Delta G°_{HNO3aq}+(0,5G_{N2gas}+1,5G_{O2gas}+G_{H2O})$=**340,2** kJ/mol;
NO_3^-	-	pKa=-1,4	**340,2**	$G_{NO3-}=\Delta G_{eqHNO3}-G_{H3O}+(G_{HNO3}+G_{H2O})$=**340,2** kJ/mol ;
NO_3^-	$E°_{NO3-OH}$	**-0,3380** V	**354,696**	$NO_2^-+2OH^-=NO_3^-+H_2O$+**2e**$^-$; $E°_{NO3-H2O}$=**-0,3380** V
NO_3^-	**-204,59**	**-318,8**	**-109,55**	**BioTherm2006**
NO_{gas}	91,3	210,8	87,6	CRC
NO_{gas}	Solubility	product -	**61,024**	$G_{NOgas}=G_{H2O}+G_{NOaq}-(\Delta G_{sp})$=**0**+**86,55**-(**25,526**)=**61,024** kJ/mol ;
NO_{aq}	-	-	**86,55**	**BioTherm2006**
NO_{aq}	$E°_{NO(g)H3O+}$	=**0,8695**	**178,28**	$NO_{aq}+6H_2O=NO_3^-+4H_3O^+$+**3e**$^-$;
NH_4^+	On data of	Alberty	**232,9**	
NH_4^++OH^-	-361,2	165,6	-254	$\Delta G°_{NH4+OH}$=-254<$\Delta G_{sumNH4+OH}$=**232,9**+77,36= **310,26** kJ/mol ;

$HNO_2+4H_2O=NO_3^-+3H_3O^+$+**2e**$^-$; $E°_{NO3-H3O+}$=**0,8495** V Kortly, Shucha pH<3,15;
$E°_{NO3-H3O+}$=E°+0,10166-0,0591/2*lg(1/$[H_2O]^4$)-0,3982=0,94+0,10166-0,02955*lg(1/55,3^4) -0,3982 =**0,8495** V;

$$E_{NO3-H3O+}=E°_{NO3-H3O+}+\frac{0.0591}{2}\bullet\log\frac{[NO_3^-]\cdot[H_3O^+]^3}{[HNO_2]\cdot[H_2O]^4}=\mathbf{0,8495}\ V+\frac{0.0591}{2}\bullet\log\frac{[NO_3^-]\cdot[H_3O^+]^3}{[HNO_2]\cdot[H_2O]^4}$$

$\Delta G_{eqNO3-H3O+}=E°_{NO3-H3O+}$•F•2=**0,8495***96485*2=**163,928** kJ/mol, <=> **163,928** kJ/mol,
$\Delta G_{eqNO3-H3O+}=G_{NO3-}+3G_{H3O}-(G_{HNO2}+4G_{H2O})$=**340,2**+3*22,44-(**243,592**+4*0)=**163,928** kJ/mol,
$G_{HNO2}=G_{NO3-}+3G_{H3O}-(\Delta G_{eqNO3-H3O+}+4G_{H2O})$=**340,2**+3*22,44-(**163,928**+4*0)=**243,592** kJ/mol;

$NO_2^- + 2OH^- = NO_3^- + H_2O + 2e^-$; $E°_{NO3–H2O}$=**-0,3380** V; pH>3,15 Suchotina

$E°_{NO3–OH}$=E°+0,10166-0,0591/2*lg([H_2O])-0,3982=0,94+0,10166-0,02955*lg(55,3^1) -0,3982 = **-0,3380** V;

$$E_{NO3–OH}=E°_{NO3–OH}+\frac{0.0591}{2}\bullet\log\frac{[NO_3^-]\cdot[H_2O]}{[NO_2^-]\cdot[OH^-]^2}=\mathbf{-0{,}3380}\ V+\frac{0.0591}{2}\bullet\log\frac{[NO_3^-]\cdot[H_2O]}{[NO_2^-]\cdot[OH^-]^2}$$

$\Delta G_{eq NO3–OH}$=E°$_{NO3–OH}$•F•2=**-0,3380***96485*2=**-65,224** kJ/mol,

$\Delta G_{eq NO3–OH}$=$G_{NO3–}$+G_{H2O}-($G_{NO2–}$+2G_{OH})=**340,2**+0-(**265,2**+2*77,36)=**-79,72** kJ/mol,

$\Delta G_{eq NO3–OH}$=$G_{NO3–}$+G_{H2O}-($G_{NO2–}$+2G_{OH})=**354,696**+0-(**265,2**+2*77,36)=**-65,224** kJ/mol,

$G_{NO3–}$=$\Delta G_{eq NO3–OH}$ -G_{H2O}+($G_{NO2–}$+2G_{OH})=**-65,224**-0+(**265,2**+2*77,36)=**354,696** kJ/mol,

$G_{NO2–}$=**354,696**+0-2*77,36+**65,224**=**256,2** kJ/mol;

Šķīdība ūdenī $NO^{(g)}$ 0,0056 g/99,6g (20 C) ; w%=0,0056/(0,0056+99,6)*100=0,00562%;

M_{NO}=30.006 g/mol ; [NO_{aq}]=(0,00562/100*996)/30,006=0,001865 M, ja tīras gāzes mol daļa ir viens [$NO^{(g)}$]=1;

Šķīdības konstante $NO^{(g)}$+H_2O=NO_{aq}; [$NO^{(g)}$]=1 mol fraction of pure gas

$K_{šķ}$=[NO_{aq}]/[$NO^{(g)}$]/[H_2O]=0,001865/1/55,3=10^(-4,472).

ΔG_{sp}=-R•T•ln(K_{sp})=-8.3144*298.15*ln(10^(-4,472))=-8.3144•298.15•-10,297=**25,526** kJ/mol

ΔG_{sp}= G_{NOaq}-(G_{H2O}+G_{NOgas})=**0+**(data Alberty **86,55**)(data CRC 87,6)-(**61,024** Solubility product)=**25,526** kJ/mol ;

G_{NOgas}=G_{NOaq}-(G_{H2O}+ΔG_{sp})=**86,55-**(**0**+**25,526**)=**61,024** kJ/mol ; if Solubility product is ΔG_{sp}=**25,526** kJ/mol ;

$NO_{aq} + 6H_2O = NO_3^- + 4H_3O^+ + 3e^-$; $E°_{NO(g)H3O+}$=**0,8695** V; Kortly, Shucha ;

$E°_{NO(g)H3O+}$=E°+0,10166-0,0591/3*lg(1/[H_2O]^6)-0,3982=0,96+0,10166-0,0197*lg(1/55,3^6) -0,3982 =**0,8695** V;

$$E_{NO(g)H3O+}=E°_{NO(g)H3O+}+0{,}0591/3\bullet\log\frac{[NO_3^-]\cdot[H_3O^+]^4}{[NO_{aq}]\cdot[H_2O]^6}=\mathbf{0{,}8695}\ V+0{,}0197\bullet\log\frac{[NO_3^-]\cdot[H_3O^+]^4}{[NO_{aq}]\cdot[H_2O]^6}$$

$\Delta G_{eq NO(g)H3O+}$=E°$_{NO(g)H3O+}$•F•3=**0,8695***96485*3=**251,68** kJ/mol,

$\Delta G_{eq NO(g)H3O+}$=$G_{NO3–}$+4G_{H3O}-(G_{NOaq}+6G_{H2O})=**340,2**+4*22,44-(**178,28**+6*0)=**251,68** kJ/mol,

G_{NOaq} =$G_{NO3–}$+4G_{H3O}-($\Delta G_{eq NO(g)H3O+}$+6G_{H2O})=**340,2**+4*22,44-(**251,68**+6*0)=**178,28** kJ/mol,

$NH_4^+ + 13H_2O = NO_3^- + 10H_3O^+ + 8e^-$; $E°_{NH4+H2O}$=**1,0198** V Suchotina

$E°_{NH4+H2O}$=E°+0,10166-0,0591/8*lg(1/[H_2O]^{13})-0,3982=0,87+0,10166-0,00739*lg(1/55,3^13) -0,3982 =**1,0198** V;

$$E_{NH4+H2O}=E°_{NH4+H2O}+0{,}0591/8\bullet\log\frac{[NO_3^-]\cdot[H_3O^+]^{10}}{[NH_4^+]\cdot[H_2O]^{13}}=\mathbf{1{,}0198}\ V+0{,}00739\bullet\log\frac{[NO_3^-]\cdot[H_3O^+]^{10}}{[NH_4^+]\cdot[H_2O]^{13}}$$

$\Delta G_{eq NH4+H2O}$=E°$_{NH4+H2O}$•F•8=**1,0198***96485*8=**787,16** kJ/mol,

$\Delta G_{eq NH4+H2O}$=$G_{NO3–}$+10G_{H3O}-(G_{NH4+}-13G_{H2O})=$G_{NO3–}$+10*22,44-(**232,9**-13***0**)=**787,16** kJ/mol,

$G_{NO3–}$=$\Delta G_{eq NH4+H2O}$-10G_{H3O}+(G_{NH4+}-13G_{H2O})=**787,16**-10*22,44+(**232,9**-13***0**)=**795,66** kJ/mol;

Nernsta potenciāla $2CO_2$ / $H_2C_2O_4$ red-oks sistēmas īpašības skābā H_3O^+ , ūdens vidē
Nernsta absolūtais standarta potenciāls. $H_2C_2O_4$ pK_{a1}=1,25; pK_{a2}=4,14;

Viela	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$, kJ/mol	$\Delta G_{H2C2O4}=\Delta H_H–T*\Delta S_H$=-829,9-298,15*-0,1098=**-747,75** kJ/mol;
$H_2C_2O_{4cr}$	-829,9	-109,8	-797,16	
$H_2C_2O_{4cr}$	-	pK_{a1}=1,25	**-602,329**	$G_{H2C2O4}=G_{HC2O4}+G_{H3O}-(\Delta G_{eq1H2C2O4}+\Delta G_{H2O})$=**-602,329** kJ/mol ;
$H_2C_2O_4$	$E°_{H2C2O4}$=	**-0,6835** V	**-595,18**	$G_{H2C2O4}=2G_{CO2}+2G_{H3O}-(\Delta G_{eqH2C2O4}+2G_{H2O})$=**-595,18** kJ/mol ;
$HC_2O_4^-$	-	pK_{a2}=4,14	**-607,687**	$G_{HC2O4}=G_{C2O4}+G_{H3O}-(\Delta G_{eq2HC2O4}+G_{H2O})$=**-607,687** kJ/mol ;
$HC_2O_4^-$	-	pK_{a2}=1,25	**-600,538**	$G_{HC2O4}=\Delta G_{eq1H2C2O4}-G_{H3O}+(G_{H2C2O4}+\Delta G_{H2O})$=**-600,538** kJ/mol ;
$HC_2O_4^-$	$E°_{HC2O4}$=	**-0,7350** V	**-607,687**	$G_{H2C2O4}=2G_{CO2}+G_{H3O}-(\Delta G_{eqH2C2O4}+G_{H2O})$=**-607,687** kJ/mol;
$C_2O_4^{2-}$	-	-	**-677,14**	**BioTherm2006**
$C_2O_4^{2-}$	-	pK_{a2}=4,14	**-596,549**	$G_{C2O4}=\Delta G_{eq2HC2O4}-G_{H3O}+(G_{HC2O4}+G_{H2O})$=**-596,549** kJ/mol ;
$C_2O_4^{2-}$	$E°_{C2O4}$=	**-0,7865** V	**-620,19**	$G_{C2O4}=2G_{CO2}-(\Delta G_{eqHC2O4})$=2*-385,98-(**-151,77**)=**-620,19** kJ/mol;
CO_{2aq}	-413,798	117,5704	-385,98	

$HC_2O_4^-+H_2O=C_2O_4^{2-}+H_3O^+$; p$K_{a2}$=4,14; $K_{eq2}=K_{a2}/[H_2O]$=10^(-4,14)/55,3=0,000001310;
$\Delta G_{eq2HC2O4}=-R•T•\ln(K_{eq2})$=-8,3144*298,15*ln(0,000001310)=$\Delta G_{C2O4}+\Delta G_{H3O}-(\Delta G_{HC2O4}+\Delta G_{H2O})$= **33,578** kJ/mol;
$\Delta G_{eq2HC2O4}=G_{C2O4}+G_{H3O}-(G_{HC2O4}+G_{H2O})$=**-596,549+22,44-(-607,687+0)=33,578** kJ/mol;
$G_{HC2O4}=G_{C2O4}+G_{H3O}-(\Delta G_{eq2HC2O4}+G_{H2O})$=**-596,549+22,44-(33,578+0)=-607,687** kJ/mol;
$G_{C2O4}=\Delta G_{eq2HC2O4}-G_{H3O}+(G_{HC2O4}+G_{H2O})$=**33,578-22,44+(-607,687+0)=-596,549** kJ/mol;

$H_2C_2O_4+H_2O=HC_2O_4^-+H_3O^+$; p$K_{a1}$=1,25; $K_{eq1}=K_{a1}/[H_2O]$=10^(-1,25)/55,3= 0,0010169;
$\Delta G_{eq1H2C2O4}=-R•T•\ln(K_{eq1})$=-8,3144*298,15*ln(0,0010169)=$\Delta G_{HC2O4}+\Delta G_{H3O}-(\Delta G_{HC2O4}+\Delta G_{H2O})$=**17,08** kJ/mol;
$\Delta G_{eq1H2C2O4}=G_{HC2O4}+G_{H3O}-(G_{H2C2O4}+\Delta G_{H2O})$=**-600,538+22,44-(-595,18+0)=17,082** kJ/mol;
$G_{H2C2O4}=G_{HC2O4}+G_{H3O}-(\Delta G_{eq1H2C2O4}+\Delta G_{H2O})$=**-600,538+22,44-(17,082+0)=-595,18** kJ/mol;
$G_{HC2O4}=\Delta G_{eq1H2C2O4}-G_{H3O}+(G_{H2C2O4}+\Delta G_{H2O})$=**17,082-22,44+(-595,18+0)=-600,538** kJ/mol;

$\Delta G_{eq1H2C2O4}=-R•T•\ln(K_{eq1})$=-8,3144*298,15*ln(0,0010169)=$\Delta G_{HC2O4}+\Delta G_{H3O}-(\Delta G_{HC2O4}+\Delta G_{H2O})$=**17,08** kJ/mol;
$\Delta G_{eq1H2C2O4}=G_{HC2O4}+G_{H3O}-(G_{H2C2O4}+\Delta G_{H2O})$=**-607,687+22,44-(-602,329+0)= 17,082** kJ/mol;
$G_{H2C2O4}=G_{HC2O4}+G_{H3O}-(\Delta G_{eq1H2C2O4}+\Delta G_{H2O})$=**-607,687+22,44-(17,082+0)=-602,329** kJ/mol;
$G_{HC2O4}=\Delta G_{eq1H2C2O4}-G_{H3O}+(G_{H2C2O4}+\Delta G_{H2O})$=**17,082-22,44+(-602,329+0)= -607,687** kJ/mol;

pH<=1,25 $H_2C_2O_4+2H_2O=2CO_2+2H_3O^++2e^-$; $E°_{H2C2O4}$=**-0,6835** V Suchotina [17]
$E°_{H2C2O4}=E°+0,10166+0,0591/2*\lg([H_2O]^2)-0,3982$=-0,49+0,10166-0,02955*lg(1/55,3²)-0,3982=**-0,6835** V;
Absolute Nernst's Standard potential $E°_{H2C2O4}$=**-0,6835** V; Suchotina [17]

$$E_{H2C2O4}=E°_{H2C2O4}+\frac{0.0591}{2}\bullet\lg\frac{[CO_2]^2\cdot[H_3O^+]^2}{[H_2C_2O_2]\cdot[H_2O]^2}=-0,6835\text{ V}+\frac{0.0591}{2}\bullet\lg\frac{[CO_2]^2\cdot[H_3O^+]^2}{[H_2C_2O_2]\cdot[H_2O]^2}$$

$\Delta G_{eqH2C2O4}=E°_{H2C2O4}•F•2$=**-0,6835***96485*2=**-131,895** kJ/mol,
$\Delta G_{eqH2C2O4}=2G_{CO2}+2G_{H3O}-(G_{H2C2O4}+2G_{H2O})$=2*-385,98+2***22,44-(-595,185**+2*0)=**-131,9** kJ/mol,
$G_{H2C2O4}=2G_{CO2}+2G_{H3O}-(\Delta G_{eqH2C2O4}+2G_{H2O})$=2*-385,98+2***22,44-(-131,9**+2*0)=**-595,18** kJ/mol;

1,25<pH<=4,14; $HC_2O_4^-+H_2O$ = $2CO_2+H_3O^++2e^-$;
Absolute Nernst's Standard potential $E°_{H2C2O4}$=**-0,7350** V Suchotina [17]
$E°_{HC2O4}=E°+0,10166-0,0591/2*\lg(1/[H_2O]^1)-0,3982$=-0,49+0,10166-0,0591/2*lg(1/55,3^1)-0,3982=**-0,7350** V;
$\Delta G_{eqHC2O4}=E°_{HC2O4}•F•2$=**-0,7350***96485*2=**-141,833** kJ/mol,
$\Delta G_{eqHC2O4}=2G_{CO2}+G_{H3O}-(G_{HC2O4}+G_{H2O})$=2*-385,98+**22,44-(-607,687**+0)=**-141,833** kJ/mol,
$G_{HC2O4}=2G_{CO2}+G_{H3O}-(\Delta G_{eqHC2O4}+G_{H2O})$=2*-385,98+**22,44-(-141,833**+0)=**-607,687** kJ/mol;

4,14 <pH; $C_2O_4^{2-}$ = $2CO_2+2e^-$; Absolute Nernst's Standard potential $E°_{C2O4}$=**-0,7865** V; Suchotina [17]
$E°_{C2O4}=E°+0,10166-0,0591/2*\lg([1/H_2O]^0)-0,3982$=-0,49+0,10166-0,0591/2*lg(1/55,3⁰)-0,3982=**-0,6835** V;
$\Delta G_{eqC2O4}=E°_{C2O4}•F•2$=**-0,7865***96485*2=**-151,77** kJ/mol,
$\Delta G_{eqC2O4}=2G_{CO2}-(G_{C2O4})$=2*-385,98-(**-620,19**)=**-151,77** kJ/mol,
$G_{C2O4}=2G_{CO2}-(\Delta G_{eqHC2O4})$=2*-385,98-(**-151,77**)=**-620,19** kJ/mol;

Nernsta potenciāla $Cr_2O_7^{2-}$ / $2Cr^{3+}$ red-oks sistēmas īpašības skābā H_3O^+ , ūdens vidē
Nernsta absolūtais standarta potenciāls. $\log K_D=2.05$; $K_D=10$^$2{,}05$; $2HCrO_4^-=Cr_2O_7^{2-}+H_2O$;

$\Delta G_D=-R\bullet T\bullet \ln(K_D*[H_2O])=-8{,}3144*298{,}15*\ln(10\text{^}2{,}05*55{,}3)=G_{Cr2O7}+G_{H2O}-(2G_{HCrO4})=$ **-21,65** kJ/mol;

$2G_{HCrO4}=G_{Cr2O7}+G_{H2O}-(\Delta G_D)=G_{Cr2O7}+0-($**-21,65**$)=???$ kJ/mol;

$pK_a=1{,}8$; $HCr_2O_7^-+H_2O=Cr_2O_7^{2-}+H_3O^+$; $K_{eq}=K_a/[H_2O]=10\text{^}(-1{,}8)/55{,}3=0{,}0002866$;

$\Delta G_{eq}=-R\bullet T\bullet \ln(K_{eq})=-8{,}3144*298{,}15*\ln(0{,}0002866)=G_{Cr2O7}+G_{H3O}-(G_{HCr2O7}+G_{H2O})=$**20,22** kJ/mol;

$G_{HCr2O7}=G_{Cr2O7}+G_{H3O}-(\Delta G_{eq}+G_{H2O})=G_{Cr2O7}+22{,}44-($**20,22**$+0)=???$ kJ/mol;

Instability constant $[CrOH]^{2+}+H_2O=Cr^{3+}+OH^-$; $K_{inst}=10\text{^}^{(-9{,}77)}$; $K_{eq}=K_{inst}/[H_2O]=10\text{^}^{(-9{,}88)}/55{,}3=10\text{^}^{(-11{,}51)}$;

$\Delta G_{eqinst}=-R\bullet T\bullet \ln(K_{eqinst})=-8{,}3144*298{,}15*\ln(10\text{^}^{(-11{,}51)})=G_{Cr3+}+G_{OH}-(G_{[CrOH]2+}+G_{H2O})=$ **65,7** kJ/mol;

$G_{[CrOH]2+}=G_{Cr3+}+G_{OH}-(\Delta G_{eqinst}+G_{H2O})=G_{Cr3+}+77{,}36-($**65,7**$+0)=???$ kJ/mol;

Instability $[Cr(OH)_2]^++2H_2O=Cr^{3+}+2OH^-$; $K_{inst}=10\text{^}^{(-17{,}3)}$; $K_{eqinst}=K_{inst}/[H_2O]^2=10\text{^}^{(-17{,}3)}/55{,}3\text{^}2=10\text{^}^{(-20{,}785)}$;

$\Delta G_{eqinst}=-R\bullet T\bullet \ln(K_{eqinst})=-8{,}3144*298{,}15*\ln(10\text{^}^{(-20{,}785)})=G_{Cr3+}+2G_{OH}-(G_{Cr(OH)2}+2G_{H2O})=$**118,64** kJ/mol;

$G_{Cr(OH)2}=G_{Cr3+}+2G_{OH}-(\Delta G_{eqinst}+2G_{H2O})=G_{Cr3+}+2*77{,}36-($**118,64**$+2*0)=???$ kJ/mol;

Instability constant $[Cr(OH)_3]+3H_2O=Cr^{3+}+3OH^-$; $K_{inst}=10\text{^}^{(-24)}$; $K_{eq}=K_{inst}/[H_2O]=10\text{^}^{(-24)}/55{,}3=10\text{^}^{(-29{,}23)}$;

$\Delta G_{eqinst}=-R\bullet T\bullet \ln(K_{eqinst})=-8{,}3144*298{,}15*\ln(10\text{^}^{(-29{,}23)})=G_{Cr3+}+3G_{OH}-(G_{[Cr(OH)3]}+3G_{H2O})=$**166,8** kJ/mol;

$G_{[Cr(OH)3]}=G_{Cr3+}+3G_{OH}-(\Delta G_{eqinst}+3G_{H2O})=G_{Cr3+}+3*77{,}36-($**166,8**$+3*0)=???$ kJ/mol;

$2Cr^{3+}+21H_2O=Cr_2O_7^{2-}+14H_3O^++6e^-$; $1<pH<7$; Standard potential $E°_{Cr2O72}=$**1,3939** V Kortly, Shucha [18]

$E°_{Cr2O72}=E°+0{,}10166-0{,}0591/6*\lg(1/[H_2O]^{21})-0{,}3982=1{,}33+0{,}10166-0{,}0591/6*\lg(1/55{,}3\text{^}^{21})-0{,}3982=$**1,3939** V;

$$E_{Cr2O72-/2Cr3+}=E°_{Cr2O72-/2Cr3+}+\frac{0.0591}{6}\bullet\lg\frac{[Cr_2O_7^{2-}]\cdot[H_3O^+]^{14}}{[Cr^{3+}]^2\cdot[H_2O]^{21}}=\mathbf{1{,}3939}\text{ V}+\frac{0.0591}{6}\bullet\lg\frac{[Cr_2O_7^{2-}]\cdot[H_3O^+]^{14}}{[Cr^{3+}]^2\cdot[H_2O]^{21}}$$

$\Delta G_{eqCr2O72-/2Cr3+}=E°_{Cr2O72-/2Cr3+}\bullet F\bullet 6=$**1,3939**$*96485*6=$**806,9** kJ/mol,

$\Delta G_{eqCr2O72-/2Cr3+}=G_{Cr2O72-}+14G_{H3O}-(2G_{2Cr3+}+21G_{H2O})=G_{Cr2O72-}+14*$**22,44**$-(2G_{2Cr3+}+21*0)=$**806,9** kJ/mol,

$2G_{2Cr3+}=G_{Cr2O72-}+14*$**22,44-(806,9**$+21*0)=$**???** kJ/mol;

$Cr^{3+}+11H_2O=HCrO_4^-+7H_3O^+$**+3e**$^-$;; pH>7 ; Standard potential $E°_{Cr2O72}=$**1,2811** V Kortly, Shucha [18]

$E°_{CrO4}=E°+0{,}10166-0{,}0591/3*\lg(1/[H_2O]^{11})-0{,}3982=1{,}2+0{,}10166-0{,}0591/3*\lg(1/55{,}3\text{^}^{11})-0{,}3982=$**1,2811** V;

$\Delta G_{eqCrO4/Cr3+}=E°_{CrO4/Cr3+}\bullet F\bullet 3=$**1,2811**$*96485*3=$**370,8** kJ/mol,

$\Delta G_{eqH2C2O4}=G_{CrO4-}+14G_{H3O}-(2G_{2Cr3+}+21G_{H2O})=G_{CrO4-}+14*$**22,44**$-(2G_{2Cr3+}+21*0)=$ **370,8** kJ/mol,

$2G_{2Cr3+}=G_{CrO4-}+14*$**22,44-(370,8**$+21*0)=$**???** kJ/mol;

$Cr(OH)_3\downarrow+5OH^-=CrO_4^{2-}+4H_2O+3e^-$; pH>9 ; $E°_{CrO42-OH}=$ **-0,5639** V Suchotina [17]

$E°_{CrO42-OH}=E°-0{,}0591/3*\lg([H_2O]^4)+0{,}10166-0{,}3982=-0{,}13-0{,}0591/3*\lg(55{,}3\text{^}^4)+0{,}10166-0{,}3982=$ **-0,5639** V;

$\Delta G_{eqCrO42-OH}=E°_{CrO42-OH}\bullet F\bullet 3=$**0,5639**$*96485*3=$ **163,2** kJ/mol,

$\Delta G_{eqCrO42-OH}=G_{CrO4-}+4G_{H3O}-(G_{Cr(OH)3}+5G_{OH})=G_{CrO4-}+4*$**22,44**$-(2G_{2Cr3+}+5*77{,}36)=$ **163,2** kJ/mol,

$G_{Cr(OH)3}=G_{CrO4-}+14*$**22,44-(163,2**$+21*0)=$**???** kJ/mol;

$$E_{CrO42-/Cr(OH)3\downarrow}=E°_{CrO42-/Cr(OH)3\downarrow}+\frac{0.0591}{3}\bullet\lg\frac{[CrO_4^{2-}]\cdot[H_2O]^4}{[Cr(OH)_3]\cdot[OH^-]^5}=\mathbf{-0{,}5639}\text{ V}+\frac{0.0591}{3}\bullet\lg\frac{[CrO_4^{2-}]\cdot[H_2O]^4}{[Cr(OH)_3]\cdot[OH^-]^5}\text{ V;}$$

Solubility product $Cr(OH)_3+4H_2O=Cr^{3+}+3OH^-$; $K_{sp}=6{,}7*10\text{^}^{(-31)}$; $K_{eq}=K_{sp}/[H_2O]^4=6{,}7*10\text{^}^{(-31)}/55{,}3\text{^}^4=10\text{^}^{(-37{,}14)}$;

$\Delta G_{eqsp}=-R\bullet T\bullet \ln(K_{eqsp})=-8{,}3144*298{,}15*\ln(10\text{^}^{(-37{,}14)})=G_{Cr3+}+3G_{OH}-(G_{Cr(OH)3}+4G_{H2O})=$**211,99** kJ/mol;

$G_{Cr(OH)3}=G_{Cr3+}+3G_{OH}-(\Delta G_{eqsp}+4G_{H2O})=G_{Cr3+}+3*77{,}36-($**211,99**$+4*0)=???$ kJ/mol;

Viela	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$, 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	-
$Cr_2O_{3(cr)}$	-1139,7	81,2	1058,1

$2G_{HCrO4}=G_{Cr2O7}+0-($**-21,65**$)=???$ kJ/mol;

$G_{HCr2O7}=G_{Cr2O7}+22{,}44-($**20,22**$+0)=???$ kJ/mol;

$G_{[CrOH]2+}=G_{Cr3+}+77{,}36-($**65,7**$+0)=???$ kJ/mol;

$G_{Cr(OH)2}=G_{Cr3+}+2*77{,}36-($**118,64**$+2*0)=???$ kJ/mol;

$G_{[Cr(OH)3]}=G_{Cr3+}+3*77{,}36-($**166,8**$+3*0)=???$ kJ/mol;

$2G_{2Cr3+}=G_{Cr2O72-}+14*$**22,44-(806,9**$+21*0)=$**???** kJ/mol;

$2G_{2Cr3+}=G_{CrO4-}+14*$**22,44-(370,8**$+21*0)=$**???** kJ/mol;

$G_{Cr(OH)3}=G_{CrO4-}+14*$**22,44-(163,2**$+21*0)=$**???** kJ/mol;

$G_{Cr(OH)3}=G_{Cr3+}+3*77{,}36-($**211,99**$+4*0)=???$ kJ/mol;

Nernsta potenciāla BiO_3^- / Bi^{3+} red-oks sistēmas īpašības skābā H_3O^+ , ūdens vidē
Nernsta absolūtais standarta potenciāls.

$E°_{Bi2O3-/Bi}=E_o-0,0591/6*lg([H_2O]^3)+0,10166-0,3982=-0,46-0,0591/6*lg(55,3^{\wedge 3})+0,10166-0,3982=\mathbf{-0,808}$ V ;

$E°_{Bi2O3-/Bi}=E_o-0,0591/6*lg([H_2O]^6)+0,10166-0,3982=-0,46-0,0591/6*lg(55,3^{\wedge 6})+0,10166-0,3982=\mathbf{-0,8595}$ V ;

Viela	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$, kJ/mol
Bi^{3+}	-	82,8	-
Bi	**308,3**	56,7	**-83,57**
Bi_2	219,7	-	-
$BiOH^{2+}$	-	-146,4	-
Cl^-	-167,08	56,6	**-183,955**
$Cl_{(g)}$	-121,301	165,19	
Cl_2	-	223,081	
$BiCl_{3(s)}$	-379,1	177	-315,0
$BiClO_{(s)}$	-366,9	120,5	-322,1
Bi_2O_3	-573,9	151,5	-493.7
$Bi(OH)_3$	-711,3	-	-

$2Bi+6OH^-=Bi_2O_3+3H_2O+6e^-$; pH>7; Suchotina [1

$2Bi+6OH^-=Bi_2O_3+6H_2O+6e^-$; pH>7; Suchotina [17]

$\mathbf{\Delta H_{Bi\_BiClO}=\Delta G+\Delta S*T=-83,57}+56,7*298,15=\mathbf{308,3}$ kJ/mol,

$$E_{Bi2O3-/Bi}=E°_{Bi2O3-/Bi}+\frac{0.0591}{6}\bullet lg\frac{[Bi_2O_3]\cdot[H_2O]^3}{[Bi]^2\cdot[OH^-]^6}=$$

$=\mathbf{-0,808}+0,0591/6*lg([Bi_2O_3]*[H_2O]^3/[Bi]^2/[OH^-]^6)$

$G_{Bi}=G_{BiCl}+3G_{H2O}-(\Delta G_{eqBiCl3-Bi}+3G_{Cl})=\mathbf{306,2}$ kJ/mol,

$G_{Bi}=G_{BiClO}+2G_{H3O}-(\Delta G_{eqBiClO-Bi}+3H_2O+G_{Cl})=\mathbf{291,44}$ kJ/mol,

$=\mathbf{-0,8595}+0,0591/6*lg([Bi_2O_3]*[H_2O]^6/[Bi]^2/[OH^-]^6)$

$$E_{Bi2O3-/Bi}=E°_{Bi2O3-/Bi}+\frac{0.0591}{6}\bullet lg\frac{[Bi_2O_3]\cdot[H_2O]^6}{[Bi]^2\cdot[OH^-]^6}=$$

$\Delta G_{eqBi2O3-/Bi}=E°_{Bi2O3-/Bi}\bullet F\bullet 6=\mathbf{-0,808}*96485*6=\mathbf{-467,76}$ kJ/mol,

$\Delta G_{eqBi2O3-/Bi}=G_{Bi2O3}+3G_{H2O}-(2G_{Bi}+6G_{OH})=-493,7+3*\mathbf{0}-(2*G_{Bi}+6*77,36)=\mathbf{-467,76}$ kJ/mol,

$G_{Bi}=(G_{Bi2O3}+3G_{H2O}-(\Delta G_{eqBi2O3-/Bi}+6G_{OH}))/2=(-493,7+3*\mathbf{0}-(\mathbf{-467,76}+6*77,36))/2=\mathbf{-245,05}$ kJ/mol,

$\Delta G_{eqBi2O3-/Bi}=E°_{Bi2O3-/Bi}\bullet F\bullet 6=\mathbf{-0,8595}*96485*6=\mathbf{-497,57}$ kJ/mol,

$\Delta G_{eqBi2O3-/Bi}=G_{Bi2O3}+6G_{H2O}-(2G_{Bi}+6G_{OH})=-493,7+3*\mathbf{0}-(2*G_{Bi}+6*77,36)=\mathbf{-497,57}$ kJ/mol,

$G_{Bi}=(G_{Bi2O3}+6G_{H2O}-(\Delta G_{eqBi2O3-/Bi}+6G_{OH}))/2=(-493,7+6*\mathbf{0}-(\mathbf{-497,57}+6*77,36))/2=\mathbf{-246,985}$ kJ/mol,

$Bi+3Cl^-=BiCl_{3(s)}+3H_2O+3e^-$; 1<pH<7 ; Suchotina [17]

$E°_{BiCl3-/Bi}=E_o-0,0591/3*lg([H_2O]^3)+0,10166-0,3982=0,16-0,0591/3*lg(55,3^{\wedge 3})+0,10166-0,3982=\mathbf{-0,2395}$ V ;

$\Delta G_{eqBiCl3-Bi}=E°_{eqBiCl3-Bi}\bullet F\bullet 3=\mathbf{-0,2395}*96485*3=\mathbf{-69,32}$ kJ/mol,

$\Delta G_{eqBiCl3-Bi}=G_{BiCl}+3G_{H2O}-(G_{Bi}+3G_{Cl})=-315+3*\mathbf{0}-(G_{Bi}+3*\mathbf{-183,955})=\mathbf{-69,32}$ kJ/mol,

$G_{Bi}=G_{BiCl3}+3G_{H2O}-(\Delta G_{eqBiCl3-Bi}+3G_{Cl})=-315+3*\mathbf{0}-(\mathbf{-69,32}+3*\mathbf{-183,955})=\mathbf{306,2}$ kJ/mol,

$Bi+3Cl^-=BiCl_3+2H_2O+3e^-$; 1<pH<7 ; Suchotina [17]

$E°_{BiCl3-/Bi}=E_o-0,0591/3*lg([H_2O]^2)+0,10166-0,3982=0,16-0,0591/3*lg(55,3^{\wedge 2})+0,10166-0,3982=\mathbf{-0,2052}$ V ;

$\Delta G_{eqBiCl3-Bi}=E°_{eqBiCl3-Bi}\bullet F\bullet 3=\mathbf{-0,2052}*96485*3=\mathbf{-59,40}$ kJ/mol,

$\Delta G_{eqBiCl3-Bi}=G_{BiCl}+2G_{H2O}-(G_{Bi}+3G_{Cl})=-315+3*\mathbf{0}-(G_{Bi}+3*\mathbf{-183,955})=\mathbf{-59,40}$ kJ/mol,

$G_{Bi}=G_{BiCl3}+2G_{H2O}-(\Delta G_{eqBiCl3-Bi}+3G_{Cl})=-315+3*\mathbf{0}-(\mathbf{-59,40}+3*\mathbf{-183,955})=\mathbf{296,3}$ kJ/mol,

$Bi+3H_2O+Cl^-=BiClO_{(s)}+2H_3O^++3e^-$; Suchotina [17]

$E°_{BiClO/Bi}=E_o-0,0591/3*lg(1/[H_2O]^3)+0,10166-0,3982=0,16-0,0591/3*lg(1/55,3^{\wedge 3})+0,10166-0,3982=\mathbf{-0,0335}$ V ;

$\Delta G_{eqBiClO-Bi}=E°_{eqBiClO-Bi}\bullet F\bullet 3=\mathbf{-0,0335}*96485*3=\mathbf{-9,697}$ kJ/mol,

$\Delta G_{eqBiClO-Bi}=G_{BiClO}+2G_{H3O}-(G_{Bi}+3H_2O+G_{Cl})=-322,1+2*\mathbf{22,44}-(G_{Bi}+\mathbf{3*0-183,955})=\mathbf{-9,697}$ kJ/mol,

$G_{Bi}=G_{BiClO}+2G_{H3O}-(\Delta G_{eqBiClO-Bi}+3H_2O+G_{Cl})=-322,1+2*\mathbf{22,44}-(\mathbf{-9,697+3*0-183,955})=\mathbf{-83,57}$ kJ/mol,

$BiO^++6H_2O=BiO_3^-+4H_3O^++2e^-$; 1<pH<7 ; Suchotina [17]

$E°_{BiO3-/BiO+}=E_o-0,0591/2*lg(1/[H_2O]^6)+0,10166-0,3982=1,80-0,0591/2*lg(1/55,3^{\wedge 6})+0,10166-0,3982=\mathbf{1,812}$ V ;

$$E_{BiO3-/BiO+}=E°_{BiO3-/BiO+}+\frac{0.0591}{2}\bullet lg\frac{[BiO_3^-]\cdot[H_3O^+]^4}{[BiO^+]\cdot[H_2O]^6}=\mathbf{1,812}\ V+\frac{0.0591}{2}\bullet lg\frac{[BiO_3^-]\cdot[H_3O^+]^4}{[BiO^+]\cdot[H_2O]^6}$$

$\Delta G_{eqBiO3-/BiO+}=E°_{eqBiO3-/BiO+}\bullet F\bullet 3=\mathbf{1,812}*96485*2=\mathbf{349,7}$ kJ/mol,

$\Delta G_{eqBiO3-/BiO+}=G_{BiO3-}+4G_{H3O}-(G_{BiO+}+6H_2O)=G_{BiO3-}+4*\mathbf{22,44}-(G_{BiO+}+\mathbf{6*0})=\mathbf{349,7}$ kJ/mol,

$G_{BiO+}=G_{BiO3-}+4G_{H3O}-(\Delta G_{eqBiO3-/BiO+}+6H_2O)=G_{BiO3-}+4*\mathbf{22,44}-(\mathbf{349,7+6*0})$=??? kJ/mol,

$G_{Bi}=\mathbf{-245,05}$ kJ/mol, $G_{Bi}=\mathbf{-246,985}$ kJ/mol, $G_{Bi}=\mathbf{306,2}$ kJ/mol; $G_{Bi}=\mathbf{296,3}$ kJ/mol, $G_{Bi}=\mathbf{-83,57}$ kJ/mol,

$G_{Bi}=(G_{Bi2O3}+3G_{H2O}-(\Delta G_{eqBi2O3-/Bi}+6G_{OH}))/2=(-493,7+3*\mathbf{0}-(\mathbf{-467,76}+6*77,36))/2=\mathbf{-245,05}$ kJ/mol,

$G_{Bi}=(G_{Bi2O3}+6G_{H2O}-(\Delta G_{eqBi2O3-/Bi}+6G_{OH}))/2=(-493,7+6*\mathbf{0}-(\mathbf{-497,57}+6*77,36))/2=\mathbf{-246,985}$ kJ/mol,

$G_{Bi}=G_{BiCl3(s)}+3G_{H2O}-(\Delta G_{eqBiCl3-Bi}+3G_{Cl})=-315+3*\mathbf{0}-(\mathbf{-69,32}+3*\mathbf{-183,955})=\mathbf{306,2}$ kJ/mol,

$G_{Bi}=G_{BiCl3}+2G_{H2O}-(\Delta G_{eqBiCl3-Bi}+3G_{Cl})=-315+3*\mathbf{0}-(\mathbf{-59,40}+3*\mathbf{-183,955})=\mathbf{296,3}$ kJ/mol,

$G_{Bi}=G_{BiClO}+2G_{H3O}-(\Delta G_{eqBiClO-Bi}+3H_2O+G_{Cl})=-322,1+2*\mathbf{22,44}-(\mathbf{-9,697+3*0-183,955})=\mathbf{-83,57}$ kJ/mol,

Nernsta absolūtais standarta **potenciāla** $PbO_2\downarrow / Pb^{2+}$ red-oks sistēmas īpašības skābā H_3O^+ , ūdens vidē

$Pb^{2+} + 6H_2O = PbO_2\downarrow + 4\,H_3O^+ + 2e^-$; 1< pH<7 ; $E°_{PbO_2\downarrow Pb^{2+}}=$**1,4674 V;**

$E°_{PbO_2\downarrow Pb^{2+}}=E°+0{,}10166-0{,}0591/2*\lg(1/[H_2O]^6)=1{,}8+0{,}10166-0{,}02955*\lg(1/55{,}3^{\wedge 6})-0{,}3982=$**1,4674** V;

$\Delta G_{eqPbO_2\downarrow Pb^{2+}}=E°_{PbO_2\downarrow Pb^{2+}}\bullet F\bullet 3=$**1,4674***96485*3=**424,746** kJ/mol,

$\Delta G_{eqPbO_2\downarrow Pb^{2+}}=G_{PbO_2}+4G_{H_3O^+}-(G_{Pb^{2+}}+6G_{H_2O})=-217{,}3+4*$**22,44**-($G_{Pb^{2+}}$+6***0**)= **424,746** kJ/mol,

$G_{Pb^{2+}}=G_{PbO_2}+4G_{H_3O^+}-(\Delta G_{eqPbO_2\downarrow Pb^{2+}}+6G_{H_2O})=-217{,}3+4*$**22,44-(424,746**+6***0)=-552,286** kJ/mol,

Viela	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$, kJ/mol	
Pb	$E°_{Pb\downarrow Pb^{2+}}=$	**0,3710** V	**-480,696**	$G_{Pb}=G_{Pb^{2+}}-(\Delta G_{eqPb\downarrow Pb^{2+}}+G_{H_2O})$=**-552,286-(-71,59+0)=-480,696** kJ/mol,
Pb	-	64,8	-	
Pb^{2+}	$E°_{PbO_2\downarrow Pb^{2+}}=$	**1,4674 V**	**-552,286**	$G_{Pb^{2+}}=G_{PbO_2}+4G_{H_3O^+}-(\Delta G_{eqPbO_2\downarrow Pb^{2+}}+6G_{H_2O})$=**-552,286** kJ/mol ;
Pb^{2+}	0,92	18,5	-4,596	$\Delta G_{Pb^{2+}}=\Delta H_H-T*\Delta S_H=$**0,92**-298,15*0,0185=**-4,596** kJ/mol;
$PbO_2\downarrow$	-277,4	68,6	-217,3	
Al	-	28,3	-	
Al	$E°_{Al/Al^{3+}}=$	**-1,9242** V	**115,469**	$G_{Al}=G_{Al^{3+}}-(\Delta G_{eqAl/Al^{3+}}+G_{H_2O})$=**115,469** kJ/mol,
Al^{3+}	-538,4	-325	**-441,5**	$\Delta G_{Al^{3+}}=\Delta H_H-T*\Delta S_H=-538{,}4-298{,}15*-0{,}325=$**-441,5** kJ/mol;
$H_2AlO_3^-$	$E°_{H_2AlO_3Al}=$	**-2,6609** V	**-345,3**	$G_{H_2AlO_3}=\Delta G_{eqH_2AlO_3Al}-G_{H_2O}+(G_{Al}+4G_{OH})$=**-345,3** kJ/mol,
$NaAlO_2\downarrow$	-1133,2	70,4	-	
H_2S	**-38,6**	**126**	**-76,167**	$\Delta G_{HS^-}=\Delta H_H-T*\Delta S_H=-38{,}6-298{,}15*0{,}126=$**-76,167** kJ/mol;
HS^-	**-16,3**	**67**	**-36,276**	$\Delta G_{HS^-}=\Delta H_H-T*\Delta S_H=-16{,}3-298{,}15*0{,}067=$**-36,276** kJ/mol;
HS^-	$E°_{S\downarrow/S^{2-}}=$	**-0,8775** V	**6,33**	$G_{HS\text{-}aq}=G_{S\,rombisks}+G_{H_2O}-(\Delta G_{eqS^{2-}aq}+G_{OH})$=**6,33** kJ/mol;
HS^-	pK_{a1}=7,05	pK_{a1}=7,05	**-3,072**	$G_{HS^-}=\Delta G_{eq}-G_{H_3O}+(G_{H_2S}+G_{H_2O})$=**50,188-22,44**+(**-30,82**+0)=**-3,072** kJ/mol;
H_2S	$E°_{S\downarrow/S^{2-}}=$	**-0,9290** V	**-61,09**	$G_{H_2S\text{-}aq}=G_{S\,rombisks}+3G_{H_2O}-(\Delta G_{eqH_2S\text{-}aq}+2G_{OH})$=**-61,09** kJ/mol;
H_2S	$E°_{S\downarrow/H_2S}=$	**-0,6715** V	**88,82**	$G_{H_2Saq}=G_{S\,rombisks}+2G_{H_3O^+}-(\Delta G_{Hess\_H_2Saq}+2G_{H_2O})$=**88,82** kJ/mol ;
H_2S	$E°_{S\downarrow/H_2S}=$	**-0,0515** V	**-30,82**	$G_{H_2Saq}=G_{S\,rombisks}+2G_{H_3O^+}-(\Delta G_{Hess\_H_2Saq}+2G_{H_2O})$=**-30,822** kJ/mol.
S^{2-}	$E°_{S\downarrow/S^{2-}}=$	**-0,8243** V	**64,43**	$G_{S^{2-}aq}=G_{S\,rombisks}+G_{H_2O}-(\Delta G_{eqS^{2-}aq})$=**-85,64**+0-(**-150,07**)=**64,43** kJ/mol;
S^{2-}	pK_{a2}=19	pK_{a2}=19	**92,868**	$G_{S^{2-}}=\Delta G_{eq}-G_{H_3O}+(G_{HS^-}+G_{H_2O})$=**118,38 -22,44**+(**-3,072**+0)=**92,868** kJ/mol;

$$E_{PbO_2\downarrow/Pb^{2+}}=E°_{PbO_2\downarrow Pb^{2+}}+\frac{0.0591}{2}\bullet\lg\frac{[PbO_2\downarrow]\cdot[H_3O^+]^4}{[Pb^{2+}]\cdot[H_2O]^6}=1{,}4674\ V+\frac{0.0591}{2}\bullet\lg\frac{[PbO_2\downarrow]\cdot[H_3O^+]^4}{[Pb^{2+}]\cdot[H_2O]^6}$$

$Pb+H_2O = Pb^{2+} + 2e^-$; 1< pH<7 ; $E°_{Pb\downarrow Pb^{2+}}=$**-0,3710** V; Kortly, Shucha

$E°_{PbPb^{2+}}=E°-0{,}0591/2*\lg(1/[H_2O]^1)+0{,}10166-0{,}3982=-0{,}126-0{,}02955*\lg(1/55{,}3^{\wedge 1})+0{,}10166-0{,}3982=$**-0,3710** V;

$\Delta G_{eqPb\downarrow Pb^{2+}}=E°_{PbO_2\downarrow Pb^{2+}}\bullet F\bullet 2=$**-0,371***96485*2= **-71,59** kJ/mol,

$\Delta G_{eqPb\downarrow Pb^{2+}}=G_{Pb^{2+}}-(G_{Pb}+G_{H_2O})$=**-552,286-(-480,696 +0)= -71,59** kJ/mol,

$G_{Pb}=G_{Pb^{2+}}-(\Delta G_{eqPb\downarrow Pb^{2+}}+G_{H_2O})$=**-552,286-(-71,59+0)=-480,696** kJ/mol,

Nernsta absolūtais standarta **potenciāla** $H_2AlO_3^-$ / $Al\downarrow$ red-oks sistēmas īpašības skābā H_3O^+ , ūdens vidē

$Al+ H_2O=Al^{3+}+3e^-$; CRC $E°_{Al/Al^{3+}}=$**-1,9242** V;

$E°_{Al/Al^{3+}}=E°-0{,}0591/3*\lg(1/[H_2O]^1)+0{,}10166-0{,}3982=-1{,}662-0{,}0591/3*\lg(1/55{,}3^{\wedge 1})+0{,}10166-0{,}3982=$**-1,9242** V;

$\Delta G_{eqAl/Al^{3+}}=E°_{Al/Al^{3+}}\bullet F\bullet 3=$**-1,9242***96485*3=**-556,969** kJ/mol,

$\Delta G_{eqAl/Al^{3+}}=G_{Al^{3+}}-(G_{Al}+G_{H_2O})$=**-441,5-(115,469 +0)=-556,969** kJ/mol,

$G_{Al}=G_{Al^{3+}}-(\Delta G_{eqAl/Al^{3+}}+G_{H_2O})$=**-441,5-(-556,969+0)=115,469** kJ/mol,

$Al+4OH^-=H_2AlO_3^-+H_2O+3e^-$; pH>7 CRC $E°_{H_2AlO_3Al}=$**-2,6609** V;

$E°_{H_2AlO_3Al}=E°-0{,}0591/3*\lg([H_2O]^1)+0{,}10166-0{,}3982=-2{,}33-0{,}0591/3*\lg(55{,}3^{\wedge 1})+0{,}10166-0{,}3982=$**-2,6609** V;

$\Delta G_{eqH_2AlO_3Al}=E°_{H_2AlO_3Al}\bullet F\bullet 3=$**-2,6609***96485*3=**-770,21** kJ/mol,

$\Delta G_{eqH_2AlO_3Al}=G_{H_2AlO_3}+G_{H_2O}-(G_{Al}+4G_{OH})$=**-345,3**+0-(**115,469** +4***77,36**)= **-770,21** kJ/mol,

$G_{H_2AlO_3}=\Delta G_{eqH_2AlO_3Al}-G_{H_2O}+(G_{Al}+4G_{OH})$=**-770,21**-0+(**115,469** +4***77,36**)=**-345,3** kJ/mol,

$$E_{AlO_2^-/Al\downarrow}=E°_{AlO_2^-/Al\downarrow}+\frac{0.0591}{3}\bullet\lg\frac{[H_2AlO_3^-]\cdot[H_2O]}{[Al]\cdot[OH^-]^4}=-2{,}6609\ V+\frac{0.0591}{3}\bullet\lg\frac{[H_2AlO_3^-]\cdot[H_2O]}{[Al]\cdot[OH^-]^4}$$

Nernsta absolūtais standarta **potenciāla** S↓ / H_2S_{aq} red-oks sistēmas īpašības skābā H_3O^+ , ūdens vidē

$S^{2-}=S_{rombisks}+H_2O+ 2 e^-$; $E°_{S↓/S2-}$=**-0,8243** V Kortly, Shucha ;

$E°_{S↓/S2-}$=E°-0,0591/2*lg($[H_2O]^1$) +0,10166-0,3982=-0,4763-0,02955*lg(55,3^1)+0,10166-0,3982=**-0,8243** V;

$\Delta G_{eqS2-}=E°_{S2-}Fn$=-0,8243*96485*2=**-150,07** kJ/mol . $G_{Srombisks}$=**-85,64** kJ/mol;

$\Delta G_{eqS2-aq}=G_{Srombisks}+G_{H2O}-(G_{S2-aq})$=**-85,64**+0-(**64,43**)=**-150,07** kJ/mol;

$G_{S2-aq}=G_{Srombisks}+G_{H2O}-(\Delta G_{eqS2-aq})$=**-85,64**+0-(**-150,07**)=**64,43** kJ/mol;

$HS^- +OH^- = S_{rombisks} + 2H_2O + 2e^-$; CRC 2010

$E°_{S↓/HS-}$=E°-0,0591/2*lg($[H_2O]^2$) +0,10166-0,3982=-0,478-0,02955*lg(55,3^2)+0,10166-0,3982=**-0,8775** V;

$\Delta G_{eqHS-}=E_{HS-}Fn$=-0,8775*96485*2=**-169,33** kJ/mol .

$\Delta G_{eqHS-aq}=G_{Srombisks}+2G_{H2O}-(G_{HS-aq}+G_{OH})$=**-85,64**+2*0-(**6,33+77,36**)=**-169,33** kJ/mol;

$G_{HS-aq}=G_{Srombisks}+2G_{H2O}-(\Delta G_{eqHS-aq}+G_{OH})$=**-85,64**+2*0-(**-169,33+77,36**)=**6,33** kJ/mol;

$H_2S_{aq}+2H_2O=S_{rombisks}+2H_3O^++2e^-$; $E°_{S↓/H2S}$=**-0,0515** V Kortly, Shucha_1<pH< 7 ;

$E°_{S↓/H2S}$=E°-0,0591/2*lg($1/[H_2O]^2$) +0,10166-0,3982=0,142-0,02955*lg(1/55,3^2)+0,10166-0,3982=**-0,0515** V;

$\Delta G_{eqH2S}=E°_{H2S}Fn$=-0,0515*96485*2=**-9,938** kJ/mol .

$\Delta G_{eqH2Saq}=G_{Srombisks}+2G_{H3O+}-(G_{H2Saq}+2G_{H2O})$=**-85,64**+2***22,44**-(**-30,82**+2*0)=**-9,938** kJ/mol;

$G_{H2Saq}=G_{Srombisks}+2G_{H3O+}-(\Delta G_{Hess\_H2Saq}+2G_{H2O})$=**-85,64**+2***22,44**-(**-9,938**+2*0)=**-30,822** kJ/mol.

pKa=7,0 Wikipedia; CRC2010 pK_{a1}=7,05; pK_{a2}=19

pK_{a1}=7,05 $H_2S+ H_2O=HS^-+H_3O^+$; $K_{eq1}=K_{a1}/[H_2O]$=10^(-7,05)/55,3= 0,000000001612;

ΔG_{eq}=-R•T•ln(K_{eq})=-8,3144*298,15*ln(0,000000001612)= $G_{HS-}+G_{H3O}-(G_{H2S}+G_{H2O})$=**50,188** kJ/mol;

$\Delta G_{eq}=G_{HS-}+G_{H3O}-(G_{H2S}+G_{H2O})$=**-3,072** +**22,44**-(**-30,82**+0)=**50,188** kJ/mol ;

$G_{HS-}=\Delta G_{eq}-G_{H3O}+(G_{H2S}+G_{H2O})$=**50,188-22,44**+(**-30,82**+0)= **-3,072** kJ/mol ;

pK_{a2}=19 $HS^-+ H_2O=S^{2-}+H_3O^+$; $K_{eq1}=K_{a1}/[H_2O]$=10^(-19)/55,3=10^(-20,74);

ΔG_{eq}=-R•T•ln(K_{eq})=-8,3144*298,15*ln(10^(-20,74))=$G_{S2-}+G_{H3O}-(G_{HS-}+G_{H2O})$=**118,38** kJ/mol;

$\Delta G_{eq}=G_{S2-}+G_{H3O}-(G_{HS-}+G_{H2O})$=**92,868+22,44**-(**-3,072**+0)=**118,38** kJ/mol ;

$G_{S2-}=\Delta G_{eq}-G_{H3O}+(G_{HS-}+G_{H2O})$=**118,38-22,44**+(**-3,072**+0)=**92,868** kJ/mol ;

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