

Nernsta pus reakcijas oksidēšanas potenciāls un membrānas potenciāls voltos Oksidēšanās-reducēšanās balansēšana ar Nernsta pus reakcijām

Nernsts saņēma Nobela 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 pus reakcijām.

Klasificē šādus **elektrodu** veidus:

I veida: lādētu **jonu** un **elektronu** pārnese cauri fāžu **robežvirsmi**;

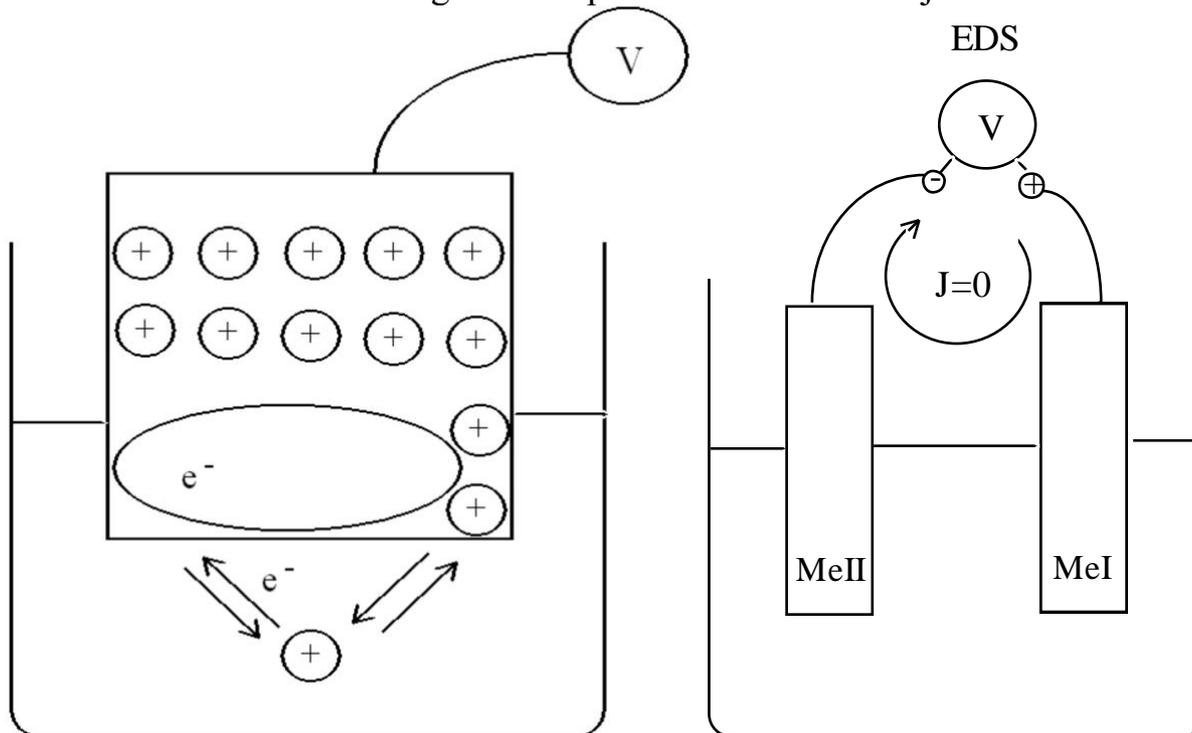
II veida : lādētu **jonu** un **elektronu** pārnese cauri fāžu **robežvirsmi**;

Red-Oks elektrodi: lādētu **jonu** un **elektronu** pārnese cauri fāžu **robežvirsmi**;

Membrānas elektrods: : lādētu **jonu** pārnese 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)**:

$$EDS = E_I - E_{II} ;$$

$$E_I = EDS + E_{II}$$

Indikatora elektrods ar E_I

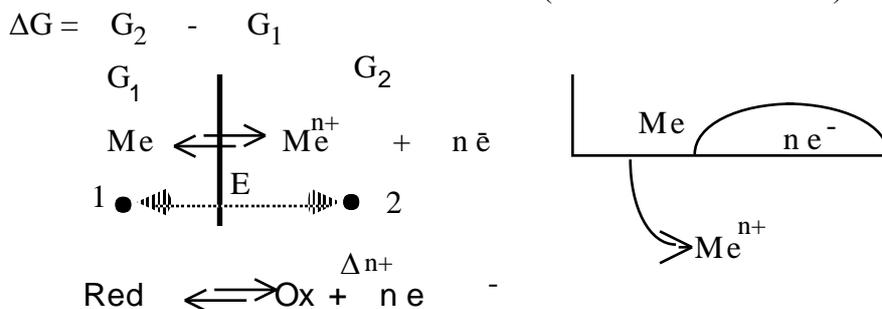
– ir mijiedarbība ar šķīdumu ,

Standarta elektrods ar $E_{II} = \text{konstants}$

– mijiedarbības ar apkārtējo vidi nav.

Pirmā (vienkāršotā) pieeja Nernsta vienādojuma izvedumam.

(Pirmā veida elektrodos)



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, $W = qE = nFE$; $W_{\text{darbs}} = nFE = -\Delta G^\circ = RT \ln K_{\text{līdzsv}}$.

Red-Ox līdzsvara konstante ir $K_{\text{līdzsv}} = \frac{[\text{Ox}] \cdot [e^{-}]^n}{[\text{Red}]}$ tātad

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

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

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

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

Otrā termodinamiskā pieeja Nernsta vienādojuma izvedumam.

Kad ir iestājies līdzsvars tad izejvielu un produktu ķīmisko potenciālu summa ir vienāda $\mu_{\text{Red}} + nF = \mu_{\text{Ox}} + n\mu_{e^{-}}$

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 $\Delta G^\circ_{\text{Ox}}$, $\Delta G^\circ_{e^{-}}$ un $\Delta G^\circ_{\text{Red}}$.

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

No šejienes var izteikt elektroda potenciāla lielumu E :

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

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

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

Standarta potenciāls $E^\circ = \frac{\Delta G^\circ_{\text{Ox}} + n \cdot \Delta G^\circ_{e^{-}} - \Delta G^\circ_{\text{Red}}}{nF}$ veido Prigožina atraktoru brīvās enerģijas izmaiņas

minimumu līdzsvarā $\Delta G_{\text{eq}} = E^\circ nF = \Delta G_{\text{eq}} = \Delta G^\circ_{\text{Ox}} + n\Delta G^\circ_{e^{-}} - \Delta G^\circ_{\text{Red}}$.

Pārejot uz decimāliem logaritmiem un termodinamisko standartu $T=298,15$ K iegūst Nernsta vienādojumu

$$\text{reakcijai : izejvielas } \underline{\text{Red}} \rightleftharpoons \underline{\text{Ox}}^{\Delta n^+} + n e^{-} \text{ Oksidēto forma produkti; } E = E^\circ + \frac{0,0591}{n} \cdot \lg \left(\frac{[\text{Ox}]}{[\text{Red}]} \right).$$

Reakcijā zaudē $n e^{-}$ elektronus tātad šķīduma virzienā tiek pārvietoti Δn^+ pozitīvi lādēti papildus joni.

Elektroni $n e^{-}$ paliek metālā elektronu gāzē. Δn^+ lādiņa pārvietošanās sistēmā produktos oksidētajā formā

$\underline{\text{Ox}}^{\Delta n^+}$ ienes ķīmiskā potenciāla elektrisko elektrona $n e^{-}$ daļu $n \mu_{\text{elektr}} = n \Delta G^\circ_{e^{-}} = -nFE$, kur $\mu_{\text{elektr}} = -FE$.

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

Atraktoram $\text{pH}=7,36$ līdzsvara stāvoklī ir patiesa $\text{pOH}=6,64$ vērtība, jo $\text{pK}_w=14=\text{pH}+\text{pOH}=7,36+6,64$. Ūdens daudzuma atlaide $[\text{H}_2\text{O}]=963/18=53,5$ M litrā sērskābes $[\text{H}_2\text{SO}_4]=[\text{H}_3\text{O}^+]=1$ M šķīduma ar $1,061$ g/mL blīvumu **ūdeņraža elektrodam** Nernsta izteiksmē ir klasiska standarta potenciāla $E_{o_classic}=0$ V atskaites vērtība:

$$\underline{\text{H(Pt)}}=\text{H}^++\text{e}^-; E_{\text{classic}}=E_{o_classic}+0,0591 \cdot \log K^{\circ}_{\text{classicH(Pt)}}=0+0,0591 \cdot \log[\text{H}^+]=0+0,0591 \cdot \log(1 \text{ M})=0 \text{ Volti. [11]}$$

Termodinamiska hidroksonija jonu uzskaitē pieprasa ūdeni: $\underline{\text{H(Pt)}}+\text{H}_2\text{O}=\text{H}_3\text{O}^++\text{e}^-$ un $E^{\circ}_{\text{H}}=0,10166$ V. Attiecība $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]=1 \text{ M}/52,5 \text{ M}=\text{X}_{\text{H}_3\text{O}^+}/\text{X}_{\text{H}_2\text{O}}$ ir mol daļa aizstājot molus litrā $[\text{H}^+]=1$ M klasiskajā potenciāla izteiksmē. Ūdens uzskaitē dod termodinamisko standartu $E^{\circ}_{\text{H}}=0,10166$ V potenciālu skalā. Nernsta izteiksme ar klasisko mērījumu nulle pieprasa termodinamisko standarta potenciālu $E^{\circ}_{\text{H}}=0,10166$ V :

$$E=E^{\circ}_{\text{H}}+\ln(10) \cdot R \cdot T / F \cdot 1 \cdot \log(\text{X}_{\text{H}_3\text{O}^+} / \text{X}_{\text{H}_2\text{O}})=E^{\circ}_{\text{H}}+0,0591 \cdot \log(1/52,5)=0,10166-0,10166=0 \text{ V.}$$

Ja attiecība ir viens $1=\text{K}_{\text{H(Pt)}}=\text{X}_{\text{H}_3\text{O}^+} / \text{X}_{\text{H}_2\text{O}}$, tad potenciāls $E^{\circ}_{\text{H}}=0,10166$ V ir termodinamiskais standarts:

$$E=E^{\circ}_{\text{H}}+\frac{\ln(10) \cdot R \cdot T}{F \cdot 1} \cdot \log \frac{\text{X}_{\text{H}_3\text{O}^+}}{\text{X}_{\text{H}_2\text{O}}} =0,10166+0,0591 \cdot \log(1)=0,10166 \text{ V.}$$

Metāla oksidēšanas brīvās enerģijas izmaiņa ir atšķirīga endoerģiska $\Delta G_{\text{eq}}=E^{\circ}_{\text{H}} \cdot F \cdot 1 \cdot 1=0,10166 \cdot 96485 \cdot 1=9,81$ kJ/mol pretstatā eksoerģiskai.

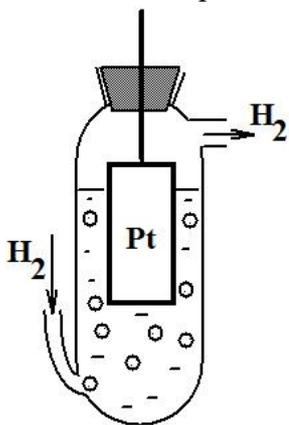
Albertija Hesa vērtība ir eksoerģiska: $\Delta G_{\text{Hess_eq}}=G_{\text{H}_3\text{O}^+}+G_{\text{e}^-}-(G_{\text{H(Pt)}}+G_{\text{H}_2\text{O}})=22,44+0-(48,56+0)=-26,12$ kJ/mol .

Brīvās enerģijas izmaiņa ir noteikta nulles atskaites skalā $G_{\text{H}_2\text{O}}=G_{\text{CO}_2\text{gas}}=G_{\text{e}^-}=0$ kJ/mol. Iteratīvi izskaitļotais absolūtajā skalā ūdeņraža standarta potenciāls ir: $E^{\circ}_{\text{H}}=\Delta G_{\text{eqH(Pt)}}/F/1=-26,12/96485/1=-0,27073$ Volti. Līdzsvara brīvās enerģijas minimums ir eksoerģisks: $\Delta G_{\text{eqH(Pt)}}=E^{\circ}_{\text{H}} \cdot F \cdot 1=-0,27073 \cdot 96485 \cdot 1=-26,12$ kJ/mol sakrīt ar Albertija datiem. Absolūtā potenciālu skala noslīd par $\Delta E=-0,27073-0,10166=-0,37239$ Voltiem zemāk attiecībā pret klasisko nulles skalu. Nernsta līdzsvara konstante ir lielāka par vienu metāla oksidēšanai par hidroksonija jonu: $\text{K}_{\text{H(Pt)_Red}}=[\text{H}_3\text{O}^+] \cdot [\text{e}^-] / [\text{H}_2\text{O}] / [\text{H(Pt)}]=\text{EXP}(-\Delta G_{\text{Alberty}}/R/T)=\text{EXP}(26120/8,3144/298,15)=37675,6$.

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

Liela ātruma protolīzes atraktori $[\text{H}_3\text{O}^+]=10^{-7,36}$ M , $\text{pH}=7,36$ un ūdens masas $[\text{H}_2\text{O}]=997/18=55,3$ M uzskaitē litrā rāda metāla ūdeņraža stipru reducējošu potenciālu: $E_{\text{pH}=7,36}=-0,27073+0,0591 \cdot \log(10^{-7,36}/55,3)=-0,8087$ V un brīvās enerģijas izmaiņas minimumu $\Delta G_{\text{eqpH}_7,36}=E^{\circ}_{\text{H}} \cdot F \cdot 1=-0,8087 \cdot 96485 \cdot 1/1000=-78,03$ kJ/mol .

Nernsta pus reakcijas metāla reducēšanas potenciāla $E^{\circ}_{\text{H}}=-0,27073$ V enerģija ir $\Delta G_{\text{eq}}=-26,12$ kJ/mol.



Platīna plāksnīte iemērta hidroksonija jonu $[\text{H}^+]=[\text{H}_3\text{O}^+]=[\text{H}_2\text{SO}_4]=1$ M sērskābes šķīdumā $\underline{\text{H(Pt)}}=\text{H}^++\text{e}^-$: $E=E^{\circ}+0,0591 \cdot \log[\text{H}^+]=0,0+0,0591 \cdot \log(1 \text{ M})=0$ V ir klasika. Attiecība $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]=1/52,5=\text{X}_{\text{H}_3\text{O}^+}/\text{X}_{\text{H}_2\text{O}}$ dod klasiskās nulles **0** vietā termodinamisko standarta potenciālu: $E^{\circ}_{\text{H}}=0,10166$ V un no Alberty datiem absolūtajā skalā absolūto standarta potenciālu $E^{\circ}_{\text{H}}=-0,27073$ Volti.

$$\begin{array}{ccc} \text{absolūti } E^{\circ}_{\text{H}}=-0,27073 \text{ V} & \text{klasiska nulle } E^{\circ}_{\text{H}}=0 \text{ V} & 0,10166 \text{ V } E, \text{V} \\ \hline E_{\text{(Pt)H/H}^+}=E^{\circ}_{\text{H}}+0,0591 \cdot \log\left(\frac{\text{X}_{\text{H}_3\text{O}^+}}{\text{X}_{\text{H}_2\text{O}}}\right) & E_{\text{H_classic}}=E^{\circ}_{\text{H}}+0,0591 \cdot \log([\text{H}_3\text{O}^+]) & \text{termodinamiskais } E^{\circ}_{\text{H}} \end{array}$$

Absolūtais standarta potenciāls $E^{\circ}_{\text{H}}=-0,27073$ V pamatojas uz Albertija ūdeņraža datiem $G_{\text{H}_2\text{gas}}=85,64$ kJ/mol un $G_{\text{H}_2\text{aq}}=103,24$ kJ/mol , kuri ir noteikti ūdens un oglekļa dioksīda gāzes nulles skalā $G_{\text{H}_2\text{O}}=G_{\text{CO}_2\text{gas}}=G_{\text{e}^-}=0$ kJ/mol. Pie $\text{pH}=7,36$, $[\text{H}_3\text{O}^+]=10^{-7,36}$ M ir stiprs

reducētājs metāls **H(Pt)** ar potenciālu $E_{\text{pH}=7,36}=-0,27073+0,0591 \cdot \log(10^{-7,36}/55,3)=-0,8087$ V. Brīvās enerģijas saturs vienā molā metāla ūdeņraža ir: $G_{\text{H(Pt)}}=48,56$ kJ/mol.

Viela	$\Delta H^{\circ}_{\text{H}}$, kJ/mol	$\Delta S^{\circ}_{\text{H}}$, J/mol/K	$\Delta G^{\circ}_{\text{H}}$, kJ/mol
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549
H₃O⁺	-285,81	-3,854	-213,2746
H_{2aq}	23,4	-130	99,13
H(Pt)_(aq)	$E^{\circ}_{\text{H}}=$	-0,27073	48,56
H_{2aq}	-5,02	-363,92	103,24
O₂aqua	-11,70	-94,2	16,4

CRC 2010

2006, Massachusetts Technology Inst. Alberty $\text{pH}=7,36$ [8]

Mischenko 1972, Himia, Leningrad [26]

CRC 2010 [1]

$\Delta G_{\text{Hess_eq}}=G_{\text{H}_3\text{O}^+}-(G_{\text{H(Pt)}}+G_{\text{H}_2\text{O}})=22,44-(48,56+0)=-26,12$ kJ/mol.

2006, Massachusetts Technology Inst. Alberty $\text{pH}=7,36$ [8]

Gāzveida ūdeņraža šķīdība $\text{H}_{2\text{gas}}+\text{H}_2\text{O}=\text{H}_{2\text{aq}}$ kompensē ($\text{H}_{2\text{gas}}+2\text{H}_2\text{O}=\text{H}_{2\text{aq}}+\text{H}_2\text{O}=2\text{H}_3\text{O}^++2\text{e}^-$) vienu ūdens molekulu Nernsta ūdeņraža oksidēšanā par hidroksoniju un ir patvaļīga, jo **absolūtās** brīvās enerģijas izmaiņa ir negatīva. $\Delta G_{\text{Hess, H}_3\text{O}^+}=2G_{\text{H}_3\text{O}^+}+2G_{\text{e}^-}-(G_{\text{H}_{2\text{aq}}}+G_{\text{H}_2\text{O}})=2*22,44+2*0-(103,24+0)=-58,36 \text{ kJ/mol}$. Ar grafitu oksidē $\text{H}_{2\text{aq}}$ šķīdumu par hidroksoniju ar **absolūto** standarta potenciālu:

$$E^\circ_{\text{H}_{2\text{aq}}}=-58,36*1000/96485/2=-0,3024 \text{ V.}$$

Nernsta un inversās pus reakciju summa: $\text{H}_{2\text{aq}}+\text{H}_2\text{O}=2\text{H}_3\text{O}^++2\text{e}^-$; $2\text{H}_3\text{O}^++2\text{e}^-=2\text{H(Pt)}+2\text{H}_2\text{O}$

parāda ūdeņraža šķīdību platīna kristāla režģī $\text{H}_{2\text{aq}}=2\text{H(Pt)}+\text{H}_2\text{O}$;

Ūdeņraža šķīduma oksidēšanas $\text{H}_{2\text{aq}}+\text{H}_2\text{O}=2\text{H}_3\text{O}^++2\text{e}^-$ potenciāls $E^\circ_{\text{H}_{2\text{aq}}}=-0,302 \text{ V}$ plus inversais potenciāls: $-E^\circ_{\text{H(Pt)}}=+0,27073 \text{ V}$ metāla elektroķīmiskā šķīdībā $2\text{H}_3\text{O}^++2\text{e}^-=2\text{H(Pt)}+2\text{H}_2\text{O}$ parāda ūdeņraža mola daļas $[\text{H}_{2\text{aq}}]/[\text{H}_2\text{O}]$ šķīdību platīnā eksoergisku, patvaļīgu:

$$\Delta G_{\text{spH(Pt)}}=\Delta E^\circ_{\text{spH(Pt)}}*F*2=(E^\circ_{\text{H}_{2\text{aq}}}-E^\circ_{\text{H(Pt)}})*F*2=c(-0,302+0,27073)*96485*2=-0,03128*96485*2=-6,03 \text{ kJ/mol};$$

$$K_{\text{spH(Pt)}}=[\text{H(Pt)}]^2*[\text{H}_2\text{O}]/[\text{H}_{2\text{aq}}]=\text{EXP}(-\Delta G_{\text{spH(Pt)}}/R/T)=\text{EXP}(6036,1/8,3144/298,15)=11,415 .$$

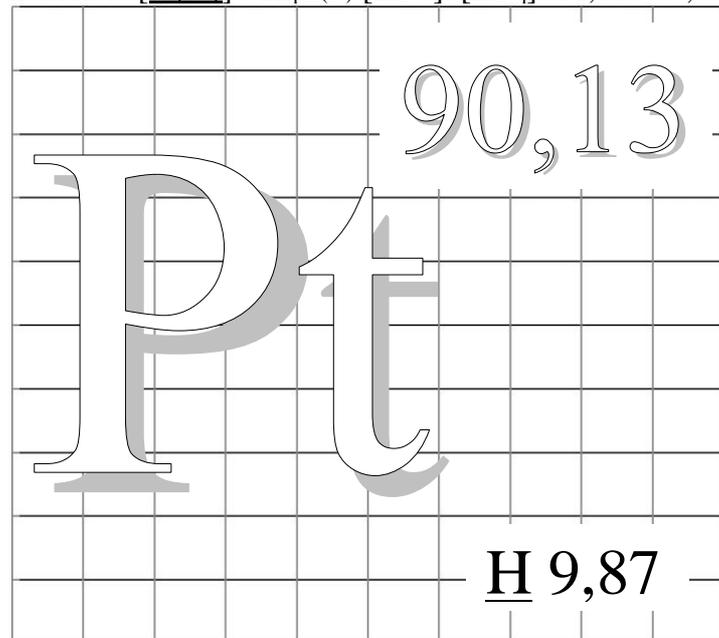
Šķīdība platīnā $\text{H}_{2\text{aq}}=2\text{H(Pt)}+\text{H}_2\text{O}$ parāda par ūdeņraža elektroķīmisko šķīdības produktu metālā nedaudz eksoergiskāku, labvēlīgāku: $\Delta G_{\text{sp, H(Pt)}}=2G_{\text{H(Pt)}}+G_{\text{H}_2\text{O}}-(G_{\text{H}_{2\text{aq}}})=2*48,56+0-(103,24)=-6,12 \text{ kJ/mol}$ un konstanti eksoergiskāku, labvēlīgāku:

$$K_{\text{sp, H(Pt)}}=[\text{H(Pt)}]^2/[\text{H}_{2\text{aq}}]*[\text{H}_2\text{O}]=\text{EXP}(-\Delta G_{\text{spH(Pt)}}/R/T)=\text{EXP}(6120/8,3144/298,15)=11,808 .$$

Attiecība $K_{\text{H}_{2\text{sp}}}=[\text{H}_{2\text{aq}}]/[\text{H}_2\text{O}]/X_{\text{H}_{2\text{gas}}}=\text{EXP}(-\Delta G_{\text{H}_{2\text{sp}}}/R/T)=\text{EXP}(-17600/8,3144/298,15)=0,0008253$ dod šķīdību $[\text{H}_{2\text{aq}}]=K_{\text{H}_{2\text{sp}}*}[\text{H}_2\text{O}]*X_{\text{H}_{2\text{gas}}}=0,0008253*55,3*1=0,04564 \text{ M}$, ja tīras gāzes mola daļa ir viens $X_{\text{H}_{2\text{gas}}}=1$.

Saskaņā ar **Albertija** matemātisko datu pielietojumu bioķīmijā, molu daļās bez mērvienībām konstante ir $K_{\text{H}_{2\text{sp}}}=[\text{H}_{2\text{aq}}]/[\text{H}_2\text{O}]/X_{\text{H}_{2\text{gas}}}=\text{EXP}(-\Delta G_{\text{H}_{2\text{sp}}}/R/T)=\text{EXP}(-17600/8,3144/298,15)=0,0008253$ endoergiska, nelabvēlīga: $\Delta G_{\text{H}_{2\text{sp}}\text{Alberty}}=G_{\text{H}_{2\text{aq}}}-G_{\text{H}_{2\text{gas}}}-G_{\text{H}_2\text{O}}=103,24-85,64-0=17,6 \text{ kJ/mol}$ gāzes šķīdībai $\text{H}_{2\text{gas}}+\text{H}_2\text{O}=\text{H}_{2\text{aq}}$.

No attiecības $[\text{H(Pt)}]^2/[\text{H}_{2\text{aq}}]=K_{\text{sp, H(Pt)}}/[\text{H}_2\text{O}]=11,808/55,3=0,21353$ iegūst H(Pt) laukuma mola daļas kvadrātu: $[\text{H(Pt)}]^2=K_{\text{spH(Pt)}}/[\text{H}_2\text{O}]*[\text{H}_{2\text{aq}}]=11,808/55,3*0,04564=0,009745$. Piesātināta šķīdība platīnā



$[\text{H(Pt)}]=\text{SQRT}(0,009745)=0,0987$ molu daļās ir ūdeņraža atomu virsmas molu daļa 9,87% dalīta ar platīna atomu molu daļu 90,13% kopējā 100% kristāla režģa virsmā. Šķīdības $\text{H}_{2\text{aq}}\text{Alberty}=2\text{H(Pt)}+\text{H}_2\text{O}$ molu daļas koncentrācijas ir bez mērvienībām tā pat kā konstante bez mērvienībām $K_{\text{sp, H(Pt)}}=11,808$.

Atomu rādiusi ir Pt 0,135 nm un H 0,053 nm. Rādiusa kvadrāta laukums ir Pt 0,0729 nm², H 0,0112 nm². 0,0729+0,0112=0,0841 nm² kopējā 100% virsma tiek iedalīta platīna un ūdeņraža atomiem 0,0729/0,0841=86,7% un 0,0112/0,0841=9,53% atbilstoši. [25] H(Pt) šķīdība ūdenī ir mazāka par vienu, endoergiska: $2\text{H(Pt)}+\text{H}_2\text{O}=\text{H}_{2\text{aq}}\text{Alberty}$;

$K_{\text{spH(Pt)}_{\text{H}_{2\text{aq}}}}=[\text{H}_{2\text{aq}}]/[\text{H(Pt)}]^2/[\text{H}_2\text{O}]=0,08469$; un pozitīva $\Delta G_{\text{Alberty}}=G_{\text{H}_{2\text{aq}}}-2G_{\text{H(Pt)}}-G_{\text{H}_2\text{O}}=6,12 \text{ kJ/mol}$; nelabvēlīga, nepatvaļīga. Tas uztur metāla režģi piesātinātu ar ūdeņradi 9,87 %.

$$K_{\text{sp, H(Pt)}}=[\text{H}_{2\text{aq}}]/[\text{H(Pt)}]^2/[\text{H}_2\text{O}]=\text{EXP}(-\Delta G_{\text{sp, H(Pt)}}/R/T)=\text{EXP}(-6120/8,3144/298,15)=0,08469 \text{ nelabvēlīga.}$$

Ūdens oksidēšana par skābekli pus reakcijas $5\text{H}_2\text{O}=\text{O}_{2\text{aq}}+4\text{H}_3\text{O}^++4\text{e}^-$ Hesa brīvās enerģijas izmaiņa ir:

$$\Delta G_{\text{O}_{2\text{aq}}\text{Alberty}}=G_{\text{O}_{2\text{aq}}}+4G_{\text{H}_3\text{O}^+}-5G_{\text{H}_2\text{O}}=329,68-4*22,44-5*0=419,44 \text{ kJ/mol}, \text{ jo aqua mol daļa}$$

$\text{O}_{2\text{gas AIR}}+\text{H}_2\text{O}=\text{O}_{2\text{aq}}$ kompensē vienu ūdens molekulu no sešām $6\text{H}_2\text{O}=\text{O}_{2\text{gas AIR}}+\text{H}_2\text{O}+4\text{H}_3\text{O}^++4\text{e}^-$ un Nernsta pus reakcijā paliek piecas: $5\text{H}_2\text{O}=\text{O}_{2\text{aq}}+4\text{H}_3\text{O}^++4\text{e}^-$ ar absolūto standarta potenciālu $E^\circ_{\text{O}_{2\text{aq}}}=1,0868 \text{ V}$.

Tā ir identiska brīvās enerģijas izmaiņas minimumam elektroķīmiskos aprēķinos lietojot absolūto Nernsta standarta potenciālu: $\Delta G_{\text{eqO}_{2\text{aq}}}=\text{E}^\circ_{\text{O}_{2\text{aq}}}\cdot F\cdot n_{\text{e}}=1,0868*96485*4=419,44 \text{ kJ/mol}$.

Metāla ūdeņraža H(Pt) pus reakcijas $\text{H(Pt)}+\text{H}_2\text{O}=\text{H}_3\text{O}^++\text{e}^-$ Hesa brīvās enerģijas izmaiņa ir:

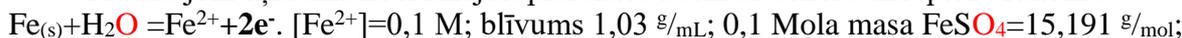
$$\Delta G_{\text{H(Pt)eqAlberty}}=G_{\text{H}_3\text{O}^+}+G_{\text{e}^-}-(G_{\text{H}_2\text{O}}+G_{\text{H(Pt)}})=22,44+0-(48,56+0)=-26,12 \text{ kJ/mol} .$$

Tā sakrīt ar elektroķīmiskiem brīvās enerģijas izmaiņas minimuma aprēķiniem lietojot **absolūto** Nernsta standarta potenciālu $E^\circ_{\text{H(Pt)}}=-0,27073 \text{ Volti}$:

$$\Delta G_{\text{eqH(Pt)}}=\text{E}^\circ_{\text{H(Pt)}}\cdot F\cdot n_{\text{e}}=-0,27073*96485*1=-26,12 \text{ kJ/mol}$$
 iekļaujoties Albertija datos. [8,15]

Metāls iegremdēts savu jonu šķīdumā Nernsta oksidēšanas pus reakcijā veido Elektroda potenciālu Volto.

Metālu joni šķīdumā koordinējas. piesaistot ūdeni ar donoru akceptoru saitēm .



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

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

Atšķirības $-0,74048 \text{ V}$ ir skaitlī **4** $-0,74059 \text{ V}$ $\Delta G_{\text{eq, Fe}} = E^\circ_{\text{Fe}} \cdot F \cdot 2 = -0,65943 * 96485 * 2 = -127,25 \text{ kJ/mol}$,

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

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

$E_{\text{Fe}} = E^\circ_{\text{Fe}/\text{Fe}^{2+}} + 0,0591/2 * \log([\text{Fe}^{2+}]/[\text{Fe}]/([\text{H}_2\text{O}] - 6[\text{Fe}^{2+}])) = -0,65943 + 0,0591/2 * \log(0,1/1/(56,38 - 0,6)) = -0,74059 \text{ V}$;

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

Viela	$\Delta H^\circ_{\text{H}} \text{ kJ/mol}$	$\Delta S^\circ_{\text{H}} \text{ J/mol/K}$	$\Delta G^\circ_{\text{H}} \text{ kJ/mol}$
Fe	$E^\circ_{\text{Fe}} =$	-0,6594 V	45,11
Fe ²⁺	-87,45	-17,8	-82,14
Fe ²⁺	-89,1	-137,7	-78,9
Fe ³⁺	-44,79	-110	-11,99
Fe ³⁺	-48,5	-315,9	-4,7
Cu	$E^\circ_{\text{Cu}} =$	0,1243 V	70,02
Cu ²⁺	64,8	-98	94,0187
Zn	$E^\circ_{\text{Zn}} =$	-0,98098 V	68,65
Zn ²⁺	-153,39	-109,8	-120,653

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

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

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

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

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

Reakcijā $\text{Cu}(\text{Hg}) + \text{H}_2\text{O} = \text{Cu}^{2+} + (\text{Hg}) + 2\text{e}^-$; $[\text{Cu}^{2+}] = 1 \text{ M}$ blīvums $1,19 \text{ g/mL}$; $1 \text{ Mola masa } M_{\text{CuSO}_4} = 159,602 \text{ g/mol}$;

$E^\circ_{\text{Cu}/\text{Cu}^{2+}} = E^\circ_{\text{Cu}} + 0,0591/2 * \log(1/([\text{H}_2\text{O}])) = 0,3435 - 0,0591/2 * \log(1/55,3) + 0,10166 - 0,37239 = 0,1243 \text{ V}$.

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

$E_{\text{Cu}} = E^\circ_{\text{Cu}} + 0,0591/2 * \log([\text{Cu}^{2+}]/[\text{Cu}]/([\text{H}_2\text{O}] - 4[\text{Cu}^{2+}])) = 0,1253 + 0,0591/2 * \log(1/1/(57,24 - 4)) = 0,0733 \text{ V}$;

Atšķirības $0,0728 \text{ V}$ ir skaitlī **2** $0,0733 \text{ V}$

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

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

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

$\text{Zn} + \text{H}_2\text{O} = \text{Zn}^{2+} + 2\text{e}^-$; $\text{ZnSO}_4 = 161,44 \text{ g/mol}$ $[\text{Zn}^{2+}] = C_{\text{ZnSO}_4} = 2 \text{ M}$ blīvums $1,31 \text{ g/mL}$; $m_{\text{ZnSO}_4} = 2 * 161,44 = 322,88 \text{ g}$;

$E^\circ_{\text{Zn}/\text{Zn}^{2+}} = E^\circ_{\text{Zn}} + 0,0591/2 * \log(1/([\text{H}_2\text{O}])) = -0,7628 - 0,0591/2 * \log(1/55,3) + 0,10166 - 0,37239 = -0,98098 \text{ V}$.

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

Atšķirības skaitlī $-1,0215 \text{ V}$ ir ceturtajā zīmē $-1,02358 \text{ V}$ 2 M ;

Šķīdība $57,7 \text{ g}/100 \text{ g}$ simts gramos ūdens; $w\% = 57,7 / 157,7 * 100 = 36,6\%$;

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

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

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

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

$\text{Cr} + \text{H}_2\text{O} = \text{Cr}^{3+} + 3\text{e}^-$; $\text{Cr}_2(\text{SO}_4)_2 = 159,602 \text{ g/mol}$; $C_{\text{Cr}_2(\text{SO}_4)_2} = 0,5 \text{ M}$ $[\text{Cr}^{3+}] = 2 * C_{\text{Cr}_2(\text{SO}_4)_2} = 1 \text{ M}$ density $1,172 \text{ g/mL}$;

$E^\circ_{\text{Cr}/\text{Cr}^{3+}} = E^\circ_{\text{Cr}} + 0,0591/3 * \log(1/([\text{H}_2\text{O}])) = -0,744 - 0,0591/3 * \log(1/55,3) + 0,10166 - 0,37239 = -0,9793 \text{ V}$.

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

Atšķirības skaitlī $-1,0136 \text{ V}$ ir ceturtajā zīmē $-1,01246 \text{ V}$ 1 M ; $2,32 \text{ M}$.

$m_{\text{H}_2\text{O}} = m_{\text{L}} - m_{\text{Cr}_2(\text{SO}_4)_2} = 1172 - 196,08 = 975,92 \text{ g}$; $m_{\text{Cr}_2(\text{SO}_4)_3} = 392,16 / 2 = 196,08$;

$[\text{Cr}^{3+}] = 2 * C_{\text{Cr}_2(\text{SO}_4)_2} = 1 \text{ M}$ density $1,172 \text{ g/mL}$; $m_{\text{Cr}_2(\text{SO}_4)_3} = 196,08 \text{ g}$; $[\text{H}_2\text{O}] = 975,92 \text{ g} / 18 \text{ g/mol} = 54,21778 \text{ M}$

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

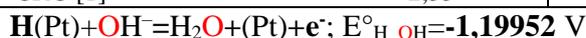
Šķīdība $64 \text{ g}/100 \text{ g}$ simts gramos ūdens; $w\% = 64 / 164 * 100 = 39\%$, $[\text{H}_2\text{O}] = 714,93 \text{ g} / 18 \text{ g/mol} = 39,718 \text{ M}$;

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

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

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

	Reducētā forma = Oksidētā forma + n e ⁻ ; [avoti klasiskie]	H ₂ O atlaide klasiskā nulle E _o	Termodinamiskā skala 0,10166 V	Absolūtā skala -0,37239
H	$\underline{\text{H}}(\text{Pt}) + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + (\text{Pt}) + e^-$; CRC [1]	klasiskā nulle 0	0,10166	-0,27073
	$\underline{\text{H}}(\text{Pt}) + \text{OH}^- = \text{H}_2\text{O} + (\text{Pt}) + e^-$; CRC [1]	-0,8277	-0,8282	-1,1995
	$\underline{\text{H}}(\text{Pt}) + \text{OH}^- = \text{H}_2\text{O} + (\text{Pt}) + e^-$; koriģēts CRC -0.8277+-0.10449	-0,9322	-0,93375	-1,30508
	$\text{H}_{2\text{aq}} + \text{H}_2\text{O} = 2\text{H}_3\text{O}^+ + 2e^-$; grafīta elektrods	-0,1343	0,07039	-0,302
O	$5\text{H}_2\text{O} = \text{O}_{2\text{aq}} + 4\text{H}_3\text{O}^+ + 4e^-$; Suchotina [17]	1,2288	1,4592	1,0868
	$\text{H}_2\text{O}_2 + 2\text{H}_2\text{O} = \text{O}_{2\text{aqua}} + 2\text{H}_3\text{O}^+ + e^-$; David A. Harris [21]	1,2764	1,4811	1,1087
	$4\text{H}_2\text{O} = \text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2e^-$; Suchotina [17]	1,776	2,0837	1,7113
	$\text{H}_2\text{O}_{2\text{aqua}} + 2\text{H}_2\text{O} = \text{O}_{2\text{aqua}} + 2\text{H}_3\text{O}^+ + 2e^-$ University Alberta	0,6945	0,8992	0,5268
CHO	$\text{C}_6\text{H}_{12}\text{O}_6 + 42\text{H}_2\text{O} = 24\text{H}_3\text{O}^+ + 6\text{H}_3\text{CO}_3^- + 6\text{HCO}_3^- + 24e^-$	-0,04915	0,2328	-0,13964
	$\text{HOO}^- + \text{H}_2\text{O} = \text{O}_{2\text{aqua}} + \text{H}_3\text{O}^+ + 2e^-$;	0,3155	0,4686	0,09625
N	$\text{NO}_2^- + 2\text{OH}^- = \text{NO}_3^- + \text{H}_2\text{O} + 2e^-$; pH>3,15 Suchotina [17]	0,01	0,0602	-0,3112
	$\text{HNO}_2 + 4\text{H}_2\text{O} = \text{NO}_3^- + 3\text{H}_3\text{O}^+ + 2e^-$; pH<3,15 [18]	0,94	1,2477	0,8763
	$\text{NO}_2 + 3\text{H}_2\text{O} = \text{NO}_3^- + 2\text{H}_3\text{O}^+ + 2e^-$; David A. Harris [21]	0,835	1,09115	0,71981
	$\text{NO}_{\text{aq}} + 5\text{H}_2\text{O} = \text{NO}_3^- + 4\text{H}_3\text{O}^+ + 3e^-$; pH>3,15 [18]	0,96	1,2333	0,8609
	$\text{NH}_4^+ + 13\text{H}_2\text{O} = \text{NO}_3^- + 10\text{H}_3\text{O}^+ + 8e^-$; Suchotina [17]	0,87	1,4180	1,0466
Br	$2\text{Br}^- = \text{Br}_2(\text{aq}) + 2e^-$; CRC [1]	1,0873	1,18896	0,8176
Bi	$\text{BiO}^+ + 6\text{H}_2\text{O} = \text{BiO}_3^- + 4\text{H}_3\text{O}^+ + 2e^-$; Suchotina [17]	1,80	2,21065	1,83826
Mn H⁺	$\text{Mn}^{2+} + 12\text{H}_2\text{O} = \text{MnO}_4^- + 8\text{H}_3\text{O}^+ + 5e^-$; Kortly, Shucha [18]	1,51	1,85885	1,4865
	$\text{MnO}_2 + 4\text{OH}^- = \text{MnO}_4^- + 2\text{H}_2\text{O} + 3e^-$; Suchotina [17]	0,603	0,6360	0,2636
	$\text{MnO}_4^{2-} = \text{MnO}_4^- + e^-$; Suchotina [17]	0,558	0,65966	0,2873
Pb	$\text{Pb}^{2+} + 6\text{H}_2\text{O} = \text{PbO}_2(\text{s}) + 4\text{H}_3\text{O}^+ + 2e^-$; Kortly, Shucha [18]	1,455	1,86565	1,49326
	$\text{Pb} + \text{H}_2\text{O} = \text{Pb}^{2+} + 2e^-$; pH<7 Kortly, Shucha [18]	-0,126	0,02716	-0,3452
S	$\text{SO}_2^{\text{g}} + \text{H}_2\text{O} = \text{H}_2\text{SO}_{3\text{aq}}; \text{H}_2\text{SO}_3 + 3\text{H}_2\text{O} = \text{HSO}_4^- + 3\text{H}_3\text{O}^+ + 2e^-$; [17]	0,172	0,42815	0,10726
	$\text{HSO}_3^- + 4\text{H}_2\text{O} = \text{SO}_4^{2-} + 3\text{H}_3\text{O}^+ + 2e^-$; 2=<pH<7 Suchotina [17]	0,172	0,47965	0,10726
	$\text{SO}_3^{2-} + 2\text{OH}^- = \text{SO}_4^{2-} + \text{H}_2\text{O} + 2e^-$; pH > 7 Suchotina [17]	-0,93	-0,87984	-1,2522
	$\text{S}^{2-} = \text{S}_{\text{rombisks}} + \text{H}_2\text{O} + 2e^-$; CRC [1]	-0,4763	-0,4261	-0,7985
	$\text{HS}^- + \text{OH}^- = \text{S}_{\text{rombisks}} + 2\text{H}_2\text{O} + 2e^-$; CRC [1]	-0,478	-0,4793	-0,8517
	$\text{H}_2\text{S}_{\text{aq}} + 2\text{H}_2\text{O} = \text{S}_{\text{rombisks}} + 2\text{H}_3\text{O}^+ + 2e^-$; CRC [1]; [17]	0,142	0,3467	-0,025735
	$2\text{S}_2\text{O}_3^{2-} = \text{S}_4\text{O}_6^{2-} + 2e^-$; Suchotina [17]	0,08	0,1817	-0,1907
Fe	$\text{Fe}^{2+} = \text{Fe}^{3+} + e^-$; Suchotina [17]	0,769	0,8707	0,4983
	$\text{Fe}_{(\text{s})} + \text{H}_2\text{O} = \text{Fe}^{2+} + 2e^-$; Suchotina [17]	-0,4402	-0,2870	-0,6594
Ag	$\text{Ag} + \text{H}_2\text{O} = \text{Ag}^+ + e^-$; Kortly, Shucha [18]	0,7994	1,00406	0,6327
	$\text{Ag}(\text{s}) + \text{Cl}^- = \text{AgCl}(\text{s}) + \text{H}_2\text{O} + e^-$; Kortly, Shucha [18]	0,2223	0,2210	-0,1514
	$\text{Ag} + 2\text{NH}_{3\text{aq}} = \text{Ag}(\text{NH}_3)_2^+ + \text{H}_2\text{O} + e^-$; Suchotina [17]	0,373	0,57766	0,2053
	$2\text{Ag} + 2\text{OH}^- = \text{Ag}_2\text{O}(\text{s}) + \text{H}_2\text{O} + 2e^-$; Suchotina [17]	0,345	0,39516	0,02277
Hg	$2\text{Hg} + \text{H}_2\text{O} = \text{Hg}_2^{2+} + 2e^-$; Kortly, Shucha [18]	0,907	1,0602	0,6888
	$2\text{Hg} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{H}_2\text{O} + 2e^-$; Suchotina ; [17]	0,2676	0,2663	-0,1059
	$2\text{Hg} + \text{SO}_4^{2-} = \text{Hg}_2\text{SO}_4(\text{s}) + \text{H}_2\text{O} + 2e^-$; Kortly, Shucha ; [18]	0,614	0,6642	0,2918
	$\text{Hg} + 2\text{OH}^- = \text{HgO} + \text{H}_2\text{O} + 2e^-$; Suchotina ; [17]	0,098	0,1482	-0,2242
I	$3\text{I}^- = \text{I}_3^- + 2e^-$; Kortly, Shucha [18]	0,6276	0,72926	0,35687
Cu	$\text{Cu}(\text{Hg}) + \text{H}_2\text{O} = \text{Cu}^{2+} + (\text{Hg}) + 2e^-$; Kortly, Shucha [18]	0,3435	0,4967	0,1243
F	$2\text{F}^- = \text{F}_2(\text{g}) + 2e^-$; Kortly, Shucha [18]	2,87	2,97166	2,5993
Cl	$2\text{Cl}^- = \text{Cl}_2(\text{g}) + 2e^-$; Kortly, Shucha [18]	1,358	1,45966	1,0873
Cl	$\text{Cl}_2(\text{g}) + 4\text{H}_2\text{O} = 2\text{HOCl} + 2\text{H}_3\text{O}^+ + 2e^-$; Kortly, Shucha [18]	1,63	1,93765	1,5653
Cr	$2\text{Cr}^{3+} + 21\text{H}_2\text{O} = \text{Cr}_2\text{O}_7^{2-} + 14\text{H}_3\text{O}^+ + 6e^-$; Kortly, Shucha [18]	1,33	1,7921	1,41975
	$\text{Cr}^{3+} + 11\text{H}_2\text{O} = \text{HCrO}_4^- + 7\text{H}_3\text{O}^+ + 3e^-$; Kortly, Shucha [18]	1,20	1,6793	1,30692
	$\text{Cr}(\text{OH})_3 + 5\text{OH}^- = \text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3e^-$; pH>9 ; Suchotina [17]	-0,13	-0,1657	-0,53806
C	$\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} = 2\text{CO}_2 + 2\text{H}_3\text{O}^+ + 2e^-$; Suchotina [17]	-0,49	-0,2853	-0,6577
Cr	$\text{Cr} + \text{H}_2\text{O} = \text{Cr}^{3+} + 3e^-$; Suchotina [17]	-0,744	-0,60801	-0,97935
Zn	$\text{Zn} + \text{H}_2\text{O} = \text{Zn}^{2+} + 2e^-$; Kortly, Shucha [18]	-0,763	-0,6096	-0,98098
Al	$\text{Al} + \text{H}_2\text{O} = \text{Al}^{3+} + 3e^-$; CRC [1]	-1,662	-1,52601	-1,8984
	$\text{Al} + 4\text{OH}^- = \text{H}_2\text{AlO}_3^- + \text{H}_2\text{O} + 3e^-$; CRC [1]	-2,35	-2,28267	-2,63506



Absolūtais potenciāls tiek koriģēts ar hidroksīda $G_{\text{OH}^-} = 77,36 \text{ kJ/mol}$ brīvās enerģijas uzskaiti Hesa aprēķinā:

$$\Delta G_{\text{AlbertyH,OH}} = G_{\text{H}_2\text{O}} - (G_{\text{H}(\text{Pt})} + G_{\text{OH}^-}) = 0 - (48,56025 + 77,36) = -125,92 \text{ kJ/mol}$$

un aprēķina izteiksmē izlaboto absolūto potenciālu: $E^\circ_{\text{H}} = \Delta G_{\text{eq}}/F = -125920/96485 = -1,30508 \text{ V}$.

Ūdens daudzuma atlaide $[\text{H}_2\text{O}] = 963/18 = 53,5 \text{ M}$ litrā sērskābes $[\text{H}_2\text{SO}_4] = [\text{H}_3\text{O}^+] = 1 \text{ M}$ šķīdumam ar $1,061 \text{ g/mL}$ blīvumu **ūdenraža elektrodam** ir klasiska $E_{\text{o,classic}} = -0,8277 \text{ V}$ un absolūtā standarta potenciāls ir:

$$E^\circ_{\text{H,OH}} = E^\circ - 0,0591/1 * \lg([\text{H}_2\text{O}]^1) + 0,10166 - 0,37239 = -0,8277 - 0,0591/1 * \lg(53,5^1) + 0,10166 - 0,37239 = -1,1995 \text{ V};$$

$$\text{dati koriģē } \Delta G_{\text{eqH,OH}} = E^\circ_{\text{H,OH}} \cdot F \cdot 1 = -1,30508 * 96485 * 1 = -125,92 \text{ kJ/mol}$$

uz $E^\circ_{\text{H}} = -0,8277 - 0,10449 = -0,9322 \text{ V}$.

$$E^\circ_{\text{H,OH}} = E^\circ - 0,0591/1 * \lg([\text{H}_2\text{O}]^1) + 0,10166 - 0,37239 = -0,9322 - 0,0591/1 * \lg(53,5^1) + 0,10166 - 0,37239 = -1,30508 \text{ V};$$

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

Skābeklis šķīstot ūdenī $O_{2(gas)}+H_2O=O_{2(aq)}$ kompensē vienu ūdens molekulu $6H_2O=O_{2(gas)}+H_2O+4H_3O^++4e^-$ Nernsta pus reakcijā $5H_2O=O_{2(aq)}+4H_3O^++4e^-$, veidojot absolūto standarta potenciālu $E^{\circ}_{5HOH}=1,0868$ V.

$$E^{\circ}_{5HOH}=E^{\circ}-0,0591/4*\lg(1/[H_2O]^5)+0,10166-0,37238=1,2288-0,0591/4*\lg(1/53,5^{5})+0,10166-0,37239=1,0868$$
 V;

Viela	$\Delta H^{\circ}_H, \text{ kJ/mol}$	$\Delta S^{\circ}_H, \text{ J/mol/K}$	$\Delta G^{\circ}_H, \text{ kJ/mol}$
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549
H₃O⁺	-285,81	-3,854	-213,2746
H₂(aq)	23,4	-130	99,13
H(Pt)_(aq)	$E^{\circ}_H-E^{\circ}_{O_2}$	-1,3575	48,56
H₂(aq)	-5,02	-363,92	103,24
O₂aqua	-11,70	-94,2	16,4
O₂aqua	-11,715	110,876	16,4

$$\Delta G_{Hess}=2\Delta G^{\circ}_{H_2O}-4\Delta G^{\circ}_{(Pt)H}-\Delta G^{\circ}_{O_2aqua}=-689=2*(-344,521) \text{ kJ/mol};$$

$$=2*(-237,191)-(4*99,13/2+16,4)=-689=2*344,5 \text{ kJ/mol. CRC 2010}$$

2006, Massachusetts Technology Inst. Alberty [8]

Mischenko 1972, Himia, Leningrad [26]

CRC 2010 [1]

$$G_{H(Pt)}=(2G_{H_2O}-\Delta G_{eq2H_2O}-G_{O_2aqua})/4=48,56 \text{ kJ/mol};$$

Alberty 2006 Biochem. Thermodyn. Massachusetts Technology Inst.

Ūdens koncentrācijas $[H_2O]^5$ logaritms ekstrāgē no $E^{\circ}_{classic}=1,2288$ V

Nernsta izteiksmes absolūto standarta potenciālu $E^{\circ}_{5HOH}=1,0868$ V

Skābeklis $O_{2(aq)}+4H_3O^++4e^-=5H_2O$ ir stiprs oksidētājs ar inverso standarta potenciālu $-E^{\circ}_{5HOH}=-1,0868$ V:

Skābekļa oksidētā forma ar hidroksonija joniem piesaista četrus brīvos elektronus, veidojot četras ūdens molekulas reducētā formā kā produktus. Brīvās enerģijas saturs palielinās, izšķīdinot ūdenī:

$$G_{O_2aq}=G_{O_2gas}+G_{O_2šk}=303,1+26,58=330 \text{ kJ/mol}.$$

Skābekļa šķīdības brīvās enerģijas izmaiņa Hesa likumā ir eksotermiska, endoerģiska: $O_{2(gaiss)}+H_2O=O_{2(aq)}$;

kurā skābekļa mol daļa gaisā $1=[O_{2(gas)}]>[O_{2(gaiss)}]=0,2095$ un ūdenī ir bez mērvienību koncentrācijas $[O_{2(aq)}]/[H_2O]=1,22*10^{(-3)} \text{ M}/55,3 \text{ M}=2,206*10^{-5}$ un konstantes vērtība

$K_{šk}=[O_{2(aq)}]/[O_{2(gaiss)}]/[H_2O]=1,22*10^{(-3)}/1/55,3=2,206*10^{-5}$. Pozitīva enerģijas izmaiņa $\Delta G_{Hess}=\Delta G^{\circ}_{O_2aq}-\Delta G^{\circ}_{H_2O}-\Delta G^{\circ}_{O_2gas}=16,4-(0-237,191)=253,6 \text{ kJ/mol}$ ir arī abās izteiksmēs

$\Delta G_{Alberty O_2aq}=G_{O_2aq}-(G_{H_2O}+G_{O_2gas})=330-(0+303,1)=26,58 \text{ kJ/mol}$ absolūtajā enerģijas skalā

$\Delta G_{šk}=-R\cdot T\cdot \ln(K_{šk})=-8,3144*298,15*\ln(2,206*10^{-5})=26,58 \text{ kJ/mol}$. $[O_2]$ šķīdības Hesa

brīvās enerģijas izmaiņa ir pozitīva $\Delta G_{Hess}=253,6 \text{ kJ/mol}$, bet minimizējas līdzsvara maisījumā $K_{šk}=[O_{2(aq)}]/[O_{2(gas)}]/[H_2O]=2,206*10^{-5}=10^{-4,656}$. Līdzsvara stāvoklis ir atraktors

visiem nelīdzsvara stāvokļiem. Minimuma sasniegšanā iestājas līdzsvars. 53. lpp

Osmolārā $C_{osm}=0$ M, jonu spēka $I=0$ M ūdenī no gaisa 20,95% skābekļa šķīdība ir:

$$[O_{2aq}]=K_{šk}*[O_{2gas}]*[H_2O]=2,205*10^{(-5)}*0,2095*55,3=0,00025546 \text{ M}.$$

Tīra 1atm mol daļa ir $[O_{2gas}]=1$. Osmolaritāte $C_{osm}=0,305$ M, jonu spēks $I=0,25$ M, gaisa skābekli no 0 20,95% izšķīdina $[O_{2aq}]=9,768\cdot 10^{-5}$ M.

Arteriālo $[O_{2aq}]=6*10^{-5}$ M un venozo $[O_{2aq}]=0,426\cdot 10^{-5}$ M izooksiju uztur skābekļa molekulu osmoze, kuras cauri akvaporīnu kanāliem šķērso membrānas pretēji osmolārās koncentrācijas $C_{osm}=0.305$ M gradientam.

Inversa: $O_{2(aq)}+4H_3O^++4e^-=5H_2O$; $-E^{\circ}_{O_2}=-1,0868$ Volts; Nernsta: $4(Pt)H+4H_2O=4H_3O^++4e^-$; $E^{\circ}_H=-0,27073$ V

$O_{2(aqua)}+4(Pt)H=2H_2O$ elektrodu standarta potenciālu summa dod standarta brīvās enerģijas izmaiņu:

$$\Delta G_{eq2H_2O}=(E^{\circ}_H-E^{\circ}_{O_2})\cdot F\cdot 1\cdot 4=(-0,27073-1,0868)*96485*4=2*261,96=-523,925 \text{ kJ/mol};$$

Zinot līdzsvara vērtību $\Delta G_{eq2H_2O}=2G_{H_2O}-4G_{(Pt)H}-G_{O_2aqua}=2*0-(4*G_{(Pt)H}+329,68)=-523,925 \text{ kJ/mol}$, ūdeņraža metāla brīvā enerģija ir $G_{H(Pt)}=(2G_{H_2O}-\Delta G_{eq2H_2O}-G_{O_2aqua})/4=(2*0+523,925-329,68)/4=194,245/4=48,56 \text{ kJ/mol}$.

Brīvā enerģija ir $G_{H_3O^+OH}=G_{H_3O^+}+G_{OH^-}=22,44+77,36=99,8 \text{ kJ/mol}$ protolīzes reakcijā $H_2O+H_2O<=>H_3O^++OH^-$.

Bioķīmija skābekļa $O_{2(aqua)}$ brīvo enerģijas saturu $G_{O_2aqua}=329,68 \text{ kJ/mol}$ samazina līdz $G_{O_2Bio}=88,22 \text{ kJ/mol}$.

Arteriālo asiņu koncentrācijas $[O_{2aqua}]=6*10^{-5}$ M un koncentrācijas $[H_3O^+]=10^{-7,36}$ M potenciāls ir samazināts:

$$E_{O_2}=E^{\circ}+0,0591/4*\lg([O_{2aqua}]\cdot[H_3O^+]^4/[H_2O]^5)=1,0868+0,0591/4*\lg(6*10^{(-5)}*10^{(-7,36*4)}/55,346^{5})=0,46174 \text{ V}$$

par $\Delta E_{arterial}=(E_{O_2}-E^{\circ}_{O_2})=-1,0868+0,46174=-0,62506$ Voltiem un

brīvās enerģijas saturs par $\Delta G_{arterial}=\Delta E_{H_2O}\cdot F\cdot n=-0,62506*96485*4/1000=-241,24 \text{ kJ/mol}$.

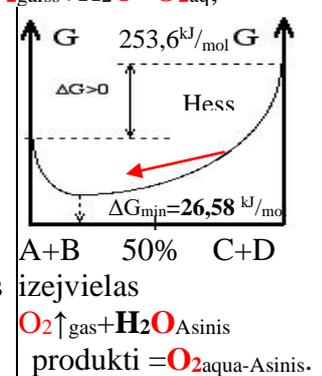
Skābekļa brīvās enerģijas saturs $O_{2(gas)} \text{ AIR}+H_2O=O_{2(Blood)}$ ar šķīdības ieguldījumu palielinās par:

$$K_{šk}=\frac{[O_{2(aqua)}]}{[O_{2(gas)}]\cdot[H_2O]}=2,205*10^{-5}; G_{O_2šk}=-R\cdot T\cdot \ln(K_{šk})=-8,3144*298,15*\ln(2,205*10^{-5})=26,58 \text{ kJ/mol}.$$

Protolīze samazina brīvo enerģiju līdz $G_{O_2arteriāla}=G_{O_2aqua}+G_{O_2šk}+\Delta G_{arteriāla}=303,1+26,58-241,456=88,22 \text{ kJ/mol}$ un skābeklis kļūst uguns drošs bioķīmisks oksidants, veidojot **arteriālo koncentrāciju** $[O_{2(aqua)}]=6*10^{-5}$ M kā bioenerģētiski drošu uzturētu izooksijas normu. [3];

1) Ūdens 55,346 M samazina potenciālu no **1,0868** V par **-0,1288** V=**0,9580-1,0868**= ΔE_{H_2O} .

$$E_{O_2}=E^{\circ}_{O_2}+0,0591/4*\lg(1/[H_2O]^5)=1,0868+0,01478*\lg(1/55,346^{5})=0,95805 \text{ V};$$



2) Paskābināšana H_3O^+ 10 reizes potenciālu un brīvās enerģijas saturu palielina par $\Delta E_{\text{H}_3\text{O}^+} = \mathbf{0,05912}$ V;

$$\Delta E_{\text{H}_3\text{O}^+} = 0,01478 \cdot \lg([\text{H}^+]^4) = \mathbf{0,05912}$$
 V un $\Delta G_{\text{max}} = \Delta E_{\text{H}_3\text{O}^+} \cdot F \cdot n = 0,05912 \cdot 96485 \cdot 4 / 1000 = \mathbf{22,817}$ kJ/mol;

3) Gaisa 20,95% aizvietojot ar 100% skābekļa $[\text{O}_{2\text{aqua}}]$ koncentrāciju 5 reizes lielāka palielina potenciālu par

$$\Delta E_{\text{O}_{2100\%}} = 0,01478 \cdot \lg(100\% [\text{O}_{2\text{aqua}}]) = 0,01478 \cdot \lg(5) = \mathbf{+0,0103}$$
 V. Brīvās enerģijas saturs

palielinās par $\Delta G_{\text{max}} = \Delta E_{\text{H}_3\text{O}^+} \cdot F \cdot n = \mathbf{0,01033} \cdot 96485 \cdot 4 / 1000 = \mathbf{3,987}$ kJ/mol. [6. lapas puse](#):

Lielā oksidatīvā stresa un tehnoloģisko briesmu dēļ 1972. gadā slēdza NASA Apollo projektu.

Nernsta glikozes oksidēšanas pus reakcijā absolūtais standarta potenciāls ir negatīvs, jo spēcīgais 24 elektronu donors reducē sešas skābekļa molekulas Nernsta reakcijā $\text{O}_{2\text{aqua}} + 4\text{H}_3\text{O}^+ + 4e^- = 5\text{H}_2\text{O}$ ar inverso absolūto standarta potenciālu $-E^\circ = \mathbf{-1,0868}$ V. No klasiskā glikozes standarta potenciāla $E^\circ = -0,04915$ V, ekstrahējot logaritma $\log(1/55,3^{42})$ 42 ūdens molekulas, glikozes absolūtais Nernsta standarta potenciāls ir

$$E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} = -0,04915 - 0,0591/24 \cdot \log(1/55,3^{42}) + 0,10166 - 0,37239 = \mathbf{-0,13964}$$
 V.



Glikozes un skābekļa inversā absolūto standarta potenciālu summa ΔE°

$\Delta E^\circ = (E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} - E^\circ_{\text{O}_2}) = \Delta G_{\text{Lehninger}} / F / n = \mathbf{-2840000} / 96485 / 24 = \mathbf{-1,2264}$ V dod standarta brīvās enerģijas izmaiņu

$$\Delta G_{\text{Lehninger}} = \Delta E^\circ \cdot F \cdot n = (E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} - E^\circ_{\text{O}_2}) \cdot F \cdot n = (\mathbf{-0,13964} - \mathbf{1,0868}) \cdot 96485 \cdot 24 = \mathbf{-2840}$$
 kJ/mol reakcijā pēc publicētajiem datiem $\text{C}_6\text{H}_{12}\text{O}_6 + 12\text{H}_2\text{O} + 6\text{O}_{2\text{aqua}} = 6\text{H}_3\text{O}^+ + 6\text{HCO}_3^-$. [1,6]

Glikozes un skābekļa absolūto standarta potenciālu summa $(E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} - E^\circ_{\text{O}_2}) = (E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} - \mathbf{1,0868}) = \mathbf{-1,22644}$ V

ļauj noteikt absolūto standarta potenciālu glikozei $E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} = \Delta E + E^\circ_{\text{O}_2} = \mathbf{-1,22644} + \mathbf{1,0868} = \mathbf{-0,13964}$ V, ko aprēķina no skābekļa inversā absolūtais standarta potenciāla vērtības $\text{O}_{2\text{aqua}} + 4\text{H}_3\text{O}^+ + 4e^- = 5\text{H}_2\text{O}$; $-E^\circ_{\text{O}_2} = \mathbf{-1,0868}$ V.

Arteriālā skābekļa $[\text{O}_{2\text{arteriālā}}] = 6 \cdot 10^{(-5)}$; hidroksonija $[\text{H}_3\text{O}^+]^{30} = 10^{(-7,36 \cdot 30)}$ M un $[\text{C}_6\text{H}_{12}\text{O}_6] = 0,005$ M glikozes koncentrācijas dod negatīvu arteriālo potenciālu:

$$E_{\text{arterial}} = E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} + \frac{0,0591}{24} \cdot \lg([\text{HCO}_3^-]^6 \cdot [\text{H}_3\text{O}^+]^{30} / [\text{H}_2\text{O}]^{42} / [\text{C}_6\text{H}_{12}\text{O}_6]) =$$

$$= \mathbf{-0,13964} + \frac{0,0591}{24} \cdot \lg(0,0154 \cdot 10^{(-7,36 \cdot 30)} / 0,005 / 55,346^{42}) = \mathbf{-0,8624}$$
 V

un inversā skābekļa pus reakcijas arteriālais absolūtais potenciāls ir $E_{\text{O}_2\text{arterial}} = \mathbf{-0,46068}$ V

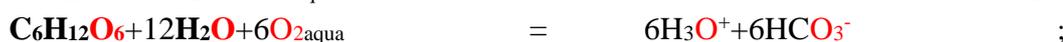
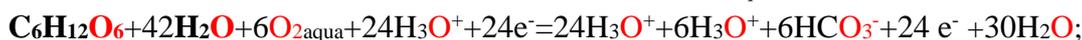
$$E_{\text{O}_2\text{arterial}} = E^\circ_{\text{O}_2} + \frac{0,0591}{4} \cdot \lg([\text{H}_2\text{O}]^5 / [\text{O}_{2\text{aqua}}] / [\text{H}_3\text{O}^+]^4) = \mathbf{-1,0868} + \frac{0,0591}{4} \cdot \log(55,346^5 / 6 / 10^{(-5)} / 10^{(-7,36 \cdot 4)}) = \mathbf{-0,46068}$$
 V.

Homeostāzes summa ir vairāk negatīva $\Delta E_{\text{arterial}} = E_{\text{C}_6\text{H}_{12}\text{O}_6\text{arterial}} + E_{\text{O}_2\text{arterial}} = \mathbf{-0,8624} - \mathbf{0,46068} = \mathbf{-1,32308}$ Volti.

Brīvās enerģijas izmaiņa $\Delta G_{\text{arterial}}$ ir vairāk negatīva kā standarta lielums $\Delta G_{\text{Lehninger}}$:

$$\Delta G_{\text{arterial}} = \Delta E \cdot F \cdot n = (E_{\text{C}_6\text{H}_{12}\text{O}_6\text{arterial}} - E_{\text{O}_2\text{arterial}}) \cdot F \cdot n = (\mathbf{-0,86237} - \mathbf{0,4607}) \cdot 96485 \cdot 24 = \mathbf{-3063,846}$$
 kJ/mol.

Vienu molu glikozes oksidē seši moli skābekļa producējot sešus molus bikarbonāta $6\text{H}_3\text{O}^+ + 6\text{HCO}_3^-$:



$$\text{G}_{\text{H}_3\text{O}^+} + \text{G}_{\text{HCO}_3^-} = \text{G}_{\text{H}_3\text{O}^+} + \text{G}_{\text{HCO}_3^-} = \mathbf{22,44} + \mathbf{56,08} = \mathbf{78,52}$$
 kJ/mol,

Glc (6. lpp.) veidošanās no elementiem $6\text{C} + 6\text{H}_{2\text{gas}} + 3\text{O}_{2\text{gas}} = \text{C}_6\text{H}_{12}\text{O}_6$ brīvās enerģijas izmaiņu aprēķina no Albertija datiem pie pH=7,36 $\Delta G^\circ_{\text{Alberty}} = \text{G}_{\text{C}_6\text{H}_{12}\text{O}_6} - (6\text{G}_{\text{Cgraph}} + 6\text{G}_{\text{H}_2\text{gas}} + 3\text{G}_{\text{O}_2\text{gas}}) = \mathbf{-402,05}$ kJ/mol.

Viela	$\Delta H^\circ_{\text{H}}$, kJ/mol	$\Delta S^\circ_{\text{H}}$, J/mol/K	$\Delta G^\circ_{\text{H}}$, kJ/mol	
$\text{C}_6\text{H}_{12}\text{O}_{6\text{aq}}$	-1263,78	269,45	-919,96	2006, Massachusetts's Technology Inst. Alberty [8] pH=7,36. CRC 2010 [1]
Glc	-1267,13	-2901,492	-402,05	$\Delta G^\circ_{\text{Alberty}} + (6\text{G}_{\text{Cgraph}} + 6\text{G}_{\text{H}_2\text{gas}} + 3\text{G}_{\text{O}_2\text{gas}}) = \text{G}_{\text{C}_6\text{H}_{12}\text{O}_6} = \mathbf{1568}$ kJ/mol;

Brīvo enerģiju glikozes oksidēšanā $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_{2\text{aqua}} + 12\text{H}_2\text{O} = 6\text{H}_3\text{O}^+ + 6\text{HCO}_3^-$ aprēķina trīs veidos:

1) Albertija datus pie pH=7,36 $\Delta G^\circ_{\text{Alberty}} = \text{G}_{\text{C}_6\text{H}_{12}\text{O}_6} - (6\text{G}_{\text{Cgraph}} + 6\text{G}_{\text{H}_2\text{gas}} + 3\text{G}_{\text{O}_2\text{gas}}) = \mathbf{-402,05}$ kJ/mol, standarta brīvās enerģijas saturs molā ir

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

2) Lēningera $\Delta G_{\text{C}_6\text{H}_{12}\text{O}_6} = 6\text{G}_{\text{H}_3\text{O}^+} + 6\text{G}_{\text{HCO}_3^-} - (\text{G}_{\text{StandardC}_6\text{H}_{12}\text{O}_6} + 6\text{G}_{\text{O}_{2\text{aqua}}} + 12\text{G}_{\text{H}_2\text{O}}) = \mathbf{-2840}$ kJ/mol standarta saturs glikozes molā $\text{G}_{\text{StandardC}_6\text{H}_{12}\text{O}_6} = 6 \cdot (\mathbf{22,44} + \mathbf{56,08}) - (\mathbf{-2840} + 6 \cdot \mathbf{330} + 12 \cdot \mathbf{0}) = \mathbf{1331}$ kJ/mol un

3) brīvās enerģijas saturs

$$\Delta G_{\text{arterial}_\text{C}_6\text{H}_{12}\text{O}_6} = 6\text{G}_{\text{H}_3\text{O}^+} + 6\text{G}_{\text{HCO}_3^-} - (\text{G}_{\text{arterial}_\text{C}_6\text{H}_{12}\text{O}_6} + 6\text{G}_{\text{O}_{2\text{aqua}}} + 12\text{G}_{\text{H}_2\text{O}}) = \mathbf{-3064}$$
 kJ/mol uz glikozes molu homeostāzē $\text{G}_{\text{arterial}_\text{C}_6\text{H}_{12}\text{O}_6} = 6 \cdot (\mathbf{22,44} + \mathbf{56,08}) - (\mathbf{-3064} + 6 \cdot \mathbf{88,22} + 12 \cdot \mathbf{85,64}) = \mathbf{1978}$ kJ/mol. [8,6]

Ģenerētie $6\text{HCO}_3^- + 6\text{H}_3\text{O}^+$ joni virza izejvielas $6\text{O}_{2\text{aqua}}$ un $6\text{H}_2\text{O}$ cauri membrānu akvaporīnu kanāliem osmozē pretēji koncentrācijas gradientiem, bet transportē jonus $6\text{HCO}_3^- + 6\text{H}_3\text{O}^+$ lejup pa gradientiem cauri membrānu bikarbonāta un protonu kanāliem lietojot producēto brīvo enerģiju $\Delta G_{\text{arteriālo}} = \mathbf{-3064}$ kJ/mol.

Absolūtās potenciālu un brīvās enerģijas vērtībās iekļauj hidroksionija H_3O^+ un ūdens H_2O uzskaiti.

Skābekļa inversā pus reakcija ar brīvo enerģiju $G_{\text{O}_2\text{aqua}}=330 \text{ kJ/mol}$ reducē $\text{O}_{2\text{aqua}}+4\text{H}_3\text{O}^++4\text{e}^-=5\text{H}_2\text{O}$ ar standarta potenciālu $-E_{\text{O}_2}=-1,0868 \text{ V}$ oksidējot četrus metāla ūdeņraža atomus ar brīvo enerģiju $G_{\text{H(Pt)}}=48,56 \text{ kJ/mol}$ Nernsta pus reakcijā: $4(\text{Pt})\text{H}+4\text{H}_2\text{O}=4\text{H}_3\text{O}^++4\text{e}^-$ un ar standarta potenciālu $E_{\text{H}}=-0,27073 \text{ V}$. Standarta brīvās enerģijas izmaiņa reakcijā $\text{O}_{2\text{aqua}}+4(\text{Pt})\text{H}=2\text{H}_2\text{O}$ ir

$$\Delta G_{\text{Hes}2\text{H}_2\text{O}}=2G_{\text{H}_2\text{O}}-4G_{\text{H(Pt)}}-G_{\text{O}_2\text{aqua}}=2*0-(4*48,56+330)=-524,24=2*-262 \text{ kJ/mol.}$$

Standarta potenciālu summa

$\Delta G_{\text{eq}2\text{H}_2\text{O}}=(E_{\text{H}}-E_{\text{O}_2})\cdot F\cdot 4=(-0,27073-1,0868)*96485*4=-1,3575*96485*4=-523,925=2*-262 \text{ kJ/mol}$ ļauj neatkarīgi no Hesa likuma aprēķinātās veidošanās no brīviem elementiem skābekļa $\text{O}_{2\text{aqua}}$ un metāla ūdeņraža (Pt)H brīvās absolūtās enerģijas izmaiņas $\Delta G_{\text{eq(Pt)H}_2\text{H}_2\text{O}}=-262 \text{ kJ/mol}$, kura ir sakrītoša ar absolūto brīvo enerģiju $G_{\text{H(Pt)}}=(2G_{\text{H}_2\text{O}}-\Delta G_{\text{eq}2\text{H}_2\text{O}}-G_{\text{O}_2\text{aqua}})/4=(2*0+523,9-329,68)/4=48,56 \text{ kJ/mol}$ un absolūto potenciāla skalu.

Ūdeņraža standarta brīvā enerģija ūdens šķīdumā $G_{\text{H}_2\text{aqua}}=103,24 \text{ kJ/mol}$ ir Albertija datos $\text{pH}=7,36$. [8]



$$\Delta G_{\text{HessCRCaqua}}=2\Delta G^{\circ}\text{H}_2\text{O}-2\Delta G^{\circ}\text{H}_{2\text{aqua}}-\Delta G^{\circ}\text{O}_{2\text{aqua}}=2*-237,191-(2*99,13/2+16,4)=-589,91=2*-295 \text{ kJ/mol. CRC [1]}$$

Viela	$\Delta H^{\circ}_{\text{H}}$, kJ/mol	$\Delta S^{\circ}_{\text{H}}$, J/mol/K	$\Delta G^{\circ}_{\text{H}}$, kJ/mol
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
H_3O^+	-285,81	-3,854	-213,2746
$\text{H}_{2\text{aq}}$	23,4	-130	99,13
$\text{H}_{2\text{aq}}$	-5,02	-363,92	103,24
$E^{\circ}(\text{Pt})\text{H}$	-0,27073	-1,0868	48,56
$\text{O}_{2\text{aqua}}$	-11,70	-94,2	16,4
$\text{O}_{2\text{aqua}}$	-11,715	110,876	16,4

CRC

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

Reakcijā $4(\text{Pt})\text{H} + \text{O}_{2\text{aqua}}=2 \text{H}_2\text{O}$; absolūtā brīvā enerģijas izmaiņa ir $|\Delta G_{\text{eq}}=-262 \text{ kJ/mol}| < |\Delta G_{\text{Hess}}=-295 \text{ kJ/mol}|$;

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$$G_{\text{H(Pt)}}=(2G_{\text{H}_2\text{O}}-\Delta G_{\text{eq}2\text{H}_2\text{O}}-G_{\text{O}_2\text{aqua}})/4=48,56 \text{ kJ/mol}$$

$$K_{\text{eqH}_2\text{O}}=K_{\text{OxRed}}=\exp(-\Delta G_{\text{OxRed}}/R/T)=\exp(261960,6/8,3144/298,15)=\exp(105,675)=7,832*10^{45};$$

Eksotermiska un eksoergiska $\text{O}_{2\text{aqua}}$ reducēšana ar metālu ūdeņradi $4(\text{Pt})\text{H}$ un H_2O_2 dismutēšanas Hesa brīvās enerģijas izmaiņa negatīva $\Delta G_{\text{HessAqua}_\text{H}_2\text{O}}=-295 \text{ kJ/mol}$, $\Delta G_{\text{AlbertyH}_2\text{O}_2}=-246 \text{ kJ/mol}$, bet minimizējas sasniedzot līdzsvaru $\Delta G_{\text{eq}2\text{H}_2\text{O}}=-262 \text{ kJ/mol}$ un $\Delta G_{\text{eqStandard}_\text{H}_2\text{O}_2}=-228,6 \text{ kJ/mol}$ konstantes $K_{\text{eqH}_2\text{O}}=7,832*10^{45}$ un $K_{\text{eqStandard}_\text{H}_2\text{O}_2}=1,11*10^{40}$ Līdzsvara stāvoklis minimums ir Prigožina atraktors visiem nelīdzsvara stāvokļiem.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvara stāvoklis.

Red $\text{H}_2\text{O}_2+2\text{H}_2\text{O}=\text{O}_{2\text{aqua}}+2\text{H}_3\text{O}^++2\text{e}^-$; $E^{\circ}\text{H}_2\text{O}_2=0,5268 \text{ V}$ Alberta University Edmontona Canada. [19] Peroksīda H_2O_2 vidē $\text{pH}=7,36$ absolūtais inversais standarta $\text{H}_2\text{O}_2+2\text{H}_3\text{O}^++2\text{e}^-=4\text{H}_2\text{O}$ potenciāls ir $-E^{\circ}\text{Ox}=-1,7113 \text{ V}$ [17];

Summārā dismutācija $2\text{H}_2\text{O}_2\text{aq}=>\text{O}_{2\text{aqua}}+2\text{H}_2\text{O}+\text{Q}+\Delta G$;



$$\text{Summa } \Delta G_{\text{eqStandard}_\text{H}_2\text{O}_2}=(E_{\text{Red}}-E_{\text{Ox}})*F*n=(0,5268-1,7113)*96485*2=(-1,1845)*96485*2=-228,57 \text{ kJ/mol};$$

$$K_{\text{eqStandard}_\text{H}_2\text{O}_2}=\frac{[\text{O}_2]_{\text{aqua}}\cdot[\text{H}_2\text{O}]^2}{[\text{H}_2\text{O}_2]_{\text{aq}}^2}=K_{\text{H}_2\text{O}_2}=\exp(-\Delta G_{\text{eq}}/R/T)=\exp(228573/8,3144/298,15)=1,11*10^{40} \dots\dots$$

$$E^{\circ}\text{H}_2\text{O}_2=E^{\circ}-0,0591/2*\lg(1/[\text{H}_2\text{O}]^2)+0,10166-0,372=0,6945-0,02955*\lg(1/55,3^2)+0,10166-0,37239=0,5268 \text{ V};$$

$$E^{\circ}\text{H}_2\text{O}_2\text{Ox}=E^{\circ}-0,0591/2*\lg(1/[\text{H}_2\text{O}]^4)+0,10166-0,372=1,776-0,02955*\lg(1/55,3^4)+0,10166-0,37239=1,7113 \text{ V};$$

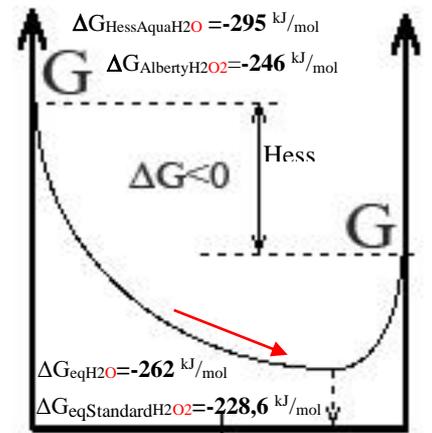
$$E_{\text{O}_2\text{H}_2\text{O}_2}=E^{\circ}\text{H}_2\text{O}_2+0,0591/2*\lg([\text{O}_{2\text{aqua}}]*[\text{H}_3\text{O}^+]^2/[\text{H}_2\text{O}_2]/[\text{H}_2\text{O}]^2)=0,5278+0,0591/2*\lg(6*10^{(-5)}*10^{(-7,36*2)}/1/55,3^2)=-0,1349 \text{ V}$$

$$E_{\text{O}_2\text{Ox}}=E^{\circ}\text{H}_2\text{O}_2\text{Ox}+0,0591/2*\lg([\text{H}_2\text{O}]^4/[\text{H}_2\text{O}_2]/[\text{H}_3\text{O}^+]^2)=-1,7113+0,0591/2*\lg(55,3^4/1/10^{(-7,36*2)})=-1,0713 \text{ V}$$

Summā Nernsta + inversā reakcija homeostāzē ir

$$\Delta G_{\text{eqBioChem}}=(E_{\text{Red}}-E_{\text{Ox}})*F*n=(-0,13493-1,0703)*96485*2=(-1,2062)*96485*2=-232,76 \text{ kJ/mol};$$

$$G_{\text{HomeostasisH}_2\text{O}_2}=(G_{\text{O}_2\text{Biochem}_\text{arteriaj}}+2*G_{\text{H}_2\text{O}_2\text{BioChemistry}}-\Delta G_{\text{Alberty}})/2=(88,04+2*85,64+232,76)/2=246,04 \text{ kJ/mol};$$



Sēra / H₂S_{aq} red-oks sistēmas. H₃O⁺ un [H₂O]=55,3 M uzskaitē absolūtās brīvās enerģijas un potenciālu skalai.

Viela	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H , kJ/mol
H ₂ S	-38,6	126	-76,167
HS ⁻	-16,3	67	-36,276
HS ⁻	$E^{\circ}_{\underline{S}/S_2} =$	-0,8517V	6,16
HS ⁻	$pK_{a1} = 7,05$	$pK_{a1} = 7,05$	-3,072
H ₂ S	$E^{\circ}_{\underline{S}/S_2} =$	-0,9290 V	-61,09
H ₂ S	$E^{\circ}_{\underline{S}/H_2S} =$	-0,6715 V	88,82
H ₂ S	$E^{\circ}_{\underline{S}/H_2S} =$	-0,025735 V	-35,794
S _{rombics}	$2(Pt)H =$	H ₂ S _{aq}	-35,997
S ²⁻	$E^{\circ}_{\underline{S}/S_2} =$	-0,79853V	68,45
S ²⁻	$pK_{a2} = 19$	$pK_{a2} = 19$	92,868

$$\Delta G_{HS} = \Delta H_H - T \cdot \Delta S_H = -38,6 - 298,15 \cdot 0,126 = -76,167 \text{ kJ/mol};$$

$$\Delta G_{HS} = \Delta H_H - T \cdot \Delta S_H = -16,3 - 298,15 \cdot 0,067 = -36,276 \text{ kJ/mol};$$

$$G_{HS-aq} = G_{Srombics} + 2G_{H_2O} - (\Delta G_{eqHS-aq} + G_{OH}) = 6,16 \text{ kJ/mol};$$

$$G_{HS} = \Delta G_{eq} - G_{H_3O} + (G_{H_2S} + G_{H_2O}) = 50,188 - 22,44 + (-30,82 + 0) = -3,072 \text{ kJ/mol};$$

$$G_{H_2S-aq} = G_{Srombics} + 3G_{H_2O} - (\Delta G_{eqH_2S-aq} + 2G_{OH}) = -61,09 \text{ kJ/mol};$$

$$G_{H_2Saq} = G_{Srombics} + 2G_{H_3O} - (\Delta G_{Hess_H_2Saq} + 2G_{H_2O}) = 88,82 \text{ kJ/mol};$$

$$G_{H_2Saq} = G_{Srhombic} + 2G_{H_3O} - (\Delta G_{Hess_H_2Saq} + 2G_{H_2O}) = -35,794 \text{ kJ/mol};$$

$$G_{H_2Saq} = \Delta G_{HessH_2S} + (2G_{H(Pt)} + G_{Srombics}) = -35,997 \text{ kJ/mol};$$

$$G_{S_2-aq} = G_{Srombics} + G_{H_2O} - (\Delta G_{eqS_2-aq}) = 68,45 \text{ kJ/mol};$$

$$G_{S_2} = \Delta G_{eq} - G_{H_3O} + (G_{HS} + G_{H_2O}) = 118,38 - 22,44 + (-3,072 + 0) = 92,868 \text{ kJ/mol};$$

$$S^{2-} = S_{rombics} + H_2O + 2e^-; E^{\circ}_{\underline{S}/S_2} = -0,79853 \text{ V Kortly, Shucha};$$

$$E^{\circ}_{\underline{S}/S_2} = E^{\circ} - 0,0591/2 \cdot \lg([H_2O]^1) + 0,10166 - 0,37239 = -0,4763 - 0,02955 \cdot \lg(55,3^{A1}) + 0,10166 - 0,37239 = -0,79853 \text{ V};$$

$$\Delta G_{eqS_2} = E^{\circ}_{S_2} \cdot F \cdot n = -0,79853 \cdot 96485 \cdot 2 = -154,09 \text{ kJ/mol}; G_{Srombics} = -85,64 \text{ kJ/mol};$$

$$\Delta G_{eqS_2-aq} = G_{Srombics} + G_{H_2O} - (G_{S_2-aq}) = -85,64 + 0 - (68,25) = -154,09 \text{ kJ/mol};$$

$$G_{S_2-aq} = G_{Srombics} + G_{H_2O} - (\Delta G_{eqS_2-aq}) = -85,64 + 0 - (-154,09) = 68,45 \text{ kJ/mol};$$

$$HS^- + OH^- = S_{rombics} + 2H_2O + 2e^-; CRC 2010; E^{\circ}_{\underline{S}/HS} = -0,8517 \text{ V};$$

$$E^{\circ}_{\underline{S}/HS} = E^{\circ} - 0,0591/2 \cdot \lg([H_2O]^2) + 0,10166 - 0,37239 = -0,478 - 0,02955 \cdot \lg(55,3^{A2}) + 0,10166 - 0,37239 = -0,8517 \text{ V};$$

$$\Delta G_{eqHS} = E_{HS} \cdot F \cdot n = -0,8517 \cdot 96485 \cdot 2 = -164,35 \text{ kJ/mol};$$

$$\Delta G_{eqHS-aq} = G_{Srombics} + 2G_{H_2O} - (G_{HS-aq} + G_{OH}) = -85,64 + 2 \cdot 0 - (1,35 + 77,36) = -164,35 \text{ kJ/mol};$$

$$G_{HS-aq} = G_{Srombics} + 2G_{H_2O} - (\Delta G_{eqHS-aq} + G_{OH}) = -85,64 + 2 \cdot 0 - (-164,35 + 77,36) = 1,35 \text{ kJ/mol};$$

$$H_2S_{aq} + 2H_2O = S_{rombics} + 2H_3O^+ + 2e^-; E^{\circ}_{\underline{S}/H_2S} = -0,025735 \text{ V Suchotina}_1 < pH < 7;$$

$$E^{\circ}_{\underline{S}/H_2S} = E^{\circ} - 0,0591/2 \cdot \lg(1/[H_2O]^2) + 0,10166 - 0,37239 = 0,142 - 0,02955 \cdot \lg(1/55,3^{A2}) + 0,10166 - 0,37239 = -0,025735 \text{ V};$$

$$\Delta G_{eqH_2S} = E^{\circ}_{H_2S} \cdot F \cdot n = -0,025735 \cdot 96485 \cdot 2 = -4,966 \text{ kJ/mol};$$

$$\Delta G_{eqH_2Saq} = G_{Srombics} + 2G_{H_3O} - (G_{H_2Saq} + 2G_{H_2O}) = -85,64 + 2 \cdot 22,44 - (-35,794 + 2 \cdot 0) = -4,966 \text{ kJ/mol};$$

$$G_{H_2Saq} = G_{Srombics} + 2G_{H_3O} - (\Delta G_{Hess_H_2Saq} + 2G_{H_2O}) = -85,64 + 2 \cdot 22,44 - (-4,966 + 2 \cdot 0) = -35,794 \text{ kJ/mol};$$

$$pK_a = 7,0 \text{ Wikipedia; CRC2010 } pK_{a1} = 7,05; pK_{a2} = 19$$

$$pK_{a1} = 7,05 \text{ H}_2\text{S} + \text{H}_2\text{O} = \text{HS}^- + \text{H}_3\text{O}^+; K_{eq1} = K_{a1}/[H_2O] = 10^{-(7,05)}/55,3 = 0,000000001612;$$

$$\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = -8,3144 \cdot 298,15 \cdot \ln(0,000000001612) = G_{HS} + G_{H_3O} - (G_{H_2S} + G_{H_2O}) = 50,188 \text{ kJ/mol};$$

$$\Delta G_{eq} = G_{HS} + G_{H_3O} - (G_{H_2S} + G_{H_2O}) = -3,072 + 22,44 - (-30,82 + 0) = 50,188 \text{ kJ/mol};$$

$$G_{HS} = \Delta G_{eq} - G_{H_3O} + (G_{H_2S} + G_{H_2O}) = 50,188 - 22,44 + (-30,82 + 0) = -3,072 \text{ kJ/mol};$$

$$pK_{a2} = 19 \text{ HS}^- + \text{H}_2\text{O} = \text{S}^{2-} + \text{H}_3\text{O}^+; K_{eq1} = K_{a1}/[H_2O] = 10^{-(19)}/55,3 = 10^{-(20,74)};$$

$$\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = -8,3144 \cdot 298,15 \cdot \ln(10^{-(20,74)}) = G_{S_2} + G_{H_3O} - (G_{HS} + G_{H_2O}) = 118,38 \text{ kJ/mol};$$

$$\Delta G_{eq} = G_{S_2} + G_{H_3O} - (G_{HS} + G_{H_2O}) = 92,868 + 22,44 - (-3,072 + 0) = 118,38 \text{ kJ/mol};$$

$$G_{S_2} = \Delta G_{eq} - G_{H_3O} + (G_{HS} + G_{H_2O}) = 118,38 - 22,44 + (-3,072 + 0) = 92,868 \text{ kJ/mol};$$

$$\text{Sēra reducēšana inversais potenciāls: } S_{rombics} + 2H_3O^+ + 2e^- = H_2S_{aq} + 2H_2O; -E^{\circ}_s = -0,025735 \text{ V};$$

$$2(Pt)H + 2H_2O = 2H_3O^+ + 2e^-; E^{\circ}_H = -0,27073 \text{ V}; S_{rombics} + 2(Pt)H = H_2S_{aq};$$

$$\Delta G_{eq} = (E^{\circ}_H - E^{\circ}_s) \cdot F \cdot 1 \cdot 2 = (-0,27073 + 0,025735) \cdot 96485 \cdot 2 = -0,244995 \cdot 96485 \cdot 2 = -47,277 \text{ kJ/mol};$$

$$G_{H_2Saq} = \Delta G_{HessH_2S} + (2G_{H(Pt)} + G_{Srombics}) = -47,277 + (2 \cdot 48,46 - 85,64) = -35,997 \text{ kJ/mol}; \text{ 2. lapas puse.}$$

Nernsta pus reakcijai: $H_2S_{aq} + 2H_2O = S_{rhombic} + 2H_3O^+ + 2e^-$ absolūtais standarta potenciāls $E^{\circ}_{H_2S} = -0,025735 \text{ V}$ brīvās enerģijas izmaiņai: $\Delta G_{eqH_2S} = E^{\circ}_{H_2S} \cdot F \cdot n = -0,025735 \cdot 96485 \cdot 2 = -4,966 \text{ kJ/mol}$.

Ūdeņraža sulfīda šķīduma pus reakcijā H₂S likuma brīvās enerģijas izmaiņas vērtība izteiksmē ir:

$$\Delta G_{Hess_H_2Saq} = G_{Srhombic} + 2G_{H_3O} - (G_{H_2Saq} + 2G_{H_2O}) = -85,64 + 2 \cdot 22,44 - (G_{H_2Saq} + 2 \cdot 0) = -4,966 \text{ kJ/mol}, \text{ tad absolūtā}$$

$$\text{vērtība ir: } G_{H_2Saq} = G_{Srhombic} + 2G_{H_3O} - (\Delta G_{Hess_H_2Saq} + 2G_{H_2O}) = -85,64 + 2 \cdot 22,44 - (-4,966 + 2 \cdot 0) = -35,794 \text{ kJ/mol}.$$

$$\text{Veidošanās no elementiem } S_{rombics} + H_2\text{gāze} = H_2\text{Sgāze}; G_{Srombics} = -85,64 \text{ kJ/mol}; [1,6]$$

$$\text{Veidošanās enerģijas izmaiņa ir } \Delta G_{Hess_H_2Sgāze} = G^{\circ}_{H_2Sgāze} - (HessG^{\circ}_{Srombics} + HessG^{\circ}_{H_2}) = -20,6 - (0 + 0) = -20,6 \text{ kJ/mol}.$$

$$\text{Sēra enerģijas saturs molā ir } G_{Srombics} = G^{\circ}_{H_2Sgāze} - (\Delta G_{Hess_H_2Sgāze} + G_{H_2gāze}) = -20,6 - (-20,6 + 85,64) = -85,64 \text{ kJ/mol};$$

Hidroksonija un ūdens uzskaitē $[H_2O]=55,3$ M absolūtās brīvās enerģijas un potenciālu skalai.

Albertija dati ir doti par elementu absolūtajām vērtībām:

$G_{S_{rombisks}}=-85,64$ kJ/mol; $G_{O_{2gas}}=303$ kJ/mol; $G_{H_{2gas}}=85,6$ kJ/mol; $\Delta G^{\circ}SO_{4Form}=-747,75$ kJ/mol; attiecībā pret ūdeni un oglekļa dioksīda gāzi nulles $G_{H_2O}=G_{CO_{2gas}}=G_{E=0}$ kJ/mol atskaites skalā. Veidošanās no brīviem elementiem:

$$S_{rombisks}+2O_{2gas}+H_{2gas}=H_2SO_4; \Delta G^{\circ}H_2SO_4Form=G_{H_2SO_4}-(G_{S_{rombisks}}+2G_{O_2}+G_{H_{2gas}})=-690,0 \text{ kJ/mol}; [1]$$

$$G_{H_2SO_4}=\Delta G^{\circ}H_2SO_4Form+(G_{S_{rombisks}}+2G_{O_2}+G_{H_{2gas}})=-690,0+(-85,64+2*303+85,6)=-84,04 \text{ kJ/mol};$$

$$S_{rombisks}+2O_{2gas}+H_{2gas}/2=HSO_4^-; \Delta G^{\circ}HSO_4Form=G_{HSO_4}-(G_{S_{rombisks}}+2G_{O_2}+0,5G_{H_{2gas}})=-755,9 \text{ kJ/mol}.$$

$$G_{HSO_4}=\Delta G^{\circ}HSO_4Form+(G_{S_{rombisks}}+2G_{O_2}+0,5G_{H_{2gas}})=-755,9+(-85,64+2*303+85,6/2)=-192,74 \text{ kJ/mol};$$

$$S_{rombisks}+2O_{2gas}=SO_4^{2-}; \Delta G^{\circ}SO_4Form=G_{SO_4}-(G_{S_{rombisks}}+2G_{O_2})=-747,75 \text{ kJ/mol};$$

$$G_{SO_4}=\Delta G^{\circ}SO_4Form+(G_{S_{rombisks}}+2G_{O_2})=-747,75-85,64+2*303=-227,39 \text{ kJ/mol};$$

Līdzsvara konstantes molu daļās $K_{eq}=K_a/[H_2O]$ aprēķina daļot skābes konstanti ar ūdeni $[H_2O]=55,3$ M.

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

$$\Delta G_{eqH_2SO_4}=-R \cdot T \cdot \ln(K_{eq})=-8,3144*298,15*\ln(11,41)=G_{HSO_4}+G_{H_3O}-(G_{H_2SO_4}+G_{H_2O})=-6,035 \text{ kJ/mol};$$

$$\Delta G_{eqH_2SO_4}=G_{HSO_4}+G_{H_3O}-(G_{H_2SO_4}+G_{H_2O})=G_{HSO_4}+22,44-(-84,04-151,549)=-6,035 \text{ kJ/mol};$$

$$G_{HSO_4}=\Delta G_{eqH_2SO_4}-G_{H_3O}+(G_{H_2SO_4}+G_{H_2O})=-6,035-22,44+(-84,04-151,549)=-264,06 \text{ kJ/mol};$$

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

$$\Delta G_{eqHSO_4}=-R \cdot T \cdot \ln(K_{eq2})=-8,3144*298,15*\ln(0,0001850)=G_{SO_4^{2-}}+G_{H_3O}-(G_{HSO_4}+G_{H_2O})=21,307 \text{ kJ/mol};$$

$$\Delta G_{eqHSO_4}=G_{SO_4^{2-}}+G_{H_3O}-(G_{HSO_4}+G_{H_2O})=-747,75+22,44-(G_{HSO_4}-151,549)=21,307 \text{ kJ/mol};$$

$$G_{HSO_4}=G_{SO_4^{2-}}+G_{H_3O}-(\Delta G_{eqHSO_4}+G_{H_2O})=-747,75+22,44-(21,307-151,549)=-595,068 \text{ kJ/mol};$$

$$\Delta G_{eqHSO_4}=G_{SO_4^{2-}}+G_{H_3O}-(G_{HSO_4}+G_{H_2O})=G_{SO_4^{2-}}+22,44-(-264,06-151,549)=21,307 \text{ kJ/mol};$$

$$G_{SO_4^{2-}}=\Delta G_{eqHSO_4}-G_{H_3O}+(G_{HSO_4}+G_{H_2O})=21,307-22,44+(-264,06-151,549)=-416,74 \text{ kJ/mol};$$

Veidošanās no brīvajiem elementiem $S_{rombisks}+1,5O_{2gas}+H_{2gas}=H_2SO_{3aq}$; un šķīdība $SO_2^{gas}+H_2O=H_2SO_{3aq}$.

$$\Delta G^{\circ}H_2SO_3Form=G_{H_2SO_3}-(G_{S_{rombisks}}+1,5\Delta G_{O_2}+G_{H_{2gas}})=G_{H_2SO_3}-(-85,64+1,5*303+85,6)=-527,3675 \text{ kJ/mol};$$

$$G_{H_2SO_3}=\Delta G^{\circ}H_2SO_3Form+(G_{S_{rombisks}}+1,5\Delta G_{O_2}+G_{H_{2gas}})=-527,3675+(-85,64+1,5*303+85,6)=-72,9075 \text{ kJ/mol};$$

$$G_{HSO_3}=\Delta G^{\circ}HSO_3Form+(G_{S_{rombisks}}+1,5\Delta G_{O_2}+G_{H_{2gas}}/2)=-486,5+(-85,64+1,5*303+85,6/2)=-74,84 \text{ kJ/mol};$$

$$G_{SO_3}=\Delta G^{\circ}SO_3Form+G_{S_{rombisks}}+1,5\Delta G_{O_2}=-490,38-85,64+1,5*303=-121,52 \text{ kJ/mol};$$

Līdzsvara konstantes molu daļās $K_{eq}=K_a/[H_2O]$ aprēķina daļot skābes konstanti ar ūdeni $[H_2O]=55,3$ M.

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

$$\Delta G_{eqH_2SO_3}=-R \cdot T \cdot \ln(K_{eq1})=-8,3144*298,15*\ln(0,0002554)=G_{HSO_3}+G_{H_3O}-(G_{H_2SO_3}+G_{H_2O})=20,5075 \text{ kJ/mol};$$

$$G_{H_2SO_3}=G_{HSO_3}+G_{H_3O}-(\Delta G_{eqH_2SO_3}+G_{H_2O})=-74,84+22,44-(20,5075+0)=-72,9075 \text{ kJ/mol};$$

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

$$\Delta G_{eqHSO_3}=-R \cdot T \cdot \ln(K_{eq2})=-8,3144*298,15*\ln(0,000000001115)=G_{SO_3^{2-}}+G_{H_3O}-(G_{HSO_3}+G_{H_2O})=51,1 \text{ kJ/mol};$$

$$G_{HSO_3}=G_{SO_3^{2-}}+G_{H_3O}-(\Delta G_{eqHSO_3}+G_{H_2O})=-121,52+22,44-(51,1+0)=-150,2 \text{ kJ/mol};$$

Sēraskābes oksidēšanas $H_2SO_3+4H_2O=HSO_4^-+3H_3O^++2e^-$ elektroda standarta potenciāls $E^{\circ}H_2SO_3=0,1073$ V.

$$E^{\circ}H_2SO_3=E^{\circ}+0,10166-0,0591/2*\lg(1/[H_2O]^4)-0,37239=0,172-0,0591/2*\lg(1/55,3^4)+0,10166-0,37239=0,10726 \text{ V};$$

$$E_{H_2SO_3}=E^{\circ}H_2SO_3+\frac{0,0591}{2} \cdot \log \frac{[HSO_4^-][H_3O^+]^4}{[H_2SO_3][H_2O]^5}=0,10726 \text{ V} + \frac{0,0591}{2} \cdot \log \frac{[HSO_4^-][H_3O^+]^4}{[H_2SO_3][H_2O]^5}$$

$$\Delta G_{eqH_2SO_3}=E^{\circ}HSO_3 \cdot F \cdot 2=0,107260*96485*2=20,69796 \text{ kJ/mol};$$

$$\Delta G_{eqH_2SO_3}=G_{HSO_4}+3G_{H_3O}-(G_{H_2SO_3}+4G_{H_2O})=-192,74+3*22,44-(-146,118+4*0)=20,69796 \text{ kJ/mol};$$

$$G_{H_2SO_3}=G_{HSO_4}+3G_{H_3O}-(\Delta G_{eqH_2SO_3}+4G_{H_2O})=-192,74+3*22,44-(20,69796+4*0)=-146,118 \text{ kJ/mol};$$

$$G_{HSO_4}=\Delta G_{eqH_2SO_3}-3G_{H_3O}+(G_{H_2SO_3}+4G_{H_2O})=20,69796-3*22,44+(-146,118+4*0)=-192,74 \text{ kJ/mol};$$

Šķīdības konstantes molu daļās $K_{eq}=K_{sp}/[H_2O]$ aprēķina daļot piesātinātu šķīdības produktu ar ūdeni $[H_2O]$.

$SO_2^{gas}+H_2O=H_2SO_{3aq}$; $K_{sp}=[H_2SO_3]/[SO_2^{gas}]/[H_2O]=1,46724/1/51,64=0,028413$, jo piesātinājuma stāvoklī izšķīst

94 g/L SO_2 M=64,066 g/mol $[SO_2]=[H_2SO_3]=94/64,066=1,46724$ M sēraskābes $M_{H_2SO_3}=82,075$ g/mol ar

blīvumu 1,05 g/mL $m_{solution}=1050$ g/L un $m_{H_2SO_3}=[SO_2]*M_{H_2SO_3}=1,46724 \text{ M}*82,075 \text{ g/mol}=120,4327$ g/L skābes

masu $m_{H_2O}=1050-120,4327=929,5673$ g. Ūdens koncentrācija ir $n_{H_2O}=929,5673/18=51,64$ M. Brīvās enerģijas

$$\text{izmaiņa ir } \Delta G_{spH_2SO_3}=-R \cdot T \cdot \ln(K_{sp})=-8,3144*298,15*\ln(0,028413)=G_{H_2SO_3}-(G_{SO_2}+G_{H_2O})=8,82727 \text{ kJ/mol};$$

Veidošanās no brīvajiem elementiem $S_{\text{rombiks}} + O_{2\text{gas}} = SO_2$: $\Delta G^{\circ}_{SO_2\text{Form}} = G_{SO_2} - (-85,64 + 303) = -370,82 \text{ kJ/mol}$;

$$G_{SO_2} = \Delta G^{\circ}_{SO_2\text{Form}} + (G_{S_{\text{rombiks}}} + G_{O_2}) = -370,82 + (-85,64 + 303) = -153,46 \text{ kJ/mol}$$

$$\Delta G_{\text{spH}_2\text{SO}_3} = G_{\text{H}_2\text{SO}_3} - (G_{SO_2} + G_{\text{H}_2\text{O}}) = -72,9075 - (-81,73477 + 0) = 8,82727 \text{ kJ/mol}$$

$$G_{SO_2} = G_{\text{H}_2\text{SO}_3} - (\Delta G_{\text{spH}_2\text{SO}_3} + G_{\text{H}_2\text{O}}) = -72,9075 - (8,82727 + 0) = -81,73477 \text{ kJ/mol}$$

$$HSO_3^- + 4H_2O = SO_4^{2-} + 3H_3O^+ + 2e^-; \quad \text{Suchotina } 2 = \text{pH} < 7 \quad E^{\circ}_{HSO_4^-} = 0,10726 \text{ V}$$

$$E^{\circ}_{HSO_3^-} = E^{\circ} + 0,10166 - 0,0591/2 * \lg(1/[H_2O]^4) - 0,37239 = 0,172 - 0,0591/2 * \lg(1/55,3^4) + 0,10166 - 0,37239 = 0,10726 \text{ V};$$

$$E_{HSO_3^-} = E^{\circ}_{HSO_3^-} + 0,0591/2 * \log([HSO_4^-] * [H_3O^+]^3 / [H_2SO_3\text{aq}] / [H_2O]^4) = 0,10726 \text{ V} + 0,0591/2 * \log \frac{[SO_4^{2-}] * [H_3O^+]^3}{[HSO_3^-] * [H_2O]^4}$$

$$\Delta G_{\text{eqSO}_4} = E^{\circ}_{HSO_4^-} * F * 2 = 0,10726 * 96485 * 2 = 20,69796 \text{ kJ/mol}$$

$$\Delta G_{\text{eqSO}_4} = G_{SO_4} + 3G_{H_3O} - (G_{HSO_3} + 4G_{H_2O}) = -119,5295 + 3 * 22,44 - (-72,9075 + 4 * 0) = 20,69796 \text{ kJ/mol}$$

$$G_{HSO_3} = G_{SO_4} + 3G_{H_3O} - (\Delta G_{\text{eqSO}_4} + 4G_{H_2O}) = -119,5295 + 3 * 22,44 - (20,69796 + 4 * 0) = -72,9075 \text{ kJ/mol}$$

$$G_{SO_4} = \Delta G_{\text{eqSO}_4} - 3G_{H_3O} + (G_{HSO_3} + 4G_{H_2O}) = 20,69796 - 3 * 22,44 + (-72,9075 + 4 * 0) = -119,5295 \text{ kJ/mol}$$

Viela	$\Delta H^{\circ}_H, \text{kJ/mol}$	$\Delta S^{\circ}_H, \text{J/mol/K}$	$\Delta G^{\circ}_H, \text{kJ/mol}$	
H ₂ SO ₄	-814,0	156,9	-690,0	CRC;
H ₂ SO ₄		formation	-84,04	$G_{\text{H}_2\text{SO}_4} = \Delta G^{\circ}_{\text{H}_2\text{SO}_4} + G_{S_{\text{rombiks}}} + 2\Delta G_{O_2} + G_{\text{H}_2\text{gas}} + G_{\text{H}_2\text{O}} = -84,04 \text{ kJ/mol}$;
H ₂ SO ₄		pK _{a1} =-2,8	-415,04	$G_{\text{H}_2\text{SO}_4} = G_{\text{HSO}_4^-} + G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqH}_2\text{SO}_4} + G_{\text{H}_2\text{O}}) = -415,04 \text{ kJ/mol}$;
HSO ₄ ⁻	-887,3	131,8	-755,9	CRC
HSO ₄ ⁻	-	pK _{a1} =-2,8	-264,06	$G_{\text{HSO}_4^-} = \Delta G_{\text{eqH}_2\text{SO}_4} - G_{\text{H}_3\text{O}^+} + (G_{\text{H}_2\text{SO}_4} + G_{\text{H}_2\text{O}}) = -264,06 \text{ kJ/mol}$;
HSO ₄ ⁻	-	pK _{a2} =1,99	-595,068	$G_{\text{HSO}_4^-} = G_{SO_4^{2-}} + G_{H_3O^+} - (\Delta G_{\text{eqHSO}_4^-} + G_{H_2O}) = -595,068 \text{ kJ/mol}$;
HSO ₄ ⁻		formation	-192,74	$G_{\text{HSO}_4^-} = \Delta G^{\circ}_{\text{HSO}_4^-} + G_{S_{\text{rombiks}}} + 2\Delta G_{O_2} + G_{\text{H}_2\text{gas}}/2 = -192,74 \text{ kJ/mol}$;
HSO ₄ ⁻	$E^{\circ}_{HSO_3^-} =$	0,10726	-192,74	$G_{\text{HSO}_4^-} = \Delta G_{\text{eqHSO}_3^-} - 3G_{H_3O^+} + (G_{\text{H}_2\text{SO}_3} + 4G_{\text{H}_2\text{O}}) = -192,74 \text{ kJ/mol}$;
SO ₄ ²⁻	-907,62	-536,2	-747,75	BioTherm2006; $\Delta G_{SO_4^{2-}} = \Delta H - T * \Delta S = -907,62 - 298,15 * -0,5362 = -747,75 \text{ kJ/mol}$;
SO ₄ ²⁻	-	formation	-227,39	$G_{SO_4^{2-}} = \Delta G^{\circ}_{SO_4^{2-}\text{Form}} + G_{S_{\text{rombiks}}} + 2\Delta G_{O_2} = -747,75 - 85,64 + 2 * 303 = -227,39 \text{ kJ/mol}$;
SO ₄ ²⁻	-	pK _{a2} =1,99	-416,74	$G_{SO_4^{2-}} = \Delta G_{\text{eqHSO}_4^-} - G_{H_3O^+} + (G_{\text{HSO}_4^-} + G_{\text{H}_2\text{O}}) = -416,74 \text{ kJ/mol}$;
SO ₄ ²⁻	$E^{\circ}_{HSO_3^-} =$	0,10726	-119,53	$G_{SO_4^{2-}} = \Delta G_{\text{eqHSO}_3^-} - 3G_{H_3O^+} + (G_{\text{HSO}_3^-} + 4G_{\text{H}_2\text{O}}) = -119,5295 \text{ kJ/mol}$;
SO ₄ ²⁻	$E^{\circ}_{SO_3^{2-}} =$	-1,2522	-213,4	$G_{SO_4^{2-}} = \Delta G_{\text{eqSO}_3^{2-}\text{-OH}} - G_{H_2O} + (G_{SO_3^{2-}} + 2G_{OH^-}) = -213,4 \text{ kJ/mol}$;
SO ₄ ²⁻	-909,3	20,1	-744,5	CRC
SO ₂ ^{gas}	-296,81	248,223	-370,82	$\Delta G_H = \Delta H_H - T * \Delta S_H = -296,81 - 298,15 * 0,248223 = -370,82 \text{ kJ/mol}$;
SO ₂ ^{gas}		formation	-153,46	$G_{SO_2} = \Delta G^{\circ}_{SO_2\text{Form}} + (G_{S_{\text{rombiks}}} + G_{O_2}) = -153,46 \text{ kJ/mol}$;
SO ₂ ^{gas}	$\Delta G_{K_{sp}} = 8,827$	0,028413	-81,735	$\Delta G_{SO_2} = G_{\text{H}_2\text{SO}_3} - (\Delta G_{\text{spH}_2\text{SO}_3} + G_{\text{H}_2\text{O}}) = -72,9075 - (8,82727 + 0) = -81,73477 \text{ kJ/mol}$;
H ₂ SO ₃		formation	-72,9075	$G_{\text{H}_2\text{SO}_3} = \Delta G^{\circ}_{\text{H}_2\text{SO}_3\text{Form}} + (G_{S_{\text{rombiks}}} + 1,5\Delta G_{O_2} + G_{\text{H}_2\text{gas}}) = -72,9075 \text{ kJ/mol}$;
H ₂ SO ₃		pK _{a1} =1,85	-72,9075	$G_{\text{H}_2\text{SO}_3\text{aq}} = -74,84 + 22,44 - (20,5075 + 0) = -72,9075 \text{ kJ/mol}$;
H ₂ SO ₃	$E^{\circ}_{HSO_3^-} =$	0,10726	-146,118	$G_{\text{H}_2\text{SO}_3} = G_{\text{HSO}_4^-} + 3G_{H_3O^+} - (\Delta G_{\text{eqHSO}_3^-} + 4G_{H_2O}) = -146,11796 \text{ kJ/mol}$;
HSO ₃ ⁻		formation	-74,84	$G_{\text{HSO}_3^-} = \Delta G^{\circ}_{\text{HSO}_3^-} + G_{S_{\text{rombiks}}} + 1,5\Delta G_{O_2} + G_{\text{H}_2\text{gas}}/2 = -74,84 \text{ kJ/mol}$;
HSO ₃ ⁻		pK _{a2} =7,21	-150,2	$G_{\text{HSO}_3\text{-aq}} = -121,52 + 22,44 - (51,1 + 0) = -150,2 \text{ kJ/mol}$;
HSO ₃ ⁻	$E^{\circ}_{HSO_3^-} =$	0,10726	-72,9075	$G_{\text{HSO}_3^-} = G_{SO_4^{2-}} + 3G_{H_3O^+} - (\Delta G_{\text{eqHSO}_3^-} + 4G_{H_2O}) = -72,9075 \text{ kJ/mol}$;
HSO ₃ ⁻	-635,5	-29	-486,5	CRC
SO ₃ ²⁻	-632,19	-474,05	-490,38	BioTherm2006 $\Delta G_{H_2SO_3^{2-}} = \Delta H_H - T * \Delta S_H = -632,1888 - 298,15 * -0,47405 = -490,85 \text{ kJ/mol}$;
SO ₃ ²⁻	-	formation	-121,52	$G_{SO_3^{2-}} = \Delta G_{\text{Form}} = \Delta G^{\circ}_{SO_3^{2-}} + G_{S_{\text{rombiks}}} + 1,5\Delta G_{O_2} = -121,52 \text{ kJ/mol}$;
SO ₃ ²⁻	$E^{\circ}_{SO_3^{2-}\text{-OH}} =$	-1,2522	-126,48	$G_{SO_3^{2-}} = G_{SO_4^{2-}} + G_{H_2O} - (\Delta G_{\text{eqSO}_3^{2-}\text{-OH}} + 2G_{OH^-}) = -126,483 \text{ kJ/mol}$;

$$G_{\text{H}_2\text{SO}_3} = \Delta G^{\circ}_{\text{H}_2\text{SO}_3\text{Form}} + (G_{S_{\text{rombiks}}} + 1,5\Delta G_{O_2} + G_{\text{H}_2\text{gas}}) = -72,9075 \text{ kJ/mol}$$

$$SO_3^{2-} + 2OH^- = SO_4^{2-} + H_2O + 2e^-; \text{pH} > 7; E^{\circ}_{SO_4^{2-}} = -1,2522 \text{ V Suchotina}$$

$$E^{\circ}_{SO_3^{2-}\text{-OH}} = E^{\circ} + 0,10166 + 0,0591/2 * \lg(1/[H_2O]) = -0,93 + 0,10166 + 0,02955 * \lg(1/55,3) - 0,37239 = -1,2522 \text{ V};$$

$$E_{SO_3^{2-}\text{-OH}} = E^{\circ}_{SO_3^{2-}\text{-OH}} + \frac{0,0591}{2} * \log \frac{[SO_4^{2-}] * [H_2O]}{[SO_3^{2-}] * [OH^-]^2} = -1,2522 \text{ V} + \frac{0,0591}{2} * \log \frac{[SO_4^{2-}] * [H_2O]}{[SO_3^{2-}] * [OH^-]^2}$$

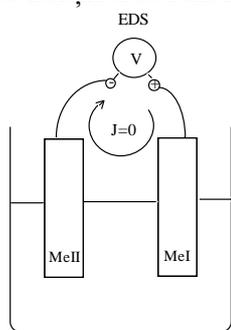
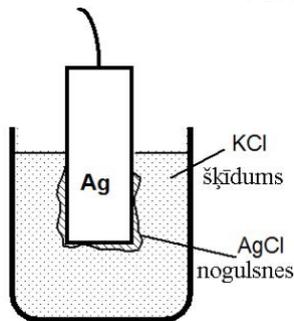
$$\Delta G_{\text{eqSO}_4^{2-}\text{-OH}} = E^{\circ}_{SO_3^{2-}\text{-OH}} * F * 2 = -1,2522 * 96485 * 2 = -241,637 \text{ kJ/mol};$$

$$\Delta G_{\text{eqSO}_3^{2-}\text{-OH}} = G_{SO_4^{2-}} + G_{H_2O} - (G_{SO_3^{2-}} + 2G_{OH^-}) = -213,4 + 0 - (-126,483 + 2 * 77,36) = -241,637 \text{ kJ/mol}$$

$$G_{SO_3^{2-}} = G_{SO_4^{2-}} + G_{H_2O} - (\Delta G_{\text{eqSO}_3^{2-}\text{-OH}} + 2G_{OH^-}) = -213,4 + 0 - (-241,637 + 2 * 77,36) = -126,483 \text{ kJ/mol}$$

$$G_{SO_4^{2-}} = \Delta G_{\text{eqSO}_3^{2-}\text{-OH}} - G_{H_2O} + (G_{SO_3^{2-}} + 2G_{OH^-}) = -241,637 - 0 + (-126,483 + 2 * 77,36) = -213,4 \text{ kJ/mol}$$

Metāls/tā nešķīstošā sāls/nešķīstošās sāls jonu šķīdums II-tipa elektrods



K^+Cl^- šķīduma ar $AgCl$ pret joniem Cl^- nešķīstošajā sāli. Nernsta pus reakcijas sudraba metālam Ag . Elektriskā potenciāla mērījumi voltos ar elektrodu pāri ir Elektro Dzinēja Spēks 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: $EI=EDS+EII$. Standarta salīdzināšanas elektrods ir EII ir ar konstantu hlorīda koncentrāciju.

$Ag(s)+H_2O=Ag^++e^-$; absolūtais standarta potenciāls $E^\circ_{Ag}=0,6317$ V; Kortly, Shucha ; [18]

$$E_{Ag/Ag^+}=E^\circ-0,0591/1*\lg(1/[H_2O]^1)+0,10166-0,37239=0,7994-0,0591/1*\lg(1/55,3^{^1})+0,10166-0,37239=0,6317$$
 V;

$$\Delta G_{eq_Ag}=E^\circ_{Ag}\cdot F\cdot 2=0,6317*96485*1=60,95$$
 kJ/mol, $\Delta G_{eq_As}=G_{Ag^+}-(G_{Ag}+G_{H_2O})=77,1-(G_{Ag}+0)=60,95$ kJ/mol ;

$$G_{Ag}=G_{Ag^+}-(\Delta G_{eq_Ag}+G_{H_2O})=77,1-(60,95+0)=16,15$$
 kJ/mol;

$$G_{Ag}=G_{Ag^+}-(\Delta G_{eq_Ag}+G_{H_2O})=103,8-(60,95+0)=42,85$$
 kJ/mol;

$$G_{Ag^+}=\Delta G_{eq_As}+(G_{Ag}+G_{H_2O})=60,95+(42,855+0)=103,8$$
 kJ/mol ;

Šķīdības līdzsvara mol daļās $AgCl(s)+2H_2O=Ag^++Cl^-$; $AgCl(s)+2H_2O-Cl^-=Ag^+$ absolūtā konstante :

$$K_{AbsoluteAgCl}=K_{spAgCl}/[H_2O]^2=[Ag^+][Cl^-]/[AgCl(s)]=1,77*10^{(-10)}/55,3^2=5,788*10^{-14}$$
 ;

$$\Delta G_{spAgCl}=-R\cdot T\cdot \ln(K_{spAgCl})=-8,3144*298,15*\ln(5,788*10^{(-14)})=75,559$$
 kJ/mol;

$$\Delta G_{spAgCl}=G_{Ag^+}+G_{Cl^-}-(G_{AgCl}+2G_{H_2O})=103,8-183,955-(-155,714+2*0)=75,559$$
 kJ/mol ;

$$G_{AgCl}=G_{Ag^+}+G_{Cl^-}-(\Delta G_{spAgCl}+2G_{H_2O})=103,8-183,955-(75,559+2*0)=-155,714$$
 kJ/mol ;

kompensē šķīdības ūdens molekulu summārajā $Ag(s)+H_2O=Ag^++e^-$; $Ag(s)+H_2O+Cl^-=AgCl(s)+2H_2O+e^-$; reakcijā $Ag_s+Cl^-=AgCl_s+H_2O+e^-$ ar absolūto standarta potenciālu $E^\circ_{Ag/AgCl}=-0,1514$ V $[Cl^-]=0,1$ M= $[K^+Cl^-]$ kālija hlorīda šķīdumā. [18]

$$E_{Ag/AgCl}=E^\circ-0,0591/1*\lg([H_2O]^1)+0,10166-0,37239=0,2223-0,0591/1*\lg(55,3^{^1})+0,10166-0,37239=-0,1514$$
 V;

$$\Delta G_{eq_Ag}=E^\circ_{Ag}\cdot F\cdot 1=-0,1514*96485*1=-14,61$$
 kJ/mol;

$$\Delta G_{eq_Ag}=G_{AgCl}+G_{H_2O}-(G_{Ag}+G_{Cl^-})=-155,71+0-(G_{Ag}-183,955)=-14,61$$
 kJ/mol ;

$$G_{Ag}=G_{AgCl}+G_{H_2O}-(\Delta G_{eq_Ag}+G_{Cl^-})=-155,71+0-(-14,61-183,955)=42,855$$
 kJ/mol ;

Šķīdība NH_3 gas un Ag kompensē katru ūdens molekulu Nernsta pus reakcijas produktos



$Ag+2NH_3aq=Ag(NH_3)_2^++H_2O+e^-$; absolūtais potenciāls $E^\circ_{Ag/Ag(NH_3)_2^+}=0,000725$ V; [17] klasiskais $E^\circ=0,373$ V;

$$E^\circ_{Ag/Ag(NH_3)_2^+}=E^\circ-0,0591/1*\lg([H_2O]^1)+0,10166-0,3=0,373-0,0591/1*\lg(55,3^{^1})+0,10166-0,37239=-0,000725$$
 V;

$$\Delta G_{Ag/Ag(NH_3)_2^+}=E^\circ_{Ag/Ag(NH_3)_2^+}\cdot F\cdot 1=-0,000725*96485*1=-0,06995$$
 kJ/mol;

$$G_{Ag(NH_3)_2^+}=\Delta G_{Ag/Ag(NH_3)_2^+}-G_{H_2O}+(G_{Ag}+2G_{NH_3aq})=-0,06995-0+(42,855-2*91,1)=-139,415$$
 kJ/mol;

$2Ag+2OH^-=Ag_2O(s)+H_2O+2e^-$; absolūtais potenciāls $E^\circ_{2Ag/Ag_2O}=0,02277$ V; [17] klasiskais $E^\circ=0,345$ V ;

$$E^\circ_{2Ag/Ag_2O}=E^\circ-0,0591/2*\lg([H_2O]^1)+0,10166-0,37239=0,345-0,0591/2*\lg(55,3^{^1})+0,10166-0,37239=0,02277$$
 V

$$\Delta G_{Ag/Ag_2O}=E^\circ_{Ag/Ag_2O}\cdot F\cdot 2=0,02277*96485*2=4,394$$
 kJ/mol;

$$\Delta G_{Ag/Ag_2O}=G_{Ag_2O}+G_{H_2O}-(2G_{Ag}+2G_{OH})=G_{Ag_2O}+0-(2*42,855-2*77,36)=4,394$$
 kJ/mol ;

$$G_{Ag_2O}=\Delta G_{Ag/Ag_2O}-G_{H_2O}+(2G_{Ag}+2G_{OH})=4,394-0+(2*42,855-2*77,36)=-64,616$$
 kJ/mol ;

$$E^\circ_{Ag/Ag(NH_3)_2^+}=0,000725$$
 V + $\frac{[Ag(NH_3)_2^+]}{[Ag]\cdot([NH_3]\cdot 2\cdot [Ag(NH_3)_2^+])^2}$ $E^\circ_{2Ag/Ag_2O}=0,02277$ V + $\frac{[Ag_2O]\cdot[H_2O]}{[Ag]^2\cdot[OH]^2}$

Viela	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H , kJ/mol
Ag	-	CRC	16,15
Ag	E°_{Ag/Ag^+}	-0,6317 V	42,85
Ag	$E^\circ_{Ag/AgCl}$	-0,1514 V	42,855
Ag+	105,6	72,7	77,1
Ag+	E°_{Ag}	0,6317 V	103,8
AgCl(s)	-127,01	96,25	-155,71
Cl-	-167,08	56,6	-183,955
$Ag(NH_3)_2^+$	$E^\circ_{Ag(NH_3)_2^+}$	-0,000725	-139,415
AgCl	-	-	-155,71
AgCl	ΔG_{spAgCl}	K_{spAgCl}	-155,714
Cl-	-	-	-183,955
$Ag_2O(s)$	-31,1	121,3	-11,2
$Ag_2O(s)$	E°_{Ag/Ag_2O}	0,02277V	-64,616

$$G_{Ag}=G_{Ag^+}-(\Delta G_{eq_Ag}+G_{H_2O})=77,1-(60,95+0)=16,15$$
 kJ/mol;

$$G_{Ag}=G_{Ag^+}-(\Delta G_{eq_Ag}+G_{H_2O})=103,8-(60,95+0)=42,85$$
 kJ/mol;

$$G_{Ag}=G_{AgCl}+G_{H_2O}-(\Delta G_{eq_Ag}+G_{Cl^-})=-155,71+0-(-14,51-183,955)=42,855$$
 kJ/mol;

CRC;

$$G_{Ag^+}=\Delta G_{eq_As}+(G_{Ag}+G_{H_2O})=60,95+(42,855+0)=103,8$$
 kJ/mol ;

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

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

$$G_{Ag(NH_3)_2^+}=\Delta G_{Ag/Ag(NH_3)_2^+}-G_{H_2O}+(G_{Ag}+2G_{NH_3aq})=-139,415$$
 kJ/mol;

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

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CRC;

$$G_{Ag_2O}=\Delta G_{Ag/Ag_2O}-G_{H_2O}+(2G_{Ag}+2G_{OH})=-64,616$$
 kJ/mol;

Nernsta potenciāla studijas $\text{Hg}/\text{Hg}_2^{2+}/\text{Hg}^{2+}$, Hg_2Cl_2 , $\text{Hg}_2\text{SO}_4(\text{s})$, HgO uzskaitot hidroksioniju H_3O^+ un ūdeni H_2O .

Viela	$\Delta H^\circ_{\text{H}}$, kJ/mol	$\Delta S^\circ_{\text{H}}$, J/mol/K	$\Delta G^\circ_{\text{H}}$, kJ/mol
Hg	HgO ; H ₂ O ₂	75,9	35,885
Hg	E° _{HgCl₂} =	-0,1059 V	35,8
Hg ₂ ²⁺	-166,87	66,74	-146,97
Hg ₂ ²⁺	E° _{Hg/Hg₂²⁺} =	0,6888 V	204,52
Hg ²⁺	-170,21	-36,19	-
Hg ₂ SO ₄ (s)	-743,1	200,7	-625,8
Hg ₂ SO ₄ (s)	K _{AbsoluteHg₂SO₄} =	10 ^{^(-9,673)}	-598,44
SO ₄ ²⁻	-907,62	-536,2	-747,75
SO ₄ ²⁻	E° _{Hg₂SO₄} =	0,2918 V	-726,54
SO ₄ ²⁻	-909,3	20,1	-744,5
Hg ₂ Cl ₂ (s)	-265,37	191,6	-210,7
Hg ₂ Cl ₂ (s)	E° _{HgCl₂} =	-0,1059 V	197,76
Hg ₂ Cl ₂ (s)	E° _{HgCl₂} =	-0,1059 V	255,1
HgCl ₂ (s)	-224,3	146	-178,6
Cl ⁻	-167,08	56,6	-183,955
Cl ⁻	K _{AbsoluteHg₂Cl₂} =	10 ^{^(-23,1)}	101,97
HgO(s)	-99,79	70,25	-60,3675
HgO(s)	-90,8	70,3	-58,5
HgO(s)	-	formation	142,3
HgO(s)	E° _{HgO} =	0,22423 V	147,25

$$(E^\circ_{\text{H}_2\text{O}_2\text{aqRed}} - E^\circ_{\text{HgO}}) \cdot F \cdot n = (0,5278 + 0,22423) = 0,7520 \text{ V}$$

$$G_{\text{Hg}} = G_{\text{eqRedOx}_2\text{H}_2\text{O}_2} - G_{\text{O}_2\text{aqua}} + (G_{\text{HgO}} + G_{\text{H}_2\text{O}_2}) = 35,885 \text{ kJ/mol};$$

$$G_{\text{Hg}} = (G_{\text{Hg}_2\text{Cl}_2} + G_{\text{H}_2\text{O}} - (2G_{\text{Cl}^-} + \Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2})) / 2 = 35,8 \text{ kJ/mol};$$

$$\Delta G_{\text{Hg}_2^{2+}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -166,87 - 298,15 \cdot 0,06674 = -146,97 \text{ kJ/mol};$$

$$G_{\text{Hg}_2^{2+}} = \Delta G_{\text{eq}_\text{Hg}} + (2G_{\text{Hg}} + G_{\text{H}_2\text{O}}) = 132,92 + (2 \cdot 35,8 + 0) = 204,52 \text{ kJ/mol};$$

CRC

CRC

$$G_{\text{Hg}_2\text{SO}_4} = G_{\text{Hg}_2^{2+}} + G_{\text{SO}_4^{2-}} - (\Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4} + 2G_{\text{H}_2\text{O}}) = -598,44 \text{ kJ/mol};$$

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$$G_{\text{SO}_4^{2-}} = G_{\text{Hg}_2\text{SO}_4} - (2G_{\text{Hg}} + \Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4}) = -726,54 \text{ kJ/mol}$$

CRC

CRC

$$G_{\text{Hg}_2\text{Cl}_2(\text{s})} = \Delta G^\circ_{\text{Hg}_2\text{Cl}_2\text{Form}} + (G_{\text{Hg}_2^{2+}} + 2 \cdot G_{\text{Cl}^-}) = 197,76 \text{ kJ/mol};$$

$$G_{\text{Hg}_2\text{Cl}_2} = \Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} - 2G_{\text{H}_2\text{O}} + (2G_{\text{Cl}^-} + 2G_{\text{Hg}}) = 255,1 \text{ kJ/mol};$$

CRC

$$\Delta G_{\text{Cl}^-} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -167,08 - 298,15 \cdot 0,0566 = -183,955 \text{ kJ/mol};$$

$$G_{\text{Cl}^-} = (-G_{\text{Hg}_2^{2+}} + \Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} + (G_{\text{Hg}_2\text{Cl}_2} + 3G_{\text{H}_2\text{O}})) / 2 = 101,97 \text{ kJ/mol};$$

$$\Delta G_{\text{HgO}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -99,79 - 298,15 \cdot 0,07025 = -60,3675 \text{ kJ/mol};$$

CRC $\Delta G_{\text{HgO}} = -58,5 \text{ kJ/mol};$

$$2G_{\text{HgO}} = 2\Delta G_{\text{HgO}} + (2 \cdot G_{\text{Hg}} + G_{\text{O}_2}) = 2 \cdot 142,3 \text{ kJ/mol}$$

$$G_{\text{HgO}} = \Delta G_{\text{eq}_\text{HgO}} - 2G_{\text{H}_2\text{O}} + (G_{\text{Hg}} + 2G_{\text{OH}^-}) = 147,15 \text{ kJ/mol};$$

$2\text{Hg} + \text{H}_2\text{O} = \text{Hg}_2^{2+} + 2\text{e}^-$; absolūtais standarta potenciāls $E^\circ_{\text{Hg}} = 0,6888 \text{ V}$; Kortly, Shucha ; [18]

$$E^\circ_{\text{Hg}} = E^\circ - 0,0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^1) + 0,10166 - 0,37239 = 0,907 - 0,0591/2 \cdot \lg(1/55,3^1) + 0,10166 - 0,37239 = 0,6888 \text{ V};$$

$$\Delta G_{\text{eq}_\text{Hg}} = E^\circ_{\text{Hg}} \cdot F \cdot 2 = 0,6888 \cdot 96485 \cdot 2 = 132,92 \text{ kJ/mol};$$

$$\Delta G_{\text{eq}_\text{Hg}} = G_{\text{Hg}_2^{2+}} - (2G_{\text{Hg}} + G_{\text{H}_2\text{O}}) = G_{\text{Hg}_2^{2+}} - (2 \cdot 35,8 + 0) = 204,52 - (2 \cdot 35,8 + 0) = 132,92 \text{ kJ/mol};$$

$$G_{\text{Hg}_2^{2+}} = \Delta G_{\text{eq}_\text{Hg}} + (2G_{\text{Hg}} + G_{\text{H}_2\text{O}}) = 132,92 + (2 \cdot 35,8 + 0) = 204,52 \text{ kJ/mol};$$

Šķīdības līdzsvara $\text{Hg}_2\text{Cl}_2(\text{s}) + 3\text{H}_2\text{O} = \text{Hg}_2^{2+} + 2\text{Cl}^-$; $2\text{Hg} + \text{H}_2\text{O} = \text{Hg}_2^{2+} + 2\text{e}^-$; absolūta šķīdības konstante :

$$K_{\text{AbsoluteHg}_2\text{Cl}_2} = K_{\text{spHg}_2\text{Cl}_2} / [\text{H}_2\text{O}]^3 = [\text{Hg}_2^{2+}] \cdot [\text{Cl}^-]^2 / [\text{Hg}_2\text{Cl}_2(\text{s})] / [\text{H}_2\text{O}]^3 = 1,43 \cdot 10^{(-18)} / 55,3^3 = 10^{-23,1};$$

$$\Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} = -R \cdot T \cdot \ln(K_{\text{AbsoluteHg}_2\text{Cl}_2}) = -8,314 \cdot 298,15 \cdot \ln(10^{(-23,1)}) = 131,85 \text{ kJ/mol};$$

$$\Delta G_{\text{Hg}_2\text{Cl}_2} = G_{\text{Hg}_2^{2+}} + 2G_{\text{Cl}^-} - (G_{\text{Hg}_2\text{Cl}_2} + 3G_{\text{H}_2\text{O}}) = 204,52 + 2G_{\text{Cl}^-} - (276,61 + 3 \cdot 0) = 204,52 + 2 \cdot 101,97 - (276,61 + 3 \cdot 0) = 131,85 \text{ kJ/mol};$$

$$G_{\text{Cl}^-} = (-G_{\text{Hg}_2^{2+}} + \Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} + (G_{\text{Hg}_2\text{Cl}_2} + 3G_{\text{H}_2\text{O}})) / 2 = (-204,52 + 131,85 + (276,61 + 3 \cdot 0)) / 2 = 101,97 \text{ kJ/mol};$$

$$\text{Hg}_2^{2+} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2(\text{s}); G_{\text{Hg}_2\text{Cl}_2(\text{s})} = \Delta G^\circ_{\text{Hg}_2\text{Cl}_2\text{Form}} + (G_{\text{Hg}_2^{2+}} + 2 \cdot G_{\text{Cl}^-}) = -210,7 + (204,52 + 2 \cdot 101,97) = 197,76 \text{ kJ/mol};$$

$$\text{Veidošanās } \text{Hg}_2^{2+} + 2\text{Cl}^-; G_{\text{Hg}_2\text{Cl}_2(\text{s})} = G_{\text{Hg}_2\text{Cl}_2(\text{s})} - (G_{\text{Hg}_2^{2+}} + 2 \cdot G_{\text{Cl}^-}) = 276,61 - (204,52 + 2 \cdot 101,97) = -131,85 \text{ kJ/mol};$$

$2\text{Hg} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{H}_2\text{O} + 2\text{e}^-$; absolūtais standarta potenciāls $E^\circ_{\text{HgCl}_2} = -0,1059 \text{ V}$; Suchotina ; [18]

$$E^\circ_{\text{HgCl}_2} = E^\circ - 0,0591/2 \cdot \lg([\text{H}_2\text{O}]^2) + 0,10166 - 0,37239 = 0,2678 - 0,0591/2 \cdot \lg(55,3^2) + 0,10166 - 0,37239 = -0,1059 \text{ V};$$

$$\Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} = E^\circ_{\text{Hg}_2\text{Cl}_2} \cdot F \cdot 2 = -0,1059 \cdot 96485 \cdot 2 = -20,44 \text{ kJ/mol};$$

$$\Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} = G_{\text{Hg}_2\text{Cl}_2} + 2G_{\text{H}_2\text{O}} - (2G_{\text{Cl}^-} + 2G_{\text{Hg}}) = 255,1 + 2 \cdot 0 - (2 \cdot 101,97 + 2 \cdot 35,8) = -20,44 \text{ kJ/mol};$$

$$G_{\text{Hg}_2\text{Cl}_2} = \Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2} - 2G_{\text{H}_2\text{O}} + (2G_{\text{Cl}^-} + 2G_{\text{Hg}}) = -20,44 - 2 \cdot 0 + (2 \cdot 101,97 + 2 \cdot 35,8) = 255,1 \text{ kJ/mol};$$

$$G_{\text{Hg}} = (G_{\text{Hg}_2\text{Cl}_2} + G_{\text{H}_2\text{O}} - (2G_{\text{Cl}^-} + \Delta G_{\text{eq}_\text{Hg}_2\text{Cl}_2})) / 2 = (255,1 + 0 - (2 \cdot 101,97 - 20,44)) / 2 = 35,8 \text{ kJ/mol};$$

Šķīdības līdzsvara $\text{Hg}_2\text{SO}_4(\text{s}) + 2\text{H}_2\text{O} = \text{Hg}_2^{2+} + \text{SO}_4^{2-}$; $2\text{Hg} + 2\text{H}_2\text{O} = \text{Hg}_2^{2+} + 2\text{e}^-$; absolūta šķīdības konstante :

$$K_{\text{AbsoluteHg}_2\text{SO}_4} = K_{\text{spHg}_2\text{SO}_4} / [\text{H}_2\text{O}]^2 = [\text{Hg}_2^{2+}] \cdot [\text{SO}_4^{2-}] / [\text{Hg}_2\text{SO}_4(\text{s})] / [\text{H}_2\text{O}]^2 = 6,5 \cdot 10^{(-7)} / 55,3^2 = 10^{-9,673};$$

$$\Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4} = -R \cdot T \cdot \ln(K_{\text{AbsoluteHg}_2\text{SO}_4}) = -8,314 \cdot 298,15 \cdot \ln(10^{(-9,673)}) = 55,21 \text{ kJ/mol};$$

$$\Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4} = G_{\text{Hg}_2^{2+}} + G_{\text{SO}_4^{2-}} - (G_{\text{Hg}_2\text{SO}_4} + 2G_{\text{H}_2\text{O}}) = 204,52 - 747,75 - (-598,44 + 2 \cdot 0) = 55,21 \text{ kJ/mol};$$

$$G_{\text{Hg}_2\text{SO}_4} = G_{\text{Hg}_2^{2+}} + G_{\text{SO}_4^{2-}} - (\Delta G_{\text{eq}_\text{Hg}_2\text{SO}_4} + 2G_{\text{H}_2\text{O}}) = 204,52 - 747,75 - (55,21 + 2 \cdot 0) = -598,44 \text{ kJ/mol};$$

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

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

$2\text{Hg} + \text{SO}_4^{2-} = \text{Hg}_2\text{SO}_4(\text{s}) + \text{H}_2\text{O} + 2\text{e}^-$; absolūtais standarta potenciāls $E^\circ_{\text{HgSO}_4} = 0,291772 \text{ V}$; Kortly, Shucha ; [18]

$$E^\circ_{\text{HgSO}_4} = E^\circ - 0,0591/2 \cdot \lg([\text{H}_2\text{O}]^1) + 0,10166 - 0,37239 = 0,614 - 0,0591/2 \cdot \lg(55,3^1) + 0,10166 - 0,37239 = 0,291772 \text{ V};$$

$$\Delta G_{\text{eq}_\text{HgSO}_4} = E^\circ_{\text{HgSO}_4} \cdot F \cdot 2 = 0,291772 \cdot 96485 \cdot 2 = 56,30 \text{ kJ/mol};$$

$$\Delta G_{\text{eq}_\text{HgSO}_4} = G_{\text{Hg}_2\text{SO}_4} - (2G_{\text{Hg}} + G_{\text{SO}_4^{2-}}) = -598,44 - (2 \cdot 35,8 - 726,54) = 56,50 \text{ kJ/mol};$$

$$G_{\text{SO}_4^{2-}} = G_{\text{Hg}_2\text{SO}_4} - (2G_{\text{Hg}} + \Delta G_{\text{eq}_\text{HgSO}_4}) = -598,44 - (2 \cdot 35,8 + 56,3) = -726,54 \text{ kJ/mol};$$

Veidošanās $2\text{Hg} + \text{O}_2 \text{ aqua} = 2\text{HgO}$; $2G_{\text{HgO}} = 2\Delta G_{\text{HgO}} + (2 \cdot G_{\text{Hg}} + G_{\text{O}_2}) = 2 \cdot -58,5 + (2 \cdot 35,8 + 330) = 2 \cdot 142,3 \text{ kJ/mol};$

$\text{Hg}+2\text{OH}^-=\text{HgO}+\text{H}_2\text{O}+2\text{e}^-$, Nernsta absolūtais standarta potenciāls $E^\circ_{\text{HgO}}=-0,2242\text{ V}$;

$E^\circ_{\text{HgO}}=E^\circ-0,0591/2*\lg([\text{H}_2\text{O}]^1)+0,10166-0,37239=0,098-0,0591/2*\lg(55,3^\wedge 1)+0,10166-0,37239=-0,22423\text{ V}$;

$\Delta G_{\text{eqHgO}}=E^\circ_{\text{HgO}}*F*n=-0,22423*96485*2=-43,27\text{ kJ/mol}$;

$\Delta G_{\text{eqHgO}}=G_{\text{HgO}}+G_{\text{H}_2\text{O}}-(G_{\text{Hg}}+2G_{\text{OH}})=G_{\text{HgO}}+0-(35,8+2*77,36)=147,25+0-(35,8+2*77,36)=-43,27\text{ kJ/mol}$;

$G_{\text{HgO}}=\Delta G_{\text{eqHgO}}-G_{\text{H}_2\text{O}}+(G_{\text{Hg}}+2G_{\text{OH}})=-43,27-0+(35,8+2*77,36)=147,25\text{ kJ/mol}$;

Reducēšanas $\text{HgO}+2\text{H}_2\text{O}+2\text{e}^-=\text{Hg}+2\text{OH}^-$, inversais standarta potenciāls $-E^\circ_{\text{HgO}}=0,22423\text{ V}$.

Oksidēšanas $\text{H}_2\text{O}_{2\text{aq}}+2\text{H}_2\text{O}=\text{O}_{2\text{aq}}+2\text{H}_3\text{O}^++2\text{e}^-$ Nernsta absolūtais standarta potenciāls $E^\circ_{\text{RedH}_2\text{O}_2}=0,5278\text{ V}$;

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

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

Summā: $\text{HgO}+\text{H}_2\text{O}_{2\text{aq}}=\text{Hg}+\text{O}_{2\text{aq}}$; katalāze $G_{\text{H}_2\text{O}_2}=279,285\text{ kJ/mol}$;

$\Delta G_{\text{eqRedOx}_\text{H}_2\text{O}_2}=(E^\circ_{\text{H}_2\text{O}_2\text{aqRed}}-E^\circ_{\text{HgO}})*F*n=(0,5278+0,22423)*96485*2=(0,7520)*96485*2=145,1\text{ kJ/mol}$;

$\Delta G_{\text{eqRedOx}_\text{H}_2\text{O}_2}=G_{\text{Hg}}+G_{\text{O}_{2\text{aq}}}-(G_{\text{HgO}}+G_{\text{H}_2\text{O}_2})=35,885+330-(-58,5+279,285)=145,1\text{ kJ/mol}$;

HgO ; $G_{\text{Hg}}=G_{\text{eqRedOx}_\text{H}_2\text{O}_2}-G_{\text{O}_{2\text{aq}}}+(G_{\text{HgO}}+G_{\text{H}_2\text{O}_2})=145,1-330+(-58,5+279,285)=35,885\text{ kJ/mol}$;

$\Delta G_{\text{eqRedOx}_\text{H}_2\text{O}_2}=G_{\text{Hg}}-G_{\text{O}_{2\text{aq}}}+(G_{\text{HgO}}+G_{\text{H}_2\text{O}_2})=$

Substance	$\Delta H^\circ_{\text{H}}$, kJ/mol	$\Delta S^\circ_{\text{H}}$, J/mol/K	$\Delta G^\circ_{\text{H}}$, kJ/mol
Pb	$E^\circ_{\text{Pb}\downarrow\text{Pb}2+}$	-0,34523 V	-349,07
Pb	-	64,8	-
Pb ²⁺	$E^\circ_{\text{PbO}_2\downarrow\text{Pb}2+}$	1,49326 V	-415,69
Pb ²⁺	0,92	18,5	-4,596
PbO ₂ ↓	-277,4	68,6	-217,3
PbO ₂ ↓	$E^\circ_{\text{PbO}_2\downarrow\text{Pb}2+}$	1,49326 V	-217,3
Al	-	28,3	-
Al	$E^\circ_{\text{Al}/\text{Al}3+}$	-1,8984 V	108
Al ³⁺	-538,4	-325	-441,5
H ₂ AlO ₃ ⁻	$E^\circ_{\text{H}_2\text{AlO}_3/\text{Al}}$	-2,63506	-345,29
NaAlO ₂ ↓	-1133,2	70,4	-

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$G_{\text{Pb}}=G_{\text{Pb}2+}-(\Delta G_{\text{eqPb}\downarrow\text{Pb}2+}+G_{\text{H}_2\text{O}})=-415,895-(-66,42+0)=-349,07\text{ kJ/mol}$;

$G_{\text{Pb}2+}=G_{\text{PbO}_2}+4G_{\text{H}_3\text{O}^+}-(\Delta G_{\text{eqPbO}_2\downarrow\text{Pb}2+}+6G_{\text{H}_2\text{O}})=-415,69\text{ kJ/mol}$;

$\Delta G^\circ_{\text{Pb}2+}=\Delta H^\circ_{\text{H}}-T*\Delta S^\circ_{\text{H}}=0,92-298,15*0,0185=-4,596\text{ kJ/mol}$;

CRC

$G_{\text{PbO}_2}=\Delta G_{\text{eqPbO}_2\downarrow\text{Pb}2+}-4G_{\text{H}_3\text{O}^+}+(G_{\text{Pb}2+}+6G_{\text{H}_2\text{O}})=-217,3\text{ kJ/mol}$;

CRC

$G_{\text{Al}}=G_{\text{Al}3+}-(\Delta G_{\text{eqAl}/\text{Al}3+}+G_{\text{H}_2\text{O}})=-441,5-(-549,5+0)=108\text{ kJ/mol}$;

$\Delta G^\circ_{\text{Pb}2+}=\Delta H^\circ_{\text{H}}-T*\Delta S^\circ_{\text{H}}=-538,4-298,15*-0,325=-441,5\text{ kJ/mol}$;

$G_{\text{H}_2\text{AlO}_3}=\Delta G_{\text{eqH}_2\text{AlO}_3/\text{Al}}-G_{\text{H}_2\text{O}}+(G_{\text{Al}}+4G_{\text{OH}})=-345,29\text{ kJ/mol}$;

CRC

Veidošanās $\text{Pb}+\text{O}_{2\text{gas}}=\text{PbO}_2(\text{s})$; $G_{\text{PbO}_2}=\Delta G_{\text{PbO}_2}+(G_{\text{Pb}}+G_{\text{O}_{2\text{gas}}})=-217,3+(35,8+303,1)=2*142,3\text{ kJ/mol}$;

$\text{Pb}^{2+}+6\text{H}_2\text{O}=\text{PbO}_2(\text{s})+4\text{H}_3\text{O}^++2\text{e}^-$; Nernsta pus reakcijas absolūtais standarta potenciāls $E^\circ_{\text{PbO}_2}=1,49326\text{ V}$;

$E^\circ_{\text{PbO}_2}=E^\circ-0,0591/2*\lg(1/[\text{H}_2\text{O}]^6)+0,10166-0,37239=1,455-0,0591/2*\lg(1/55,3^\wedge 6)+0,10166-0,37239=1,49326\text{ V}$;

$\Delta G_{\text{eqPbO}_2\downarrow\text{Pb}2+}=E^\circ_{\text{PbO}_2\downarrow\text{Pb}2+}*F*3=1,49326*96485*3=288,15\text{ kJ/mol}$;

$\Delta G_{\text{eqPbO}_2\downarrow\text{Pb}2+}=G_{\text{PbO}_2}+4G_{\text{H}_3\text{O}^+}-(G_{\text{Pb}2+}+6G_{\text{H}_2\text{O}})=-217,3+4*22,44-(-415,69+6*0)=288,15\text{ kJ/mol}$;

$G_{\text{PbO}_2}=\Delta G_{\text{eqPbO}_2\downarrow\text{Pb}2+}-4G_{\text{H}_3\text{O}^+}+(G_{\text{Pb}2+}+6G_{\text{H}_2\text{O}})=288,15-4*22,44+(-415,69+6*0)=-217,3\text{ kJ/mol}$;

$G_{\text{Pb}2+}=G_{\text{PbO}_2}+4G_{\text{H}_3\text{O}^+}-(\Delta G_{\text{eqPbO}_2\downarrow\text{Pb}2+}+6G_{\text{H}_2\text{O}})=-217,3+4*22,44-(288,15+6*0)=-415,69\text{ kJ/mol}$;

$$E_{\text{PbO}_2\downarrow/\text{Pb}2+}=E^\circ_{\text{PbO}_2\downarrow\text{Pb}2+}+\frac{0.0591}{2}\cdot\lg\frac{[\text{PbO}_2\downarrow][\text{H}_3\text{O}^+]^4}{[\text{Pb}^{2+}][\text{H}_2\text{O}]^6}=1,4674\text{ V}+\frac{0.0591}{2}\cdot\lg\frac{[\text{PbO}_2\downarrow][\text{H}_3\text{O}^+]^4}{[\text{Pb}^{2+}][\text{H}_2\text{O}]^6};$$

$\text{Pb}+\text{H}_2\text{O}=\text{Pb}^{2+}+2\text{e}^-$; pH<7 Nernsta pus reakcijas absolūtais standarta potenciāls $E^\circ_{\text{Pb}/\text{Pb}2+}=-0,3452\text{ V}$;

$E^\circ_{\text{Pb}/\text{Pb}2+}=E^\circ-0,0591/2*\lg(1/[\text{H}_2\text{O}])+0,10166-0,37239=-1,26-0,0591/2*\lg(1/55,3^\wedge 1)+0,10166-0,37239=-0,3452\text{ V}$;

$\Delta G_{\text{eqPb}\downarrow\text{Pb}2+}=E^\circ_{\text{Pb}\downarrow\text{Pb}2+}*F*n=-0,34523*96485*2=-66,62\text{ kJ/mol}$;

$\Delta G_{\text{eqPb}\downarrow\text{Pb}2+}=G_{\text{Pb}2+}-(G_{\text{Pb}}+G_{\text{H}_2\text{O}})=-415,69-(G_{\text{Pb}}+0)=-71,59=-66,62\text{ kJ/mol}$;

$G_{\text{Pb}}=G_{\text{Pb}2+}-(\Delta G_{\text{eqPb}\downarrow\text{Pb}2+}+G_{\text{H}_2\text{O}})=-415,69-(-66,62+0)=-349,07\text{ kJ/mol}$;

$\text{Al}+\text{H}_2\text{O}=\text{Al}^{3+}+3\text{e}^-$; CRC Nernsta pus reakcijas absolūtais standarta potenciāls $E^\circ_{\text{Pb}/\text{Pb}2+}=-1,8984\text{ V}$;

$E^\circ_{\text{Al}/\text{Al}3+}=E^\circ-0,0591/3*\lg(1/[\text{H}_2\text{O}])+0,10166-0,37239=-1,662-0,0591/3*\lg(1/55,3^\wedge 1)+0,10166-0,37239=-1,8984\text{ V}$;

$\Delta G_{\text{eqAl}/\text{Al}3+}=E^\circ_{\text{Al}/\text{Al}3+}*F*3=-1,8984*96485*3=-549,5\text{ kJ/mol}$;

$\Delta G_{\text{eqAl}/\text{Al}3+}=G_{\text{Al}3+}-(G_{\text{Al}}+G_{\text{H}_2\text{O}})=-441,5-(108+0)=-549,5\text{ kJ/mol}$;

$G_{\text{Al}}=G_{\text{Al}3+}-(\Delta G_{\text{eqAl}/\text{Al}3+}+G_{\text{H}_2\text{O}})=-441,5-(-549,5+0)=108\text{ kJ/mol}$;

$\text{Al}+4\text{OH}^-=\text{H}_2\text{AlO}_3^-+\text{H}_2\text{O}+3\text{e}^-$; CRC Nernsta absolūtais standarta potenciāls $E^\circ_{\text{H}_2\text{AlO}_3-\text{Al}}=-2,63506\text{ V}$;

$E^\circ_{\text{H}_2\text{AlO}_3-\text{Al}}=E^\circ-0,0591/3*\lg([\text{H}_2\text{O}])+0,10166-0,37239=-2,33-0,0591/3*\lg(55,3^\wedge 1)+0,10166-0,37239=-2,63506\text{ V}$;

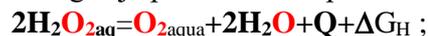
$\Delta G_{\text{eqH}_2\text{AlO}_3/\text{Al}}=E^\circ_{\text{H}_2\text{AlO}_3/\text{Al}}*F*3=-2,63506*96485*3=-762,73\text{ kJ/mol}$;

$\Delta G_{\text{eqH}_2\text{AlO}_3/\text{Al}}=G_{\text{H}_2\text{AlO}_3}+G_{\text{H}_2\text{O}}-(G_{\text{Al}}+4G_{\text{OH}})=-345,29+0-(108+4*77,36)=-762,73\text{ kJ/mol}$;

$G_{\text{H}_2\text{AlO}_3}=\Delta G_{\text{eqH}_2\text{AlO}_3/\text{Al}}-G_{\text{H}_2\text{O}}+(G_{\text{Al}}+4G_{\text{OH}})=-762,73-0+(108+4*77,36)=-345,29\text{ kJ/mol}$;

$$E_{\text{AlO}_2-\text{Al}\downarrow}=E^\circ_{\text{AlO}_2-\text{Al}\downarrow}+\frac{0.0591}{3}\cdot\lg\frac{[\text{H}_2\text{AlO}_3][\text{H}_2\text{O}]}{[\text{Al}][\text{OH}]^4}=-2,63506\text{ V}+\frac{0.0591}{3}\cdot\lg\frac{[\text{H}_2\text{AlO}_3][\text{H}_2\text{O}]}{[\text{Al}][\text{OH}]^4};$$

Liela ātruma protolīzes Aktivēto peroksīda jonu sadursmē $\text{HOO}^- < \text{OOH}$ ir liela $E_a = 79000 \text{ J/mol}$ aktivācijas enerģija, bet jonu $\text{HOO}^- \Rightarrow \text{Fe}^{3+}$ sadursmē aktivācijas enerģija ir maza $E_a = 29 \text{ J/mol}$. Elongācija peroksisomās producē $\omega = 6$, $\omega = 3$ neaizstājamās taukskābes, skābekli, ūdeni un siltumu:



Red: $\text{H}_2\text{O}_2 + 2\text{H}_2\text{O} = \text{O}_2 + 2\text{H}_3\text{O}^+ + 2e^-$; $E^\circ_{\text{H}_2\text{O}_2} = 0,5268 \text{ V}$ Nernsta absolūtais potenciāls Alberta University;

Ox: $\text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2e^- = 4\text{H}_2\text{O}$; $-E^\circ_{\text{OxH}_2\text{O}_2} = -1,7113 \text{ V}$ inversais standarta potenciāls Suhotina;

$$\Delta G_{\text{eqStandarta}_2\text{H}_2\text{O}_2} = (E^\circ_{\text{H}_2\text{O}_2\text{aqRed}} - E^\circ_{\text{H}_2\text{O}_2\text{aqOx}}) * F * n = (0,5268 - 1,7113) * 96485 * 2 = (-1,1845) * 96485 * 2 = -228,57 \text{ kJ/mol};$$

$$\Delta G_{\text{Alberty}_2\text{H}_2\text{O}_2} = G_{\text{O}_2\text{aq}} + 2 * G_{\text{H}_2\text{O}} - 2 * G_{\text{H}_2\text{O}_2} = 330 + 2 * 0 - 2 * G_{\text{H}_2\text{O}_2} = -228,57 \text{ kJ/mol}; \text{ exoergic}$$

$$G_{\text{H}_2\text{O}_2} = (G_{\text{O}_2\text{aq}} + 2 * G_{\text{H}_2\text{O}} + \Delta G_{\text{Alberty}_2\text{H}_2\text{O}_2}) / 2 = (330 + 2 * 0 + 228,57) / 2 = 558,57 / 2 = 279,285 \text{ kJ/mol};$$

$$K_{\text{eqStandart}} = \frac{[\text{O}_2]_{\text{aq}} * [\text{H}_2\text{O}]^2}{[\text{H}_2\text{O}_2]_{\text{aq}}^2} = K_{\text{H}_2\text{O}_2} = \exp(228573 / 8,3144 / 298,15) = 1,11 * 10^{40}.$$

Pus reakciju RedOx Nernsta reducēšanas un oksidēšanas elektronu balanss $2e^-$ pie $\text{pH} = 7,36$, $[\text{O}_{aq}] = 6 * 10^{-5} \text{ M}$.

$$E_{\text{Red}} = E^\circ_{\text{H}_2\text{O}_2} + 0,0591 / 2 * \lg([\text{O}_{2aq}] * [\text{H}_3\text{O}^+]^2 / [\text{H}_2\text{O}_2] / [\text{H}_2\text{O}]^2) = 0,5268 + 0,0591 / 2 * \lg(6 * 10^{(-5)} * 10^{(-7,36 * 2)} / 1 / 55,3^{(2)}) = -0,13493 \text{ V};$$

$$E_{\text{Ox}} = -E^\circ_{\text{H}_2\text{O}_2\text{Ox}} + 0,0591 / 2 * \lg([\text{H}_2\text{O}_2] * [\text{H}_3\text{O}^+]^2 / [\text{H}_2\text{O}]^4) = -1,7113 + 0,0591 / 2 * \lg(1 * 10^{(-7,36 * 2)} / 55,3^{(4)}) = -1,0703 \text{ V};$$

$$\text{H}_2\text{O}_2 \text{ izmaiņa ir } \Delta G_{\text{Homeostasis} / 2} = (E_{\text{Red}} - E_{\text{Ox}}) * F * n / 2 = (-0,13493 - 1,0703) * 96485 = (-1,2052) * 96485 = -232,76 \text{ kJ/mol};$$

$$G_{\text{HomeostasisH}_2\text{O}_2} = (G_{\text{O}_2\text{Biochem}_\text{arteriaj}} + 2 * G_{\text{H}_2\text{O}} - G_{\text{H}_2\text{O}_2\text{BioChemistry}} - \Delta G_{\text{Alberty}}) / 2 = (88,04 + 2 * 85,64 + 232,76) / 2 = 246,04 \text{ kJ/mol}$$

Viela	$\Delta H^\circ_H, \text{kJ/mol}$	$\Delta S^\circ_H, \text{J/mol/K}$	$\Delta G^\circ_H, \text{kJ/mol}$
H_3O^+	-285,81	-3,854	-213,275
O_{2aq}	-11,715	110,876	16,4
O_{2aq}	-11,70	-94,2	16,40
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
H_2O_{2aq}	-191,99	-481,688	-48,39
H_2O_{2aq}	-191,17	143,9	-134,03
H_2O_{2aq}	Formation	-48,39	340,25
H_2O_{2aq}	Formation	-134,03	254,61
H_2O_{2aq}	$\Delta E^\circ_{\text{H}_2\text{O}_2\text{aq}}$	1,1845 V	279,285
HOO^-	$\text{pK}_a = 11,75$	77,016	333,866
H_2O_2	-237,129	69,91	-237,129

$$G_{\text{H}_2\text{O}_2} = 279,285 \text{ kJ/mol}; G_{\text{HOO}^-} = 333,866 \text{ kJ/mol};$$

Mischenko 1972, Himia, Leningrad [26]

$$\text{CRC 2010}; G_{\text{O}_2\text{aq}} = 330 \text{ kJ/mol}; G_{\text{H}_2\text{O}} = 0 \text{ kJ/mol};$$

$$\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{O}_2} + 2\Delta H^\circ_{\text{H}_2\text{O}} - 2\Delta H^\circ_{\text{H}_2\text{O}_2} = -201,02 = -201,06 \text{ kJ/mol}$$

$$= -11,7 - 2 * 286,65 - (2 * -191,99) = -201,02 \text{ kJ/mol eksotermiska.}$$

$$= -11,7 - 2 * 285,85 - (2 * -191,17) = -201,06 \text{ kJ/mol}$$

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$$G_{\text{H}_2\text{O}_{2aq}} = \Delta G_{\text{H}_2\text{O}_2\text{Alberty}} + (G_{\text{O}_2\text{gas}} + G_{\text{H}_2\text{gas}} + G_{\text{H}_2\text{O}}) = 340,25 \text{ kJ/mol};$$

$$G_{\text{H}_2\text{O}_{2aq}} = \Delta G_{\text{H}_2\text{O}_2\text{Alberty}} + (G_{\text{O}_2\text{gas}} + G_{\text{H}_2\text{gas}} + G_{\text{H}_2\text{O}}) = 254,61 \text{ kJ/mol};$$

$$G_{\text{H}_2\text{O}_2} = (G_{\text{O}_2\text{aq}} + 2 * G_{\text{H}_2\text{O}} + \Delta G_{\text{Alberty}_2\text{H}_2\text{O}_2}) / 2 = 279,285 \text{ kJ/mol};$$

$$G_{\text{HOO}^-} = -G_{\text{H}_3\text{O}^+} + \Delta G_{\text{aH}_2\text{O}_2} + (G_{\text{H}_2\text{O}_2} + G_{\text{H}_2\text{O}}) = 333,866 \text{ kJ/mol};$$

CRC

$$\text{H}_2\text{O}_2 + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HOO}^-; \text{pK}_a = 11,75; G_{\text{H}_2\text{O}_2} = 279,29 \text{ kJ/mol}; G_{\text{HOO}^-} = 333,866 \text{ kJ/mol};$$

$$\Delta G_{\text{aH}_2\text{O}_2} = -R * T * \ln(K_a / [\text{H}_2\text{O}]) = -8,3144 * 298,15 * \ln(10^{(-11,75)} / 55,3) = -8,3144 * 298,15 * -31,07 = 77,016 \text{ kJ/mol};$$

$$\Delta G_{\text{aH}_2\text{O}_2} = G_{\text{H}_3\text{O}^+} + G_{\text{HOO}^-} - (G_{\text{H}_2\text{O}_2} + G_{\text{H}_2\text{O}}) = 22,44 + G_{\text{HOO}^-} - (279,29 + 0) = 77,016 \text{ kJ/mol};$$

$$G_{\text{HOO}^-} = -G_{\text{H}_3\text{O}^+} + \Delta G_{\text{aH}_2\text{O}_2} + (G_{\text{H}_2\text{O}_2} + G_{\text{H}_2\text{O}}) = -22,44 + 77,016 + (279,29 + 0) = 333,866 \text{ kJ/mol};$$

$\text{HOO}^- + \text{H}_2\text{O} = \text{O}_{2aq} + \text{H}_3\text{O}^+ + 2e^-$; Absolūtājā skalā peroksīda anjona standarta potenciāls ir: $E^\circ_{\text{NernstHOO}^-} = 0,09625 \text{ V}$.

$$\Delta G_{\text{NernstHOO}^-} = G_{\text{O}_2\text{aq}} + G_{\text{H}_3\text{O}^+} - (G_{\text{HOO}^-} + G_{\text{H}_2\text{O}}) = 330 + 22,44 - (333,866 + 0) = 18,574 \text{ kJ/mol};$$

$$E^\circ_{\text{HOO}^-} = E^\circ - 0,0591 / 2 * \lg(1 / [\text{H}_2\text{O}]) + 0,10166 - 0,37 = 0,31548 - 0,02955 * \lg(1 / 55,3^{(1)}) + 0,10166 - 0,37239 = 0,09625 \text{ V};$$

$$E^\circ_{\text{HOO}^-} = E^\circ + 0,37239 = 0,09625 + 0,37239 = 0,46864 \text{ V}; E^\circ_{\text{HOO}^-} = 0,46864 - 0,10166 = 0,36698 \text{ V};$$

$$E^\circ_{\text{HOO}^-} = 0,36698 + 0,0591 / 2 * \lg(1 / 55,3^{(1)}) = 0,31548 \text{ V};$$

Nernsta pus reakcijas absolūtais standarta potenciāls ir:

$$E^\circ_{\text{NernstHOO}^-} = \Delta G_{\text{NernstHOO}^-} / F / 1 = 18574 / 96485 / 2 = 0,09625 \text{ V}.$$

Eksotermiska, eksoerģiska H_2O_2 (aq) dismutēšanas Hesa izmaiņa $\Delta G_{\text{Alberty}_2\text{H}_2\text{O}_2}$,

-246 kJ/mol un homeostāzē $\Delta G_{\text{Homeostasis}} -232,76 \text{ kJ/mol}$ ir negatīva, bet standarta līdzsvaru

maisījumā minimizējas $\Delta G_{\text{eqStandart}} = -228,6 \text{ kJ/mol}$ sasniedzot konstanti: $K_{\text{eq}} = 1,11 * 10^{40}$.

Lešateljē princips ir Prigožina atraktors kā brīvās enerģijas izmaiņas minimums ΔG_{min}

līdzsvarā. Liela ātruma protolīzes atraktori $\text{pH} = 7,36$, skābeklis 20,95% gaisā atrodas

līdzsvara stāvoklī, kamēr neatgriezeniskā homeostāze turpinās, jo ir nelīdzsvara

stāvoklis. Prigožina atraktors ir Nobela prēmija ķīmijā 1977. gadā. KATALĀZE izdzēs

peroksīda molekulas H_2O_2 sasniedzot 100% $\omega = 6$, $\omega = 3$ taukskābju C20:4 iznākumam

elongācijas sintēzē peroksisomās. KATALĀZES reaktivitāte ir nepieciešams

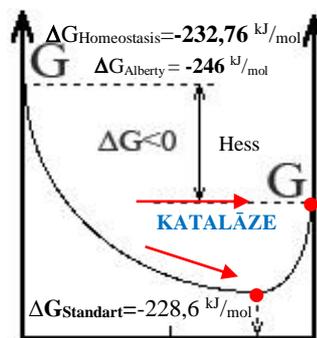
neatgriezeniskas homeostāzes Brauna molekulārs dzinējs evolūcijai un izdzīvošanai.

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

$$\text{Catalase}; G_{\text{H}_2\text{O}_{2aq}} = \Delta G_{\text{H}_2\text{O}_2\text{Alberty}} + (G_{\text{O}_2\text{gas}} + G_{\text{H}_2\text{gas}} + G_{\text{H}_2\text{O}}) = -134,03 + (85,64 + 303 + 0) = 254,61 \text{ kJ/mol};$$

$$\text{Catalase}; G_{\text{H}_2\text{O}_{2aq}} = \Delta G_{\text{H}_2\text{O}_2\text{Alberty}} + (G_{\text{O}_2\text{gas}} + G_{\text{H}_2\text{gas}} + G_{\text{H}_2\text{O}}) = -48,39 + (85,64 + 303 + 0) = 340,25 \text{ kJ/mol};$$

$$41^{\text{st}}, 54^{\text{th}} \text{ page [1,8,20]} \Delta G^\circ_{\text{UnivAlberta}} = -134,03 \text{ kJ/mol}; \Delta G^\circ_{\text{Alberty}} = -48,39 \text{ kJ/mol};$$



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

Šķīdība $N_{2gas}+H_2O+\Delta G=N_{2aq}$ palielina slāpekļa enerģiju molā no $G_{N_{2gas}}=-9,55$ kJ/mol līdz $G_{N_{2aq}}=18,7$ kJ/mol.

Publicētā Albertija slāpekļa šķīdumā **absolūtā** brīvā enerģija vienā molā ir $G_{N_{2aq}}=18,7$ kJ/mol, ja tīras gāzes mol daļa ir viens $[N_{2gas}]=1$. [8] Ūdenī Elements slāpekļi $N_{2gas}+H_2O=N_{2aq}$ ir vāji šķīstošs ar $0,00175$ g/100g H_2O izšķīdināto daudzumu $[N_{2aq}]=0,00175/100,00175*996=0,01743/28,02=10^{-3,206}$ M un blīvumu 996 g/L. [1] Šķīdības konstante mol daļās ir mazāka par vienu $K_{sp}=[N_{2aq}]/[H_2O]=10^{(-3,206)}/55,3=10^{-4,949}$, kuras brīvās enerģijas izmaiņa ir endoerģiska:

$$\Delta G_{sp}=-R\cdot T\cdot \ln(K_{sp})=-8,3144\cdot 298,15\cdot \ln(10^{(-4,949)})=28,25 \text{ kJ/mol}.$$

Hesa likuma brīvās enerģijas izmaiņa ir $\Delta G_{Hess_sp_N_{2aq}}=G_{N_{2aq}}-(G_{N_{2gas}}+G_{H_2O})=18,7-(G_{N_{2gas}}-0)=28,25$ kJ/mol sakrītoša absolūtajā enerģijas skalā. Mola $G_{N_{2gas}}=G_{N_{2aq}}-(\Delta G_{Hess_sp_N_{2aq}}+G_{H_2O})=18,7-(28,25+0)=-9,55$ kJ/mol slāpekļa gāzes enerģijas saturs ir negatīvs relatīvi zem destilētā ūdens nulles $G_{H_2O}=0$ kJ/mol. Izšķīdināta slāpekļa mola enerģijas saturs $G_{N_{2aq}}=18,7$ kJ/mol ir pozitīvs.

Prigožina enerģijas izmaiņa šķīdināto produktu reakcijās ir sakrītoši ar Hesa likuma brīvās enerģijas izmaiņām Albertija datus: $\Delta G_{Hess_sp_N_{2aq}}=G_{N_{2aq}}-(G_{N_{2gas}}+G_{H_2O})=18,7-(G_{N_{2gas}}-0)=28,25$ kJ/mol.

Slāpekļa gāzes brīvās enerģijas saturs izteiksmē ir negatīvs pret ūdens nulles atskaiti $G_{H_2O}=0$ kJ/mol skalā:

$$G_{N_{2gas}}=G_{N_{2aq}}-(\Delta G_{Hess_sp_N_{2aq}}+G_{H_2O})=18,7-(28,25+0)=-9,55 \text{ kJ/mol}.$$

$$\Delta G_{sp_N_{2aq}}=G_{N_{2aq}}-(G_{N_{2gas}}+G_{H_2O})=18,7-(-9,55+0)=28,25 \text{ kJ/mol}; [8] \text{ Albertijs}$$

Viela	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
N_{2gas}	$G_{N_{2gas}}=$	form NH_3	107,2
N_{2aq}	-10,54	98,1	18,7
N_{2gas}	$N_{2gas}+H_2O$	$=N_{2aq}$	-9,55

$$G_{N_{2gas}}=2G_{NH_3gas}-(2\Delta G_{Hess_NH_3gas}+3\cdot G_{H_2gas})=107,28 \text{ kJ/mol};$$

$$G_{N_{2gas}}=2\cdot 165,6593-(-32,8+3\cdot 85,64)=107,28 \text{ kJ/mol}; [1,8];$$

Šķīdums N_{2aq} pie $pH=7,36$ [8].

$$G_{N_{2gas}}=G_{N_{2aq}}-(\Delta G_{Hess_šk_N_{2aq}}+G_{H_2O})=18,7-(28,25+0)=-9,55 \text{ kJ/mol};$$

Veidošanās no akva elementiem $N_{2aq}+3H_{2aq}>2NH_{3aq}$ ar absolūto enerģiju $G_{N_{2aq}}=18,7$ kJ/mol; $G_{H_{2aq}}=103,2$ kJ/mol uzrāda eksoerģisku reakciju $2\Delta G_{Hess_NH_3aq}=2G_{NH_3aq}-(G_{N_{2aq}}+3\cdot G_{H_{2aq}})=2\cdot 91,1056-(18,7+3\cdot 103,24)=-146,2$ kJ/mol. [8]

Veidošanās no elementiem $N_{2gas}+3H_{2gas}>2NH_{3gas}$ dod $G_{N_{2gas}}=-9,55$ kJ/mol; $G_{H_{2gas}}=85,64$ kJ/mol ir eksoerģiska $2\Delta G_{Hess_NH_3gas}=2G_{NH_3gas}-(G_{N_{2gas}}+3\cdot G_{H_{2gas}})=2G_{NH_3gas}-(-9,55+3\cdot 85,64)=2\cdot -16,4=-32,8$ kJ/mol. [1] Enerģijas saturs molā NH_3gas ir $2G_{NH_3gas}=2\Delta G_{Hess_NH_3gas}+(G_{N_{2gas}}+3\cdot G_{H_{2gas}})=2\cdot -16,4+(-9,55+3\cdot 85,64)=214,57=2\cdot 107,285$ kJ/mol.

Klasiski, Hess pieņemot nulles enerģiju brīviem elementiem ir dota eksoerģiska izmaiņa CRC datus:

$$2\Delta G_{Hess_NH_3gas}=2G^{\circ}_{NH_3gas}-(G^{\circ}_{N_{2gas}}+3\cdot G^{\circ}_{H_2})=2\cdot -16,4-(0+3\cdot 0)=-32,8 \text{ kJ/mol} . [1]$$

Šķīdība $NH_3gas+H_2O=NH_3aq$; $G_{NH_3aq}=91,1$ kJ/mol; amonjakam pie $pH=7,36$ [8];

$$\Delta H_{Hydration}=\Delta H^{\circ}_{NH_3aq}-\Delta H^{\circ}_{NH_3gas}-\Delta H^{\circ}_{H_2O}=-132,5608+45,94-286,65=373,3 \text{ kJ/mol};$$

$$S_{Hydration}=\Delta S^{\circ}_{NH_3aq}-\Delta S^{\circ}_{NH_3gas}-\Delta S^{\circ}_{H_2O}=-739,2922-192,77-69,9565=-1002 \text{ J/mol/K};$$

$$\Delta G_{Hydrations}=\Delta H_{Hydrations}-T\cdot \Delta S_{Hydration}=-373,3-298,15\cdot -1,002=-74,5537 \text{ kJ/mol};$$

$$K_{sp}=\exp(-\Delta G_{Hydration}/R/T)=\exp(74553,7/8,3144/298,15)=10^{13,06};$$

Albertija šķīdumi amonjakam pie $pH=7,36$ $G_{NH_3aq}=91,1056$ kJ/mol un Hesa hidratācija ar izmaiņu enerģijai $\Delta G_{Hydrations}=-74,5537$ kJ/mol aprēķina absolūto enerģijas saturu gāzei NH_3gas sakrītoši vienādi:

$$G_{NH_3gas}=G_{NH_3aq}-(\Delta G_{Hydration}+G_{H_2O})=91,1056-(-74,5537+0)=165,7 \text{ kJ/mol};$$

$$G_{NH_3gas}=(2\Delta G_{Hess_NH_3gas}+(G_{N_{2gas}}+3\cdot G_{H_2}))/2=(-32,8+(107,2+3\cdot 85,64))/2=165,7 \text{ kJ/mol}; [1,8] \text{ CRC, Albertijs}$$

$$G_{NH_3gas}=(\Delta G_{Hess_NH_3gas}+(G_{N_{2gas}}+3\cdot G_{H_{2gas}}))/2=(-32,8+(-9,55+3\cdot 85,64))/2=107,285 \text{ kJ/mol};$$

Enerģiju elementam ūdeņradim $G_{H_{2gas}}=85,64$ kJ/mol, gāzei $G_{NH_3gas}=165,7$ kJ/mol; ar Hesa izmaiņu $-32,8$ kJ/mol aprēķina $G_{N_{2gas}}=2G_{NH_3gas}-(2\Delta G_{Hess_NH_3gas}+3\cdot G_{H_{2gas}})=2\cdot 165,7-(2\cdot -16,4+3\cdot 85,64)=107,28$ kJ/mol viena mola slāpekļa gāzes brīvās enerģijas saturu.

Šķīdība $NH_3gas+H_2O=NH_3aq$; $G_{NH_3aq}=91,1$ kJ/mol; $G_{NH_3gas}=107,285$ kJ/mol absolūtajā enerģijas skalā ir eksoerģiska: $\Delta G_{Hydration}=G_{NH_3aq}-(G_{NH_3gas}+G_{H_2O})=91,1056-(107,285+0)=-16,18$ kJ/mol. [1,8] CRC, Albertijs Šķīdības konstante ir $K_{sp}=\exp(-\Delta G_{Hydration}/R/T)=\exp(16179,4/8,3144/298,15)=683,17$ lielāka par vienu.

Vājas skābes $G_{NH_4+}=50,81$ kJ/mol protolīze $NH_4++H_2O=NH_3aq+H_3O+$; $pK_{eq}=10,99$; uzrāda enerģijas izmaiņu

$$\Delta G_{eq}=-R\cdot T\cdot \ln(K_{eq})=-8,3144\cdot 298,15\cdot \ln(10^{(-10,99)})=G_{NH_3Hydration}+G_{H_3O}-G_{NH_4+}-G_{H_2O}=62,73 \text{ kJ/mol} , \text{ 16th page:}$$

$$\Delta G_{eq}=G_{NH_3aq}+G_{H_3O}-(G_{NH_4+}+G_{H_2O})=91,1+22,44-G_{NH_4+}-0=62,73 \text{ kJ/mol}.$$

Amonija brīvās enerģijas saturs ir $G_{NH_4+}=G_{NH_3aq}+G_{H_3O}-(\Delta G_{eq}+G_{H_2O})=91,1+22,44-62,73-0=50,81$ kJ/mol,

Protolīzes klasiskā skābes konstante ir $NH_4+=H++NH_3aq$ $pK_a=9,25$;

Veidošanās no elementiem HNO_2 $\Delta G^{\circ}_{HNO_2}=-46$ kJ/mol un HNO_3 $\Delta G^{\circ}_{HNO_3}=-250,53$ kJ/mol Wikipedia:

$$G_{HNO_2}=\Delta G^{\circ}_{HNO_2}+0,5N_{2gas}+O_{2gas}+0,5H_{2gas}=-46+(0,5\cdot -9,55+303+0,5\cdot 85,6)=295,025 \text{ kJ/mol};$$

$$G_{N_{2gas}}=G_{N_{2aq}}-(\Delta G_{Hess_šk_N_{2aq}}+G_{H_2O})=18,7-(28,25+0)=-9,55 \text{ kJ/mol}; G_{H_{2gas}}=85,6 \text{ kJ/mol}; G_{O_{2gas}}=303 \text{ kJ/mol}; [8]$$

$$G_{NO_2Form}=\Delta G^{\circ}_{NO_2aq}+0,5G_{N_{2gas}}+G_{O_{2gas}}+G_{H_2O}=-33,01+0,5\cdot -9,55+1\cdot 303+0=265,2 \text{ kJ/mol};$$

$$G_{HNO_3Form}=\Delta G^{\circ}_{HNO_3}+(0,5G_{N_{2gas}}+1,5G_{O_{2gas}}+0,5G_{H_{2gas}})=-250,53+(0,5\cdot -9,55+1,5\cdot 303+0)=199,195 \text{ kJ/mol};$$

Skābes un protolīzes līdzsvars $K_{eq}=K_a/[H_2O]$ aprēķina dalot skābes konstanti ar ūdeni $[H_2O]=55,3$ M.

1. $HNO_2+H_2O=NO_2^-+H_3O^+$; $pK_a=3,15$; $K_{eq}=K_a/[H_2O]=10^{-(3,15)}/55,3=0,00001280$;

$$\Delta G_{eqHNO_2}=-R \cdot T \cdot \ln(K_{eq})=-8,3144 \cdot 298,15 \cdot \ln(0,0000128)=G_{NO_2^-}+G_{H_3O^+}-(G_{HNO_2}+G_{H_2O})=27,927 \text{ kJ/mol};$$

$$\Delta G_{eqHNO_2}=G_{NO_2^-}+G_{H_3O^+}-(G_{HNO_2}+G_{H_2O})=265,2+22,44-(259,713+0)=27,927 \text{ kJ/mol};$$

$$G_{NO_2^-}=\Delta G_{eqHNO_2}-G_{H_3O^+}+(G_{HNO_2}+G_{H_2O})=27,927+22,44-(259,713+0)=265,2 \text{ kJ/mol};$$

$$G_{HNO_2}=G_{NO_2^-}+G_{H_3O^+}-(\Delta G_{eqHNO_2}+G_{H_2O})=265,2+22,44-(27,927+0)=259,713 \text{ kJ/mol};$$

2. $HNO_3+H_2O=NO_3^-+H_3O^+$; $pK_a=-1,4$; $K_{eq}=K_a/[H_2O]=10^{(1,4)}/55,3=0,4542$;

$$\Delta G_{eqHNO_3}=-R \cdot T \cdot \ln(K_{eq})=-8,3144 \cdot 298,15 \cdot \ln(0,4542)=G_{NO_3^-}+G_{H_3O^+}-(G_{HNO_3}+G_{H_2O})=1,956 \text{ kJ/mol};$$

$$\Delta G_{eqHNO_3}=G_{NO_3^-}+G_{H_3O^+}-(G_{HNO_3}+G_{H_2O})=340,2+22,44-(360,684+0)=1,956 \text{ kJ/mol};$$

$$G_{HNO_3}=G_{NO_3^-}+G_{H_3O^+}-(\Delta G_{eqHNO_3}+G_{H_2O})=340,2+22,44-(1,956+0)=360,7 \text{ kJ/mol};$$

$$G_{NO_3^-}=\Delta G_{eqHNO_3}-G_{H_3O^+}+(G_{HNO_3}+G_{H_2O})=1,956-22,44+(360,684+0)=340,2 \text{ kJ/mol};$$

Viela	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
HNO_2	$E^\circ_{NO_3^-/H_3O^+}=0,8763$ V		238,42
HNO_2	-	$pK_a=3,15$	259,713
HNO_2	-79,5	254,1	-46,0
HNO_2	-	formation	295,025
NO_2^-	-	formation	265,2
NO_2^-	-	$pK_a=3,15$	265,2
NO_2^-	-104,19	-238,7	-33,01
NO_2^-			482,3
HNO_3	-207	146	-250,53
HNO_3	-	formation	199,195
HNO_3	-	$pK_a=-1,4$	360,7
NO_3^-	$E^\circ_{NH_4^+/H_2O}=0,7677$ V		601,06
NO_3^-	-206,85	146,7	-250,5886
NO_3^-	-	formation	340,2
NO_3^-	-	$pK_a=-1,4$	340,2
NO_3^-	$E^\circ_{NO_3^-/OH^-}=-0,3112$ V		359,87
NO_3^-	-204,59	-318,8	-109,55
NO_{gas}	91,3	210,8	87,6
NO_{gas}	Solubility	product -	61,024
NO_{aq}	-	-	86,55
NO_{aq}	$E^\circ_{NO(g)/H_3O^+}=0,8609$		180,77
NH_3_{gas}	$\Delta G_{Hydration}$		-74,5537
NH_3_{gas}	[1,8] CRC	Alberty	107,285
NH_3_{gas}	-45,9	192,77	-16,4
NH_3_{aq}	-132,5608	-739,2922	91,1056
NH_3_{aq}	$pK_{beq}=6,49475$		91,1
NH_4^+	$pK_{aeq}=10,99$		50,81

$$G_{HNO_2}=G_{NO_3^-}+3G_{H_3O^+}-(\Delta G_{eqNO_3}+4G_{H_2O})=238,42 \text{ kJ/mol};$$

$$G_{HNO_2}=G_{NO_2^-}-G_{H_3O^+}+(\Delta G_{eqHNO_2}+G_{H_2O})=259,713 \text{ kJ/mol};$$

$$G_{HNO_2_{gas}}=\Delta G^\circ_{HNO_2_{gas}}+0,5N_{2_{gas}}+O_{2_{gas}}+0,5H_{2_{gas}}=295,025 \text{ kJ/mol}$$

$$G_{NO_2_{form}}=\Delta G^\circ_{NO_2_{aq}}+0,5G_{N_{2_{gas}}}+G_{O_{2_{gas}}}+G_{H_2O}=265,2 \text{ kJ/mol};$$

$$G_{NO_2}=\Delta G_{eqHNO_2}-G_{H_3O^+}+(G_{HNO_2}+G_{H_2O})=265,2 \text{ kJ/mol};$$

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$$G_{NO_3^-}=\Delta G_{eqNH_4^+/H_2O}-10G_{H_3O^+}+(G_{NH_4^+}-13G_{H_2O})=580,31 \text{ kJ/mol}$$

$$\text{Wikiped } G^\circ_{NO_3^-}=\Delta H_H-T \cdot \Delta S_H=-207-298,15 \cdot 0,146=-250,5886 \text{ kJ/mol};$$

$$G_{HNO_3}=G_{NO_3^-}+G_{H_3O^+}-(\Delta G_{eqHNO_3}+G_{H_2O})=360,7 \text{ kJ/mol};$$

$$G_{NO_3^-}=\Delta G_{eqNH_4^+/H_2O}-10G_{H_3O^+}+(G_{NH_4^+}-13G_{H_2O})=601,06 \text{ kJ/mol};$$

$$\Delta G^\circ_{NO_3^-}=\Delta H_H-T \cdot \Delta S_H=-206,85-298,15 \cdot 0,1467=-250,5886 \text{ kJ/mol};$$

$$G_{NO_3_{Form}}=\Delta G^\circ_{HNO_3_{aq}}+(0,5G_{N_{2_{gas}}}+1,5G_{O_{2_{gas}}}+G_{H_2O})=340,2 \text{ kJ/mol};$$

$$G_{NO_3^-}=\Delta G_{eqHNO_3}-G_{H_3O^+}+(G_{HNO_3}+G_{H_2O})=340,2 \text{ kJ/mol};$$

$$G_{NO_3^-}=\Delta G_{eqNO_3^-/OH^-}-G_{H_2O}+(G_{NO_2^-}+2G_{OH^-})=359,87 \text{ kJ/mol};$$

BioTherm2006

CRC

$$G_{NO_{gas}}=G_{H_2O}+G_{NO_{aq}}-(\Delta G_{sp})=0+86,55-(25,526)=61,024 \text{ kJ/mol};$$

BioTherm2006

$$G_{NO_{aq}}=G_{NO_3^-}+4G_{H_3O^+}-(\Delta G_{eqNO(g)/H_3O^+}+5G_{H_2O})=180,77 \text{ kJ/mol};$$

$$G_{NH_3_{gas}}=\Delta G_{NH_3_{aq}}-(\Delta G_{Hydrations}+G_{H_2O})=91,1056-(-74,5537+0)=165,7 \text{ kJ/mol};$$

$$2G_{NH_3_{gas}}=2\Delta G_{FormNH_3_{gas}}+(G_{N_{2_{gas}}}+3G_{H_{2_{gas}}})=2 \cdot 107,285 \text{ kJ/mol};$$

$$\text{CRC [1]} G_{NH_3_{gas}}=(2 \cdot -16,4+(-9,55+3 \cdot 85,64))/2=2 \cdot 107,285 \text{ kJ/mol};$$

Amonjaks pie $pH=7,36$ [8] Albertyjs; NH_3_{aq} veidošanās

$$G_{NH_3_{aq}}=G_{NH_4^+}+G_{OH^-}-(\Delta G_{beq}+G_{H_2O})=91,1 \text{ kJ/mol}; \text{ Wikipedia [28]}$$

$$G_{NH_4^+}=G_{NH_3_{aq}}+G_{H_3O^+}-(\Delta G_{eq}+G_{H_2O})=91,1+22,44-62,73-0=50,81 \text{ kJ/mol};$$

Protolīzes $NH_3_{aq}+H_2O=NH_4^++OH^-$ konstante $K_{beq}=K_b/[H_2O]=10^{(-)}/55,3=3,20 \cdot 10^{(-7)}=10^{(-6,4947)}$ $pK_{beq}=6,4947$

klasiski izteiksmē bez ūdens uzskaites ir $K_b=[NH_4^+][OH^-]/[NH_3_{aq}]=10^{(-4,752)}=1,77 \cdot 10^{(-5)}$; $pK_b=4,752$.

Enerģija akumulējas endoerģiski produktos $G_{NH_4^+}+G_{OH^-}=50,81+77,36=128,17 \text{ kJ/mol}$:

$$\Delta G_{beq}=-R \cdot T \cdot \ln(K_{beq})=-8,3144 \cdot 298,15 \cdot \ln(10^{(-6,4947)})=G_{NH_4^+}+G_{OH^-}-(G_{NH_3_{aq}}+G_{H_2O})=37,07 \text{ kJ/mol} .$$

$$\Delta G_{Hess_{beq}}=G_{NH_4^+}+G_{OH^-}-(G_{NH_3_{aq}}+G_{H_2O})=50,81+77,36-(91,1056+0)=37,064 \text{ kJ/mol};$$

$$G_{NH_3_{aq}}=G_{NH_4^+}+G_{OH^-}-(\Delta G_{beq}+G_{H_2O})=50,81+77,36-(37,07+0)=91,1 \text{ kJ/mol};$$

Izteikta gāzes šķīdībai $NH_3_{gas}+H_2O=NH_3_{aq}$ enerģijas vērtības ir $G_{NH_3_{aq}}=91,1 \text{ kJ/mol}$, $G_{NH_3_{gas}}=107,285 \text{ kJ/mol}$.

Vāja skābe $G_{NH_4^+}=50,81 \text{ kJ/mol}$ protolīze $NH_4^++H_2O=NH_3_{aq}+H_3O^+$ $pK_{eq}=10,99$ rāda endoerģisku enerģijas

izmaiņu $\Delta G_{aeq}=-R \cdot T \cdot \ln(K_{aeq})=-8,3144 \cdot 298,15 \cdot \ln(10^{(-10,99)})=G_{NH_3_{Hydration}}+G_{H_3O^+}-G_{NH_4^+}-G_{H_2O}=62,73 \text{ kJ/mol} .$

Amonija brīvās enerģijas saturs molā ir $G_{NH_4^+}=G_{NH_3_{aq}}+G_{H_3O^+}-(\Delta G_{aeq}+G_{H_2O})=91,1+22,44-(62,73+0)=50,81 \text{ kJ/mol} .$

Nernsta potenciāla $\text{NO}_3^-/\text{NO}_2^-$ red-oks sistēmas īpašības skābā H_3O^+ ūdens un baziskā OH^- vidē



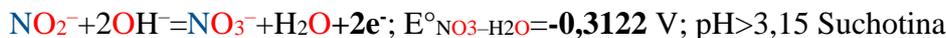
$$E^\circ_{\text{NO}_3^-} = E^\circ + 0,10166 - 0,0591/2 * \lg(1/[\text{H}_2\text{O}]^4) - 0,37239 = 0,94 + 0,10166 - 0,02955 * \lg(1/55,3^4) - 0,37239 = \mathbf{0,8753 \text{ V}};$$

$$E_{\text{NO}_3^-} = E^\circ_{\text{NO}_3^-} + \frac{0,0591}{2} \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^3}{[\text{HNO}_2] \cdot [\text{H}_2\text{O}]^4} = \mathbf{0,8753 \text{ V}} + \frac{0,0591}{2} \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^3}{[\text{HNO}_2] \cdot [\text{H}_2\text{O}]^4}$$

$$\Delta G_{\text{eqNO}_3^-} = E^\circ_{\text{NO}_3^-} \cdot F \cdot 2 = \mathbf{0,8753 * 96485 * 2 = 168,9 \text{ kJ/mol}},$$

$$\Delta G_{\text{eqNO}_3^-} = G_{\text{NO}_3^-} + 3G_{\text{H}_3\text{O}^+} - (G_{\text{HNO}_2} + 4G_{\text{H}_2\text{O}}) = \mathbf{340,2 + 3 * 22,44 - (238,62 + 4 * 0) = 168,9 \text{ kJ/mol}},$$

$$G_{\text{HNO}_2} = G_{\text{NO}_3^-} + 3G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqNO}_3^-} + 4G_{\text{H}_2\text{O}}) = \mathbf{340,2 + 3 * 22,44 - (168,9 + 4 * 0) = 238,62 \text{ kJ/mol}};$$



$$E^\circ_{\text{NO}_3^-/\text{OH}^-} = E^\circ + 0,10166 - 0,0591/2 * \lg([\text{H}_2\text{O}]) - 0,37239 = 0,01 + 0,10166 - 0,02955 * \lg(55,3^1) - 0,37239 = \mathbf{-0,3122 \text{ V}};$$

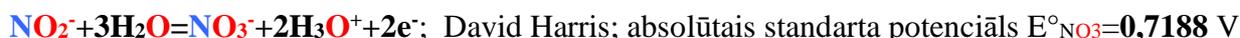
$$E_{\text{NO}_3^-/\text{OH}^-} = E^\circ_{\text{NO}_3^-/\text{OH}^-} + \frac{0,0591}{2} \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_2\text{O}]}{[\text{NO}_2^-] \cdot [\text{OH}]^2} = \mathbf{-0,3122 \text{ V}} + \frac{0,0591}{2} \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_2\text{O}]}{[\text{NO}_2^-] \cdot [\text{OH}]^2}$$

$$\Delta G_{\text{eqNO}_3^-/\text{OH}^-} = E^\circ_{\text{NO}_3^-/\text{OH}^-} \cdot F \cdot 2 = \mathbf{-0,3122 * 96485 * 2 = -60,245 \text{ kJ/mol}},$$

$$\Delta G_{\text{eqNO}_3^-/\text{OH}^-} = G_{\text{NO}_3^-} + G_{\text{H}_2\text{O}} - (G_{\text{NO}_2^-} + 2G_{\text{OH}^-}) = \mathbf{359,675 + 0 - (265,3 + 2 * 77,36) = -60,245 \text{ kJ/mol}},$$

$$G_{\text{NO}_3^-} = \Delta G_{\text{eqNO}_3^-/\text{OH}^-} - G_{\text{H}_2\text{O}} + (G_{\text{NO}_2^-} + 2G_{\text{OH}^-}) = \mathbf{-60,2455 - 0 + (265,3 + 2 * 77,36) = 359,775 \text{ kJ/mol}},$$

$$G_{\text{NO}_2^-} = G_{\text{NO}_3^-} + G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqNO}_3^-/\text{OH}^-} + 2G_{\text{OH}^-}) = \mathbf{359,675 + 0 - (-60,245 + 2 * 77,36) = 265,3 \text{ kJ/mol}};$$



$$E^\circ_{\text{NO}_3^-} = E^\circ + 0,10166 - 0,0591/2 * \lg([\text{H}_2\text{O}]^3) - 0,37239 = 0,835 + 0,10166 - 0,02955 * \lg(1/55,3^3) - 0,37239 = \mathbf{0,7188 \text{ V}}$$

$M_{\text{NO}} = 30,006 \text{ g/mol}$; šķīdība $\text{NO}^{(\text{g})}$ 0,0056 g/99,6g (20 C); w% = 0,0056 / (0,0056 + 99,6) * 100 = 0,00562%; ūdenī

$$[\text{NO}_{\text{aq}}] = (0,00562 / 100 * 996) / 30,006 = 0,001865 \text{ M, ja tūras gāzes mol daļa ir viens } [\text{NO}^{(\text{g})}] = 1;$$

Līdzsvara $\text{NO}_{\text{gas}} + \text{H}_2\text{O} = \text{NO}_{\text{aq}}$ konstante $K_{\text{eq}} = [\text{NO}_{\text{aq}}] / [\text{NO}^{(\text{g})}] / [\text{H}_2\text{O}] = 0,001865 / 1 / 55,3 = 10^{-(4,472)}$.

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 * 298,15 * \ln(10^{-(4,472)}) = -8,3144 * 298,15 * -10,297 = \mathbf{25,526 \text{ kJ/mol}}$$

$$\Delta G_{\text{eq}} = G_{\text{NO}_{\text{aq}}} - (G_{\text{H}_2\text{O}} + G_{\text{NO}_{\text{gas}}}) = \mathbf{86,55 - (0 + G_{\text{NO}_{\text{gas}}}) = 25,526 \text{ kJ/mol}};$$

$$G_{\text{NO}_{\text{gas}}} = G_{\text{NO}_{\text{aq}}} - (G_{\text{H}_2\text{O}} + \Delta G_{\text{eq}}) = \mathbf{86,55 - (0 + 25,526) = 61,024 \text{ kJ/mol}}, \text{ ja līdzsvara minimums ir } \Delta G_{\text{eq}} = \mathbf{25,526 \text{ kJ/mol}};$$

Gāzes NO_{gas} šķīdība kompensē vienu ūdens molekulu Nernsta izteiksmē no sešām $6\text{H}_2\text{O}$ uz piecām $5\text{H}_2\text{O}$:



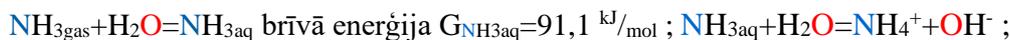
$$E^\circ_{\text{NO}_3^-/\text{NO}_{\text{aq}}} = E^\circ + 0,10166 - 0,0591/3 * \lg(1/[\text{H}_2\text{O}]^5) - 0,37239 = 0,96 + 0,10166 - 0,0197 * \lg(1/55,3^5) - 0,37239 = \mathbf{0,8609 \text{ V}};$$

$$E_{\text{NO}_3^-/\text{NO}_{\text{aq}}} = E^\circ_{\text{NO}_3^-/\text{NO}_{\text{aq}}} + 0,0591/3 \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{NO}_{\text{aq}}] \cdot [\text{H}_2\text{O}]^6} = \mathbf{0,8609 \text{ V}} + 0,0197 \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{NO}_{\text{aq}}] \cdot [\text{H}_2\text{O}]^6}$$

$$\Delta G_{\text{eqNO}_3^-/\text{NO}_{\text{aq}}} = E^\circ_{\text{NO}_3^-/\text{NO}_{\text{aq}}} \cdot F \cdot 3 = \mathbf{0,8609 * 96485 * 3 = 249,19 \text{ kJ/mol}},$$

$$\Delta G_{\text{eqNO}_3^-/\text{NO}_{\text{aq}}} = G_{\text{NO}_3^-} + 4G_{\text{H}_3\text{O}^+} - (G_{\text{NO}_{\text{aq}}} + 5G_{\text{H}_2\text{O}}) = \mathbf{340,2 + 4 * 22,44 - (180,77 + 5 * 0) = 249,19 \text{ kJ/mol}},$$

$$G_{\text{NO}_{\text{aq}}} = G_{\text{NO}_3^-} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqNO}_3^-/\text{NO}_{\text{aq}}} + 5G_{\text{H}_2\text{O}}) = \mathbf{340,2 + 4 * 22,44 - (249,19 + 5 * 0) = 180,77 \text{ kJ/mol}},$$



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$$E^\circ_{\text{NH}_4^+/\text{NO}_3^-} = E^\circ + 0,10166 - 0,0591/8 * \lg(1/[\text{H}_2\text{O}]^{13}) - 0,37239 = 0,87 + 0,10166 - 0,00739 * \lg(1/55,3^{13}) - 0,37239 = \mathbf{0,7667 \text{ V}};$$

$$E_{\text{NH}_4^+/\text{NO}_3^-} = E^\circ_{\text{NH}_4^+/\text{NO}_3^-} + 0,0591/8 \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^{10}}{[\text{NH}_4^+] \cdot [\text{H}_2\text{O}]^{13}} = \mathbf{0,76669 \text{ V}} + 0,00739 \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^{10}}{[\text{NH}_4^+] \cdot [\text{H}_2\text{O}]^{13}}$$

$$\Delta G_{\text{eqNH}_4^+/\text{NO}_3^-} = E^\circ_{\text{NH}_4^+/\text{NO}_3^-} \cdot F \cdot 8 = \mathbf{0,76669 * 96485 * 8 = 591,8 \text{ kJ/mol}},$$

$$\Delta G_{\text{eqNH}_4^+/\text{NO}_3^-} = G_{\text{NO}_3^-} + 10G_{\text{H}_3\text{O}^+} - (G_{\text{NH}_4^+} + 13G_{\text{H}_2\text{O}}) = \mathbf{601,06 + 10 * 22,44 - (232,9 + 13 * 0) = 591,8 \text{ kJ/mol}},$$

$$G_{\text{NO}_3^-} = \Delta G_{\text{eqNH}_4^+/\text{NO}_3^-} - 10G_{\text{H}_3\text{O}^+} + (G_{\text{NH}_4^+} + 13G_{\text{H}_2\text{O}}) = \mathbf{591,8 - 10 * 22,44 + (232,9 + 13 * 0) = 601,06 \text{ kJ/mol}};$$

Nernsta potenciāla studijas $5(\text{Pt})\text{H}+\text{MnO}_4^-$ uzskaitot hidroksoniju H_3O^+ un ūdeni H_2O .

Inversais Nernsta standarta potenciāls: $\text{MnO}_4^-+8\text{H}_3\text{O}^++5\text{e}^-=\text{Mn}^{2+}+12\text{H}_2\text{O}$; $E^\circ_{\text{Mn}^{2+}/\text{MnO}_4^-}=-1,4865 \text{ V}$.

Divpadsmit ūdens molekulu uzskaitē $[\text{H}_2\text{O}]=55,3 \text{ M}=(996 \frac{\text{g}}{\text{L}})/(18 \frac{\text{g}}{\text{mol}})$ palielina potenciālu līdz:

$$E^\circ_{\text{Mn}^{2+}/\text{MnO}_4^-}=E^\circ-0,0591/5 \cdot \log(1/[\text{H}_2\text{O}]^{12})=1,51-0,0591/5 \cdot \log(1/55,3^{12})+0,10166-0,37239=1,4865 \text{ V};$$

Ūdens koncentrācija $[\text{H}_2\text{O}]^{12}$ ir iekļauta klasiskā standarta potenciāla vērtībā $E^\circ=1,51 \text{ V}$ kā logaritms:

Reducētāja Nernsta absolūtais standarta potenciāls: $5(\text{Pt})\text{H}+5\text{H}_2\text{O}=5\text{H}_3\text{O}^++5\text{e}^-$; $E^\circ_{\text{H}}=-0,27073 \text{ V}$

$$E_{\text{MnO}_4^-}=-1.4865 \text{ V}+0,0591/5 \cdot \log([\text{H}_2\text{O}]^{12} \cdot [\text{Mn}^{2+}]/[\text{MnO}_4^-]/[\text{H}_3\text{O}^+]^8);$$

$$E_{\text{H}}=E^\circ_{\text{H}}+0,0591 \cdot \log([\text{H}_3\text{O}^+]/[\text{H}_2\text{O}])=-0,27073 \text{ V}+0,0591 \cdot \log([\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]);$$

Elektronu balansēšana $+n\text{e}^-=5\text{e}^-=n\text{e}^-$ summārajā Red-Ox reakcijā: $\text{MnO}_4^-+3\text{H}_3\text{O}^++5(\text{Pt})\text{H}=\text{Mn}^{2+}+7\text{H}_2\text{O}$;

$$\Delta G_{\text{HessPtH}}=\Delta G^\circ_{\text{Mn}^{2+}}+7\Delta G^\circ_{\text{H}_2\text{O}}-(\Delta G^\circ_{\text{MnO}_4^-}+3\Delta G^\circ_{\text{H}_3\text{O}^+}+5G_{(\text{Pt})\text{H}})=-228,1+7 \cdot (-237,191)-(3 \cdot (-213,2746)-447,2+5 \cdot 48,56)=-1044,21 \text{ kJ/mol};$$

$$\Delta G_{\text{HessCRC}}=\Delta G^\circ_{\text{Mn}^{2+}}+7\Delta G^\circ_{\text{H}_2\text{O}}-(\Delta G^\circ_{\text{MnO}_4^-}+3\Delta G^\circ_{\text{H}_3\text{O}^+}+5/2\Delta G^\circ_{\text{H}_2})=-228,1+7 \cdot (-237,191)-(3 \cdot (-213,2746)-447,2+5 \cdot 99,13/2)=-1049 \text{ kJ/mol};$$

$$\Delta G_{\text{Alberty}}=\Delta G^\circ_{\text{Mn}^{2+}}+7\Delta G^\circ_{\text{H}_2\text{O}}-(\Delta G^\circ_{\text{MnO}_4^-}+3\Delta G^\circ_{\text{H}_3\text{O}^+}+5/2G_{\text{H}_2})=-228,1+7 \cdot (-237,191)-(3 \cdot (-213,2746)-447,2+5 \cdot 103,24/2)=-1059,5 \text{ kJ/mol};$$

Viela	$\Delta H^\circ_{\text{H}}$, kJ/mol	$\Delta S^\circ_{\text{H}}$, J/mol/K	$\Delta G^\circ_{\text{H}}$, kJ/mol
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549
H₃O⁺	-285,81	-3,854	-213,2746
H₂(aq)	23,4	-130	99,13
H₂(aq)	-5,02	-363,92	103,24
H(Pt)(aq)	-	-	48,56
MnO₄⁻	-541,4	-191,2	-447,2
Mn²⁺	-220,8	-73,6	-228,1
O₂aqua	-11,7	-94,2	16,4

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

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

Alberty 2006 Biochem. Thermodyn Massachusetts Technology Inst.

$$\Delta G_{\text{eq}}=-847,7 \text{ kJ/mol}; \Delta G_{\text{Hess}}=-1044,2 \text{ kJ/mol}$$

kā absolūti lielumi $|\Delta G_{\text{eq}}=-847,7 \text{ kJ/mol}| < |\Delta G_{\text{Hess}}=-1043,7 \text{ kJ/mol}|$;

$$\Delta G_{\text{eqH/MnO}_4^-}=(E^\circ_{\text{H}}-E^\circ_{\text{MnO}_4^-}) \cdot F \cdot 1 \cdot 5=(-0,27073-1,4865) \cdot 96485 \cdot 5=-1,757 \cdot 96485 \cdot 5=-847,7 \text{ kJ/mol}.$$

$$K_{\text{eq}}=\exp(-\Delta G_{\text{eqH/MnO}_4^-}/R/T)=\exp(847732/8,3144/298,15)=\exp(341,96)=10^{148,5};$$

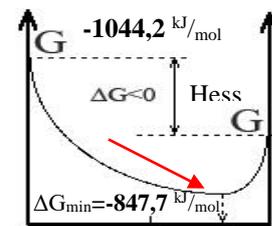
Eksotermiska un eksoergiskas MnO_4^- reducēšanas ar metālisku $5(\text{Pt})\text{H}$ Hesa brīvās enerģijas izmaiņa negatīva $\Delta G_{\text{Hess}}=\Delta G_{\text{OxRed}}=-1043,7 \text{ kJ/mol}$, bet minimizējas sasniedzot

$$\text{līdzsvara maisījumu } \Delta G_{\text{min}}=\Delta G_{\text{eq}}=-847,7 \text{ kJ/mol}; 10^{148,5}=K_{\text{eq}}=\frac{[\text{H}_2\text{O}]^7 \cdot [\text{Mn}^{2+}]}{[(\text{Pt})\text{H}]^5 \cdot [\text{MnO}_4^-] \cdot [\text{H}_3\text{O}^+]^3};$$

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

visiem bezgalīga skaita ne līdzsvara stāvokļiem

izejvielas



$5\text{A}+\text{B}+3\text{C}$ 50% $\text{D}+8\text{E}$

$5(\text{Pt})\text{H}+\text{MnO}_4^-+3\text{H}_3\text{O}^+$

produkti $\text{Mn}^{2+}+7\text{H}_2\text{O}$

$\text{MnO}_2+4\text{OH}^-=\text{MnO}_4^-+2\text{H}_2\text{O}+3\text{e}^-$; Reducētāja Nernsta absolūtais standarta potenciāls: $E^\circ_{\text{MnO}_2/\text{MnO}_4^-}=\mathbf{0,26465 \text{ V}}$

$$E^\circ_{\text{MnO}_2/\text{MnO}_4^-}=E^\circ-0,0591/3 \cdot \log([\text{H}_2\text{O}]^2)+0,10166-0,37239=0,603-0,0591/3 \cdot \log(55,3^2)+0,10166-0,37239=\mathbf{0,26465 \text{ V}};$$

$\text{MnO}_4^{2-}=\text{MnO}_4^-+\text{e}^-$; Reducētāja Nernsta absolūtais standarta potenciāls: $E^\circ_{\text{MnO}_2/\text{MnO}_4^-}=\mathbf{0,2883 \text{ V}};$

$$E^\circ_{\text{MnO}_4/\text{MnO}_4^-}=E^\circ-0,0591/3 \cdot \log([\text{H}_2\text{O}]^0)+0,10166-0,37239=0,558-0,0591/3 \cdot \log(55,3^0)+0,10166-0,37239=\mathbf{0,2883 \text{ V}};$$

2) Karbo anhidrāze CA ģenerē brīvo enerģiju no nulles $G_{\text{CO}_2+2\text{H}_2\text{O}}=0 \text{ kJ/mol}$ līdz $G_{\text{H}_3\text{O}^+\text{HCO}_3^-}=78,52 \text{ kJ/mol}$.

Šķīdība ūdenī rada brīvo enerģiju no nulles līmeņa $\text{CO}_2\text{gas}+\text{H}_2\text{O}=\text{CO}_2\text{aqua}$ līdz $G_{\text{CO}_2\text{aqua}}=18,38 \text{ kJ/mol}$ ar konstanti:

$$K_{\text{eqCO}_2\text{aqua}}=[\text{CO}_2\text{aqua}]/[\text{CO}_2\text{gas}]/[\text{H}_2\text{O}]=\text{EXP}(-G_{\text{CO}_2\text{aqua}}/R/T)=\text{EXP}(-18382,746/8,3144/298,15)=0,000601808$$

palielinot brīvo enerģiju līdz $G_{\text{CO}_2\text{aqua}}=-R \cdot T \cdot \ln(K_{\text{šķCO}_2\text{aqua}})=-8,3144 \cdot 298,15 \cdot \ln(0,000601808)=18,38 \text{ kJ/mol}$.



ātruma konstante ir $k_1\text{CO}_2\text{aqua}=1,5 \cdot 10^8 \text{ M}^{-1}\text{s}^{-1}$ un protolītiskā skābes CO_2aqua līdzsvara konstantes vērtība ir

$$\frac{[\text{HCO}_3^-]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}} \cdot [\text{H}_2\text{O}]^2}=K_{\text{eqCAHCO}_3\text{aqua}}=K_{\text{aCO}_2\text{aqua}}/[\text{H}_2\text{O}]^2=10^{-7,0512}/55,3^2=2,906 \cdot 10^{-11}. [9]$$

CA liela ātruma protolīzes konstante akumulē brīvo enerģiju produktos $\text{H}_3\text{O}^++\text{HCO}_3^-$ aktivējot tos:

$$\Delta G_{\text{eqCACO}_2\text{aqua}}=-R \cdot T \cdot \ln(K_{\text{eqCACO}_2\text{aqua}})=-8,3144 \cdot 298,15 \cdot \ln(2,90636 \cdot 10^{(-11)})/1000=60,14 \text{ kJ/mol}.$$

Kopējā brīvā enerģija palielinās aktivējot sasniedzot līdzsvara stāvokli liela ātruma protolīzē un šķīdībā:

$$G_{\text{H}_3\text{O}^+\text{HCO}_3^-}=G_{\text{H}_3\text{O}^+}+G_{\text{HCO}_3^-}=22,44+56,08=G_{\text{CO}_2\text{aqua}}+\Delta G_{\text{eqCACO}_2\text{aqua}}=18,38+60,14=78,52 \text{ kJ/mol}. [1,8,14]$$

Liela ātruma protolīzes atraktors ir $\text{pH}=7,36$. Novirze no atraktora izjauc neatgriezeniskās homeostāzes procesus, radot nekārtību un haosu.

Karbo anhidrāzes CA sintēze nepieciešams aktīvas biosfēras atraktors.

Karboanhidrāzes reaktivitāte un radītā fizioloģiskā bufera šķīduma protolīzes līdzsvara-atractora vērtība $\text{pH}=7,36$ ir pašorganizējošais biosfēras atraktors. Reakcijas $\text{CO}_2+2\text{H}_2\text{O}$ uzkrātā brīvā enerģija produktos ($\text{CO}_{2\text{aqua}}$) $\text{H}_3\text{O}^++\text{HCO}_3^-$ akumulē brīvo enerģiju $G_{\text{H}_3\text{O}^++\text{HCO}_3^-}=18,38+60,14=78,52$ kJ/, kas nepieciešama ķermeņa funkcionālai darbībai, tas ir bikarbonāta bufera sistēma ideālai reakciju secībai neatgriezeniskas homeostāzes kompleksajos procesos.

CO_2 nereaģē ar ūdeni H_2O bez CA klātbūtnes. CO_2 ir mazšķīstošs un lēni reaģē ar OH^- .

[Wikipedia](#) [27] mol masa $M_{\text{CO}_2}=44,009$ g/mol. Šķīdība $\text{CO}_{2\text{gas}}+\text{H}_2\text{O}=\text{CO}_{2\text{aqua}}$ 1,45 g/L pie 0,99 atm un pie 1 atm $m_{\text{CO}_2}=100*1,45/99=1,4646$ g/L ar koncentrāciju $[\text{CO}_{2\text{aqua}}]=m_{\text{CO}_2}/M_{\text{CO}_2}=1,4646/44,009=0,03328$ M.

Šķīdība ir $K_{\text{spCO}_{2\text{aqua}}}=[\text{CO}_{2\text{aqua}}]/[\text{CO}_{2\text{gas}}]=0,03328$ M bet līdzsvara konstante molu daļās ir bez mērvienības

$$K_{\text{eqCO}_{2\text{aqua}}}=[\text{CO}_{2\text{aqua}}]/[\text{CO}_{2\text{gas}}]/[\text{H}_2\text{O}]=K_{\text{spCO}_{2\text{aqua}}}/[\text{H}_2\text{O}]=0,03328 \text{ M}/55,3 \text{ M}=0,000601808.$$

Brīvā enerģija $\Delta G_{\text{eqCO}_{2\text{aqua}}}=-R\cdot T\cdot \ln(K_{\text{eqCO}_{2\text{aqua}}})=-8,3144\cdot 298,15\cdot \ln(0,000601808)/1000=18,38$ kJ/mol ir minimumā ar šķīdības līdzsvara vērtību $G_{\text{CO}_{2\text{aqua}}}=\Delta G_{\text{eqCO}_{2\text{aqua}}}+(G_{\text{CO}_{2\text{gas}}}+G_{\text{H}_2\text{O}})=18,38+(0+0)=18,38$ kJ/mol.

No gaisa 0,04 % mol daļas $[\text{CO}_{2\text{gas}}]=0,0004$ izšķīdinātā koncentrācija ir:

$$[\text{CO}_{2\text{aqua}}]=K_{\text{eqCO}_{2\text{aqua}}}\cdot [\text{H}_2\text{O}]\cdot [\text{CO}_{2\text{gas}}]=0,000601808\cdot 55,3457\cdot 0,0004=0,000753 \text{ M}.$$

Oglekļa dioksīds $\text{CO}_{2\text{aqua}}$ reaģē ar OH^- joniem reizes $10^{16,54}$ lēnāk par bikarbonāta HCO_3^- neitralizācijas reakciju: $\text{H}_3\text{O}^++\text{HCO}_3^-\Rightarrow\text{CO}_{2\text{aqua}}+2\text{H}_2\text{O}$, jo neitralizācijas ātruma konstante ir $k_2=5,16885\cdot 10^{18} \text{ M}^{-2}\text{s}^{-1}$, bet OH^- joniem $\text{CO}_{2\text{aqua}}+\text{OH}^-\Rightarrow\text{HCO}_3^-$ ir ātruma konstante $k_{1\text{OH}}$ no $1,5\cdot 10^2 \text{ M}^{-2}\text{s}^{-1}$. Reakcija ir labvēlīga:

$$\Delta G_{\text{HessHCO}_3^-}=G_{\text{HCO}_3^-}-(G_{\text{CO}_{2\text{aqua}}}+G_{\text{OH}^-})=56,08-(18,38+77,36)=-39,66 \text{ kJ/mol}$$
 ar līdzsvara konstanti

$k_{1\text{OH}}/k_{2\text{HCO}_3^-}=[\text{HCO}_3^-]/[\text{CO}_{2\text{aqua}}]/[\text{OH}^-]=K_{\text{eqHCO}_3^-}=\text{EXP}(-\Delta G_{\text{eqHCO}_3^-}/R/T)=\text{EXP}(39659/8,3144/298,15)=8875,3$, eksotermiski izdalot siltumu Q $\Delta H_{\text{Hess}}=\Delta H^\circ_{\text{HCO}_3^-}-\Delta H^\circ_{\text{CO}_2}-\Delta H^\circ_{\text{OH}^-}=-48,68$ kJ/mol. Inversā $\text{HCO}_3^-\Rightarrow\text{CO}_{2\text{aqua}}+\text{OH}^-$ reakcija ir nelabvēlīga $k_{2\text{HCO}_3^-}=k_{1\text{OH}}/K_{\text{eqHCO}_3^-}=1,5\cdot 10^2/8875,3=0,0169$. Sadalīšanās $\text{HCO}_3^-\Rightarrow\text{CO}_{2\text{aqua}}+\text{OH}^-$ ātruma konstante $k_{2\text{HCO}_3^-}$ ir desmit triljoni 10^{13} reizes lēnāka par CA ātruma konstanti $k_{1\text{CO}_{2\text{aqua}}}=1,5\cdot 10^8 \text{ M}^{-1}\text{s}^{-1}$.

CA protolītiskā reaktivitāte rada funkcionāli aktīvu bikarbonāta bufera pašorganizēšanas atraktoru $\text{pH}=7,36$ ar ģenerētiem koncentrācijas gradientiem transportam H_3O^+ , HCO_3^- , $\text{CO}_{2\text{aqua}}$ un $\text{O}_{2\text{aqua}}$, H_2O osmozei cauri akvaporīnu kanāliem. [9]

CA liela ātruma protolīzē reaģē $\text{CO}_{2\text{aqua}}$ ar divām ūdens molekulām:

$\text{CO}_{2\text{aqua}}+2\text{H}_2\text{O}+\Delta G+Q=v_1\text{CAH}_3\text{O}^++\text{HCO}_3^-$, kurā ātruma konstante ir: $k_{1\text{CO}_{2\text{aqua}}}=1,5\cdot 10^8 \text{ M}^{-1}\text{s}^{-1}$. [9] Neitralizācijas $\text{H}_3\text{O}^++\text{HCO}_3^-\xrightarrow{\text{CA}}\text{CO}_{2\text{aqua}}+2\text{H}_2\text{O}$ ātruma konstante ir reizes $10^{10,54}$ lielāka par karbo anhidrāzes ātruma konstanti: $k_2/k_{1\text{CO}_{2\text{aqua}}}=5,16885\cdot 10^{18}/1,5/10^8=34459000000=10^{10,537}$. CA protolīzes līdzsvara konstanti aprēķina ātruma konstanšu attiecības izteiksmē:

$$K_{\text{eqCAHCO}_3\text{aqua}}=k_{1\text{CO}_{2\text{aqua}}}/k_2=K_{\text{aCO}_{2\text{aqua}}}/[\text{H}_2\text{O}]^2=10^{-(7,0512)}/55,3^2=2,906\cdot 10^{-11}=10^{-10,54}.$$

Bikarbonāta bufera skābes protolīzes konstante $\text{pK}_{\text{aCO}_{2\text{aqua}}}=7,0512$ ir draudzīga atractora vērtībai $\text{pH}=7,36$:

$$K_{\text{aCO}_{2\text{aqua}}}=K_{\text{eqCAHCO}_3\text{aqua}}\cdot [\text{H}_2\text{O}]^2=\frac{[\text{HCO}_3^-]_{\text{aqua}}\cdot [\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}}}=10^{-7,0512}=10^{-\text{pK}_{\text{aCO}_{2\text{aqua}}}}. \text{ Oriģinālā } \text{pK}_{\text{aCO}_{2\text{aqua}}}=7,0512$$

vērtība iegūta un aprēķināta [BUFERA šķīdumam](#). Hesa brīvās enerģijas izmaiņa ir eksoerģiska negatīva:

$$\Delta G_{\text{Hess}}=2\Delta G^\circ_{\text{H}_2\text{O}}+\Delta G^\circ_{\text{CO}_2}-(\Delta G^\circ_{\text{H}_3\text{O}^+}+\Delta G^\circ_{\text{HCO}_3^-})=2\cdot -237,191-385,98-(-213,2746-544,9688)=-102 \text{ kJ/mol} . [1]$$

Neitralizācijas: $\text{H}_3\text{O}^++\text{HCO}_3^-\Rightarrow\text{CO}_{2\text{aqua}}+2\text{H}_2\text{O}$ konstante ir inversa protolīzei un labvēlīga:

$$K_{\text{eqNeitralizācija}}=1/K_{\text{eqCAHCO}_3\text{aqua}}=[\text{HCO}_3^-]\cdot [\text{H}_3\text{O}^+]/[\text{CO}_{2\text{aqua}}]/[\text{H}_2\text{O}]^2=1/2,90636/10^{-(11)}=34407299853.$$

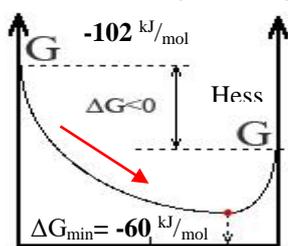
$$\Delta G_{\text{Absolute}}=2G_{\text{H}_2\text{O}}+G_{\text{CO}_2\text{aqua}}-G_{\text{H}_3\text{O}^+}-G_{\text{HCO}_3^-}=2\cdot 0+18,38-22,44-56,08=-60,14 \text{ kJ/mol}$$
 un

entalpijas Hesa izmaiņa ir eksotermiska: $\Delta H_{\text{Hess}}=2\Delta H^\circ_{\text{H}_2\text{O}}+\Delta H^\circ_{\text{CO}_2}-\Delta H^\circ_{\text{H}_3\text{O}^+}-\Delta H^\circ_{\text{HCO}_3^-}=-7,2$ kJ/mol.

Neitralizācija ir labvēlīga reakcija. Brīvās enerģijas izmaiņas minimums izteiksmē ir negatīvs:

$$\Delta G_{\text{eqNeitralizācija}}=-R\cdot T\cdot \ln(K_{\text{eqNeitralizācija}})=-8,3144\cdot 298,15\cdot \ln(34407299853)=-60,14 \text{ kJ/mol}, \text{ bet } \text{CO}_{2\text{aqua}} \text{ protolīzes minimums kā neitralizācijas inversā reakcija ir pozitīva:}$$

$$\Delta G_{\text{eqCAHCO}_3\text{aqua}}=-R\cdot T\cdot \ln(K_{\text{eqCAHCO}_3\text{aqua}})=-8,3144\cdot 298,15\cdot \ln(1/34407299853)=60,14 \text{ kJ/mol}.$$



Atractora Zīm. 2. Eksotermiska un eksoerģiska neitralizācijā Hesa brīvās enerģijas izmaiņa $\Delta G_{\text{eqNeitralizācija}}$ negatīva -102 kJ/mol, bet $\Delta G_{\text{eqNeitralizācija}}=-60,14$ kJ/mol minimizējas sasniedzot līdzsvara maisījumu: $K_{\text{eq}}=34407299853$ CA karbo anhidrāzes klātienē. Oglekļa dioksīds reakcija ar hidroksīda anjonu ir lēna, jo mazi reizinātāji: ātruma konstante $k_{1\text{OH}}=1,5\cdot 10^2 \text{ M}^{-2}\text{s}^{-1}$, koncentrācijas $[\text{CO}_{2\text{aqua}}]=0,000753$ M, $[\text{OH}^-]=10^{-6,64}$ M. Karbo anhidrāzes sintēze atrisina bioenerģētikā perfektu kārtību homeostāzei kā pašorganizējošs atraktors. [3,4]

A+B 50 % C+2D.

Reaktanti $\text{H}_3\text{O}^++\text{HCO}_3^-$, produkti $\text{CO}_{2\text{aqua}}+2\text{H}_2\text{O}$.

2CO₂ / H₂C₂O₄ / CH_{4gas} šķīdība un protolīze iekļauj hidroksionija H₃O⁺ un ūdens H₂O uzskaiti.

Oglekļa dioksīda veidošanās no brīviem elementiem C_{gr}+O_{2gas}=CO_{2gas} standarta brīvās enerģijas izmaiņa ir negatīva ΔG_{Hess_CO2gas}=-394,36 kJ/mol. [1] Ja fona līmenis bioķīmijas absolūtās enerģijas skalai ir nulle, tad Hesa likumā grafitam absolūtās brīvās enerģijas saturs ir G_{gr}=-ΔG^o_{Hess_CO2gas}-G_{O2gas}=394,36-303,1=91,26 kJ/mol.

Standarta brīvās enerģijas izmaiņas metāna veidošanai no brīvajiem elementiem C_{gr}+2H_{2gas}>CH_{4gas} [1,8] ir

$$\Delta G_{\text{Hess_CH4gas}} = G_{\text{CH4gas}} - (G_{\text{Cgr}} + 2 * G_{\text{H2}}) = G_{\text{CH4gas}} - (91,26 + 2 * 85,64) = -50,5 \text{ kJ/mol un}$$

brīvās enerģijas saturs uz vienu molu metāna, kas paliek neizmantots no brīvajiem elementiem Hesa likumā ir

$$G_{\text{CH4gas}} = \Delta G_{\text{Hess_CH4gas}} + (G_{\text{Cgr}} + 2 * G_{\text{H2}}) = -50,5 + (91,26 + 2 * 85,64) = 212,04 \text{ kJ/mol.}$$

Tas ļauj mums aprēķināt absolūto brīvo enerģiju uz grafitā elementa molu, izmantojot Albertija enerģijas datus:

$$G^{\circ}_{\text{CgrCH4gas}} = G^{\circ}_{\text{CH4gas}} - \Delta G_{\text{Hess_CH4gas}} - 2 * G^{\circ}_{\text{H2gas}} = 212,04 - (-50,5 + 2 * 85,64) = 91,26 \text{ kJ/mol ,}$$

kas sakrīt ar oglekļa dioksīda gāzes nulles fonu G^o_{CO2gas}=0 kJ/mol bioķīmijas absolūtās enerģijas skalā.

Metāna šķīdība CH_{4gas}+H₂O=CH_{4aq} ir 22,7 mg/L un metāna mol masa ir M_{CH4}=16,043 g/mol. Ūdens uzskaitē

[H₂O]=996/18=55,3 M aprēķina konstanti K_{eq}=K_{sp}/[H₂O]=0,001414947 M/55,3 M=10^{^(-4,592)}. Albertija dati

aprēķina šķīdības enerģijas izmaiņu ΔG_{eqCH4gas}=G_{CH4aq}-(G_{CH4gas}+G_{H2O})=238,25-(212,04+0)=26,21 kJ/mol .

$$G_{\text{CH4aq}} = \Delta G_{\text{eqCH4}} + (G_{\text{H2O}} + G_{\text{CH4gas}}) = 26,21 + (0 + 212,04) = 238,25 \text{ kJ/mol;}$$

Metāna šķīdības [CH₄]=0,0227/16,043=0,001414947 M līdzsvaram absolūtā brīvās enerģijas izmaiņa ir

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(0,001414947/55,3) = -8,3144 \cdot 298,15 \cdot -6,592 = 26,21 \text{ kJ/mol .}$$

Līdzsvara enerģijas izmaiņa ΔG_{eqCH4}=G_{CH4aq}-(G_{H2O}+G_{CH4gas})=G_{CH4aq}-(0+212,04)=26,21 kJ/mol ļauj aprēķināt

absolūto brīvās enerģijas saturu metānam ūdenī (aqua): G_{CH4aq}=G_{CH4gas}+G_{CH4sp}=212,04+26,21=238,25 kJ/mol;

Viela	ΔH ^o _H kJ/mol	ΔS ^o _H J/mol/K	ΔG ^o _H kJ/mol	ΔG _{H2C2O4} =ΔH _H -T*ΔS _H =-829,9-298,15*-0,1098=-747,75 kJ/mol;
H ₂ O	-285,85	69,9565	-237,191	CRC
H ₃ O ⁺	-285,81	-3,854	-213,2746	CRC Mischenko 1972, Himia, Leningrad [26]
H ₂ C ₂ O _{4cr}	-829,9	-109,8	-797,16	CRC
H ₂ C ₂ O _{4cr}	formation		76,96	G _{H2C2O4cr} =ΔG ^o _{H2C2O4crForm} +(2G _{Cgr} +2G _{O2gas} +G _{H2gas})=76,96 kJ/mol;
H ₂ C ₂ O _{4sq}	ΔG _{eq_sp} = 9,0161		85,976	G _{H2C2O4aq} =ΔG _{eq_sp} +(G _{H2O} +G _{H2C2O4cr})=85,976 kJ/mol;
H ₂ C ₂ O _{4sq}	E ^o _{H2C2O4} = -0,6577 V		171,78	G _{H2C2O4} =2G _{CO2} +2G _{H3O} -(ΔG _{eqH2C2O4} +2G _{H2O})=171,78 kJ/mol;
HC ₂ O ₄ ⁻	17,08 pK _{a2} =1,25		80,618	G _{HC2O4} =ΔG _{eq1H2C2O4} -G _{H3O} +(G _{H2C2O4} +ΔG _{H2O})=80,618 kJ/mol ;
HC ₂ O ₄ ⁻	E ^o _{HC2O4} = -0,7092 V		159,028	G _{HC2O4} =2G _{CO2} +G _{H3O} -(ΔG _{eqHC2O4} +G _{H2O})=159,028 kJ/mol;
C ₂ O ₄ ²⁻	-	-	-677,14	Alberty 2006 Biochem.Thermodyn Massachusetts Techn. Inst.
C ₂ O ₄ ²⁻	33,578 pK _{a2} =4,14		91,756	G _{C2O4} =ΔG _{eq2HC2O4} -G _{H3O} +(G _{HC2O4} +G _{H2O})=91,756 kJ/mol ;
C ₂ O ₄ ²⁻	E ^o _{C2O4} = -0,7607 V		146,79	G _{C2O4} =2G _{CO2} -(ΔG _{eqC2O4})=2*0-(-146,79)=146,79 kJ/mol;
CH _{4gas}	-74,6	186,3	-50,5	Wikipedia CRC [1]
CH _{4gas}	formation	-50,5	212,04	G _{CH4gas} =ΔG _{Hess_CH4gas} +(G _{Cgr} +2*G _{H2})=212,04 kJ/mol;
CH _{4gas}	Alberty 2006		120,56	G ^o _{CgrCH4gas} =G ^o _{CH4gas} -G _{Hess_CH4gas} -2*G ^o _{H2gas} =91,26 kJ/mol;
CH _{4aq}	Solubility	26,21	238,25	G _{CH4aq} = G _{CH4gas} + G _{CH4sp} =212,04+26,21=238,25 kJ/mol;
CH _{4aq}	Alberty 2006		136,95	Alberty 2006 Biochem.Thermodyn Massachusetts Techn. Inst.
C _{gr}	background	Biochemistry	91,26	G ^o _{Cgr0CO2} =-ΔG ^o _{Hess_CO2gas} -G ^o _{O2gas0} =394,36-303,1=91,26 kJ/mol;
CO _{2gas}	-393,509	213,74	-394,359	CRC [1]
CO _{2aq}	-413,798	117,5704	-385,98	CRC [1]
CO _{2aq}	E ^o _{H2C2O4} = -0,6577 V		-42,90	2G _{CO2} = ΔG _{eqH2C2O4} -2G _{H3O} +(G _{H2C2O4} +2G _{H2O})=2*-42,902 kJ/mol;
CO _{2aq}	E ^o _{HC2O4} = -0,7092 V		-97,514	2G _{CO2} = ΔG _{eqHC2O4} -G _{H3O} +(G _{HC2O4} +G _{H2O})=2*-97,514 kJ/mol;
CO _{2aq}	E ^o _{C2O4} = -0,7607 V		-27,517	2G _{CO2} =ΔG _{eqC2O4} +(G _{C2O4})=-27,517 kJ/mol;
CO _{2aq}	K _{eqCO2aqua}	šķīdība	18,38	G _{CO2aqua} =ΔG _{eqCO2aqua} +(G _{CO2gas} +G _{H2O})=18,38+(0+0)=18,38 kJ/mol .

Veidošanās no brīviem elementiem $2C_{gr}+2O_{2gas}+H_{2gas}=H_2C_2O_{4cr}$ un šķīdība $H_2C_2O_4^{cr}+H_2O=H_2C_2O_{4aq}$:
 $G_{H_2C_2O_{4cr}}=\Delta G^\circ_{H_2C_2O_{4cr}Form}+(2G_{C_{gr}}+2G_{O_{2gas}}+G_{H_{2gas}})=-797,16+(2*91,26+2*303+85,6)=76,96$ kJ/mol.

Skābeņskābes šķīdības 118 g/L $H_2C_2O_4^{cr}+H_2O=H_2C_2O_{4aq}$ konstanti iegūst no CRC, Wikipēdijas datiem
 $K_{eq_sp}=[H_2C_2O_{4aq}]/[H_2C_2O_4^{cr}]/[H_2O]=1,3106/1/49,77=0,026329$. [1,29]

Mola masa $M_{H_2C_2O_4}=90,034$ g/mol; $[H_2O]=982/18=49,777$ M; koncentrācija $[H_2C_2O_4]=118/90,034=1,3106$ M un masas daļa procentos $w\%=118/(118+982)*100=10,7272\%$, ja tīra kristāla mol daļa ir viens $[H_2C_2O_4^{cr}]=1$.

Skābeņskābes šķīdības brīvās enerģijas izmaiņa līdzsvarā ir nelabvēlīga $K_{eq_sp}=0,026329$:

pozitīva $\Delta G_{eq_sp}=-R\cdot T\cdot \ln(K_{eq_sp})=-8,3144*298,15*\ln(0,026329)=-8,3144*298,15\cdot -3,637=9,0161$ kJ/mol .

Hesa izmaiņā $\Delta G_{eq_sp}=G_{H_2C_2O_{4aq}}-(G_{H_2O}+G_{H_2C_2O_4^{cr}})=G_{H_2C_2O_{4aq}}-(0+76,96)=9,0161$ kJ/mol aprēķina saturu brīvai enerģijai $G_{H_2C_2O_{4aq}}=\Delta G_{eq_sp}+(G_{H_2O}+G_{H_2C_2O_4^{cr}})=9,0161+(0+76,96)=85,976$ kJ/mol [29] [Wikipedia](#).

1. Vājas skābes protolīze $H_2C_2O_4+H_2O=HC_2O_4^-+H_3O^+$; $pK_{a1}=1,25$; $K_{eq1}=K_{a1}/[H_2O]=10^{-(1,25)}/55,3=0,0010169$;
 $\Delta G_{eq1H_2C_2O_4}=-R\cdot T\cdot \ln(K_{eq1})=-8,3144*298,15*\ln(0,0010169)=\Delta G_{HC_2O_4}+\Delta G_{H_3O}-(\Delta G_{H_2C_2O_4}+\Delta G_{H_2O})=17,08$ kJ/mol;
 $\Delta G_{eq1H_2C_2O_4}=G_{HC_2O_4}+G_{H_3O}-(G_{H_2C_2O_4}+\Delta G_{H_2O})=G_{HC_2O_4}+22,44-(85,976+0)=17,082$ kJ/mol;
 $G_{HC_2O_4}=\Delta G_{eq1H_2C_2O_4}-G_{H_3O}+(G_{H_2C_2O_4}+\Delta G_{H_2O})=17,082-22,44+(85,976+0)=80,618$ kJ/mol;

2. Vājas skābes protolīze $HC_2O_4^-+H_2O=C_2O_4^{2-}+H_3O^+$; $pK_{a2}=4,14$; $K_{eq2}=K_{a2}/[H_2O]=10^{-(4,14)}/55,3=0,000001310$;
 $\Delta G_{eq2HC_2O_4}=-R\cdot T\cdot \ln(K_{eq2})=-8,3144*298,15*\ln(0,000001310)=\Delta G_{C_2O_4}+\Delta G_{H_3O}-(\Delta G_{HC_2O_4}+\Delta G_{H_2O})=33,578$ kJ/mol;
 $\Delta G_{eq2HC_2O_4}=G_{C_2O_4}+G_{H_3O}-(G_{HC_2O_4}+\Delta G_{H_2O})=G_{C_2O_4}+22,44-(80,618+0)=33,578$ kJ/mol;
 $G_{C_2O_4}=\Delta G_{eq2HC_2O_4}-G_{H_3O}+(G_{HC_2O_4}+\Delta G_{H_2O})=33,578-22,44+(80,618+0)=91,756$ kJ/mol;

$pH\leq 1,25$ $H_2C_2O_4+2H_2O=2CO_2+2H_3O^++2e^-$; $E^\circ_{H_2C_2O_4}=-0,6577$ V Suchotina [17]

$E^\circ_{H_2C_2O_4}=E^\circ+0,10166-0,0591/2*\lg(1/[H_2O]^2)-0,37239=-0,49+0,10166-0,02955*\lg(1/55,3^2)-0,37239=-0,6577$ V;

Absolute Nernst's Standard potential $E^\circ_{H_2C_2O_4}=-0,6577$ V; Suchotina [17]

$$E_{H_2C_2O_4}=E^\circ_{H_2C_2O_4}+\frac{0,0591}{2}\cdot \lg\frac{[CO_2]^2\cdot [H_3O^+]^2}{[H_2C_2O_4]\cdot [H_2O]^2}=-0,6577\text{ V}+\frac{0,0591}{2}\cdot \lg\frac{[CO_2]^2\cdot [H_3O^+]^2}{[H_2C_2O_4]\cdot [H_2O]^2}$$

$$\Delta G_{eqH_2C_2O_4}=E^\circ_{H_2C_2O_4}\cdot F\cdot 2=-0,6577*96485*2=-126,9\text{ kJ/mol},$$

$$\Delta G_{eqH_2C_2O_4}=2G_{CO_2}+2G_{H_3O}-(G_{H_2C_2O_4}+2G_{H_2O})=2*0+2*22,44-(85,976+2*0)=-126,9\text{ kJ/mol};$$

$$G_{H_2C_2O_4}=2G_{CO_2}+2G_{H_3O}-(\Delta G_{eqH_2C_2O_4}+2G_{H_2O})=2*0+2*22,44-(-126,9+2*0)=171,78\text{ kJ/mol};$$

$1,25 < pH \leq 4,14$; $HC_2O_4^-+H_2O=2CO_2+H_3O^++2e^-$;

Absolute Nernst's Standard potential $E^\circ_{HC_2O_4}=-0,7092$ V Suchotina [17]

$E^\circ_{HC_2O_4}=E^\circ+0,10166-0,0591/2*\lg(1/[H_2O]^1)-0,37239=-0,49+0,10166-0,0591/2*\lg(1/55,3^1)-0,37239=-0,709$ V;

$$\Delta G_{eqHC_2O_4}=E^\circ_{HC_2O_4}\cdot F\cdot 2=-0,7092*96485*2=-136,85\text{ kJ/mol},$$

$$\Delta G_{eqHC_2O_4}=2G_{CO_2}+G_{H_3O}-(G_{HC_2O_4}+G_{H_2O})=2*0+22,44-(80,618+0)=-136,85\text{ kJ/mol},$$

$$G_{HC_2O_4}=2G_{CO_2}+G_{H_3O}-(\Delta G_{eqHC_2O_4}+G_{H_2O})=2*0+22,44-(-136,85+0)=159,028\text{ kJ/mol},$$

$4,14 < pH$; $C_2O_4^{2-}=2CO_2+2e^-$; Absolute Nernst's Standard potential $E^\circ_{C_2O_4}=-0,7607$ V; Suchotina [17]

$E^\circ_{C_2O_4}=E^\circ+0,10166-0,0591/2*\lg([1/H_2O]^0)-0,37239=-0,49+0,10166-0,0591/2*\lg(1/55,3^0)-0,37239=-0,7607$ V;

$$\Delta G_{eqC_2O_4}=E^\circ_{C_2O_4}\cdot F\cdot 2=-0,7607*96485*2=-146,79\text{ kJ/mol},$$

$$\Delta G_{eqC_2O_4}=2G_{CO_2}-(G_{C_2O_4})=2*0-(G_{C_2O_4})=-146,79\text{ kJ/mol},$$

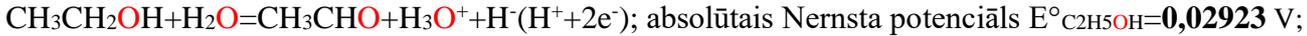
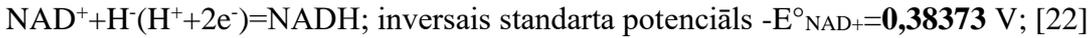
$$G_{C_2O_4}=2G_{CO_2}-(\Delta G_{eqC_2O_4})=2*0-(-146,79)=146,79\text{ kJ/mol},$$

Nernsta potenciāla studijas reducējot ar vitamīnu B3 etanālu $\text{H}_3\text{CCH}=\text{O}$ un oksidējot $\text{H}_3\text{CCH}_2\text{OH}$ etanolu



$$\Delta\text{G}_{\text{Hess}}=\Delta\text{G}^{\circ}_{\text{H}_3\text{O}}+\Delta\text{G}^{\circ}_{\text{CH}_3\text{CHO}}+\Delta\text{G}^{\circ}_{\text{NADH}}-\Delta\text{G}^{\circ}_{\text{CH}_3\text{CH}_2\text{OH}}-\Delta\text{G}^{\circ}_{\text{H}_2\text{O}}-\Delta\text{G}^{\circ}_{\text{NAD}^+}=159,1 \text{ kJ/mol};$$

$$\Delta\text{G}_{\text{Hess}}=32,2824+1175,5732-151,549-(75,2864+1059,11-237,191)=159,1 \text{ kJ/mol endoergiska};$$



$$\text{E}^{\circ}_{\text{C}_2\text{H}_5\text{OH}}=\text{E}^{\circ}-0,0591/2\cdot\log(1/[\text{H}_2\text{O}]^1)=0,19-0,0591/2\cdot\log(1/55,3^1)+0,10166-0,37239=\mathbf{0,02923 \text{ V}}$$

$$\text{Summa: } \text{E}^{\circ}_{\text{C}_2\text{H}_5\text{OH}}-\text{E}^{\circ}_{\text{NAD}^+}=\mathbf{0,02923+0,38373}=0,3545 \text{ V}, n=2; \Delta\text{G}_{\text{eq}}=\Delta\text{E}^{\circ}\cdot\text{F}\cdot n=0,3545\cdot 96485\cdot 2=\mathbf{68,4 \text{ kJ/mol}};$$

Novērtētajā balansā $n=2=m$ ar elektronu skaitu 2e^- donors $\text{E}^{\circ}_{\text{C}_2\text{H}_5\text{OH}}=\mathbf{0,02923 \text{ V}}$ plus elektronu akceptors

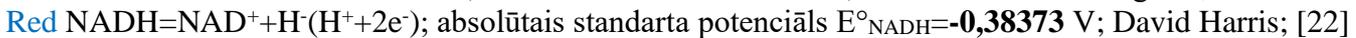
$-\text{E}^{\circ}_{\text{NAD}^+}=\mathbf{0,38373 \text{ V}}$, jo $-\text{E}^{\circ}_{\text{NAD}^+}=\mathbf{0,38373 \text{ V}}$ akceptē elektronus no etanola $\text{E}^{\circ}_{\text{C}_2\text{H}_5\text{OH}}=\mathbf{0,02923 \text{ V}}$:

$$\Delta\text{G}_{\text{eq}}=-\text{R}\cdot\text{T}\cdot\ln(\text{K}_{\text{eq}})=\mathbf{68,4 \text{ kJ/mol}}; \text{K}_{\text{eq}}=\frac{[\text{NADH}]\cdot[\text{CH}_3\text{CHO}]\cdot[\text{H}_3\text{O}^+]}{[\text{NAD}^+]\cdot[\text{CH}_3\text{CH}_2\text{OH}]\cdot[\text{H}_2\text{O}]}=e^{-\frac{\Delta\text{G}_{\text{eq}}}{\text{R}\cdot\text{T}}}=e^{-\frac{68408}{8,314\cdot 298,15}}=1,036\cdot 10^{-12}=10^{-11,985};$$



$$\Delta\text{G}_{\text{Hess}}=\Delta\text{G}^{\circ}_{\text{CH}_3\text{CH}_2\text{OH}}+\Delta\text{G}^{\circ}_{\text{H}_2\text{O}}+\Delta\text{G}^{\circ}_{\text{NAD}^+}-\Delta\text{G}^{\circ}_{\text{H}_3\text{O}}-\Delta\text{G}^{\circ}_{\text{CH}_3\text{CHO}}-\Delta\text{G}^{\circ}_{\text{NADH}}=-159,1 \text{ kJ/mol};$$

$$\Delta\text{G}_{\text{Hess}}=75,2864+1059,11-237,191-(32,2824+1175,5732-151,549)=-159,1 \text{ kJ/mol endoergiska};$$



$$\text{E}^{\circ}_{\text{NADH}}=\text{E}^{\circ}-0,0591/2\cdot\log(1/[\text{H}_2\text{O}]^0)=-0,113-0,0591/2\cdot\log(1/55,3^0)+0,10166-0,37239=\mathbf{-0,38373 \text{ V}}$$



Summa:

$$\Delta\text{E}^{\circ}=\text{E}^{\circ}_{\text{NADH}}-\text{E}^{\circ}_{\text{CH}_3\text{CHO}}=\mathbf{-0,38373+0,02923}=-0,3545 \text{ V}, \Delta\text{G}_{\text{eq}}=\Delta\text{E}^{\circ}\cdot\text{F}\cdot n=-0,3545 \text{ V}\cdot 2 \text{ mol}\cdot 96485 \text{ C/mol}=\mathbf{-68,4 \text{ kJ/mol}};$$

Novērtētajā balansā $n=2=m$ ar elektronu skaitu 2e^- donors $\text{E}^{\circ}_{\text{NADH}}=\mathbf{-0,38373 \text{ V}}$ plus elektronu akceptors

$-\text{E}^{\circ}_{\text{CH}_3\text{CHO}}=\mathbf{0,02923 \text{ V}}$, jo $-\text{E}^{\circ}_{\text{CH}_3\text{CHO}}=\mathbf{0,02923 \text{ V}}$ akceptē elektronus no B3 vitamīna $\text{E}^{\circ}_{\text{NADH}}=\mathbf{-0,38373 \text{ V}}$.

$$\Delta\text{G}_{\text{eq}}=-\text{R}\cdot\text{T}\cdot\ln(\text{K}_{\text{eq}})=\mathbf{-68,408 \text{ kJ/mol}}; \text{K}_{\text{eq}}=\frac{[\text{NAD}^+]\cdot[\text{CH}_3\text{CH}_2\text{OH}]\cdot[\text{H}_2\text{O}]}{[\text{NADH}]\cdot[\text{CH}_3\text{CHO}]\cdot[\text{H}_3\text{O}^+]}=e^{-\frac{\Delta\text{G}_{\text{eq}}}{\text{R}\cdot\text{T}}}=e^{-\frac{-68408}{8,314\cdot 298,15}}=10^{11,985}.$$

Aerobā organismā $\text{O}_{2\text{aqua}}$ NADH oksidāze reda attiecību $[\text{NAD}^+]/[\text{NADH}]=10^6$;

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

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

Līdzsvars novirzīts izejvielās kā aerobā konstante $\text{K}_{\text{eq}}=10^{-11,985}$ un ir inversa anaerobi produktos konstantē $\text{K}_{\text{eq}}=10^{11,985}$. Aerobā endotermiskā un endoergiskā etanola

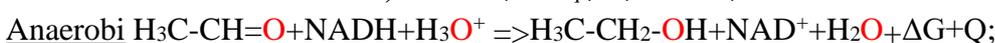
oksidēšanā Hesa likuma brīvās enerģijas izmaiņa ir pozitīva $\Delta\text{G}_{\text{Hess}}=159 \text{ kJ/mol}$ un asimetriski negatīva etanāla anaerobai reducēšanai $\Delta\text{G}_{\text{Hess}}=-159 \text{ kJ/mol}$, bet minimizējas

sasniedzot līdzsvaru $\Delta\text{G}_{\text{min}}=\Delta\text{G}_{\text{eq}}=68,4 \text{ kJ/mol}$ aerobi izejvielas_

un asimetriski anaerobi $\Delta\text{G}_{\text{min}}=\Delta\text{G}_{\text{eq}}=\mathbf{-68,4 \text{ kJ/mol}}$ sasniedzot līdzsvara produkti_ maisījumu ar asimetriskām konstantēm $10^{-11,985}=\text{K}_{\text{eq}}$ un $10^{11,985}=\text{K}_{\text{eq}}$.

Prigožina atraktors ir brīvās enerģijas izmaiņas absolūts minimums $\Delta\text{G}_{\text{min}}$ sasniedzot

$$\text{līdzsvaru: } \Delta\text{G}_{\text{min}}=\mathbf{68,4 \text{ kJ/mol}}=|\Delta\text{G}_{\text{eq}}|<|\Delta\text{G}_{\text{Hess}}|=159 \text{ kJ/mol}.$$



$$\text{reducēšana labvēlīgi } \Delta\text{G}_{\text{eq}}=\Delta\text{E}^{\circ}\cdot\text{F}\cdot n=-0,3545 \text{ V}\cdot 2 \text{ mol}\cdot 96485 \text{ C/mol}=\mathbf{-68,408 \text{ kJ/mol}}.$$

Anaerobā etanola oksidēšana nelabvēlīga zemās $\text{O}_{2\text{aqua}}$ koncentrācijas hipoksijā, bet etanāla reducēšana par etanolu labvēlīga $[\text{H}_3\text{CCH}_2\text{OH}]/[\text{H}_3\text{CCH}=\text{O}]=1/10$ homeostāzē ar NADH reduktāzes enzīmu kā negatīva brīvās enerģijas izmaiņa

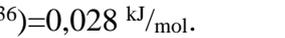
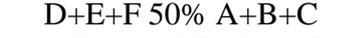
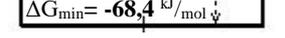
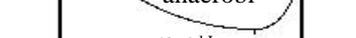
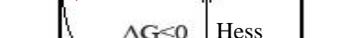
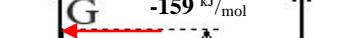
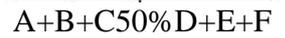
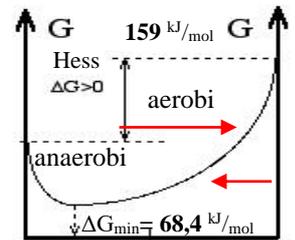
$$\Delta\text{G}_{\text{Homeostāze}}=-27,86 \text{ kJ/mol}$$

Anaerobā attiecība homeostāzē virs c labvēlīga reducēšanai:

$$\Delta\text{G}_{\text{Homeostāze}}=-68,41+8,3144\cdot 298,15\cdot \ln(\text{K}_{\text{Homeostāze}})=-68,41+40,54=-27,86 \text{ kJ/mol}$$

$$\Delta\text{G}_{\text{Homeostāze}}=-68,41+8,3144\cdot 298,15\cdot \ln\left(\frac{1}{10}\cdot \frac{1}{10}\cdot \frac{55,333}{10^{-7,36}}\right)=-27,86 \text{ kJ/mol}; \text{K}_{\text{Homeostāze}}=\frac{[\text{NAD}^+]\cdot[\text{CH}_3\text{CH}_2\text{OH}]\cdot[\text{H}_2\text{O}]}{[\text{NADH}]\cdot[\text{CH}_3\text{CHO}]\cdot[\text{H}_3\text{O}^+]}$$

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



Stikla $\text{SiO}_2 \downarrow \text{SiO}_2 \text{SiO}_2 \downarrow$ 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) kristāliskās virsmas silīcijskābes protolīzes reakcijā $\text{SiO}_2\text{-SiO}_3\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{SiO}_2\text{-SiO}_3^- + \text{H}_3\text{O}^+$. Stikla elektroda potenciāla rašanās izskaidrojama sekojoši.

Uz stikla virsmas atrodas silīcijskābes anjonu funkcionālās grupas $\text{SiO}_2\text{-SiO}_3^-$. Stikla virsmā iestājas protolītiskais līdzsvars stāvoklis starp kristālisku silīcijskābi $\text{SiO}_2\text{-SiO}_3\text{H}$ un silikāta anjonu grupām $\text{SiO}_2\text{-SiO}_3^-$. Silīcijskābe ir ūdenī nešķīstoša skābe un ļoti vājš protolīts: $\text{SiO}_2\text{-SiO}_3\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{SiO}_2\text{-SiO}_3^- + \text{H}_3\text{O}^+$.

Tā kā kristāliskai membrānai ir iekšējās virsmas līdzsvars un uz ārējās membrānas virsmas ir ārējais līdzsvars, kurš ir mainīgs no mērāmās vides H_3O^+ koncentrācijas testa eksperimentos.



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

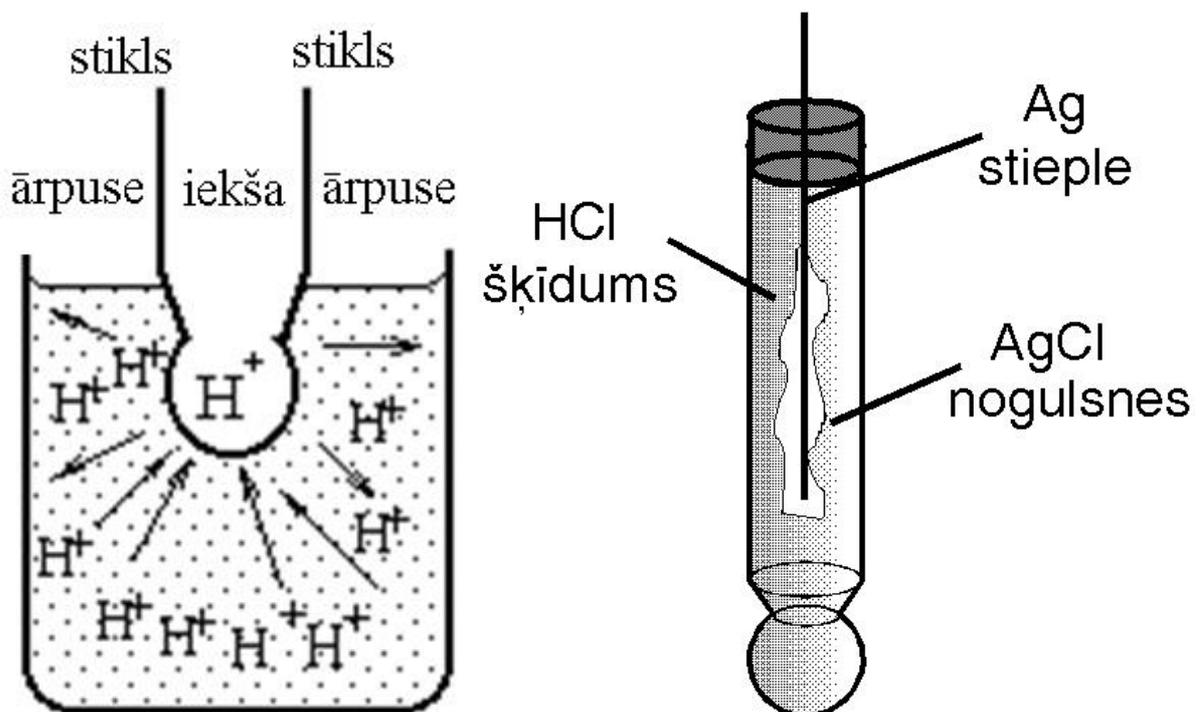
$$K_{\text{iekš.}} = \frac{[\text{H}_2\text{O}]}{[\text{H}_3\text{O}^+]_{\text{iekš.}}}; \quad K_{\text{ārēj.}} = \frac{[\text{H}_3\text{O}^+]_{\text{ārēj.}}}{[\text{H}_2\text{O}]}; \quad K_{\text{iekš.}} \cdot K_{\text{ārēj.}} = K_{\text{membr.}} = \frac{[\text{H}_3\text{O}^+]_{\text{ārēj.}}}{[\text{H}_3\text{O}^+]_{\text{iekš.}}};$$

$$E_{\text{membr.}} = \frac{0,0591}{n} \log \frac{[\text{H}_3\text{O}^+]_{\text{ārēj.}}}{[\text{H}_3\text{O}^+]_{\text{iekš.}}} = 0,0591 (\log[\text{H}_3\text{O}^+]_{\text{ārēj.}} - \log[\text{H}_3\text{O}^+]_{\text{iekš.}}) = E_{\text{const.}} - 0,0591 \cdot \text{pH},$$

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 $E_{\text{const.}} = -0,0591 \cdot \log[\text{H}_3\text{O}^+]_{\text{iekš.}}$. Membrānas potenciāls ir atkarīgs tikai no šķīduma ūdeņraža joniem $\text{H}_3\text{O}^+_{\text{ārēj.}}$ vai $\text{pH} = -\log[\text{H}_3\text{O}^+_{\text{ārēj.}}]$.

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

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 HCl šķīdums ar zināmu koncentrāciju. Ārpusi iegremdē pētāmajā šķīdumā nomēra šķīduma pH.



Stikla membrāna $\text{HSiO}_3\text{-SiO}_2 \downarrow \text{SiO}_2 \text{SiO}_2 \downarrow \text{SiO}_2\text{-SiO}_3\text{H}$ un elektroda komplekts ar sudraba stiepli.

Elektrisko kontaktu ar stikla membrānu iekšējā šķīdumā iegremdē sudraba stiepli, kas izveido otrā veida elektroda potenciālu $E_{\text{AgCl iekš.}}$ virknē ar membrānas potenciālu $E_{\text{membr.}} + E_{\text{AgCl iekš.}}$. Potenciāls ir atkarīgs tikai no ārējā – pētāmā šķīduma pH, jo sālskābes koncentrācija ir konstanta.

EDS (Elektro Dzinēja Spēku) mēra noslēgtai elektriskai ķēdei. To panāk ārējā šķīdumā iemērcot salīdzināšanas elektrodu ar standarta potenciālu 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 $E_{\text{AgCl iekš.}}$;
- 2) stikla membrānas elektrods $E_{\text{membr.}} = E_{\text{const.}} + 0,0591 \cdot \log[\text{H}_3\text{O}^+_{\text{outer}}] = E_{\text{const.}} - 0,0591 \cdot \text{pH}$;
- 3) salīdzināšanas elektrods ar standarta potenciālu E_{AgCl} .

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

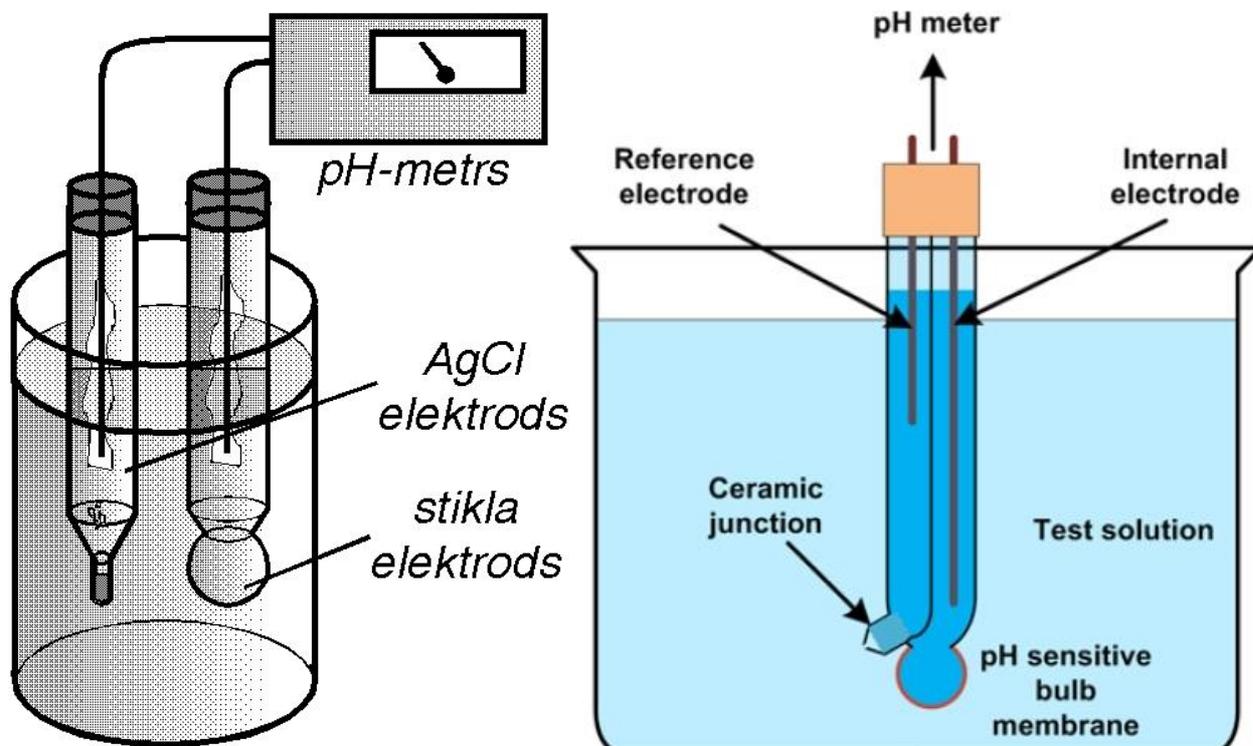
$$\text{EDS} = E_{\text{AgCl}} + E_{\text{membr.}} + E_{\text{AgCl iekš.}} = (E_{\text{AgCl}} + E_{\text{AgCl iekš.}} E_{\text{const.}}) + 0,0591 \cdot \lg [\text{H}_3\text{O}^+_{\text{ārēj.}}] = E'_{\text{const.}} - 0,0591 \cdot \text{pH} ;$$

$$\text{EDS} = E'_{\text{const.}} - 0,0591 \cdot \text{pH} .$$

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) nepārtraukti kontrolē pH izmaiņas pētāmajā sistēmā.



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

Nernsta potenciāla $\text{Cr}_2\text{O}_7^{2-} / 2\text{Cr}^{3+}$ red-oks sistēmas īpašības skābā H_3O^+ , ūdens vidē

Nernsta absolūtais standarta potenciāls. $\log K_D=2,05$; $K_D=10^{2,05}$; $2\text{HCrO}_4^- = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$;

$$\Delta G_D = -R \cdot T \cdot \ln(K_D \cdot [\text{H}_2\text{O}]) = -8,3144 \cdot 298,15 \cdot \ln(10^{2,05} \cdot 55,3) = G_{\text{Cr}_2\text{O}_7} + G_{\text{H}_2\text{O}} - (2G_{\text{HCrO}_4}) = \mathbf{-21,65 \text{ kJ/mol}}$$

$$2G_{\text{HCrO}_4} = G_{\text{Cr}_2\text{O}_7} + G_{\text{H}_2\text{O}} - (\Delta G_D) = G_{\text{Cr}_2\text{O}_7} + 0 - (-21,65) = \text{??? kJ/mol}$$

$$pK_a = 1,8; \text{HCr}_2\text{O}_7^- + \text{H}_2\text{O} = \text{Cr}_2\text{O}_7^{2-} + \text{H}_3\text{O}^+; K_{eq} = K_a / [\text{H}_2\text{O}] = 10^{(-1,8)} / 55,3 = 0,0002866;$$

$$\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = -8,3144 \cdot 298,15 \cdot \ln(0,0002866) = G_{\text{Cr}_2\text{O}_7} + G_{\text{H}_3\text{O}^+} - (G_{\text{HCr}_2\text{O}_7} + G_{\text{H}_2\text{O}}) = \mathbf{20,22 \text{ kJ/mol}}$$

$$G_{\text{HCr}_2\text{O}_7} = G_{\text{Cr}_2\text{O}_7} + G_{\text{H}_3\text{O}^+} - (\Delta G_{eq} + G_{\text{H}_2\text{O}}) = G_{\text{Cr}_2\text{O}_7} + 22,44 - (20,22 + 0) = \text{??? kJ/mol}$$

Instability constant $[\text{Cr}(\text{OH})_2]^{2+} + \text{H}_2\text{O} = \text{Cr}^{3+} + \text{OH}^-$; $K_{inst} = 10^{(-9,77)}$; $K_{eq} = K_{inst} / [\text{H}_2\text{O}] = 10^{(-9,88)} / 55,3 = 10^{(-11,51)}$;

$$\Delta G_{eqinst} = -R \cdot T \cdot \ln(K_{eqinst}) = -8,3144 \cdot 298,15 \cdot \ln(10^{(-11,51)}) = G_{\text{Cr}^{3+}} + G_{\text{OH}^-} - (G_{[\text{Cr}(\text{OH})_2]^{2+}} + G_{\text{H}_2\text{O}}) = \mathbf{65,7 \text{ kJ/mol}}$$

$$G_{[\text{Cr}(\text{OH})_2]^{2+}} = G_{\text{Cr}^{3+}} + G_{\text{OH}^-} - (\Delta G_{eqinst} + G_{\text{H}_2\text{O}}) = G_{\text{Cr}^{3+}} + 77,36 - (65,7 + 0) = \text{??? kJ/mol}$$

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

$$\Delta G_{eqinst} = -R \cdot T \cdot \ln(K_{eqinst}) = -8,3144 \cdot 298,15 \cdot \ln(10^{(-20,785)}) = G_{\text{Cr}^{3+}} + 2G_{\text{OH}^-} - (G_{[\text{Cr}(\text{OH})_2]^{2+}} + 2G_{\text{H}_2\text{O}}) = \mathbf{118,64 \text{ kJ/mol}}$$

$$G_{[\text{Cr}(\text{OH})_2]^{2+}} = G_{\text{Cr}^{3+}} + 2G_{\text{OH}^-} - (\Delta G_{eqinst} + 2G_{\text{H}_2\text{O}}) = G_{\text{Cr}^{3+}} + 2 \cdot 77,36 - (118,64 + 2 \cdot 0) = \text{??? kJ/mol}$$

Instability constant $[\text{Cr}(\text{OH})_3] + 3\text{H}_2\text{O} = \text{Cr}^{3+} + 3\text{OH}^-$; $K_{inst} = 10^{(-24)}$; $K_{eq} = K_{inst} / [\text{H}_2\text{O}] = 10^{(-24)} / 55,3 = 10^{(-29,23)}$;

$$\Delta G_{eqinst} = -R \cdot T \cdot \ln(K_{eqinst}) = -8,3144 \cdot 298,15 \cdot \ln(10^{(-29,23)}) = G_{\text{Cr}^{3+}} + 3G_{\text{OH}^-} - (G_{[\text{Cr}(\text{OH})_3]} + 3G_{\text{H}_2\text{O}}) = \mathbf{166,8 \text{ kJ/mol}}$$

$$G_{[\text{Cr}(\text{OH})_3]} = G_{\text{Cr}^{3+}} + 3G_{\text{OH}^-} - (\Delta G_{eqinst} + 3G_{\text{H}_2\text{O}}) = G_{\text{Cr}^{3+}} + 3 \cdot 77,36 - (166,8 + 3 \cdot 0) = \text{??? kJ/mol}$$

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

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

$$E_{\text{Cr}_2\text{O}_7 / 2\text{Cr}^{3+}} = E^\circ_{\text{Cr}_2\text{O}_7 / 2\text{Cr}^{3+}} + \frac{0,0591}{6} \cdot \lg \frac{[\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{H}_3\text{O}^+]^{14}}{[\text{Cr}^{3+}]^2 \cdot [\text{H}_2\text{O}]^{21}} = \mathbf{1,41975 \text{ V}} + \frac{0,0591}{6} \cdot \lg \frac{[\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{H}_3\text{O}^+]^{14}}{[\text{Cr}^{3+}]^2 \cdot [\text{H}_2\text{O}]^{21}}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

$$E_{\text{CrO}_4 / \text{Cr}(\text{OH})_3 \downarrow} = E^\circ_{\text{CrO}_4 / \text{Cr}(\text{OH})_3 \downarrow} + \frac{0,0591}{3} \cdot \lg \frac{[\text{CrO}_4^{2-}] \cdot [\text{H}_2\text{O}]^4}{[\text{Cr}(\text{OH})_3] \cdot [\text{OH}^-]^5} = \mathbf{-0,563806 \text{ V}} + \frac{0,0591}{3} \cdot \lg \frac{[\text{CrO}_4^{2-}] \cdot [\text{H}_2\text{O}]^4}{[\text{Cr}(\text{OH})_3] \cdot [\text{OH}^-]^5} \text{ V}$$

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

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

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

Viela	$\Delta H^\circ_{\text{H}} \text{ kJ/mol}$	$\Delta S^\circ_{\text{H}} \text{ J/mol/K}$	$\Delta G^\circ_{\text{H}} \text{ kJ/mol}$
$\text{CrCl}_2(\text{cr})$	-395,4	115,3	-356
$\text{CrCl}_3(\text{cr})$	-556,5	123	-486,1
Cr	-	23,8	-
$\text{CrO}_3(\text{l})$	-292,9	266,2	-
$\text{Cr}_2\text{O}_3(\text{cr})$	-1139,7	81,2	1058,1

$$2G_{\text{HCrO}_4} = G_{\text{Cr}_2\text{O}_7} + 0 - (-21,65) = \text{??? kJ/mol}$$

$$G_{\text{HCr}_2\text{O}_7} = G_{\text{Cr}_2\text{O}_7} + 22,44 - (20,22 + 0) = \text{??? kJ/mol}$$

$$G_{[\text{Cr}(\text{OH})_2]^{2+}} = G_{\text{Cr}^{3+}} + 77,36 - (65,7 + 0) = \text{??? kJ/mol}$$

$$G_{\text{Cr}(\text{OH})_2} = G_{\text{Cr}^{3+}} + 2 \cdot 77,36 - (118,64 + 2 \cdot 0) = \text{??? kJ/mol}$$

$$G_{[\text{Cr}(\text{OH})_3]} = G_{\text{Cr}^{3+}} + 3 \cdot 77,36 - (166,8 + 3 \cdot 0) = \text{??? kJ/mol}$$

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

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

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

$$G_{\text{Cr}(\text{OH})_3} = G_{\text{Cr}^{3+}} + 3 \cdot 77,36 - (211,99 + 4 \cdot 0) = \text{??? kJ/mol}$$

Nernsta potenciāla $\text{BiO}_3^- / \text{Bi}^{3+}$ Nernsta absolūtais standarta potenciāls. $2\text{Bi}+6\text{OH}^-=\text{Bi}_2\text{O}_3+3\text{H}_2\text{O}+6\text{e}^-$; $\text{pH}>7$; [7]
 $E^\circ_{\text{Bi}_2\text{O}_3^-/\text{Bi}}=E^\circ_{\text{O}_2/\text{H}_2\text{O}}-0,0591/6*\lg([\text{H}_2\text{O}]^3)+0,10166-0,37239=-0,46-0,0591/6*\lg(55,3^{3^3})+0,10166-0,37239=-0,78223 \text{ V}$;
 $E^\circ_{\text{Bi}_2\text{O}_3^-/\text{Bi}}=E^\circ_{\text{O}_2/\text{H}_2\text{O}}-0,0591/6*\lg([\text{H}_2\text{O}]^6)+0,10166-0,37239=-0,46-0,0591/6*\lg(55,3^{3^6})+0,10166-0,37239=-0,8337 \text{ V}$;
 $2\text{Bi}+3\text{OH}^-+3\text{H}_2\text{O}=\text{Bi}_2\text{O}_3+3\text{H}_3\text{O}^++6\text{e}^-$; $\text{pH}=7$; Suchotina [17].

Viela	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol
Bi^{3+}	-	82,8	-
Bi	$E^\circ_{\text{Bi}_2\text{O}_3^-/\text{Bi}}$	-0,78223V	-249,6
Bi	$E^\circ_{\text{Bi}_2\text{O}_3^-/\text{Bi}}$	-0,67923V	-132,6
Bi	$E^\circ_{\text{BiCl}_3^-/\text{Bi}}$	-0,21372V	298,725
Bi	$E^\circ_{\text{BiCl}_4^-/\text{Bi}}$	-0,17939V	288,795
Bi	$E^\circ_{\text{BiClO}/\text{Bi}}$	-0,007735V	-91,03
Bi	-74,125	56,7	-91,03
Bi_2	219,7	-	-
Bi(OH)^{2+}	-	-146,4	-
Cl^-	-167,08	56,6	-183,955
$\text{Cl}_{(\text{g})}$	-121,301	165,19	
Cl_2	-	223,081	
$\text{BiCl}_{3(\text{s})}$	-379,1	177	-315,0
$\text{BiClO}_{(\text{s})}$	-366,9	120,5	-322,1
Bi_2O_3	-573,9	151,5	-493,7
Bi(OH)_3	-711,3	-	-

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

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

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

$$G_{\text{Bi}}=G_{\text{BiCl}_4}+2G_{\text{H}_2\text{O}}-(\Delta G_{\text{eqBiCl}_4^-/\text{Bi}}+3G_{\text{Cl}})=288,795 \text{ kJ/mol};$$

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

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

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

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

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

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

$$=-0,67923+0,0591/6*\lg([\text{Bi}_2\text{O}_3]*[\text{H}_3\text{O}^+]^3/[\text{Bi}]^2/[\text{OH}]^3/[\text{H}_2\text{O}]^3)=$$

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

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

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

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

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

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

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

$$\text{Bi}+3\text{Cl}^-=\text{BiCl}_{3(\text{s})}+3\text{H}_2\text{O}+3\text{e}^-; \text{pH}=7; \text{Suchotina [17]}$$

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

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

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

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

$$\text{Bi}+4\text{Cl}^-=\text{BiCl}_{4^-}+2\text{H}_2\text{O}+3\text{e}^-; \text{pH}=7; \text{Suchotina [17]}$$

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

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

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

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

$$\text{Bi}+3\text{H}_2\text{O}+\text{Cl}^-=\text{BiClO}_{(\text{s})}+2\text{H}_3\text{O}^++3\text{e}^-; \text{Suchotina [17]}$$

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

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

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

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

$$\text{BiO}^++6\text{H}_2\text{O}=\text{BiO}_3^-+4\text{H}_3\text{O}^++2\text{e}^-; 1<\text{pH}<7; \text{Suchotina [17]}$$

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

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

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

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

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

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

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