

Protolītiskā šķīdība ūdenī saista absolūto elektrodu potenciālu ar absolūtās brīvās enerģijas skalas nulli  $G_{\text{H}_2\text{O}} = G_{\text{CO}_2\text{gas}} = 0 \text{ kJ/mol}$  un ir atkarīga no absolūtās temperatūras. Šķīdības un protolīzes reakcijās ar ūdens molekulām klasisko molāro koncentrāciju vietā termodinamikā ir jāizmanto ūdens, šķīstošo reaģentu un produktu molu daļas.

Gāzu šķīdība: skābeklis  $\text{O}_{2\text{gas}} + \text{H}_2\text{O} = \text{O}_{2\text{aq}}$ ; ūdeņradis  $\text{H}_{2\text{gas}} + \text{H}_2\text{O} = \text{H}_{2\text{aq}}$ ; slāpekļis  $\text{N}_{2\text{gas}} + \text{H}_2\text{O} = \text{N}_{2\text{aq}}$ ; sērūdeņradis  $\text{H}_2\text{S}_{\text{gas}} + \text{H}_2\text{O} = \text{H}_2\text{S}_{\text{aq}}$ ; sēra dioksīds  $\text{SO}_{2\text{gas}} + \text{H}_2\text{O} = \text{H}_2\text{SO}_{3\text{aq}}$ ;  
Metāla elektrodi: metāls ūdeņradis  $\text{H}(\text{Pt}) + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{e}^-$ ; dzelzs  $\text{Fe}_{(\text{s})} + \text{H}_2\text{O} = \text{Fe}^{2+} + 2\text{e}^-$ ;  
cinks  $\text{Zn} + \text{H}_2\text{O} = \text{Zn}^{2+} + 2\text{e}^-$ ; vara amalgama  $\text{Cu}(\text{Hg}) + \text{H}_2\text{O} = \text{Cu}^{2+} + (\text{Hg}) + 2\text{e}^-$ ; sudrabs  $\text{Ag}_{(\text{s})} + \text{H}_2\text{O} = \text{Ag}^+ + \text{e}^-$ ;  
hroms  $\text{Cr} + \text{H}_2\text{O} = \text{Cr}^{3+} + 3\text{e}^-$ ;

Cietvielu šķīdība: sudraba hlorīds  $\text{AgCl}_{(\text{s})} + 2\text{H}_2\text{O} = \text{Ag}^+ + \text{Cl}^-$ ; kalomels  $\text{Hg}_2\text{Cl}_{2(\text{s})} + 3\text{H}_2\text{O} = \text{Hg}_2^{2+} + 2\text{Cl}^-$ ; dzīvsudraba(II) oksīds  $\text{Hg} + \text{H}_2\text{O} + 2\text{OH}^- = \text{HgO} + 2\text{H}_2\text{O} + 2\text{e}^-$ , dzīvsudraba sulfāts  $\text{Hg}_2\text{SO}_{4(\text{s})} + 2\text{H}_2\text{O} = \text{Hg}_2^{2+} + \text{SO}_4^{2-}$ ;  
Protolīze: peroksīds  $\text{H}_2\text{O}_2 + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HOO}^-$   $pK_a = 11,75$ ; ūdens  $2\text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$   $pK_w = 14$ .

Gāzveida skābekļa šķīdība ūdenī  $\text{O}_{2\text{gas}} + \text{H}_2\text{O} = \text{O}_{2\text{aq}}$  kompensē vienu ūdens molekulu oksidēšanas pus reakcijā  $6\text{H}_2\text{O} = \text{O}_{2\text{gas}} + 4\text{H}_3\text{O}^+ + 4\text{e}^-$  no sešām uz piecām  $5\text{H}_2\text{O} = \text{O}_{2\text{aq}} + 4\text{H}_3\text{O}^+ + 4\text{e}^-$ . Tas samazina metāla ūdeņraža brīvās enerģijas nomērīto saturu no  $G_{\text{H}(\text{Pt})} = 51,05 \text{ kJ/mol}$  uz  $G_{\text{H}(\text{Pt})} = 48,56 \text{ kJ/mol}$ . Absolūtā potenciāla skalas atskaites vērtība palielinās no  $E^\circ_{\text{H}} = -0,29654 \text{ V}$  uz  $E^\circ_{\text{H}} = -0,27073 \text{ V}$  mazāk negatīva. Absolūtā potenciāla skalas izmaiņa no termodinamiskās  $0,10166 \text{ V}$  uz  $-0,37239 \text{ V}$  ir savienota summā  $\Delta E^\circ = +0,10166 - 0,37239$ .

Standarta potenciāls samazinās līdz vērtībai  $E^\circ_{\text{O}_2} = 1,0868 \text{ V}$  skābeklim un glikozei  $E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} = -0,13858 \text{ V}$ .

Darbību secība divu ūdens molekulu oksidēšanā par skābekli  $5\text{H}_2\text{O} = \text{O}_{2\text{aq}} + 4\text{H}_3\text{O}^+ + 4\text{e}^-$  absolūtā standarta potenciāla  $E^\circ_{\text{O}_2} = 1,0868 \text{ Volti}$  noteikšanai.

No Nernsta klasiskās vērtības  $E^\circ_{\text{classic O}_2} = 1,2288 \text{ V}$  atņem  $E^\circ_{\text{H}_2\text{O}} = -0,0591/4 * \log(1/55,3^{15}) = 0,1287$  piecu ūdens molekulu logaritmisko vērtību. Ūdens koncentrācija vienā litrā ir  $55,3 \text{ M}$ , ja šķīdumu summārās koncentrācijas ir mazākas par  $<0,1 \text{ M}$ . Tad pieskaita savienoto summu  $\Delta E^\circ = +0,10166 - 0,37239$ . Absolūtais standarta potenciāls tiek summēts no trim komponentiem klasiskais  $E^\circ_{\text{klasiskais}} +$  ūdens logaritma uzskaitē  $+ \Delta E^\circ$ :

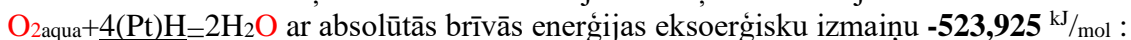
$$E^\circ_{\text{O}_2} = E^\circ_{\text{klasiskais O}_2} - 0,0591/4 * \log(1/55,3^{15}) + \Delta E^\circ = 1,2288 + 0,1287 + 0,10166 - 0,37239 = 1,0868 \text{ Volti.}$$

Tādējādi Nernsta pus reakcijai  $5\text{H}_2\text{O} = \text{O}_{2\text{aq}} + 4\text{H}_3\text{O}^+ + 4\text{e}^-$  iegūst absolūtā potenciāla izteiksmi vienādojumā:

$$E_{\text{O}_2} = E^\circ_{\text{O}_2} + 0,0591/4 * \log \frac{[\text{O}_2]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]^4}{[\text{H}_2\text{O}]^5} = 1,0868 + 0,0591/4 * \log \frac{[\text{O}_2]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]^4}{55,3^{15}} \text{ Volti.}$$

Skābekļa reducēšanas  $\text{O}_{2\text{aq}} + 4\text{H}_3\text{O}^+ + 4\text{e}^- = 5\text{H}_2\text{O}$  inversais standarta potenciāls ir ar mīnusa zīmi  $-E^\circ_{\text{O}_2}$ .

Skābekļa reducēšanas reakcija ir eksoerģiska  $\Delta G_{\text{eq O}_2} = E^\circ_{\text{O}_2} \cdot F \cdot n = -1,0868 * 96485 * 4 / 1000 = -419,44 \text{ kJ/mol}$ ;  
 $\Delta G_{\text{eq O}_2} = 5G_{\text{H}_2\text{O}} - (G_{\text{O}_2\text{aqua}} + 4G_{\text{H}_3\text{O}^+}) = 5 * 0 - (329,68 + 4 * 22,44) = -419,44 \text{ kJ/mol}$ ; un sakrīt ar absolūto potenciālu skalu, Enerģijas saturs  $G_{\text{O}_2\text{gas}} = 303,1 \text{ kJ/mol}$  ūdenī palielinās uz  $G_{\text{O}_2\text{aqua}} = G_{\text{O}_2\text{gas}} + G_{\text{O}_2\text{sp}} = 303,1 + 26,58 = 329,68 \text{ kJ/mol}$ .  
Nernsta pus reakcijas ūdeņraža oksidēšanas  $4(\text{Pt})\text{H} + 4\text{H}_2\text{O} = 4\text{H}_3\text{O}^+ + 4\text{e}^-$  standarta absolūtais potenciāls ir  $E^\circ_{\text{H}} = -0,27073 \text{ Volti}$ . Summā skābekļa reducēšanas reakcijā ar ūdeņradi sintezējas divas ūdens molekulas:



$$\Delta G_{\text{eq}} = (E^\circ_{\text{H}} - E^\circ_{\text{O}_2}) \cdot F \cdot 1 \cdot 4 = (-0,27073 - 1,0868) * 96485 * 4 = -1,3575 * 96485 * 4 / 1000 = 2 * 261,96 = -523,925 \text{ kJ/mol.}$$

Izmaiņa  $\Delta G_{\text{eq } 2\text{H}_2\text{O}} = 2G_{\text{H}_2\text{O}} - 4G_{(\text{Pt})\text{H}} - G_{\text{O}_2\text{aqua}} = 2 * 0 - (4 * G_{(\text{Pt})\text{H}} + 329,68) = -523,925 \text{ kJ/mol}$  dod metāla ūdeņraža brīvās enerģijas saturu  $G_{\text{H}(\text{Pt})} = (2G_{\text{H}_2\text{O}} - \Delta G_{\text{eq } 2\text{H}_2\text{O}} - G_{\text{O}_2\text{aqua}}) / 4 = (2 * 0 + 523,925 - 329,68) / 4 = 194,2355 / 4 = 48,56 \text{ kJ/mol}$ .

Ūdeņraža elektroda atskaites punkta  $E^\circ_{\text{H}} = -0,27073 \text{ V}$  noteikšana absolūtā potenciāla un absolūtās brīvās enerģijas skalā Nernsta pus reakcijā pamatojas **inversās simetrijas** īpašībā: Inversās reakcijas potenciāls un brīvās enerģijas izmaiņa pieder vienam un tam pašam skaitlim ar pretēju zīmi abās absolūtās skalās.

**Absolūtās un inversās** brīvās enerģijas un potenciāla mēroga noteikšanai nepieciešama ūdens un hidroksionija uzskaitē, kuras pamatā ir Albertija dati par ūdeņraža gāzi un šķīduma absolūtās brīvās enerģijas vērtību.[8]

Nernsta pus reakcijā  $\text{H}(\text{Pt}) + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{e}^-$  standarta absolūtais potenciāls ir  $E^\circ_{\text{H}} = -0,27073 \text{ V}$ .

Ūdeņraža standarta oksidēšana **absolūtajā** potenciālu skalā producētā brīvās enerģijas izmaiņa ir eksoerģiska:  $\Delta G_{\text{eq}} = E^\circ_{\text{H}} \cdot F \cdot 1 \cdot 1 = -0,27073 * 96485 * 1 = -26,12 \text{ kJ/mol}$  un ir identiska Hesa likumā aprēķinātās absolūtās brīvās enerģijas izmaiņai skalā, kas attiecināta uz ūdens brīvās enerģijas nulles saturu  $G_{\text{H}_2\text{O}} = 0 \text{ kJ/mol}$ :

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

**Absolūtais** standarta potenciāls  $E^\circ_{\text{H}} = -0,27073 \text{ Voltos}$  sakrīt ar Albertija datiem absolūtai brīvai enerģijai. [8,15]

I veida elektrodus ūdeņraža metāla  $\underline{\text{H}}(\text{Pt})$  robežvirsmā / ar tā katjona  $\text{H}_3\text{O}^+$  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 daudzums litrā ir  $[\text{H}_2\text{O}]=963/18=53,5$  M sērskābes  $[\text{H}_2\text{SO}_4]=[\text{H}_3\text{O}^+]=1$  M šķīduma ar  $1,061 \text{ g/mL}$  blīvumu **ūdeņraža elektrodam** Nernsta izteiksmē ir klasiska standarta potenciāla  $E_{o\_classic}=0$  V atskaites vērtība:

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

Termodinamiska hidroksonija jonu uzskaitē pieprasa ūdeni:  $\underline{\text{H}}(\text{Pt})+\text{H}_2\text{O}=\text{H}_3\text{O}^++\text{e}^-$  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 :

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

Ja attiecība ir viens  $1=\text{K}_{\text{H}}(\text{Pt})=\text{X}_{\text{H}_3\text{O}^+}/\text{X}_{\text{H}_2\text{O}}$ , 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  $\Delta G_{\text{eq}}=E^{\circ}_{\text{H}} \cdot F \cdot 1=0,10166 \cdot 96485 \cdot 1=9,81 \text{ kJ/mol}$  pretstatā eksoerģiskai.

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

Brīvās enerģijas izmaiņa ir noteikta nulles atskaites skalā  $G_{\text{H}_2\text{O}}=G_{\text{CO}_2\text{gas}}=G_{\text{e}^-}=0 \text{ kJ/mol}$ . Iteratīvi izskaitļotais absolūtajā skalā ūdeņraža standarta potenciāls ir  $E^{\circ}_{\text{H}}=\Delta G_{\text{eqH}}(\text{Pt})/F/1=-26,12/96485/1=-0,27073$  Volti. Līdzsvara brīvās enerģijas minimums ir eksoerģisks  $\Delta G_{\text{eqH}}(\text{Pt})=E^{\circ}_{\text{H}} \cdot F \cdot 1=-0,27073 \cdot 96485 \cdot 1=-26,12 \text{ kJ/mol}$  sakrītot 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  $\text{K}_{\text{H}}(\text{Pt})_{\text{Red}}=[\text{H}_3\text{O}^+][\text{e}^-]/[\text{H}_2\text{O}]/[\text{H}(\text{Pt})]=\text{EXP}(-\Delta G_{\text{Alberty}}/R/T)=\text{EXP}(26120/8,3144/298,15)=37675,6$  labvēlīga.

I veida elektrodus metāls  $\underline{\text{H}}(\text{Pt})$  / iegremdēts tā katjonu  $\text{H}_3\text{O}^+$  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 potenciāl  $E_{\text{pH}=7,36}=-0,27073+0,0591 \cdot \log(10^{-7,36}/55,3)=-0,8087$  V un brīvās enerģijas izmaiņu homeostāzē eksoerģisku  $\Delta G_{\text{eqpH},7,36}=E^{\circ}_{\text{H}} \cdot F \cdot 1=-0,8087 \cdot 96485 \cdot 1/1000=-78,03 \text{ kJ/mol}$ .

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

Platīna plāksnīte iemērta hidroksonija jonu  $[\text{H}^+]=[\text{H}_3\text{O}^+]=[\text{H}_2\text{SO}_4]=1$  M sērskābes šķīdumā  $\underline{\text{H}}(\text{Pt})=\text{H}^++\text{e}^-$ :  $E=E^{\circ}+0,0591 \cdot \log[\text{H}^+]=0,0+0,0591 \cdot \log(1 \text{ M})=0$  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.

$$\text{absolūti } E^{\circ}_{\text{H}}=-0,27073 \text{ V} \qquad \text{klasiska nulle } E^{\circ}_{\text{H}}=0 \text{ V} \qquad 0,10166 \text{ V } E, \text{V}$$

$$E_{(\text{Pt})\text{H}/\text{H}^+}=E^{\circ}_{\text{H}}+0,0591 \cdot \log\left(\frac{\text{X}_{\text{H}_3\text{O}^+}}{\text{X}_{\text{H}_2\text{O}}}\right) \quad E_{\text{H,classic}}=E^{\circ}_{\text{H}}+0,0591 \cdot \log([\text{H}_3\text{O}^+]) \quad \text{termodinamiskais } E^{\circ}_{\text{H}}$$

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

reducētājs metāls  $\underline{\text{H}}(\text{Pt})$  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:  $G_{\text{H}}(\text{Pt})=48,56 \text{ kJ/mol}$ .

Viela	$\Delta H^{\circ}_{\text{H}}, \text{kJ/mol}$	$\Delta S^{\circ}_{\text{H}}, \text{J/mol/K}$	$\Delta G^{\circ}_{\text{H}}, \text{kJ/mol}$	$\Delta G^{\circ}_{\text{H}_2\text{O}}=G_{\text{H}_2\text{O}}-(G_{\text{H}_2\text{aq}}+G_{\text{O}_2\text{aq}}/2)=-0-(103,24+88,04/2)=-147,26 \text{ kJ/mol}$
$\text{H}_2\text{O}$	-285,85	69,9565	-237,191	$G_{\text{H}_2\text{O}}=\Delta G_{\text{H}_2\text{O}}\text{Alberty}-(\Delta G^{\circ}_{\text{H}_2\text{O}})=-151,549-(-237,191)=85,6 \text{ kJ/mol}$ [8]
$\text{H}_2\text{O}$	-286,65	-453,188	-151,549	$\Delta G_{\text{H}}=\Delta H_{\text{H}}-T \cdot \Delta S_{\text{H}}=-286,65-298,15 \cdot (-0,453188)=-151,5 \text{ kJ/mol}$ ;
$\text{H}_3\text{O}^+$	-285,81	-3,854	-213,2746	$\Delta G^{\circ}_{\text{H}_3\text{O}^+}, \text{kJ/mol}$ <b>Mischenko</b> 1972, Himia, Leningrad [26]
$\text{H}_{2\text{gas}}$	<b>Alberty</b>	$\text{pH}=7,36$	<b>85,64</b>	Biochem. Thermodyn. Massachusetts Technology Inst. [8]
$\text{H}(\text{Pt})_{(\text{aq})}$	$E^{\circ}_{\text{H}}=$	-0,27073	<b>48,56</b>	$\Delta G_{\text{Hess,eq}}=G_{\text{H}_3\text{O}^+}-(G_{\text{H}}(\text{Pt})+G_{\text{H}_2\text{O}})=22,44-(48,56+0)=-26,12 \text{ kJ/mol}$ .
$\text{H}_{2\text{aq}}$	<b>-5,02</b>	<b>-363,92</b>	<b>103,24</b>	2006, Massachusetts Technology Inst. Alberty $\text{pH}=7,36$ [8]
$\text{O}_{2\text{aqua}}$	<b>-11,70</b>	<b>-94,2</b>	<b>16,4</b>	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  $\Delta G_{\text{Hess}_\text{H}_3\text{O}^+}=2G_{\text{H}_3\text{O}^+}+2G_{\text{e}^-}-(G_{\text{H}_{2\text{aq}}}+G_{\text{H}_2\text{O}})=2*22,44+2*0-(103,24+0)=-58,36 \text{ kJ/mol}$ .

Ar grafiņa elektrodu 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 ar līdzsvara konstantes vērtību  $K_{\text{spH(Pt)}}$ , kas ir lielāka par vienu:

$$\Delta G_{\text{spH(Pt)}}=\Delta E^\circ_{\text{spH(Pt)}}\cdot F\cdot 2=(E^\circ_{\text{H}_{2\text{aq}}}-E^\circ_{\text{H(Pt)}})\cdot F\cdot 2=c(-0,302+0,27073)*96485*2=-0,03128*96485*2=-6,03 \text{ kJ/mol}$$
 un konstanti  $K_{\text{spH(Pt)}}=\frac{[\text{H(Pt)}]^2\cdot[\text{H}_2\text{O}]}{[\text{H}_{2\text{aq}}]}=\text{EXP}(-\Delta G_{\text{spH(Pt)}}/R/T)=\text{EXP}(6036,1/8,3144/298,15)=11,415$  .

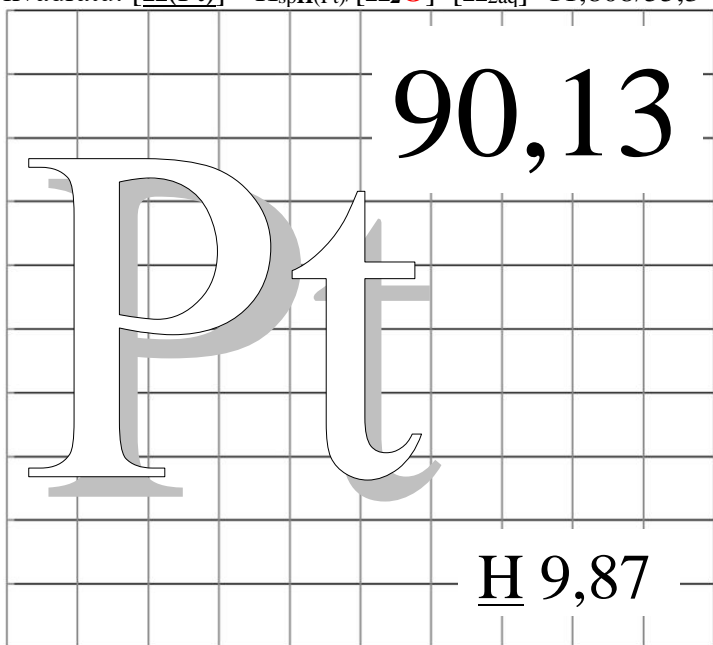
Šķīdība platīnā  $\text{H}_{2\text{aq}}=2\text{H(Pt)}+\text{H}_2\text{O}$  parāda ūdeņraža elektroķīmisko šķīdības produktu metālā eksoergisku, labvēlīgu  $\Delta G_{\text{sp}_\text{H(Pt)}}=2G_{\text{H(Pt)}}+G_{\text{H}_2\text{O}}-(G_{\text{H}_{2\text{aq}}})=2*48,56+0-(103,24)=-6,12 \text{ kJ/mol}$  un konstanti  $>1$

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

Konstante šķīdībai ūdenī  $\text{H}_{2\text{gas}}+\text{H}_2\text{O}=\text{H}_{2\text{aq}}$  ir  $\Delta G_{\text{H}_2\text{spAlberty}}=G_{\text{H}_{2\text{aq}}}-G_{\text{H}_{2\text{gas}}}-G_{\text{H}_2\text{O}}=103,24-85,64-0=17,6 \text{ kJ/mol}$  ir nelabvēlīga  $K_{\text{H}_2\text{sp}}=\frac{[\text{H}_{2\text{aq}}]}{[\text{H}_2\text{O}]\cdot X_{\text{H}_{2\text{gas}}}}=\text{EXP}(-\Delta G_{\text{H}_2\text{sp}}/R/T)=\text{EXP}(-17600/8,3144/298,15)=0,0008253$ .

Tā aprēķina šķīdību  $[\text{H}_{2\text{aq}}]=K_{\text{H}_2\text{sp}}\cdot[\text{H}_2\text{O}]\cdot X_{\text{H}_{2\text{gas}}}=0,0008253*55,3*1=0,04564 \text{ M}$ , ja tīras gāzes mola daļa ir viens  $X_{\text{H}_{2\text{gas}}}=1$ .

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



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

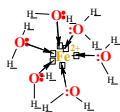
$\text{H(Pt)}$  šķīdība ūdenī ir mazāka par vienu, endoergiska:  $2\text{H(Pt)}+\text{H}_2\text{O}=\text{H}_{2\text{aqAlberty}}$ ;

$K_{\text{spH(Pt)}_\text{H}_{2\text{aq}}}=\frac{[\text{H}_{2\text{aq}}]}{[\text{H(Pt)}]^2\cdot[\text{H}_2\text{O}]}=0,08469$  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 9,87 % ar ūdeņradi, jo pozitīva  $6,12 \text{ kJ/mol}$  vērtība ar konstanti mazāku par vienu 0,08469 ir nelabvēlīga ūdeņraža izšķīšanai

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

Metāla dzelzs I-veida elektrods  $[\text{Fe}^{2+}]=0,1 \text{ M}$  šķīdumā, blīvums  $1,03 \text{ g/mL}$ ;  $0,1 \text{ Mola masa FeSO}_4=15,191 \text{ g}$ .  $\text{Fe(s)}+\text{H}_2\text{O}=\text{Fe}^{2+}+2\text{e}^-$ . Absolūto standarta potenciālu sastāda standarta potenciāls  $E^\circ_{\text{klasiskais}}=-0,4402 \text{ V}$  [17], ūdens uzskaites logaritms  $-0,0591/2*\log(1/(55,3))=0,0515$  un saistītā summa  $\Delta E^\circ=+0,10166-0,37239$  izteiksmē:

$$E^\circ_{\text{Fe/Fe}^{2+}}=E^\circ_{\text{klasiskais}}-0,0591/2*\log(1/([\text{H}_2\text{O}]))+\Delta E^\circ=-0,4402+0,0515+0,10166-0,37239=-0,65943 \text{ V.}$$



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

$$\Delta G_{\text{eq}_\text{Fe}}=E^\circ_{\text{Fe}}\cdot F\cdot 2=-0,65943*96485*2=-127,25 \text{ kJ/mol,}$$

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

$G_{\text{Fe}}=G_{\text{Fe}^{2+}}-(\Delta G_{\text{eq}_\text{Fe}}+G_{\text{H}_2\text{O}})=-82,14-(-127,25+0)=45,11 \text{ kJ/mol}$ ; Atšķirība  $-0,74048 \text{ V}$  ir **4. ciparā**  $-0,74059 \text{ V}$ .

$E_{\text{Fe}}=E^\circ_{\text{Fe/Fe}^{2+}}+0,0591/2*\log([\text{Fe}^{2+}]/[\text{Fe}]/([\text{H}_2\text{O}]-6[\text{Fe}^{2+}]))=-0,65943+0,0591/2*\log(0,1/1/(56,38-0,6))=-0,74059 \text{ V;}$   
 $[\text{H}_2\text{O}]=55,3 \text{ M}=(996\text{g/L})/(18\text{g/mol})$ ;  $m_{\text{H}_2\text{O}}=m_{\text{L}}-m_{\text{FeSO}_4}=1030-15,191=1014,8 \text{ g}$ ;  $[\text{H}_2\text{O}]=1014,8 \text{ g}/18 \text{ g/mol}=56,38 \text{ M}$ .

Koordinatīvie metāla jonu aqua kompleksi ir heksagonāli kā heksa akva dzelzs(II) jons  $[\text{Fe}^{2+}(\text{H}_2\text{O})_6]$  un tetragonāli kā tetra akva vara(II) jons  $[\text{Cu}^{2+}(\text{H}_2\text{O})_4]$ .

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

$G_{Fe} = G_{Fe^{2+}} - (\Delta G_{eq, Fe} + G_{H_2O}) = -82,14 - (-127,25 + 0) = 45,11$  kJ/mol;  
 [8] Biochem. Thermodyn. Massachusetts Technology Inst. pH=7,36  
 CRC 2010 [1]  
 [8] Biochem. Thermodyn. Massachusetts Technology Inst. pH=7,36  
 CRC 2010 [1]  
 $G_{Cu} = G_{Cu^{2+}} - (\Delta G_{eq, Cu} + G_{H_2O}) = 94,0187 - (24,0 + 0) = 70,02$  kJ/mol;  
 [1]  $\Delta G_{Cu^{2+}} = \Delta H_H - T \cdot \Delta S_H = 64,8 - 298,15 \cdot (-0,098) = 94,0187$  kJ/mol;  
 $G_{Zn} = G_{Zn^{2+}} - (\Delta G_{eq, Zn} + G_{H_2O}) = -120,653 - (-189,3 + 0) = 68,65$  kJ/mol;  
 [1]  $\Delta G_{Zn^{2+}} = \Delta H_H - T \cdot \Delta S_H = -153,39 - 298,15 \cdot (-0,1098) = -120,65$  kJ/mol;

Metāla vara I-veida elektrods [Cu<sup>2+</sup>]=1 M šķīdumā, blīvums 1,19 g/mL, 1 Mola masa M<sub>CuSO<sub>4</sub></sub>=159,602 g/mol;  
 Cu(Hg)+H<sub>2</sub>O=Cu<sup>2+</sup>+(Hg)+2e<sup>-</sup>; Absolūto standarta potenciālu sastāda standarta potenciāls E<sup>o</sup><sub>Klasiskais</sub>=0,3435 V  
 [18], ūdens uzskaites logaritms -0,0591/2\*log(1/([H<sub>2</sub>O]))=0,0515 un saistītā summa ΔE<sup>o</sup><sub>Cu</sub>=0,10166-0,371339:

$E^\circ_{Cu/Cu^{2+}} = E^\circ_{Klasiskais} - 0,0591/2 \cdot \log(1/([H_2O])) + \Delta E^\circ_{Cu} = 0,3435 + 0,0515 + 0,10166 - 0,371339 = 0,1243$  V.  
 $E_{Cu} = E^\circ_{Cu} + 0,0591/2 \cdot \log([Cu^{2+}]/[Cu]/([H_2O])) = 0,1243 + 0,0591/2 \cdot \log(1/1/(55,3)) = 0,0728$  V;  
 $E_{Cu} = E^\circ_{Cu} + 0,0591/2 \cdot \log([Cu^{2+}]/[Cu]/([H_2O] - 4[Cu^{2+}])) = 0,1253 + 0,0591/2 \cdot \log(1/1/(57,24 - 4)) = 0,0733$  V;  
 Atšķirība 0,0728 V ir otrajā 2. ciparā 0,0733 V.

$m_{H_2O} = (m_L - m_{CuSO_4})/18 = 1190 - 159,602 = 1030,4/18 = 57,24 - 4 = 53,24$  mol;  
 $\Delta G_{eq, Cu} = E^\circ_{Cu} \cdot F \cdot 2 = 0,1243 \cdot 96485 \cdot 2 = 24,0$  kJ/mol,  $\Delta G_{eq, Cu} = G_{Cu^{2+}} - (G_{Cu} + G_{H_2O}) = 94,0187 - (G_{Cu} + 0) = 24,0$  kJ/mol;  
 $G_{Cu} = G_{Cu^{2+}} - (\Delta G_{eq, Cu} + G_{H_2O}) = 94,0187 - (24,0 + 0) = 70,02$  kJ/mol;

Metāla cinka I-veida elektrods [Zn<sup>2+</sup>]=C<sub>ZnSO<sub>4</sub></sub>=2 M šķīdumā, blīvums 1,31 g/mL, Mola masa ZnSO<sub>4</sub>=161,44 g/mol,  
 masa diviem moliem m<sub>ZnSO<sub>4</sub></sub>=2\*161,44=322,88 g; Zn+H<sub>2</sub>O=Zn<sup>2+</sup>+2e<sup>-</sup>, standarta potenciāls E<sup>o</sup><sub>Zn/Zn<sup>2+</sup></sub>=-0,98098 V.  
 Absolūto standarta potenciālu sastāda klasiskais standarta potenciāls E<sup>o</sup><sub>Klasiskais</sub>=-0,7628 V [18], ūdens uzskaites  
 logaritms -0,0591/2\*log(1/([H<sub>2</sub>O]))=0,0515 un absolūtā potenciāla saistītā summa ΔE<sup>o</sup><sub>Cu</sub>=0,10166-0,371339:

$E^\circ_{Zn/Zn^{2+}} = E^\circ_{Klasiskais} - 0,0591/2 \cdot \log(1/([H_2O])) + \Delta E^\circ_{Cu} = -0,7628 + 0,0515 + 0,10166 - 0,371339 = -0,98098$  V.  
 $E_{Zn} = E^\circ_{Zn/Zn^{2+}} + 0,0591/2 \cdot \log([Zn^{2+}]/[Zn]/([H_2O])) = -0,980981 + 0,0591/2 \cdot \log(2/1/(55,3)) = -1,0215$  V  
 Atšķirība -1,0215 V ir ceturtajā ciparā -1,02358 V 2M;  
 Šķīdība 57,7 g/100g simts gramos ūdens; w%=57,7/157,7\*100=36,6%;

$m_{H_2O} = m_L - m_{ZnSO_4} = 1310 - 161,44 \cdot 2 = 987,12$  g;  $m_{ZnSO_4} = 2 \cdot 161,44 = 322,88$  g;  $[H_2O] = 987,12/18 = 54,84$  M.

$E_{Zn} = E^\circ_{Zn/Zn^{2+}} + 0,0591/2 \cdot \log \frac{[Zn^{2+}]}{[Zn] \cdot ([H_2O] - 4 \cdot [Zn^{2+}])} = -0,980981 + 0,0591/2 \cdot \log(2/1/(54,84 - 4 \cdot 2)) = -1,02358$  V;

$\Delta G_{eq, Zn} = E^\circ_{Zn} \cdot F \cdot 2 = -0,980981 \cdot 96485 \cdot 2 = -189,3$  kJ/mol,  $\Delta G_{eq, Zn} = G_{Zn^{2+}} - (G_{Zn} + G_{H_2O}) = -120,653 - (G_{Zn} + 0) = -189,3$  kJ/mol;  
 $G_{Zn} = G_{Zn^{2+}} - (\Delta G_{eq, Zn} + G_{H_2O}) = -120,653 - (-189,3 + 0) = 68,65$  kJ/mol;

Metāla hroma I-veida elektrods [Cr<sup>3+</sup>]=1 M šķīdumā, blīvums 1,172 g/mL, Mola masa Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>=392,16 g/mol.  
 Masa ūdenim m<sub>H<sub>2</sub>O</sub>=m<sub>L</sub>-m<sub>Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub></sub>=1172-392,16=779,84 g un moli litrā [H<sub>2</sub>O]=779,84 g/18 g/mol=43,3244 M.  
 Cr+H<sub>2</sub>O=Cr<sup>3+</sup>+3e<sup>-</sup>, absolūtais standarta potenciāls E<sup>o</sup><sub>Cr/Cr<sup>3+</sup></sub>=-0,9793 V. Absolūto standarta potenciālu sastāda  
 klasiskais standarta potenciāls E<sup>o</sup><sub>Klasiskais</sub>=-0,744 V [18], logaritms -0,0591/3\*log(1/([H<sub>2</sub>O]))=0,03433 ūdens  
 uzskaitē un absolūtā potenciāla saistītā summa ΔE<sup>o</sup><sub>Cu</sub>=0,10166-0,371339:

$E^\circ_{Cr/Cr^{3+}} = E^\circ_{Klasiskais} - 0,0591/3 \cdot \log(1/([H_2O])) + \Delta E^\circ_{Cr} = -0,744 + 0,03433 + 0,10166 - 0,371339 = -0,9793$  V.  
 $E_{Cr} = E^\circ_{Cr} + 0,0591/3 \cdot \log([Cr^{3+}]/[Cr]/([H_2O])) = -0,9793 + 0,0591/3 \cdot \log(1/1/55,3) = -1,0136$  V;  
 Atšķirība -1,0136 V [Cr<sup>3+</sup>]=1 M; ir trešajā ciparā -1,00208 V [Cr<sup>3+</sup>]=2,32 M.

$E_{Cr} = E^\circ_{Cr} + 0,0591/3 \cdot \log \frac{[Cr^{3+}]}{[Cr] \cdot ([H_2O] - 6 \cdot [Cr^{3+}])} = -0,9793 + 0,0591/3 \cdot \log(2,343/1/(39,59 - 6 \cdot 1)) = -1,00208$  V.

-1,010268 V;

Šķīdība 64 g/100g simts gramos ūdens; w%=64/164\*100=39,2 %;

39,2/100g=X/1172/g/L; 39,2/100\*1172=459,4=X g/L; C<sub>Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub></sub>=459,4/392,16\*2=2,343 M ;

m<sub>H<sub>2</sub>O</sub>=m<sub>L</sub>-m<sub>Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub></sub>=1172-459,4=712,6 g; m<sub>Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub></sub>=459,4 g; [H<sub>2</sub>O]=714,93 g/18 g/mol=39,59 M;

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

Skābekļa gāzes šķīdība  $O_{2\text{gas}}+H_2O=O_{2\text{aq}}$  kompensē vienu ūdens molekulu  $6H_2O=O_{2\text{gas}}+H_2O+4H_3O^++4e^-$  Nernsta pus reakcijā  $5H_2O=O_{2\text{aq}}+4H_3O^++4e^-$ , veidojot absolūto standarta potenciālu  $E^\circ_{5HOH}=1,0868$  V.

$$E^\circ_{5HOH}=E^\circ_{\text{klasiskais } O_2}+0,0591/4 \cdot \log(1/[H_2O]^5)+\Delta E^\circ=1,2288+0,1287+0,10166-0,37239=1,0868$$
 V;

Skābeklis  $O_{2\text{aq}}+4H_3O^++4e^-=5H_2O$  ir stiprs oksidētājs ar inverso standarta potenciālu  $-E^\circ_{5HOH}=-1,0868$  V.

Skābeklis piesaista četrus brīvos elektronus ar četriem protoniem no hidroksonijs joniem, veidojot divas ūdens molekulas reducētos produktus. Šķīdinot brīvās enerģijas saturs pieaug **26,58** kJ/mol no **303,1** kJ/mol līdz **330** kJ/mol:

Viela	$\Delta H^\circ_H, \text{kJ/mol}$	$\Delta S^\circ_H, \text{J/mol/K}$	$\Delta G^\circ_H, \text{kJ/mol}$
<b>H<sub>2</sub>O</b>	-285,85	69,9565	-237,191
<b>H<sub>2</sub>O</b>	<b>-286,65</b>	<b>-453,188</b>	<b>-151,549</b>
<b>H<sub>3</sub>O<sup>+</sup></b>	-285,81	-3,854	-213,2746
<b>H<sub>2</sub>gas</b>	<a href="#">Alberty</a>	pH=7,36	<b>85,64</b>
<b>H<sub>2</sub>(aq)</b>	23,4	-130	99,13
<b>H(Pt)(aq)</b>	$E^\circ_H-E^\circ_{O_2}$	-1,3575	<b>48,56</b>
<b>H<sub>2</sub>(aq)</b>	<b>-5,02</b>	<b>-363,92</b>	<b>103,24</b>
<b>O<sub>2</sub>aqua</b>	<b>-11,70</b>	<b>-94,2</b>	<b>16,4</b>
<b>O<sub>2</sub>aqua</b>	-11,715	110,876	16,4

$$G_{O_{2\text{aq}}}=G_{O_{2\text{gas}}}+G_{O_{2\text{šk}}}=303,1+26,58=329,68=330 \text{ kJ/mol}$$

$$G_{O_{2\text{gas}}}=2(G_{H_2O}-(G_{H_2\text{gas}}-\Delta G^\circ_{H_2O}))=2*(0-(85,64-237,19))=303,1 \text{ kJ/mol}$$

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

[Mischenko](#) 1972, Himia, Leningrad [26]

Biochem. Thermodyn. Massachusetts Technology Inst. [8]

CRC 2010 [1]

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

pH=7,36 [8] Biochem. Thermodyn. Massachusetts Technology Inst.

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

CRC [1]

$$G_{O_{2\text{gas}}}=303 \text{ kJ/mol}, G_{O_{2\text{aq}}}=329,68 \text{ kJ/mol}$$

Skābekļa šķīdības brīvās enerģijas izmaiņa ir eksotermiska, endoergiska:  $O_{2\text{gaiss}}+H_2O=O_{2\text{aq}}$ , kurā skābekļa mol daļai gāzei  $[O_{2\text{gaiss}}]=1$  un ūdenī  $[O_{2\text{aq}}]/[H_2O]=1,22*10^{(-3)}/55,3=2,206*10^{-5}$  mērvienības nav.  $K_{\text{šk}}=[O_{2\text{aq}}]/[O_{2\text{gaiss}}]/[H_2O]=2,206*10^{-5}/1=2,206*10^{-5}$  konstantes arī ir mol daļās.

Izmaiņa  $\Delta G_{Hess}=\Delta G^\circ_{O_{2\text{aq}}}-\Delta G^\circ_{H_2O}-\Delta G^\circ_{O_{2\text{gas}}}=16,4-(0-237,191)=253,6$  kJ/mol ir pozitīva arī

$\Delta G_{\text{Alberty } O_{2\text{aq}}}=G_{O_{2\text{aq}}}-G_{H_2O}+G_{O_{2\text{gas}}}=330-(0+303,1)=26,58$  kJ/mol absolūtajā enerģijas skalā

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

brīvās enerģijas izmaiņa ir pozitīva  $\Delta G_{Hess}=253,6$  kJ/mol, bet minimizējas līdzsvara

maisījumā  $K_{\text{šk}}=[O_{2\text{aq}}]/[O_{2\text{gas}}]/[H_2O]=2,206*10^{-5}$ . Līdzsvara stāvoklis ir atraktors visiem nelīdzsvara stāvokļiem. Minimuma sasniegšanā iestājas līdzsvars. [53. lpp](#)

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

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

Tīra 1atm mol daļa ir  $[O_{2\text{gas}}]=1$ . Osmolaritāte  $C_{\text{osm}}=0,305$  M, jonu spēks  $I=0,25$  M, gaisa skābekli no 0 20,95% izšķīdina  $[O_{2\text{aq}}]=9,768 \cdot 10^{-5}$  M. Tāpēc  $K_{O_{2\text{spAIR}}}=[O_{2\text{aq}}]/[O_{2\text{air}}]=9,768 \cdot 10^{-5}/0,2095=4,663*10^{-4}$  M ir šķīdība gaisā.

Arteriālo  $[O_{2\text{aq}}]=6*10^{-5}$  M un venozo  $[O_{2\text{aq}}]=0,426 \cdot 10^{-5}$  M izooksiju uztur skābekļa molekulu osmoze, kuras cauri akvaporīnu kanāliem šķērso membrānas pretēji osmolārās koncentrācijas  $C_{\text{osm}}=0,305$  M gradientam.

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

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

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

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

Brīvā enerģija  $G_{H_3O^++OH}=G_{H_3O^+}+G_{OH}=22,44+77,36=99,8$  kJ/mol protolīzes reakcijā  $H_2O+H_2O \rightleftharpoons H_3O^++OH^-$  bioķīmijas skābekļa  $O_{2\text{aqua}}$  brīvo enerģijas saturu  $G_{O_{2\text{aqua}}}=329,68$  kJ/mol samazina līdz  $G_{O_{2\text{Bio}}}=88,22$  kJ/mol.

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

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

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

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

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

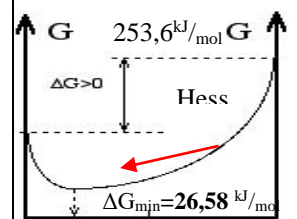
$$K_{\text{šk}}=\frac{[O_{2\text{aqua}}]}{[O_{2\text{gas}}] \cdot [H_2O]}=2,205*10^{-5}; G_{O_{2\text{šk}}}=-R \cdot T \cdot \ln(K_{\text{šk}})=-8,3144*298,15*\ln(2,205*10^{-5})=26,58 \text{ kJ/mol}$$

Protolīze samazina brīvo enerģiju līdz  $G_{O_{2\text{arteriāla}}}=G_{O_{2\text{aqua}}}+G_{O_{2\text{šk}}}+\Delta G_{\text{arteriāla}}=303,1+26,58-241,456=88,22$  kJ/mol un skābeklis kļūst uguns drošs bioķīmisks oksidants, veidojot [arteriālo koncentrāciju](#)  $[O_{2\text{aqua}}]=6*10^{-5}$  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**= $\Delta E_{H_2O}$ .

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

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



A+B 50% C+D  
izejvielas  
 $O_{2\text{gas}}+H_2O$  Asinis  
produkts =  $O_{2\text{aqua}}$ -Asinis.

$$\Delta E_{H_3O} = 0,01478 \cdot \log([H^+]^4) = 0,05912 \text{ V un } \Delta G_{\max} = \Delta E_{H_3O} \cdot F \cdot n = 0,05912 \cdot 96485 \cdot 4 / 1000 = 22,817 \text{ kJ/mol};$$

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

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

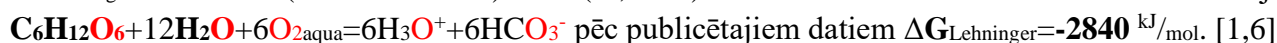
palielinās par  $\Delta G_{\max} = \Delta E_{H_3O} \cdot F \cdot n = 0,01033 \cdot 96485 \cdot 4 / 1000 = 3,987 \text{ kJ/mol}$ . [6. lapas puse](#):

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

Glikozes un skābekļa inversā absolūto un standarta potenciālu summa  $\Delta E^\circ = (E^\circ_{C_6H_{12}O_6} - E^\circ_{O_2})$

$\Delta E^\circ = (E^\circ_{C_6H_{12}O_6} - E^\circ_{O_2}) = \Delta G_{\text{Lehninger}} / F \cdot n = -2840000 / 96485 / 24 = -1,2264 \text{ V}$  dod standarta brīvās enerģijas izmaiņu

$$\Delta G_{\text{Lehninger}} = \Delta E^\circ \cdot F \cdot n = (E^\circ_{C_6H_{12}O_6} - E^\circ_{O_2}) \cdot F \cdot n = (-1,2264) \cdot 96485 \cdot 24 = -2840 \text{ kJ/mol}$$
 oksidēšanas reakcijā



Glikozes un skābekļa absolūto standarta potenciālu summa  $(E^\circ_{C_6H_{12}O_6} - E^\circ_{O_2}) = (E^\circ_{C_6H_{12}O_6} - 1,0868) = -1,22644 \text{ V}$

ļauj noteikt absolūto standarta potenciālu glikozei  $E^\circ_{C_6H_{12}O_6} = \Delta E + E^\circ_{O_2} = -1,22644 + 1,0868 = -0,13964 \text{ V}$ , ko

aprēķina no skābekļa reducēšanas inversā absolūtais standarta potenciāla vērtības  $-E^\circ_{O_2} = -1,0868 \text{ V}$ .

Nernsta glikozes oksidēšanas pus reakcijā absolūtais standarta potenciāls ir negatīvs, jo spēcīgais 24 elektronu

donors reducē sešas skābekļa molekulas Nernsta reakcijā  $O_{2\text{aqua}} + 4H_3O^+ + 4e^- = 5H_2O$  ar inverso absolūto standarta

potenciālu  $-E^\circ_{O_2} = -1,0868 \text{ V}$ . Saskaitot glikozes klasisko standarta potenciālu  $E^\circ_{\text{klasiskais}} = -0,04915 \text{ V}$ , uzskaitot

ūdens logaritmu  $-0,0591/24 \cdot \log(1/55,3^{42}) = 0,18024$  un savienoto summu  $\Delta E^\circ = +0,10166 - 0,37239$  potenciāls ir

$E^\circ_{C_6H_{12}O_6} = E^\circ_{\text{klasiskais}} - 0,0591/24 \cdot \log(1/55,3^{42}) + \Delta E^\circ = -0,04915 + 0,18024 + 0,10166 - 0,37239 = -0,13964 \text{ V}$ .



Arteriālā skābekļa  $[O_{2\text{arteriālā}}] = 6 \cdot 10^{(-5)}$ ; hidroksonija  $[H_3O^+]^{30} = 10^{(-7,36 \cdot 30)}$  M un  $[C_6H_{12}O_6] = 0,005 \text{ M}$

glikozes koncentrācijas asinīs dod negatīvu arteriālo potenciālu:

$$E_{\text{arteriāls}} = E^\circ_{C_6H_{12}O_6} + 0,0591/24 \cdot \log([HCO_3^-]^6 \cdot [H_3O^+]^{30} / [H_2O]^{42} / [C_6H_{12}O_6]) =$$

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

un inversā skābekļa pus reakcijas arteriālais absolūtais potenciāls ir  $E_{O_{2\text{arteriāls}}} = -0,46068 \text{ V}$

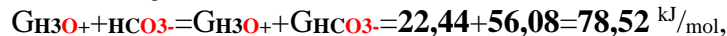
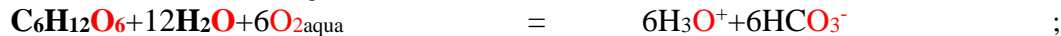
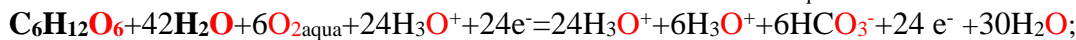
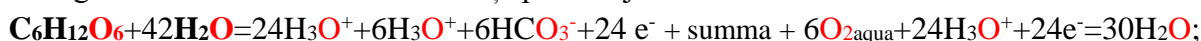
$$E_{O_{2\text{arteriāls}}} = E^\circ_{O_2} + 0,0591/4 \cdot \lg([H_2O]^5 / [O_{2\text{aqua}}] / [H_3O^+]^4) = -1,0868 + 0,0591/4 \cdot \log(55,346^5 / 6 / 10^{(-5)} / 10^{(-7,36 \cdot 4)}) = -0,46068 \text{ V.}$$

Homeostāzes summa ir vairāk negatīva  $\Delta E_{\text{arteriāls}} = E_{C_6H_{12}O_6\text{arteriāls}} + E_{O_{2\text{arteriāls}}} = -0,8624 - 0,46068 = -1,32308 \text{ Volti}$ .

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

$$\Delta G_{\text{arteriāls}} = \Delta E \cdot F \cdot n = (E_{C_6H_{12}O_6\text{arteriāls}} - E_{O_{2\text{arteriāls}}}) \cdot F \cdot n = (-0,86237 - 0,4607) \cdot 96485 \cdot 24 = -3063,846 \text{ kJ/mol}$$

Vienu molu glikozes oksidē seši moli skābekļa producējot sešus molus bikarbonāta  $6H_3O^+ + 6HCO_3^-$ :



**Glc** (6. lpp.) veidošanās no elementiem  $6C + 6H_{2\text{gas}} + 3O_{2\text{gas}} = C_6H_{12}O_6$  brīvās enerģijas izmaiņu aprēķina no

Albertija datiem pie  $pH=7,36$   $\Delta G^\circ_{\text{Alberty}} = G_{C_6H_{12}O_6} - (6G_{C\text{graph}} + 6 \cdot G_{H_2\text{gas}} + 3 \cdot G_{O_2\text{gas}}) = -402,05 \text{ kJ/mol}$ .

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

Viela	$\Delta H^\circ_H, \text{kJ/mol}$	$\Delta S^\circ_H, \text{J/mol/K}$	$\Delta G^\circ_H, \text{kJ/mol}$
$C_6H_{12}O_{6aq}$	-1263,78	269,45	-919,96
$pH=7,36 \text{ Glc}$	-1267,13	-2901,492	-402,05

CRC 2010 [1]

[8]  $\Delta G^\circ_{\text{Alberty}} + (6G_{C\text{graph}} + 6 \cdot G_{H_2\text{gas}} + 3 \cdot G_{O_2\text{gas}}) = G_{C_6H_{12}O_6} = 1568 \text{ kJ/mol};$

Brīvo enerģiju glikozes oksidēšanā  $C_6H_{12}O_6 + 6O_{2\text{aqua}} + 12H_2O = 6H_3O^+ + 6HCO_3^-$  aprēķina trīs veidos:

1) Albertija datus pie  $pH=7,36$   $\Delta G^\circ_{\text{Alberty}} = G_{C_6H_{12}O_6} - (6G_{C\text{graph}} + 6 \cdot G_{H_2\text{gas}} + 3 \cdot G_{O_2\text{gas}}) = -402,05 \text{ kJ/mol}$ , standarta

brīvās enerģijas saturs molā ir

$$G_{C_6H_{12}O_6} = \Delta G^\circ_{\text{Alberty}} + (6G_{C\text{graph}} + 6 \cdot G_{H_2\text{gas}} + 3 \cdot G_{O_2\text{gas}}) = -402,05 + (6 \cdot 91,26 + 6 \cdot 85,6 + 3 \cdot 303) = 1568 \text{ kJ/mol}$$

2) Lahningera  $\Delta G_{C_6H_{12}O_6} = 6 \cdot G_{H_3O^+} + 6 \cdot G_{HCO_3^-} - (G_{\text{Standard } C_6H_{12}O_6} + 6 \cdot G_{O_{2\text{aqua}}} + 12 \cdot G_{H_2O}) = -2840 \text{ kJ/mol}$  standarta

saturs glikozes molā  $G_{\text{Standard } C_6H_{12}O_6} = 6 \cdot (22,44 + 56,08) - (-2840 + 6 \cdot 330 + 12 \cdot 0) = 1331 \text{ kJ/mol}$  un

3) brīvās enerģijas saturs

$$\Delta G_{\text{arteriāls } C_6H_{12}O_6} = 6 \cdot G_{H_3O^+} + 6 \cdot G_{HCO_3^-} - (G_{\text{arteriāls } C_6H_{12}O_6} + 6 \cdot G_{O_{2\text{aqua}}} + 12 \cdot G_{H_2O}) = -3064 \text{ kJ/mol}$$
 uz glikozes molu

$$\text{homeostāzē } G_{\text{arteriāls } C_6H_{12}O_6} = 6 \cdot (22,44 + 56,08) - (-3064 + 6 \cdot 88,22 + 12 \cdot 85,64) = 1978 \text{ kJ/mol. [8,6]}$$

Ģenerētie  $6HCO_3^- + 6H_3O^+$  joni virza izejvielas  $6O_{2\text{aqua}}$  un  $6H_2O$  cauri membrānu akvaporīnu kanāliem osmozē

pretēji koncentrācijas gradientiem, bet transportē jonus  $6HCO_3^- + 6H_3O^+$  lejup pa gradientiem cauri membrānu

bikarbonāta un protonu kanāliem lietojot producēto brīvo enerģiju  $\Delta G_{\text{arteriāls}} = -3064 \text{ kJ/mol}$ .

Absolūtās potenciālu un brīvās enerģijas vērtībās iekļauj hidroksionija  $\text{H}_3\text{O}^+$  un ūdens  $\text{H}_2\text{O}$  uzskaiti.

Skābeklis inversā pus reakcijā ar brīvo enerģiju  $G_{\text{O}_2\text{aqua}}=330 \text{ kJ/mol}$  tiek reducēts līdz  $\text{O}_{2\text{aqua}}+4\text{H}_3\text{O}^++4\text{e}^-=5\text{H}_2\text{O}$  ar inverso potenciālu  $-E_{\text{O}_2}=-1,0868 \text{ V}$ , oksidējot četrus metāla ūdeņraža atomus ar brīvās enerģijas saturu molā  $G_{\text{H(Pt)}}=48,56 \text{ kJ/mol}$  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 absolūto potenciālu  $E_{\text{H}}=-0,27073 \text{ V}$ . Standarta brīvās enerģijas izmaiņa aqua reakcijā  $\text{O}_{2\text{aq}}+4(\text{Pt})\text{H}=2\text{H}_2\text{O}$  no elementiem 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  $\Delta G_{\text{eq}2\text{H}_2\text{O}}=(E_{\text{H}}-E_{\text{O}_2})\cdot F\cdot n=(-0,27073-1,0868)*96485*4=-1,3575*96485*4=-523,925=2*-262 \text{ kJ/mol}$  ļauj neatkarīgi no Hesa likuma aprēķinātās veidošanās no elementiem ūdenī skābekļa  $\text{O}_{2\text{aqua}}$  un metāla ūdeņraža  $(\text{Pt})\text{H}$  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  $G_{\text{H(Pt)}}=(2G_{\text{H}_2\text{O}}-\Delta G_{\text{eq}2\text{H}_2\text{O}}-G_{\text{O}_2\text{aqua}})/4=(2*0+523,9-330,68)/4=48,56 \text{ kJ/mol}$  un absolūto potenciāla skalu. Ūdeņraža standarta brīvā enerģija ūdens šķīdumā  $G_{\text{H}_2\text{aqua}}=103,24 \text{ kJ/mol}$  ir pie  $\text{pH}=7,36$ . [8]

$\text{O}_{2\text{aq}}+2\text{H}_{2\text{aq}}=2\text{H}_2\text{O}$ ; Brīvās enerģijas standarta izmaiņa Hesa likumā no aqua elementiem veidojoties ir

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

Hesa likumā izmaiņas aprēķina no CRC datiem, kad tīri reaģenti pārvēršas tīros produktos un ir maksimāli iespējama izmaiņa lielāka par standarta izmaiņu  $\Delta G_{\text{HessCRCaqua}}=-295 \text{ kJ/mol} > \Delta G_{\text{eq(Pt)H}_2\text{H}_2\text{O}}=-262 \text{ kJ/mol}$ .

Veidošanās no elementiem ūdenī  $\Delta G^{\circ}\text{H}_2\text{O}=-151,55 \text{ kJ/mol}$  Albertija [8] un homeostāzē  $\Delta G^{\circ}\text{H}_2\text{O}=-147,26 \text{ kJ/mol}$ .

Viela	$\Delta H^{\circ}_{\text{H}}$ , kJ/mol	$\Delta S^{\circ}_{\text{H}}$ , J/mol/K	$\Delta G^{\circ}_{\text{H}}$ , kJ/mol	$\Delta G^{\circ}\text{H}_2\text{O}=G_{\text{H}_2\text{O}}-(G_{\text{H}_2\text{aq}}+G_{\text{O}_2\text{aq}}/2)=0-(103,24+88,22/2)=-147,35 \text{ kJ/mol}$
$\text{H}_2\text{O}$	-285,85	69,9565	-237,191	$G_{\text{H}_2\text{O}}=\Delta G_{\text{H}_2\text{O}}\text{Alberty}-(\Delta G^{\circ}\text{H}_2\text{O})=-151,549-(-237,191)=85,6 \text{ kJ/mol}$ [8]
$\text{H}_2\text{O}$	-286,65	-453,188	-151,549	$\Delta G_{\text{H}}=\Delta H_{\text{H}}-T*\Delta S_{\text{H}}=-286,65-298,15*-0,453188=-151,5 \text{ kJ/mol}$ ;
$\text{H}_3\text{O}^+$	-285,81	-3,854	-213,2746	$\Delta G^{\circ}\text{H}_3\text{O}^+$ , kJ/mol <a href="#">Mischenko</a> 1972, Himia, Leningrad [26]
$\text{H}_{2\text{aq}}$	23,4	-130	99,13	CRC [1]
$\text{H}_{2\text{aq}}$	-5,02	-363,92	103,24	$\text{pH}=7,36$ [8] Biochem. Thermodyn Massachusetts Technology Inst.
$E^{\circ}(\text{Pt})\text{H}=-0,27073 \text{ V}$	-1,0868	48,56		$G_{\text{H(Pt)}}=(2G_{\text{H}_2\text{O}}-\Delta G_{\text{eq}2\text{H}_2\text{O}}-G_{\text{O}_2\text{aqua}})/4=48,56 \text{ kJ/mol}$
$\text{O}_{2\text{aqua}}$	-11,70	-94,2	16,4	$\text{pH}=7,36$ [8] Biochem. Thermodyn Massachusetts Technology Inst.
$\text{O}_{2\text{aqua}}$	-11,715	110,876	16,4	CRC [1] Līdzsvara konstante ir labvēlīga lielāka par vienu:

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

Eksotermiska un eksoergiska  $\text{O}_{2\text{aqua}}$  reducēšana ar metālu ūdeņradi

$4(\text{Pt})\text{H}$  un  $\text{H}_2\text{O}_2$  dismutēšanas Hesa brīvās enerģijas izmaiņa negatīva

$\Delta G_{\text{HessAqua}_\text{H}_2\text{O}}=-295 \text{ kJ/mol}$ , bet sasniedzot  $\Delta G_{\text{eq}2\text{H}_2\text{O}}=-262 \text{ kJ/mol}$  līdzsvara stāvokli

minimumā konstante ir lielāka par vienu  $K_{\text{eqH}_2\text{O}}=7,832*10^{45}$ . Līdzsvara stāvoklis

ir Prigožina atraktors visiem nelīdzsvara stāvokļiem. Brīvās enerģijas izmaiņas

minimuma sasniegšanā iestājas līdzsvara stāvoklis.

Peroksīdam oksidēšana un reducēšana ir absolūtais standarta  $E^{\circ}\text{H}_2\text{O}_2\text{Ox}=0,5268 \text{ V}$

Ox  $\text{H}_2\text{O}_2+2\text{H}_2\text{O}=\text{O}_{2\text{aqua}}+2\text{H}_3\text{O}^++2\text{e}^-$  un inversais standarta  $-E^{\circ}\text{H}_2\text{O}_2\text{Red}=-1,7113 \text{ V}$

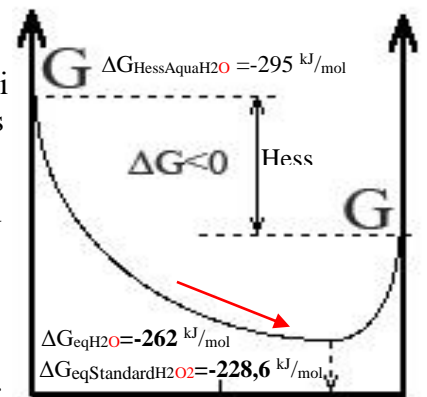
Red  $\text{H}_2\text{O}_2+2\text{H}_3\text{O}^++2\text{e}^-=4\text{H}_2\text{O}$  potenciāls. Dismutācija ir eksoergiska, labvēlīga

un eksotermiska  $2\text{H}_2\text{O}_{2\text{aq}}=>\text{O}_{2\text{aqua}}+2\text{H}_2\text{O}+Q+\Delta G$  standartu summā

$(E^{\circ}\text{H}_2\text{O}_2\text{Ox}-E^{\circ}\text{H}_2\text{O}_2\text{Red})=(0,5268-1,7113)=-1,1845 \text{ V}$   $\Delta G_{\text{eqStandard}_\text{H}_2\text{O}_2}=-228,57 \text{ kJ/mol}$ .

Reaktanti  $4(\text{Pt})\text{H} + \text{O}_{2\text{aqua}}$  un produkti  $2\text{H}_2\text{O}$   $4A+B$   $50\%$   $2D$

Reaktanti  $2\text{H}_2\text{O}_{2\text{aq}}$  un produkti  $\text{O}_{2\text{aqua}}+2\text{H}_2\text{O}$   $2A$   $50\%$   $B+2C$



Peroksīda oksidēšanas klasiskais standarta potenciāls  $E^{\circ}\text{klasiskaisH}_2\text{O}_2\text{Ox}=0,6945 \text{ V}$  [19], plus 2 ūdens uzskaitē

$-0,0591/2*\log(1/[\text{H}_2\text{O}]^2)=0,103$  un saistītās summas  $\Delta E^{\circ}=+0,10166-0,37239$  izteiksmē absolūtais potenciāls ir

$E^{\circ}\text{H}_2\text{O}_2=E^{\circ}\text{klasiskais}-0,0591/2*\log(1/[\text{H}_2\text{O}]^2)+\Delta E^{\circ}=0,6945+0,103+0,10166-0,37239=0,5268 \text{ V}$ ;

Peroksīda reducēšanas klasiskais standarta potenciāls  $E^{\circ}\text{klasiskaisH}_2\text{O}_2\text{Red}=1,776 \text{ V}$  [17], plus 4 ūdens uzskaitē

$-0,0591/2*\log(1/[\text{H}_2\text{O}]^4)=0,206$  un saistītās summas  $\Delta E^{\circ}=+0,10166-0,37239$  izteiksmē absolūtais potenciāls ir

$E^{\circ}\text{H}_2\text{O}_2\text{Ox}=E^{\circ}\text{klasiskais}-0,0591/2*\log(1/[\text{H}_2\text{O}]^4)+0,10166-0,372=1,776+0,206+0,10166-0,37239=1,7113 \text{ V}$ ;

Peroksīda oksidēšanas un inversā reducēšanas standarta potenciālu summa aprēķina enerģijas izmaiņu:

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

$$G_{\text{AlbertyH}_2\text{O}_2}=(G_{\text{O}_2\text{Biochem}_\text{arterial}}+2\cdot G_{\text{H}_2\text{O}}\text{BioChemistry}-\Delta G_{\text{eqBioChem}})/2=(330+2*0+228,57)/2=279,285 \text{ kJ/mol.}$$

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

$$E_{\text{H}_2\text{O}_2}=E^{\circ}\text{H}_2\text{O}_2+0,0591/2\cdot\lg([\text{O}_2]_{\text{aqua}}\cdot[\text{H}_3\text{O}^+]^2/[\text{H}_2\text{O}_2]/[\text{H}_2\text{O}]^2)=0,5268+0,0591/2\cdot\lg(6*10^{(-5)}*10^{(-7,36*2)}/1/55,3^2)=-0,1359 \text{ V}$$

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

Summā Nernsta + inversā reakcija homeostāzē absolūtā brīvās enerģijas elektroķīmiskā izmaiņa ir ar enerģijas saturu

$$\Delta G_{\text{eqBioChem}}=(E_{\text{Red}}-E_{\text{Ox}})\cdot F\cdot n=(0,1359-1,0703)*96485*2=(-0,9344)*96485*2=-180,3 \text{ kJ/mol}$$
 vienā molā

**Liela ātruma protolīze peroksīda anjonu sadursmēs** peroksisomās producē neizstājamās taukskābes  $\omega=6$ ,  $\omega=3$  ar 100% iznākumu, skābekli, ūdeni un siltumu:  $2\text{H}_2\text{O}_{2aq}=\text{O}_{2aq}+2\text{H}_2\text{O}+\text{Q}+\Delta G_H$ .

Sadursmes  $\text{H}^++\text{HOO}^- \rightarrow \text{OOH}+\text{H}^+$  ūdenī aktivācijas enerģija ir liela  $E_a=79000 \text{ J/mol}$  ar lēnu reakcijas ātrumu.

Sadursmē  $\text{HOO}^- \Rightarrow \text{Fe}^{3+}$  ar dzelzs(III) jonu peroksīda aktivācijas enerģija  $E_a=29 \text{ J/mol}$  ir maza. Tas palielina reakcijas ātrumu trīsdesmit miljonus reizes.  $\text{H}_2\text{O}_2$  veidošanās no aqua elementiem  $\text{O}_{2aq}+\text{H}_{2aq}=\text{H}_2\text{O}_2$  negatīva

eksoerģiska  $\Delta G_{\text{HessH}_2\text{O}_2}=\Delta G^\circ_{\text{H}_2\text{O}_2}-\Delta G^\circ_{\text{H}_2\text{O}}-\Delta G^\circ_{\text{O}_2}=-237,129-(99,13+16,4)=-352,66 \text{ kJ/mol}$ . [1] Dismutācijas

reakcija  $\Delta G_{\text{Hess}2\text{H}_2\text{O}_2}=2\Delta G^\circ_{\text{H}_2\text{O}_2}-2\Delta G^\circ_{\text{H}_2\text{O}}-2\Delta G^\circ_{\text{O}_2}=2*(-237,129)-(2*237,191+16,4)=-303,094 \text{ kJ/mol}$ . [1]

Albertija dati Hesa izteiksmē  $\Delta G_{\text{Alberty}2\text{H}_2\text{O}_2}=2G_{\text{H}_2\text{O}}+G_{\text{O}_2}-(2G_{\text{H}_2\text{O}_2})=2*0+330-(2*279,285)=-228,57 \text{ kJ/mol}$ . [8]

Viela	$\Delta H^\circ_H, \text{kJ/mol}$	$\Delta S^\circ_H, \text{J/mol/K}$	$\Delta G^\circ_H, \text{kJ/mol}$
$\text{H}_2\text{O}_{2aq}$	-191,99	-481,688	-48,39
$\text{H}_2\text{O}_{2aq}$	-191,17	143,9	-134,03
$\text{H}_2\text{O}_{2aq}$	Formation	-48,39	340,25
$\text{H}_2\text{O}_{2aq}$	Formation	-134,03	254,61
$\text{H}_2\text{O}_{2aq}$	$\Delta E^\circ_{\text{H}_2\text{O}_2}$	1,1845 V	279,285
$\text{HOO}^-$	$\text{pK}_a=11,75$	77,016	333,866
$\text{H}_2\text{O}_2$	-237,129	69,91	-237,129

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

Biochem. Thermodynamic 2006 Massachusetts Technology Inst.[8]

University Alberta 1997. [19]

$G_{\text{H}_2\text{O}_2aq}=\Delta G_{\text{H}_2\text{O}_2\text{Alberty}}+(G_{\text{O}_2\text{gas}}+G_{\text{H}_2\text{gas}})=340,25 \text{ kJ/mol}$ ;

$G_{\text{H}_2\text{O}_2aq}=\Delta G_{\text{H}_2\text{O}_2\text{Alberty}}+(G_{\text{O}_2\text{gas}}+G_{\text{H}_2\text{gas}})=254,61 \text{ kJ/mol}$ ;

$G_{\text{H}_2\text{O}_2}=(G_{\text{O}_2aq}+2*G_{\text{H}_2\text{O}}+\Delta G_{\text{Alberty}_2\text{H}_2\text{O}_2})/2=279,285 \text{ kJ/mol}$ ;

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

CRC [1]

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

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

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

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

$\text{HOO}^-+\text{H}_2\text{O}=\text{O}_{2aq}+\text{H}_3\text{O}^++2e^-$  Peroksīda anjona pus reakcijas brīvās enerģijas izmaiņa ir iegūta standarta

$\Delta G_{\text{NernstHOO}^-}=G_{\text{O}_{2aq}}+G_{\text{H}_3\text{O}^+}-(G_{\text{HOO}^-}+G_{\text{H}_2\text{O}})=330+22,44-(333,866+0)=18,574 \text{ kJ/mol}$ ; potenciālam  $E^\circ_{\text{HOO}^-}$

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

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

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

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

Eksotermiska, eksoerģiska  $\text{H}_2\text{O}_2(aq)$  dismutēšanas Hesa  $\Delta G_{\text{Hess}2\text{H}_2\text{O}_2}=-303,09 \text{ kJ/mol}$

izmaiņa ir negatīva, bet standarta līdzsvaru maisījumā  $\Delta G_{\text{eqStandart}}=-228,6 \text{ kJ/mol}$

minimizējas sasniedzot labvēlīgu konstanti  $\text{K}_{\text{eq}}=1,11*10^{40}$ . Lešateljē princips ir

Prigožina atraktors kā brīvās enerģijas izmaiņas minimums  $\Delta G_{\text{min}}$  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

$\text{H}_2\text{O}_2$  sasniedzot 100%  $\omega=6$ ,  $\omega=3$  taukskābju  $\text{C}_{20:4}$  iznākumu elongācijas sintēzē

peroksisomās. KATALĀZES reaktivitāte ir nepieciešams neatgriezeniskas homeostāzes

Brauna molekulārs dzinējs evolūcijai un izdzīvošanai.  $\text{H}_2\text{O}_2$  veidošanās no elementiem

$\text{O}_{2\text{gas}}+\text{H}_{2\text{gas}}=\text{H}_2\text{O}_{2aq}$ ;  $\Delta G^\circ_{\text{UnivAlberta}}=-134,03 \text{ kJ/mol}$ , [19]  $\Delta G^\circ_{\text{Alberty}}=-48,39 \text{ kJ/mol}$ . [8] No

Albertija datiem  $\Delta G_{\text{HessH}_2\text{O}_2}=G_{\text{H}_2\text{O}_2}-G_{\text{H}_2\text{gas}}-G_{\text{O}_2\text{gas}}=279,285-(85,64+303)=-109,155 \text{ kJ/mol}$

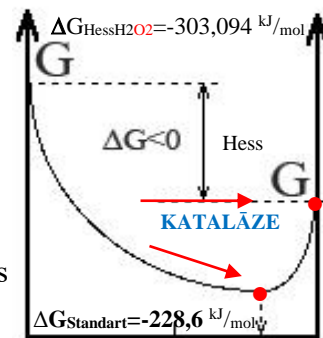
iegūtās vērtības  $G_{\text{H}_2\text{O}_2}$ ;  $G_{\text{H}_2\text{gas}}$ ;  $G_{\text{O}_2\text{gas}}$  atrodas starp  $\Delta G^\circ_{\text{UnivAlberta}}=-134,03 \text{ kJ/mol}$  un  $\Delta G^\circ_{\text{Alberty}}=-48,39 \text{ kJ/mol}$  daudz

tuvāk kā CRC dati. [1] Analogiski dati absolūtajā brīvo enerģiju skalā  $G_{\text{AlbertyH}_2\text{O}_2}=279,285 \text{ kJ/mol}$  atrodas starp

saturu molā  $G_{\text{H}_2\text{O}_2aq}=254,61 \text{ kJ/mol}$ , [19] un  $G_{\text{H}_2\text{O}_2aq}=340,25 \text{ kJ/mol}$  [8]:

$G_{\text{H}_2\text{O}_2aq}=\Delta G_{\text{H}_2\text{O}_2\text{CRC}}+(G_{\text{O}_2\text{gas}}+G_{\text{H}_2\text{gas}})=-134,03+(303+85,64+0)=254,61 \text{ kJ/mol}$ ; [19]

$G_{\text{H}_2\text{O}_2aq}=\Delta G_{\text{H}_2\text{O}_2\text{Alberty}}+(G_{\text{O}_2\text{gas}}+G_{\text{H}_2\text{gas}})=-48,39+(303+85,64+0)=340,25 \text{ kJ/mol}$ ; [8] 41.,54. lpp. [1,8,20]



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



Sēra / H<sub>2</sub>S<sub>aq</sub> red-oks sistēmas. H<sub>3</sub>O<sup>+</sup> un [H<sub>2</sub>O]=55,3 M uzskaitē absolūtās brīvās enerģijas un potenciālu skalai.

Viela	$\Delta H^{\circ}_H$ kJ/mol	$\Delta S^{\circ}_H$ J/mol/K	$\Delta G^{\circ}_H$ kJ/mol
H <sub>2</sub> S <sub>gas</sub>	formation	-81,96	<b>7,1636</b>
H <sub>2</sub> S <sub>gas</sub>	Solubility	promote	<b>38,1196</b>
H <sub>2</sub> S <sub>gas</sub>		-20,6	-81,96
H <sub>2</sub> S <sub>aq</sub>		-38,6	-76,167
H <sub>2</sub> S <sub>aq</sub>		<b>-22,9596</b>	<b>53,3896</b>
H <sub>2</sub> S <sub>aq</sub>	S+2(Pt)H=	H <sub>2</sub> S <sub>aq</sub>	<b>84,343</b>
HS <sup>-</sup>		-16,3	-36,276
HS <sup>-</sup>	E <sup>o</sup> <sub>S<sub>2</sub>/S<sup>2-</sup></sub>	<b>-0,8517V</b>	<b>90,5336</b>
HS <sup>-</sup>	pK <sub>a1</sub> =7.05	favored	<b>81,138</b>
HS <sup>-</sup>	pK <sub>a2</sub> =19	-	<b>92,65</b>
S <sub>rhombic</sub>	formation	gas-81,96	<b>3,5436</b>
S <sub>rhombic</sub>	E <sup>o</sup> <sub>S<sub>2</sub>/H<sub>2</sub>S<sub>aq</sub></sub>	<b>-0,025735 V</b>	<b>3,5436</b>
S <sup>2-</sup>	E <sup>o</sup> <sub>S<sub>2</sub>/S<sup>2-</sup></sub>	<b>-0,79853V</b>	<b>157,63</b>

G<sub>H2gas</sub>=**85,6** kJ/mol; G<sub>H2Saq</sub>=**53,3896** kJ/mol; G<sub>Srhombic</sub>=**3,5436** kJ/mol;  
 favored G<sub>H2Sgas</sub>=ΔG<sup>o</sup><sub>H2Sgas</sub>+(G<sub>Srhombic</sub>+G<sub>H2</sub>)=**7,1636** kJ/mol;  
 G<sub>H2Sgas</sub>=G<sub>H2Saq</sub>-(ΔG<sub>eq</sub>+G<sub>H2O</sub>)=**53,3896**-(**15,27**+0)=**38,1196** kJ/mol;  
 CRC [1] ΔG<sub>H2Sgas</sub>=ΔH<sub>H</sub>-T\*ΔS<sub>H</sub>=-81,96 kJ/mol;  
 CRC [1] ΔG<sub>HS</sub>=ΔH<sub>H</sub>-T\*ΔS<sub>H</sub>=-76,167 kJ/mol;  
 2006, Massachusetts Technology Inst. pH=7,36 Alberty [8]  
 G<sub>H2Saq</sub>=ΔG<sub>HessH2S</sub>+(2G<sub>H(Pt)</sub>+G<sub>Srhombic</sub>)=**84,343** kJ/mol;  
 CRC [1] ΔG<sub>HS</sub>=ΔH<sub>H</sub>-T\*ΔS<sub>H</sub>=-16,3-298,15\*0,067=-36,276 kJ/mol;  
 G<sub>HS-<sub>aq</sub></sub>=G<sub>Srhombic</sub>+2G<sub>H2O</sub>-(ΔG<sub>eqHS-<sub>aq</sub></sub>+G<sub>OH</sub>)=**90,5336** kJ/mol;  
 favored G<sub>HS</sub>=ΔG<sub>eq</sub>-G<sub>H3O</sub>+(G<sub>H2S</sub>+G<sub>H2O</sub>)=**81,138** kJ/mol;  
 G<sub>HS</sub>=G<sub>S2</sub>+G<sub>H3O</sub>-(ΔG<sub>eq</sub>+G<sub>H2O</sub>)=**92,65** kJ/mol;  
 G<sub>Srhombic</sub>=G<sub>H2Sgas</sub>-(ΔG<sub>Hess\_H2Sgas</sub>+G<sub>H2</sub>)=**3,5436** kJ/mol;  
 favored G<sub>Srhombic</sub>=ΔG<sub>eqH2Saq</sub>-2G<sub>H3O</sub>+(G<sub>H2Saq</sub>+2G<sub>H2O</sub>)=**3,544** kJ/mol;  
 G<sub>S2-<sub>aq</sub></sub>=G<sub>Srhombic</sub>+G<sub>H2O</sub>-(ΔG<sub>eqS2-<sub>aq</sub></sub>)=**157,63** kJ/mol;

Veidošanās no elementiem S<sub>rhombic</sub>+H<sub>2</sub>gas=H<sub>2</sub>S<sub>gas</sub> uzrāda enerģijas saturu G<sub>H2Sgas</sub>=**7,1636** kJ/mol;

Enerģijas saturs ir G<sub>H2Sgas</sub>=ΔG<sup>o</sup><sub>H2Sgas</sub>+(G<sub>Srhombic</sub>+G<sub>H2</sub>)=-81,98+(**3,5436**+**85,6**)=**7,1636** kJ/mol. [1,8]

Enerģijas saturs ir G<sub>Srhombic</sub>=G<sub>H2Sgas</sub>-(ΔG<sup>o</sup><sub>H2Sgas</sub>+G<sub>H2</sub>)=**7,1636**-(-81,98+**85,6**)=**3,5436** kJ/mol. [1,8]

Šķīdības H<sub>2</sub>S<sub>gas</sub>+H<sub>2</sub>O=H<sub>2</sub>S<sub>aq</sub> 3,98 g/L 20° C [30] M<sub>H2S</sub>=34,08 g/mol produkts K<sub>sp</sub>=[H<sub>2</sub>S<sub>aq</sub>]=3,98/34,08=0,11678 M līdzsvara konstante ir K<sub>eq</sub>=K<sub>sp</sub>/[H<sub>2</sub>O]=0,116784/55,3=0,0021118 ar endoerģisku brīvās enerģijas izmaiņu pozitīvu ΔG<sub>eq</sub>=-R•T•ln(K<sub>eq</sub>)=-8,3144\*298,15\*ln(0,0021118)=G<sub>H2Saq</sub>-(G<sub>H2Sgas</sub>+G<sub>H2O</sub>)=**15,27** kJ/mol.

Brīvās enerģijas saturs molā sērūdeņraža ir G<sub>H2Sgas</sub>=G<sub>H2Saq</sub>-(ΔG<sub>eq</sub>+G<sub>H2O</sub>)=**53,3896**-(**15,27**+0)=**38,1196** kJ/mol.

S<sup>2-</sup>=S<sub>rhombic</sub>+H<sub>2</sub>O+2e<sup>-</sup>; Klasiskais standarta potenciāls E<sup>o</sup><sub>klasiskais</sub>=-0,4763 V [1], plus ūdens uzskaitē -0,0591/2\*log([H<sub>2</sub>O]<sup>1</sup>)=-0,0515 un saistītā summa ΔE<sup>o</sup>=+0,10166-0,37239 izteiksmē absolūtais potenciāls ir

E<sup>o</sup><sub>S<sub>2</sub>/S<sup>2-</sup></sub>=E<sup>o</sup><sub>klasiskais</sub>-0,0591/2\*log([H<sub>2</sub>O]<sup>1</sup>)+ΔE<sup>o</sup>=-0,4763-0,0515+0,10166-0,37239=**-0,79853 V**;

ΔG<sub>eqS2</sub>=E<sup>o</sup><sub>S<sub>2</sub>/S<sup>2-</sup></sub>•Fn=**-0,79853**\*96485\*2=**-154,09** kJ/mol . G<sub>Srhombic</sub>=**3,5436** kJ/mol;

ΔG<sub>eqS2-<sub>aq</sub></sub>=G<sub>Srhombic</sub>+G<sub>H2O</sub>-(G<sub>S2-<sub>aq</sub></sub>)=**3,5436**+0-(**157,63**)=**-154,09** kJ/mol;

G<sub>S2-<sub>aq</sub></sub>=G<sub>Srhombic</sub>+G<sub>H2O</sub>-(ΔG<sub>eqS2-<sub>aq</sub></sub>)=**3,5436**+0-(**-154,09**)=**157,63** kJ/mol;

HS<sup>-</sup>+OH<sup>-</sup>=S<sub>rhombic</sub>+2H<sub>2</sub>O+2e<sup>-</sup>; Klasiskais standarta potenciāls E<sup>o</sup><sub>klasiskais</sub>=-0,478 V [1], plus ūdens uzskaitē -0,0591/2\*log([H<sub>2</sub>O]<sup>2</sup>)=-0,103 un saistītā summa ΔE<sup>o</sup>=+0,10166-0,37239 izteiksmē absolūtais potenciāls ir

E<sup>o</sup><sub>S<sub>2</sub>/HS<sup>-</sup></sub>=E<sup>o</sup><sub>klasiskais</sub>-0,0591/2\*log([H<sub>2</sub>O]<sup>2</sup>)+ΔE<sup>o</sup>=-0,478-0,103+0,10166-0,37239=**-0,8517 V**;

ΔG<sub>eqHS</sub>=E<sub>HS</sub>•Fn=**-0,8517**\*96485\*2=**-164,35** kJ/mol .

ΔG<sub>eqHS-<sub>aq</sub></sub>=G<sub>Srhombic</sub>+2G<sub>H2O</sub>-(G<sub>HS-<sub>aq</sub></sub>+G<sub>OH</sub>)=**3,5436**+2\*0-(**90,5336**+**77,36**)=**-164,35** kJ/mol;

G<sub>HS-<sub>aq</sub></sub>=G<sub>Srhombic</sub>+2G<sub>H2O</sub>-(ΔG<sub>eqHS-<sub>aq</sub></sub>+G<sub>OH</sub>)=**3,5436**+2\*0-(**-164,35**+**77,36**)=**90,5336** kJ/mol;

H<sub>2</sub>S<sub>aq</sub>+2H<sub>2</sub>O=S<sub>rhombic</sub>+2H<sub>3</sub>O<sup>+</sup>+2e<sup>-</sup>; Klasiskais standarta potenciāls E<sup>o</sup><sub>klasiskais</sub>=0,142 V [1], plus ūdens uzskaitē -0,0591/2\*log(1/[H<sub>2</sub>O]<sup>2</sup>)=0,103 un saistītā summa ΔE<sup>o</sup>=+0,10166-0,37239 izteiksmē absolūtais potenciāls ir

E<sup>o</sup><sub>S<sub>2</sub>/H<sub>2</sub>S</sub>=E<sup>o</sup><sub>klasiskais</sub>-0,0591/2\*log(1/[H<sub>2</sub>O]<sup>2</sup>)+ΔE<sup>o</sup>=0,142+0,103+0,10166-0,37239=**-0,025735 V**;

ΔG<sub>eqH2S</sub>=E<sup>o</sup><sub>H2S</sub>•Fn=**-0,025735**\*96485\*2=**-4,966** kJ/mol .

ΔG<sub>eqH2Saq</sub>=G<sub>Srhombic</sub>+2G<sub>H3O</sub>-(G<sub>H2Saq</sub>+2G<sub>H2O</sub>)=**-85,64**+2\***22,44**-(**53,3896**+2\*0)=-**4,966** kJ/mol;

G<sub>Srhombic</sub>=ΔG<sub>eqH2Saq</sub>-2G<sub>H3O</sub>+(G<sub>H2Saq</sub>+2G<sub>H2O</sub>)=**-4,966**-2\***22,44**+(**53,3896**+2\*0)=-**4,966** kJ/mol; favored

pK<sub>a</sub>=7,0 Wikipedia; [1] pK<sub>a1</sub>=7,05; pK<sub>a2</sub>=19

pK<sub>a1</sub>=7,05 H<sub>2</sub>S+H<sub>2</sub>O=HS<sup>-</sup>+H<sub>3</sub>O<sup>+</sup>; K<sub>eq1</sub>=K<sub>a1</sub>/[H<sub>2</sub>O]=10<sup>-(7,05)</sup>/55,3= 0,000000001612;

ΔG<sub>eq</sub>=-R•T•ln(K<sub>eq</sub>)=-8,3144\*298,15\*ln(0,000000001612)= G<sub>HS</sub>+G<sub>H3O</sub>-(G<sub>H2S</sub>+G<sub>H2O</sub>)=**50,188** kJ/mol;

ΔG<sub>eq</sub>=G<sub>HS</sub>+G<sub>H3O</sub>-(G<sub>H2S</sub>+G<sub>H2O</sub>)=**81,138**+**22,44**-(**53,3896**+0)=-**50,188** kJ/mol ;

G<sub>HS</sub>=ΔG<sub>eq</sub>-G<sub>H3O</sub>+(G<sub>H2S</sub>+G<sub>H2O</sub>)=**50,188**-**22,44**+(**53,3896**+0)=-**81,138** kJ/mol ;

pK<sub>a2</sub>=19 HS<sup>-</sup>+H<sub>2</sub>O=S<sup>2-</sup>+H<sub>3</sub>O<sup>+</sup>; K<sub>eq1</sub>=K<sub>a1</sub>/[H<sub>2</sub>O]=10<sup>-(19)</sup>/55,3=10<sup>-(20,74)</sup>;

ΔG<sub>eq</sub>=-R•T•ln(K<sub>eq</sub>)=-8,3144\*298,15\*ln(10<sup>-(20,74)</sup>)=G<sub>S2</sub>+G<sub>H3O</sub>-(G<sub>HS</sub>+G<sub>H2O</sub>)=**118,38** kJ/mol;

ΔG<sub>eq</sub>=G<sub>S2</sub>+G<sub>H3O</sub>-(G<sub>HS</sub>+G<sub>H2O</sub>)=**188,59**+**22,44**-(**92,65**+0)=-**118,38** kJ/mol ;

G<sub>HS</sub>=G<sub>S2</sub>+G<sub>H3O</sub>-(ΔG<sub>eq</sub>+G<sub>H2O</sub>)=**188,59**+**22,44**-(**118,38**+0)=-**92,65** kJ/mol ;

Sēra reducēšana inversais potenciāls: S<sub>rhombic</sub>+2H<sub>3</sub>O<sup>+</sup>+2e<sup>-</sup>=H<sub>2</sub>S<sub>aq</sub>+2H<sub>2</sub>O; -E<sup>o</sup><sub>S</sub>=**0,025735 V**;

2(Pt)H+2H<sub>2</sub>O=2H<sub>3</sub>O<sup>+</sup>+2e<sup>-</sup>; E<sup>o</sup><sub>H</sub>=**-0,27073 V**; S<sub>rhombic</sub>+2(Pt)H=H<sub>2</sub>S<sub>aq</sub>;

ΔG<sub>eq</sub>=(E<sup>o</sup><sub>H</sub>-E<sup>o</sup><sub>S</sub>)•F•1•2=(**-0,27073**+**0,025735**)\*96485\*2=-**0,244995**\*96485\*2=-**47,277** kJ/mol;

G<sub>H2Saq</sub>=ΔG<sub>HessH2S</sub>+(2G<sub>H(Pt)</sub>+G<sub>Srhombic</sub>)=-**47,277**+(2\***48,56**+**34,5**)=**84,343** kJ/mol . [2. lapas puse.](#)

Albertija [8] un CRC [1] dati:  $G_{H2gas}=85,6$  kJ/mol,  $G_{H2saq}=53,3896$  kJ/mol [8] un  $\Delta G^{\circ}H_2O=-237,191$  kJ/mol,  $\Delta G^{\circ}H_2S_{gas}=-81,98$  kJ/mol [1] ļauj aprēķināt vielu absolūtās vērtības brīvās enerģijas saturam  $G_{Srombiskis}=3,5436$  kJ/mol,  $G_{O2gas}=303$  kJ/mol utt. 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 sērskābei un sulfātiem:

$S_{rombiskis}+2O_{2gas}+H_{2gas}=H_2SO_4$ ;  $\Delta G^{\circ}H_2SO_4Form=G_{H_2SO_4}-(G_{Srombiskis}+2G_{O_2}+G_{H_2gas})=-690,0$  kJ/mol; [1] Saturs molā sērskābes ir  $G_{H_2SO_4}=\Delta G^{\circ}H_2SO_4Form+(G_{Srombiskis}+2G_{O_2}+G_{H_2gas})=-690,0+(3,5436+2*303+85,6)=5,1436$  kJ/mol;

$S_{rombiskis}+2O_{2gas}+H_{2gas}/2=HSO_4^-$ ;  $\Delta G^{\circ}HSO_4Form=G_{HSO_4}-(G_{Srombiskis}+2G_{O_2}+0,5G_{H_2gas})=-755,9$  kJ/mol. Saturs molā  $HSO_4^-$  ir  $G_{HSO_4}=\Delta G^{\circ}HSO_4Form+(G_{Srombiskis}+2G_{O_2}+0,5G_{H_2gas})=-755,9+(3,5436+2*303+85,6/2)=-103,56$  kJ/mol.

$S_{rombiskis}+2O_{2gas}=SO_4^{2-}$ ;  $\Delta G^{\circ}SO_4Form=G_{SO_4}-(G_{Srombiskis}+2G_{O_2})=-747,75$  kJ/mol. Saturs molā  $SO_4^{2-}$  ir  $G_{SO_4}=\Delta G^{\circ}SO_4Form+(G_{Srombiskis}+2G_{O_2})=-747,75+(3,5436+2*303)=-138,2$  kJ/mol.

Protolīzes līdzsvaru  $H_2SO_4+H_2O=HSO_4^-+H_3O^+$  molu daļās aprēķina  $K_{eq1}=K_{a1}/[H_2O]=10^{-(2,8)}/55,3=11,41$  dalot skābes konstanti  $K_{a1}$  ( $pK_{a1}=-2,8$ ) ar ūdeni  $[H_2O]=55,3$  M. Brīvās enerģijas izmaiņa ir

$\Delta G_{eqH_2SO_4}=-R \cdot T \cdot \ln(K_{eq1})=-8,3144 \cdot 298,15 \cdot \ln(11,41)=G_{HSO_4}+G_{H_3O}-(G_{H_2SO_4}+G_{H_2O})=-6,035$  kJ/mol no Hesa likuma brīvās enerģijas izteiksmes  $\Delta G_{eqH_2SO_4}=G_{HSO_4}+G_{H_3O}-(G_{H_2SO_4}+G_{H_2O})=G_{HSO_4}+22,44-(5,1436+0)=-6,035$  kJ/mol saturs  $HSO_4^-$  anjona molam ir  $G_{HSO_4}=\Delta G_{eqH_2SO_4}-G_{H_3O}+(G_{H_2SO_4}+G_{H_2O})=-6,035-22,44+(5,1436+0)=-23,33$  kJ/mol.

Protolīzes līdzsvara  $HSO_4^-+H_2O=SO_4^{2-}+H_3O^+$   $pK_{a2}=1,99$   $K_{eq2}=K_{a2}/[H_2O]=10^{-(1,99)}/55,3=0,0001850$  brīvā enerģija ir  $\Delta G_{eqHSO_4}=-R \cdot T \cdot \ln(K_{eq2})=-8,3144 \cdot 298,15 \cdot \ln(0,0001850)=G_{SO_4^{2-}}+G_{H_3O}-(G_{HSO_4}+G_{H_2O})=21,307$  kJ/mol.

Hesa brīvās enerģijas izteiksmē  $\Delta G_{eqHSO_4}=G_{SO_4^{2-}}+G_{H_3O}-(G_{HSO_4}+G_{H_2O})=G_{SO_4^{2-}}+22,44-(-23,33+0)=21,307$  kJ/mol enerģija  $SO_4^{2-}$  anjona molam ir  $G_{SO_4^{2-}}=\Delta G_{eqHSO_4}-G_{H_3O}+(G_{HSO_4}+G_{H_2O})=21,307-22,44+(-23,33+0)=-24,46$  kJ/mol.

Veidošanās no brīvajiem elementiem  $S_{rombiskis}+1,5O_{2gas}+H_{2gas}=H_2SO_3aq$ ; un šķīdība  $SO_2^{gas}+H_2O=H_2SO_3aq$ .  $\Delta G^{\circ}H_2SO_3Form=G_{H_2SO_3}-(G_{Srombiskis}+1,5\Delta G_{O_2}+G_{H_2gas})=-56,94-(3,5436+1,5*303+85,6)=-600,58$  kJ/mol;

$G_{HSO_3}=\Delta G^{\circ}HSO_3Form+(G_{Srombiskis}+1,5\Delta G_{O_2}+G_{H_2gas}/2)=-486,5+(3,5436+1,5*303+85,6/2)=-74,84$  kJ/mol;

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

Protolīzes līdzsvaru molu daļās  $K_{eq}=K_a/[H_2O]$  aprēķina dalot skābes konstanti ar ūdeni  $[H_2O]=55,3$  M.

$H_2SO_3+H_2O=HSO_3^-+H_3O^+$ ;  $pK_{a1}=1,85$ ;  $K_{eq1}=K_{a1}/[H_2O]=10^{-(1,85)}/55,3=0,0002554$  brīvās enerģijas izmaiņa ir  $\Delta G_{eqH_2SO_3}=-R \cdot T \cdot \ln(K_{eq1})=-8,3144 \cdot 298,15 \cdot \ln(0,0002554)=G_{HSO_3}+G_{H_3O}-(G_{H_2SO_3}+G_{H_2O})=20,5075$  kJ/mol;

$G_{HSO_3}=\Delta G_{eqH_2SO_3}-G_{H_3O}+(G_{H_2SO_3}+G_{H_2O})=20,5075-22,44+(-56,93796+0)=-58,87$  kJ/mol;  $pH=1,85$

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

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

$G_{SO_3^{2-}}=\Delta G_{eqHSO_3}+G_{H_3O}-(G_{HSO_3}+G_{H_2O})=51,1-22,44+(-58,87+0)=-30,21$  kJ/mol;  $pH=7,21$

$H_2SO_3+4H_2O=HSO_4^-+3H_3O^++2e^-$  Klasiskais standarta potenciāls  $E^{\circ}_{klasiskais}=0,172$  V [1], plus ūdens uzskaitē  $-0,0591/2 \cdot \log(1/[H_2O]^4)=0,206$  un saistītā summa  $\Delta E^{\circ}=+0,10166-0,37239$  izteiksmē absolūtais potenciāls ir  $E^{\circ}_{H_2SO_3}=E^{\circ}_{klasiskais}-0,0591/2 \cdot \log(1/[H_2O]^4)+\Delta E^{\circ}=0,172+0,206+0,10166-0,37239=0,10726$  V;

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

$\Delta G_{eqH_2SO_3}=E^{\circ}_{HSO_3} \cdot F \cdot 2=0,10726 \cdot 96485 \cdot 2=20,69796$  kJ/mol;

$\Delta G_{eqH_2SO_3}=G_{HSO_4}+3G_{H_3O}-(G_{H_2SO_3}+4G_{H_2O})=-103,56+3*22,44-(-56,93796+4*0)=20,69796$  kJ/mol ;

$G_{H_2SO_3}=G_{HSO_4}+3G_{H_3O}-(\Delta G_{eqH_2SO_3}+4G_{H_2O})=-103,56+3*22,44-(20,69796+4*0)=-56,94$  kJ/mol ;

$G_{HSO_4}=\Delta G_{eqH_2SO_3}-3G_{H_3O}+(G_{H_2SO_3}+4G_{H_2O})=20,69796-3*22,44+(-56,93796+4*0)=-103,56$  kJ/mol ;

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

$SO_2^{gas}+H_2O=H_2SO_3aq$ ;  $K_{eq}=[H_2SO_3]/[SO_2^{gas}]/[H_2O]=1,46724/1/51,64=0,028413$ , 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 sērskābes  $M_{H_2SO_3}=82,075$  g/mol ar blīvumu 1,05 g/mL  $m_{solution}=1050$  g/L un  $m_{H_2SO_3}=[SO_2]*M_{H_2SO_3}=1,46724$  M\*82,075 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

izmaiņa ir  $\Delta G_{eqH_2SO_3}=-R \cdot T \cdot \ln(K_{eq})=-8,3144 \cdot 298,15 \cdot \ln(0,028413)=G_{H_2SO_3}-(G_{SO_2}+G_{H_2O})=8,82727$  kJ/mol;

$\Delta G_{eqH_2SO_3}=G_{H_2SO_3}-(G_{SO_2}+G_{H_2O})=-72,9075-(-81,73477+0)=8,82727$  kJ/mol;

$G_{SO_2}=G_{H_2SO_3}-(\Delta G_{eqH_2SO_3}+G_{H_2O})=-72,9075-(8,82727+0)=-81,73477$  kJ/mol ;  $pH < 2$  [1]

$G_{SO_2}=G_{H_2SO_3}-(\Delta G_{eqH_2SO_3}+G_{H_2O})=-56,93796-(8,82727+0)=-65,76523$  kJ/mol ;  $2 < pH < 7$  [17]

$\Delta G_{eqH_2SO_3}=G_{H_2SO_3}-(G_{SO_2}+G_{H_2O})=-56,93796-(-65,76523+0)=8,82727$  kJ/mol;

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

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

$HSO_3^- + 4H_2O = SO_4^{2-} + 3H_3O^+ + 2e^-$ ; Klasiskais standarta potenciāls  $E^{\circ}_{\text{klasiskais}} = 0,172 \text{ V}$  [17], plus ūdens uzskaitē  $-0,0591/2 * \log(1/[H_2O]^4) = 0,206$  un saistītā summa  $\Delta E^{\circ} = +0,10166 - 0,37239$  izteiksmē absolūtais potenciāls ir

$$E^{\circ}_{HSO_3^-} = E^{\circ} - 0,0591/2 * \log(1/[H_2O]^4) + \Delta E^{\circ} = 0,172 + 0,206 + 0,10166 - 0,37239 = 0,10726 \text{ V}$$

$$2 = <pH < 7 \quad E_{HSO_3^-} = E^{\circ}_{HSO_3^-} + 0,0591/2 * \log \frac{[SO_4^{2-}] \cdot [H_3O^+]^3}{[HSO_3^-] \cdot [H_2O]^4} = 0,10726 \text{ V} + 0,0591/2 * \log \frac{[SO_4^{2-}] \cdot [H_3O^+]^3}{[HSO_3^-] \cdot [H_2O]^4}$$

$$\Delta G_{\text{eq}SO_4} = E^{\circ}_{HSO_4^-} \cdot F \cdot 2 = 0,10726 * 96485 * 2 = 20,69796 \text{ kJ/mol}$$

$$\Delta G_{\text{eq}SO_4} = G_{SO_4} + 3G_{H_3O} - (G_{HSO_3} + 4G_{H_2O}) = -24,46 + 3 * 22,44 - (22,16 + 4 * 0) = 20,7 \text{ kJ/mol}$$

$$G_{HSO_3} = G_{SO_4} + 3G_{H_3O} - (\Delta G_{\text{eq}SO_4} + 4G_{H_2O}) = -24,46 + 3 * 22,44 - (20,69796 + 4 * 0) = 22,16 \text{ kJ/mol}$$

$$G_{SO_4} = \Delta G_{\text{eq}SO_4} - 3G_{H_3O} + (G_{HSO_3} + 4G_{H_2O}) = 20,69796 - 3 * 22,44 + (22,16 + 4 * 0) = -24,46 \text{ kJ/mol}$$

Viela	$\Delta H^{\circ}_H, \text{kJ/mol}$	$\Delta S^{\circ}_H, \text{J/mol/K}$	$\Delta G^{\circ}_H, \text{kJ/mol}$	
H <sub>2</sub> SO <sub>4</sub>	-814,0	156,9	-690,0	CRC [1];
H <sub>2</sub> SO <sub>4</sub>	favored	formation	<b>5,1436</b>	$G_{H_2SO_4} = \Delta G^{\circ} H_2SO_4 + G_{S_{\text{rombisks}}} + 2\Delta G_{O_2} + G_{H_2\text{gas}} + G_{H_2O} = 5,1436 \text{ kJ/mol}$ ;
HSO <sub>4</sub> <sup>-</sup>	-887,3	131,8	-755,9	CRC [1]
HSO <sub>4</sub> <sup>-</sup>	-	pK <sub>a1</sub> = -2,8	<b>-23,33</b>	$G_{HSO_4^-} = \Delta G_{\text{eq}H_2SO_4} - G_{H_3O} + (G_{H_2SO_4} + G_{H_2O}) = -23,33 \text{ kJ/mol}$ ;
HSO <sub>4</sub> <sup>-</sup>	pH < 2	formation	<b>-103,56</b>	$G_{HSO_4^-} = \Delta G^{\circ} HSO_4^- + G_{S_{\text{rombisks}}} + 2\Delta G_{O_2} + G_{H_2\text{gas}}/2 = -103,56 \text{ kJ/mol}$ ;
SO <sub>4</sub> <sup>2-</sup>	<b>-907,62</b>	<b>-536,2</b>	<b>-747,75</b>	BioTherm2006 pH=7.36 [8] $\Delta G_{SO_4^{2-}} = \Delta H - T * \Delta S = -747,75 \text{ kJ/mol}$ ;
SO <sub>4</sub> <sup>2-</sup>	-	formation	<b>-138,2</b>	$G_{SO_4} = \Delta G^{\circ} SO_4\text{Form} + G_{S_{\text{rombisks}}} + 2\Delta G_{O_2} = -747,75 - 85,64 + 2 * 303 = -138,2 \text{ kJ/mol}$ ;
SO <sub>4</sub> <sup>2-</sup>	2 = <pH < 7	pK <sub>a2</sub> = 1,99	<b>-24,46</b>	$G_{SO_4^{2-}} = \Delta G_{\text{eq}HSO_4^-} - G_{H_3O} + (G_{HSO_4^-} + G_{H_2O}) = -24,46 \text{ kJ/mol}$ ;
SO <sub>4</sub> <sup>2-</sup>	E <sup>o</sup> <sub>HSO<sub>3</sub><sup>-</sup></sub> =	<b>0,10726</b>	<b>-24,46</b>	$G_{SO_4} = \Delta G_{\text{eq}SO_4} - 3G_{H_3O} + (G_{HSO_3} + 4G_{H_2O}) = -24,46 \text{ kJ/mol}$ ; 2 = <pH < 7
SO <sub>4</sub> <sup>2-</sup>	E <sup>o</sup> <sub>SO<sub>3</sub><sup>2-</sup></sub> =	<b>-1,2522</b>	<b>-213,4</b>	$G_{SO_4^{2-}} = \Delta G_{\text{eq}SO_3^{2-} - OH} - G_{H_2O} + (G_{SO_3^{2-}} + 2G_{OH}) = -213,4 \text{ kJ/mol}$ ;
SO <sub>4</sub> <sup>2-</sup>	-909,3	20,1	-744,5	CRC [1]
SO <sub>2</sub> <sup>gas</sup>	-296,81	248,223	-370,82	[1] $\Delta G_H = \Delta H_H - T * \Delta S_H = -296,81 - 298,15 * 0,248223 = -370,82 \text{ kJ/mol}$ ;
SO <sub>2</sub> <sup>gas</sup>		formation	<b>-153,46</b>	$G_{SO_2} = \Delta G^{\circ} SO_2\text{Form} + (G_{S_{\text{rombisks}}} + G_{O_2}) = -153,46 \text{ kJ/mol}$ ;
SO <sub>2</sub> <sup>gas</sup>	$\Delta G_{K_{sp}} = 8,827$	pH < 2	<b>-81,735</b>	$\Delta G_{SO_2} = G_{H_2SO_3} - (\Delta G_{\text{eq}H_2SO_3} + G_{H_2O}) = -72,9075 - (8,82727 + 0) = -81,73477 \text{ kJ/mol}$ ;
SO <sub>2</sub> <sup>gas</sup>	$\Delta G_{K_{sp}} = 8,827$	2 < pH < 7	<b>-65,765</b>	$G_{SO_2} = G_{H_2SO_3} - (\Delta G_{\text{eq}H_2SO_3} + G_{H_2O}) = -65,76523 \text{ kJ/mol}$ ;
H <sub>2</sub> SO <sub>3</sub>	Alberty [8]	pH = 7,36	<b>-600,58</b>	$\Delta G^{\circ} H_2SO_3\text{Form} = G_{H_2SO_3} - (G_{S_{\text{rombisks}}} + 1,5\Delta G_{O_2} + G_{H_2\text{gas}}) = -600,58 \text{ kJ/mol}$ ;
H <sub>2</sub> SO <sub>3</sub>		formation	<b>-72,9075</b>	$G_{H_2SO_3} = \Delta G^{\circ} H_2SO_3\text{Form} + (G_{S_{\text{rombisks}}} + 1,5\Delta G_{O_2} + G_{H_2\text{gas}}) = -72,9075 \text{ kJ/mol}$ ;
H <sub>2</sub> SO <sub>3</sub>	E <sup>o</sup> <sub>H<sub>2</sub>SO<sub>3</sub><sup>-</sup></sub> =	<b>0,10726</b>	<b>-56,93796</b>	$G_{H_2SO_3} = G_{HSO_4^-} + 3G_{H_3O} - (\Delta G_{\text{eq}H_2SO_3} + 4G_{H_2O}) = -56,938 \text{ kJ/mol}$ ; pH < 2
HSO <sub>3</sub> <sup>-</sup>	E <sup>o</sup> <sub>HSO<sub>3</sub><sup>-</sup></sub> =	<b>0,10726</b>	<b>22,16</b>	$G_{HSO_3^-} = G_{SO_4} + 3G_{H_3O} - (\Delta G_{\text{eq}SO_4} + 4G_{H_2O}) = 22,16 \text{ kJ/mol}$ ;
HSO <sub>3</sub> <sup>-</sup>		formation	<b>-74,84</b>	$G_{HSO_3^-} = \Delta G^{\circ} HSO_3^- + G_{S_{\text{rombisks}}} + 1,5\Delta G_{O_2} + G_{H_2\text{gas}}/2 = -74,84 \text{ kJ/mol}$ ;
HSO <sub>3</sub> <sup>-</sup>		pK <sub>a1</sub> = 1,85	<b>-58,87</b>	$G_{HSO_3^-} = \Delta G_{\text{eq}H_2SO_3} - G_{H_3O} + (G_{H_2SO_3} + G_{H_2O}) = -58,87 \text{ kJ/mol}$ ;
HSO <sub>3</sub> <sup>-</sup>	-635,5	-29	-486,5	CRC [1]
SO <sub>3</sub> <sup>2-</sup>	<b>-632,19</b>	<b>-474,05</b>	<b>-490,38</b>	BioTherm2006 [8] $\Delta G_{H_2SO_3^{2-}} = \Delta H_H - T * \Delta S_H = -632,1888 - 298,15 * -0,47405 = -490,85 \text{ kJ/mol}$ ;
SO <sub>3</sub> <sup>2-</sup>	-	formation	<b>-121,52</b>	$G_{SO_3} = \Delta G_{\text{Form}} = \Delta G^{\circ} SO_3 + G_{S_{\text{rombisks}}} + 1,5\Delta G_{O_2} = -121,52 \text{ kJ/mol}$ ;
SO <sub>3</sub> <sup>2-</sup>		pK <sub>a2</sub> = 7,21	<b>-30,21</b>	$G_{SO_3^{2-}} = \Delta G_{\text{eq}HSO_3^-} + G_{H_3O} - (G_{HSO_3^-} + G_{H_2O}) = -30,21 \text{ kJ/mol}$ ;
SO <sub>3</sub> <sup>2-</sup>	E <sup>o</sup> <sub>SO<sub>3</sub><sup>2-</sup> - OH</sub> =	<b>-1,2522</b>	<b>62,457</b>	$G_{SO_3^{2-}} = G_{SO_4^{2-}} + G_{H_2O} - (\Delta G_{\text{eq}SO_3^{2-} - OH} + 2G_{OH}) = 62,457 \text{ kJ/mol}$ ; pH > 7

$$G_{H_2SO_3} = \Delta G^{\circ} H_2SO_3\text{Form} + (G_{S_{\text{rombisks}}} + 1,5\Delta G_{O_2} + G_{H_2\text{gas}}) = -72,9075 \text{ kJ/mol}$$

$SO_3^{2-} + 2OH^- = SO_4^{2-} + H_2O + 2e^-$ ; pH > 7; Klasiskais standarta potenciāls  $E^{\circ}_{\text{klasiskais}} = -0,93 \text{ V}$  [17], ūdens uzskaitē  $-0,0591/2 * \log([H_2O]) = 0,0515$  un saistītā summa  $\Delta E^{\circ} = +0,10166 - 0,37239$  izteiksmē absolūtais potenciāls ir

$$E^{\circ}_{SO_3^{2-} - OH} = E^{\circ} - 0,0591/2 * \log([H_2O]) + \Delta E^{\circ} = -0,93 + 0,0515 + 0,10166 - 0,37239 = -1,2522 \text{ V}$$

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

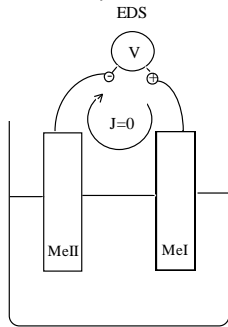
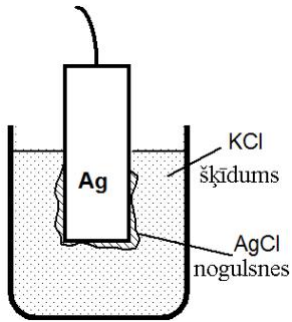
$$\Delta G_{\text{eq}SO_4^{2-} - OH} = E^{\circ}_{SO_3^{2-} - OH} \cdot F \cdot 2 = -1,2522 * 96485 * 2 = -241,637 \text{ kJ/mol}$$

$$\Delta G_{\text{eq}SO_3^{2-} - OH} = G_{SO_4^{2-}} + G_{H_2O} - (G_{SO_3^{2-}} + 2G_{OH}) = 24,46 + 0 - (62,457 + 2 * 77,36) = -241,637 \text{ kJ/mol}$$

$$G_{SO_3^{2-}} = G_{SO_4^{2-}} + G_{H_2O} - (\Delta G_{\text{eq}SO_3^{2-} - OH} + 2G_{OH}) = -24,46 + 0 - (-241,637 + 2 * 77,36) = 62,457 \text{ kJ/mol}$$

$$G_{SO_4^{2-}} = \Delta G_{\text{eq}SO_3^{2-} - OH} - G_{H_2O} + (G_{SO_3^{2-}} + 2G_{OH}) = -241,637 - 0 + (62,457 + 2 * 77,36) = -24,46 \text{ kJ/mol}$$

Metāla nešķīstošā sāls un sāls anjONU šķīdums II-veida elektrods.



$K^+Cl^-$  šķīduma ar nešķīstošās sāls  $AgCl$  pret joniem  $Cl^-$  un sudraba metāla  $Ag$  elektrodu. Elektriskā potenciāla mērījumi voltos ar elektrodu pāri ir Elektro Dzinēja Spēks EDS volti. Starp indikatora elektrodu MeI un MeII salīdzināšanas elektrodu savienotiem noslēgtā elektriskā ķēdē aprēķina MeI indikatora elektroda potenciālu EI kā summu:  $EI=EDS+EII$ . Standarta salīdzināšanas elektrods EII kalpo par konstantu potenciālu ar hlorīda koncentrāciju.

Sudraba I-veida elektroda:  $Ag(s)+H_2O=Ag^++e^-$  absolūtais

potenciāls satur standarta potenciālu  $E^{\circ}_{klasisko}=0,7994$  V [18], logaritmu  $-0,0591/1*\lg(1/55,3^{A1})=-0,103$  un summu  $\Delta E^{\circ}: E_{Ag/Ag^+}=E^{\circ}_{klasisko}-0,0591/1*\lg(1/[H_2O]^1)+\Delta E^{\circ}=0,7994-0,103+0,10166-0,37239=0,6317$  V.

$$\Delta G_{eq\_Ag}=E^{\circ}_{Ag^+}\cdot F\cdot 2=0,6317*96485*1=60,95 \text{ kJ/mol}, \Delta G_{eq\_As}=G_{Ag^+}-(G_{Ag}+G_{H_2O})=77,1-(G_{Ag}+0)=60,95 \text{ kJ/mol};$$

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

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

$$G_{Ag^+}=\Delta G_{eq\_As}+(G_{Ag}+G_{H_2O})=60,95+(42,85+0)=103,8 \text{ kJ/mol}; [8]$$

Veidošanās  $2Ag^++Cl_2=2AgCl(s); 2\Delta G_{eq\_AgCl}=2G_{AgCl}-(2G_{Ag}+G_{Cl_2})=2G_{AgCl}-(2*42,85+394,2)=-155,71 \text{ kJ/mol}; [1]$

$$G_{AgCl}=(2\Delta G_{eq\_AgCl}+(2G_{Ag}+G_{Cl_2}))/2=(2*(-155,71)+(2*42,85+394,2))/2=84,24 \text{ kJ/mol};$$

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

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

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

$$\Delta G_{spAgCl}=G_{Ag^+}+G_{Cl^-}-(G_{AgCl}+2G_{H_2O})=103,8+101,97-(130,211+2*0)=75,559 \text{ kJ/mol};$$

$$G_{AgCl}=G_{Ag^+}+G_{Cl^-}-(\Delta G_{spAgCl}+2G_{H_2O})=103,8+101,97-(75,559+2*0)=130,211 \text{ kJ/mol};$$

$[Cl^-]=0,1$  M= $[K^+Cl^-]$  šķīduma  $Ag(s)+H_2O=Ag^++e^-; Ag(s)+H_2O+Cl^-=AgCl(s)+2H_2O+e^-$ ; summārajā reakcijā.

$Ag_s+Cl^-=AgCl_s+H_2O+e^-$ ; Absolūtā standarta potenciāla aprēķins satur  $E^{\circ}_{klasisko}=0,2223$  V [18], ūdens logaritmu un  $\Delta E^{\circ}: E_{Ag/AgCl}=E^{\circ}_{klasiskais}-0,0591/1*\lg([H_2O]^1)+\Delta E^{\circ}=0,2223-0,103+0,10166-0,37239=-0,1514$  V;

$$\Delta G_{eq\_Ag}=E^{\circ}_{Ag^+}\cdot F\cdot 1=-0,1514*96485*1=-14,61 \text{ kJ/mol};$$

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

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

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

$NH_3gas+H_2O=NH_3aq; Ag+H_2O=Ag^++e^-; Ag+H_2O+2NH_3aq=Ag(NH_3)_2^++2H_2O+e^-$ ; Absolūtais standarta potenciāls

ar standartu  $E^{\circ}_{klasisko}=0,373$  V [17], ūdens  $-0,0591/1*\log([H_2O]^1)=-0,103$  logaritmu un summu  $\Delta E^{\circ}$ :

$$E^{\circ}_{Ag/Ag(NH_3)_2^+}=E^{\circ}_{klasiskais}-0,0591/1*\log([H_2O]^1)+\Delta E^{\circ}=0,373-0,103+0,10166-0,37239=-0,000725$$
 V;

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

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

$2Ag+2OH^-=Ag_2O(s)+H_2O+2e^-$ ; Absolūtā standarta potenciāla aprēķins satur  $E^{\circ}_{klasisko}=0,345$  V [17], ūdens

logaritmu un  $\Delta E^{\circ}: E^{\circ}_{2Ag/Ag_2O}=E^{\circ}_{klasiskais}-0,0591/2*\lg([H_2O]^1)+\Delta E^{\circ}=0,345-0,0515+0,10166-0,37239=0,02277$  V

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

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

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

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

Viela	$\Delta H^{\circ}_H$ kJ/mol	$\Delta S^{\circ}_H$ J/mol/K	$\Delta G^{\circ}_H$ , kJ/mol	jons $G_{Ag^+}=103,8$ kJ/mol virs $G_{Ag}=42,855$ kJ/mol elementa <b>60,945</b> ; [8]
Ag	$E^{\circ}_{Ag/Ag^+}$	<b>-0,6317</b> V	<b>16,15</b>	CRC[1] $G_{Ag}=G_{Ag^+}-(\Delta G_{eq\_Ag}+G_{H_2O})=77,1-(60,95+0)=16,15$ kJ/mol;
Ag	$E^{\circ}_{Ag/Ag^+}$	<b>-0,6317</b> V	<b>42,85</b>	$G_{Ag}=G_{Ag^+}-(\Delta G_{eq\_Ag}+G_{H_2O})=103,8-(60,95+0)=42,85$ kJ/mol; [8]
Ag	$E^{\circ}_{Ag/AgCl}$	<b>-0,1514</b> V	<b>42,855</b>	$G_{Ag}=G_{AgCl}+G_{H_2O}-(\Delta G_{eq\_Ag}+G_{Cl^-})=-155,71+0-(-14,61-183,955)=42,855$ kJ/mol;
Ag+	105,6	72,7	77,1	CRC; [1] jona $G_{Ag^+}=77,1$ kJ/mol elementa nulles $\Delta G^{\circ}_{Ag}=0$ kJ/mol;
Ag+	$E^{\circ}_{Ag}$	<b>0,6317</b> V	<b>103,8</b>	$G_{Ag^+}=\Delta G_{eq\_As}+(G_{Ag}+G_{H_2O})=60,95+(42,855+0)=103,8$ kJ/mol;
AgCl(s)	-127,01	96,25	-155,71	$\Delta G_{AgCl}=\Delta H_H-T\cdot \Delta S_H=-127,01-298,15*0,09625=-155,71$ kJ/mol; [1]
AgCl(s)	formation	-	<b>84,24</b>	$G_{AgCl}=(2\Delta G_{eq\_AgCl}+(2G_{Ag}+G_{Cl_2}))/2=84,24$ kJ/mol;
AgCl(s)	$K_{spAgCl}$	$5,788*10^{-14}$	<b>130,2</b>	$G_{AgCl}=G_{Ag^+}+G_{Cl^-}-(\Delta G_{spAgCl}+2G_{H_2O})=130,2$ kJ/mol;
Cl-	$K_{spHg_2Cl_2}$	$10^{(-23,1)}$	<b>101,97</b>	$G_{Cl^-}=(-G_{Hg_2^{2+}}+\Delta G_{eqHg_2Cl_2}+(G_{Hg_2Cl_2}+3G_{H_2O}))/2=101,97$ kJ/mol;
Ag(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	$E^{\circ}_{Ag(NH_3)_2^+}$	<b>-0,000725</b>	<b>-139,415</b>	$G_{Ag(NH_3)_2^+}=\Delta G_{Ag/Ag(NH_3)_2^+}-G_{H_2O}+(G_{Ag}+2G_{NH_3aq})=-139,415$ kJ/mol;
AgCl	$\Delta G_{spAgCl}$	$K_{spAgCl}$	<b>-155,714</b>	$G_{AgCl}=G_{Ag^+}+G_{Cl^-}-(\Delta G_{spAgCl}+2G_{H_2O})=-155,714$ kJ/mol;
Ag <sub>2</sub> O(s)	-31,1	121,3	-11,2	CRC; [1]
Ag <sub>2</sub> O(s)	$E^{\circ}_{Ag/Ag_2O}$	<b>0,02277</b> V	<b>-64,616</b>	$G_{Ag_2O}=\Delta G_{Ag/Ag_2O}-G_{H_2O}+(2G_{Ag}+2G_{OH})=-64,616$ kJ/mol;

Nernsta potenciāla studijas  $\text{Hg}/\text{Hg}_2^{2+}/\text{Hg}^{2+}$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{Hg}_2\text{SO}_4(\text{s})$ ,  $\text{HgO}$  uzskaitot hidroksoniņu  $\text{H}_3\text{O}^+$  un ūdeni  $\text{H}_2\text{O}$ .

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 <sub>2</sub> O <sub>2</sub>	75,9	35,885
Hg	$E^\circ_{\text{HgCl}_2}$	-0,1059 V	35,8
Hg <sub>2</sub> <sup>2+</sup>	-166,87	66,74	-146,97
Hg <sub>2</sub> <sup>2+</sup>	$E^\circ_{\text{Hg}/\text{Hg}_2^{2+}}$	0,6888 V	204,52
Hg <sup>2+</sup>	-170,21	-36,19	-
Hg <sub>2</sub> SO <sub>4</sub> (s)	-743,1	200,7	-625,8
Hg <sub>2</sub> SO <sub>4</sub> (s)	$K_{\text{AbsoluteHg}_2\text{SO}_4}$	$10^{(-9,673)}$	-598,44
SO <sub>4</sub> <sup>2-</sup>	-907,62	-536,2	-747,75
SO <sub>4</sub> <sup>2-</sup>	$E^\circ_{\text{Hg}_2\text{SO}_4}$	0,2918 V	-726,54
SO <sub>4</sub> <sup>2-</sup>	-909,3	20,1	-744,5
Cl <sub>2</sub>	formation	Hg <sub>2</sub> Cl <sub>2</sub> (s)	394,2
Hg <sub>2</sub> Cl <sub>2</sub> (s)	-265,37	191,6	-210,7
Hg <sub>2</sub> Cl <sub>2</sub> (s)	$E^\circ_{\text{HgCl}_2}$	-0,1059 V	255,1
HgCl <sub>2</sub> (s)	-224,3	146	-178,6
Cl <sup>-</sup>	-167,08	56,6	-183,955
Cl <sup>-</sup>	$K_{\text{AbsoluteHg}_2\text{Cl}_2}$	$10^{(-23,1)}$	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)	$E^\circ_{\text{HgO}}$	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 [1]

CRC [1]

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

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

CRC [1]

$$G_{\text{Cl}_2} = G_{\text{Hg}_2\text{Cl}_2(\text{s})} - (2G_{\text{Hg}} + \Delta G^\circ_{\text{Hg}_2\text{Cl}_2\text{Form}}) = 394,2 \text{ kJ/mol};$$

CRC [1]  $\Delta G^\circ_{\text{Hg}_2\text{Cl}_2\text{Form}} = G_{\text{Hg}_2\text{Cl}_2(\text{s})} - (2G_{\text{Hg}} + G_{\text{Cl}_2}) = -210,7 \text{ kJ/mol};$

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

CRC [1]

$$\Delta G_{\text{Cl}^-} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -167,08 - 298,15 \cdot 0,0566 = -183,955 \text{ kJ/mol}; [1]$$

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

$$\Delta G_{\text{HgO}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -99,79 - 298,15 \cdot 0,07025 = -147,25 \text{ kJ/mol};$$

CRC [1]  $\Delta G_{\text{HgO}} = -58,5 \text{ kJ/mol};$

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

$$G_{\text{HgO}} = \Delta G_{\text{eq}_\text{HgO}} - 2G_{\text{H}_2\text{O}} + (G_{\text{Hg}} + 2G_{\text{OH}^-}) = 147,25 \text{ kJ/mol};$$

$2\text{Hg} + \text{H}_2\text{O} = \text{Hg}_2^{2+} + 2\text{e}^-$ ; Absolūtā potenciāla aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = 0,907 \text{ V}$  [18], ūdens logaritmu un  $\Delta E^\circ$ :  $E^\circ_{2\text{Hg}} = E^\circ_{\text{klasiskais}} - 0,0591 / 2 \cdot \lg(1/[\text{H}_2\text{O}]^1) + \Delta E^\circ = 0,907 + 0,0515 + 0,10166 - 0,37239 = 0,6888 \text{ V};$

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

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

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

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

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

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

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

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

Veidošanās  $2\text{Hg} + \text{Cl}_2 = \text{Hg}_2\text{Cl}_2(\text{s})$ ;  $\Delta G^\circ_{\text{Hg}_2\text{Cl}_2\text{Form}} = G_{\text{Hg}_2\text{Cl}_2(\text{s})} - (2G_{\text{Hg}} + G_{\text{Cl}_2}) = 255,1 - (2 \cdot 35,8 + G_{\text{Cl}_2}) = -210,7 \text{ kJ/mol};$

$$G_{\text{Cl}_2} = G_{\text{Hg}_2\text{Cl}_2(\text{s})} - (2G_{\text{Hg}} + \Delta G^\circ_{\text{Hg}_2\text{Cl}_2\text{Form}}) = 255,1 - (2 \cdot 35,8 - 210,7) = 394,2 \text{ kJ/mol};$$

$2\text{Hg} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^-$ ; Absolūtais aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = 0,2678 \text{ V}$  [18], ūdens logaritmu un  $\Delta E^\circ$ :  $E^\circ_{\text{HgCl}_2} = E^\circ_{\text{klasisko}} - 0,0591 / 2 \cdot \lg([\text{H}_2\text{O}]^2) + \Delta E^\circ = 0,2678 - 0,103 + 0,10166 - 0,37239 = -0,1059 \text{ V};$

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

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

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

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

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

$$K_{\text{AbsoluteHg}_2\text{SO}_4} = K_{\text{spHg}_2\text{SO}_4} / [\text{H}_2\text{O}]^2 = [\text{Hg}_2^{2+}] \cdot [\text{SO}_4^{2-}] / [\text{Hg}_2\text{SO}_4(\text{s})] / [\text{H}_2\text{O}]^2 = 6,5 \cdot 10^{(-7)} / 1 / 55,3^2 = 10^{-9,673};$$

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

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

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

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

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

$2\text{Hg} + \text{SO}_4^{2-} = \text{Hg}_2\text{SO}_4(\text{s}) + \text{H}_2\text{O} + 2\text{e}^-$ ; Absolūtais aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = 0,614 \text{ V}$  [18], ūdens logaritmu un  $\Delta E^\circ$ :  $E^\circ_{\text{HgSO}_4} = E^\circ_{\text{klasisko}} - 0,0591 / 2 \cdot \lg([\text{H}_2\text{O}]^1) + \Delta E^\circ = 0,614 - 0,0515 + 0,10166 - 0,37239 = 0,2918 \text{ V};$

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

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

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

Veidošanās  $2\text{Hg} + \text{O}_2 \text{ aqua} = 2\text{HgO}$ ;  $2\text{G}_{\text{HgO}} = 2\Delta\text{G}_{\text{HgO}} + (2\text{G}_{\text{Hg}} + \text{G}_{\text{O}_2}) = 2 \cdot (-58,5) + (2 \cdot 35,8 + 330) = 2 \cdot 142,3 \text{ kJ/mol}$ ;  
 $\text{Hg} + 2\text{OH}^- = \text{HgO} + \text{H}_2\text{O} + 2\text{e}^-$ , Absolūtais aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = 0,098 \text{ V}$  [17], ūdens  
logaritmu un  $\Delta E^\circ$ :  $E^\circ_{\text{HgO}} = E^\circ - 0,0591/2 \cdot \lg([\text{H}_2\text{O}]^1) + \Delta E^\circ = 0,098 - 0,0515 + 0,10166 - 0,37239 = -0,22423 \text{ V}$ ;

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

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

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

**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  $\text{G}_{\text{H}_2\text{O}_2} = 279,285 \text{ kJ/mol}$ ;

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

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

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

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Substance	$\Delta\text{H}^\circ_{\text{H}}$ , kJ/mol	$\Delta\text{S}^\circ_{\text{H}}$ , J/mol/K	$\Delta\text{G}^\circ_{\text{H}}$ , kJ/mol
Pb	$E^\circ_{\text{Pb} \downarrow \text{Pb}^{2+}} = -0,34523 \text{ V}$	-0,34523 V	62,024
Pb	-	64,8	-
$\text{Pb}^{2+}$	$E^\circ_{\text{PbO}_2 \downarrow \text{Pb}^{2+}} = 1,49326 \text{ V}$	1,49326 V	-4,596
$\text{Pb}^{2+}$	0,92	18,5	-4,596
$\text{PbO}_2 \downarrow$	-277,4	68,6	-217,3
$\text{PbO}_2 \downarrow$	$E^\circ_{\text{PbO}_2 \downarrow \text{Pb}^{2+}} = 1,49326 \text{ V}$	1,49326 V	193,794
$\text{PbO}_2 \downarrow$	formation	-	147,824
Al	-	28,3	-
Al	$E^\circ_{\text{Al}/\text{Al}^{3+}} = -1,8984 \text{ V}$	-1,8984 V	108
$\text{Al}^{3+}$	-538,4	-325	-441,5
$\text{H}_2\text{AlO}_3^-$	$E^\circ_{\text{H}_2\text{AlO}_3^-/\text{Al}} = -2,63506$	-2,63506	-345,29
$\text{NaAlO}_2 \downarrow$	-1133,2	70,4	-

Veidošanās  $\text{Pb} + \text{O}_{2\text{gas}} = \text{PbO}_2(\text{s})$ ;  $\text{G}_{\text{PbO}_2} = \Delta\text{G}_{\text{PbO}_2} + (\text{G}_{\text{Pb}} + \text{G}_{\text{O}_{2\text{gas}}}) = -217,3 + (62,024 + 303,1) = 147,824 \text{ kJ/mol}$ ;

$\text{Pb}^{2+} + 6\text{H}_2\text{O} = \text{PbO}_2(\text{s}) + 4\text{H}_3\text{O}^+ + 2\text{e}^-$ ; Absolūtais aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = 1,455 \text{ V}$  [18], ūdens  
logaritmu un  $\Delta E^\circ$ :  $E^\circ_{\text{PbO}_2} = E^\circ_{\text{klasisko}} - 0,0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^6) + \Delta E^\circ = 1,455 + 0,309 + 0,10166 - 0,37239 = 1,49326 \text{ V}$ ;

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

$\Delta\text{G}_{\text{eqPbO}_2 \downarrow \text{Pb}^{2+}} = \text{G}_{\text{PbO}_2} + 4\text{G}_{\text{H}_3\text{O}^+} - (\text{G}_{\text{Pb}^{2+}} + 6\text{G}_{\text{H}_2\text{O}}) = 193,794 + 4 \cdot 22,44 - (-4,596 + 6 \cdot 0) = 288,15 \text{ kJ/mol}$ ;

$\text{G}_{\text{PbO}_2} = \Delta\text{G}_{\text{eqPbO}_2 \downarrow \text{Pb}^{2+}} - 4\text{G}_{\text{H}_3\text{O}^+} + (\text{G}_{\text{Pb}^{2+}} + 6\text{G}_{\text{H}_2\text{O}}) = 288,15 - 4 \cdot 22,44 + (-4,596 + 6 \cdot 0) = 193,794 \text{ kJ/mol}$ ;

$\text{G}_{\text{Pb}^{2+}} = \text{G}_{\text{PbO}_2} + 4\text{G}_{\text{H}_3\text{O}^+} - (\Delta\text{G}_{\text{eqPbO}_2 \downarrow \text{Pb}^{2+}} + 6\text{G}_{\text{H}_2\text{O}}) = 193,794 + 4 \cdot 22,44 - (288,15 + 6 \cdot 0) = -4,596 \text{ kJ/mol}$ ;

$$E_{\text{PbO}_2 \downarrow \text{Pb}^{2+}} = E^\circ_{\text{PbO}_2 \downarrow \text{Pb}^{2+}} + \frac{0,0591}{2} \cdot \log \frac{[\text{PbO}_2] \cdot [\text{H}_3\text{O}^+]^4}{[\text{Pb}^{2+}] \cdot [\text{H}_2\text{O}]^6} = 1,49326 \text{ V} + \frac{0,0591}{2} \cdot \log \frac{[\text{PbO}_2] \cdot [\text{H}_3\text{O}^+]^4}{[\text{Pb}^{2+}] \cdot [\text{H}_2\text{O}]^6};$$

$\text{Pb} + \text{H}_2\text{O} = \text{Pb}^{2+} + 2\text{e}^-$ ;  $\text{pH} < 7$  Absolūtais aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = -0,126 \text{ V}$  [18], ūdens  
logaritmu un  $\Delta E^\circ$ :  $E^\circ_{\text{Pb}/\text{Pb}^{2+}} = E^\circ_{\text{klasisko}} - 0,0591/2 \cdot \log(1/[\text{H}_2\text{O}]) + \Delta E^\circ = -1,26 + 0,0515 + 0,10166 - 0,37239 = -0,3452 \text{ V}$ ;

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

$\Delta\text{G}_{\text{eqPb} \downarrow \text{Pb}^{2+}} = \text{G}_{\text{Pb}^{2+}} - (\text{G}_{\text{Pb}} + \text{G}_{\text{H}_2\text{O}}) = -4,596 - (62,024 + 0) = -71,59 = -66,62 \text{ kJ/mol}$ ;

$\text{G}_{\text{Pb}} = \text{G}_{\text{Pb}^{2+}} - (\Delta\text{G}_{\text{eqPb} \downarrow \text{Pb}^{2+}} + \text{G}_{\text{H}_2\text{O}}) = -4,596 - (-66,62 + 0) = 62,024 \text{ kJ/mol}$ ;

$\text{Al} + \text{H}_2\text{O} = \text{Al}^{3+} + 3\text{e}^-$ ; Absolūtā potenciāla aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = -1,662 \text{ V}$  [1], ūdens  
logaritmu un  $\Delta E^\circ$ :  $E^\circ_{\text{Al}/\text{Al}^{3+}} = E^\circ_{\text{klasisko}} - 0,0591/3 \cdot \log(1/[\text{H}_2\text{O}]) + \Delta E^\circ = -1,662 + 0,0343 + 0,10166 - 0,37239 = -1,8984 \text{ V}$ ;

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

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

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

$\text{Al} + 4\text{OH}^- = \text{H}_2\text{AlO}_3^- + \text{H}_2\text{O} + 3\text{e}^-$  Absolūtā potenciāla aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = -2,33 \text{ V}$  [1], ūdens  
logaritmu un  $\Delta E^\circ$ :  $E^\circ_{\text{H}_2\text{AlO}_3^-/\text{Al}} = E^\circ_{\text{klasisko}} - 0,0591/3 \cdot \log([\text{H}_2\text{O}]) + \Delta E^\circ = -2,33 - 0,0343 + 0,10166 - 0,37239 = -2,63506 \text{ V}$ ;

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

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

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

$$E_{\text{AlO}_2^-/\text{Al}} = E^\circ_{\text{AlO}_2^-/\text{Al}} + \frac{0,0591}{3} \cdot \log \frac{[\text{H}_2\text{AlO}_3^-] \cdot [\text{H}_2\text{O}]}{[\text{Al}] \cdot [\text{OH}^-]^4} = -2,63506 \text{ V} + \frac{0,0591}{3} \cdot \log \frac{[\text{H}_2\text{AlO}_3^-] \cdot [\text{H}_2\text{O}]}{[\text{Al}] \cdot [\text{OH}^-]^4};$$

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  $G_{N_{2aqua}}=18,7$  kJ/mol, ja tīras gāzes mol daļa ir viens  $[N_{2gas}]=1$ . [8] Ūdenī Elements slāpekļis  $N_{2gas}+H_2O=N_{2aqua}$  ir vāji šķīstošs ar  $0,00175$  g/100g  $H_2O$  izšķīdināto daudzumu  $[N_{2aqua}]=0,00175/100,00175*996=0,01743/28,02=10^{-3,206}$  M un blīvumu  $996$  g/L. [1] Šķīdības konstante mol daļās ir mazāka par vienu  $K_{sp}=[N_{2aqua}]/[H_2O]=10^{(-3,206)}/55,3=10^{-4,949}$ , 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  $\Delta G_{Hess\_sp\_N_{2aqua}}=G_{N_{2aqua}}-(G_{N_{2gas}}+G_{H_2O})=18,7-(G_{N_{2gas}}-0)=28,25$  kJ/mol sakrītoša absolūtajā enerģijas skalā. Mola  $G_{N_{2gas}}=G_{N_{2aqua}}-(\Delta G_{Hess\_sp\_N_{2aqua}}+G_{H_2O})=18,7-(28,25+0)=-9,55$  kJ/mol slāpekļa gāzes enerģijas saturs ir negatīvs relatīvi zem destilētā ūdens nulles  $G_{H_2O}=0$  kJ/mol. Izšķīdināta slāpekļa mola enerģijas saturs  $G_{N_{2aqua}}=18,7$  kJ/mol ir pozitīvs. [8] **Albertijs**

Viela	$\Delta H^{\circ}_H$ kJ/mol	$\Delta S^{\circ}_H$ J/mol/K	$\Delta G^{\circ}_H$ kJ/mol
$N_{2gas}$	$G_{N_{2gas}}=$	form $NH_3$	<b>107,2</b>
$N_{2aq}$	<b>-10,54</b>	<b>98,1</b>	<b>18,7</b>
$N_{2gas}$	$N_{2gas}+H_2O=N_{2aq}$ pH=7,36		<b>-9,55</b>
$NH_{3gas}$	$\Delta G_{Hydration}$	<b>-74,5537</b>	<b>165,7</b>
$NH_{3gas}$	[1,8]	formation	<b>107,285</b>
$NH_{3gas}$	-45,9	192,77	-16,4
$NH_{3aq}$	<b>-132,5608</b>	<b>-739,2922</b>	<b>91,1056</b>
$NH_{3aq}$	$pK_{beq}=$	6,49475	<b>91,1</b>
$NH_4^+$	$pK_{aeq}=$	10,99	<b>50,81</b>

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

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

Šķīdums  $N_{2aq}$  pie pH=7,36 [8].

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

$$G_{NH_{3gas}}=\Delta G_{NH_{3aq}}-(\Delta G_{Hydrations}+G_{H_2O})=91,1056-(-74,5537+0)=165,7 \text{ kJ/mol;}$$

$$2G_{NH_{3gas}}=2\Delta G_{FormNH_{3gas}}+(G_{N_{2gas}}+3 \cdot G_{H_2gas})=2 \cdot 107,285 \text{ kJ/mol;}$$

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

Amonjaks pie pH=7,36 [8] **Albertijs**;  $NH_{3aq}$  veidošanās

$$G_{NH_{3aq}}=G_{NH_4^+}+G_{OH^-}-(\Delta G_{beq}+G_{H_2O})=91,1 \text{ kJ/mol; Wikipedia [28]}$$

$$G_{NH_4^+}=G_{NH_{3aq}}+G_{H_3O^+}-(\Delta G_{eq}+G_{H_2O})=91,1+22,44-62,73-0=50,81 \text{ kJ/mol;}$$

Veidošanās  $N_{2aq}+3H_{2aq}>2NH_{3aq}$  no elementiem ar absolūto enerģiju  $G_{N_{2aq}}=18,7$  kJ/mol;  $G_{H_{2aq}}=103,2$  kJ/mol ir eksoerģiska reakcija  $2\Delta G_{Hess\_NH_{3aq}}=2G_{NH_{3aq}}-(G_{N_{2aq}}+3 \cdot G_{H_{2aq}})=2 \cdot 91,1056 - (18,7 + 3 \cdot 103,24) = 2 \cdot -73,1$  kJ/mol. [8] Veidošanās  $N_{2gas}+3H_{2gas}>2NH_{3gas}$  no elementiem  $G_{N_{2gas}}=-9,55$  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  $NH_{3gas}$  molam ir pozitīvs  $G_{NH_{3gas}}=107,285$  kJ/mol:

$$2G_{NH_{3gas}}=2\Delta G_{Hess\_NH_{3gas}}+(G_{N_{2gas}}+3 \cdot G_{H_{2gas}})=2 \cdot -16,4 + (-9,55 + 3 \cdot 85,64) = 214,57 = 2 \cdot 107,285 \text{ kJ/mol.}$$

Gāzes šķīdības dalībnieki  $NH_{3gas}+H_2O=NH_{3aq}$  ir ar enerģijas vērtībām  $G_{NH_{3aq}}=91,1$  kJ/mol,  $G_{NH_{3gas}}=107,285$  kJ/mol.

Klasiskās amonjaka protolītiskās bāzes  $NH_{3aq}+H_2O=NH_4^++OH^-$  konstantes izteiksme, neņemot vērā ūdeni, ir  $K_b=[NH_4^+][OH^-]/[NH_{3aq}]=10^{(-4,752)}$  ar eksponenta vērtību  $pK_b=4,752$ . [1] Klasiskā bāzes konstante ir iegūta no protolīzes līdzsvara konstantes, ņemot vērā ūdens daudzumu reaģentos

$$K_{beq}=K_b/[H_2O]=10^{(-4,752)}/55,3=3,20 \cdot 10^{(-7)}=10^{(-6,4947)}.$$

Amonjaka protolīzes līdzsvara konstantes eksponenta aprēķinātā vērtība ir  $pK_{beq}=6,4947$  endoerģiska, jo absolūtās brīvās enerģijas izmaiņas Prigožina izteiksmē un Hesa izteiksmē ir pozitīvas un identiskas:

$$\Delta G_{beq}=-R \cdot T \cdot \ln(K_{beq})=-8,3144 \cdot 298,15 \cdot \ln(10^{(-6,4947)})=G_{NH_4^+}+G_{OH^-}-(G_{NH_{3aq}}+G_{H_2O})=37,064 \text{ kJ/mol;}$$

$$\Delta G_{Hess\_beq}=G_{NH_4^+}+G_{OH^-}-(G_{NH_{3aq}}+G_{H_2O})=50,81+77,36-(G_{NH_{3aq}}+0)=37,064 \text{ kJ/mol.}$$

Brīvās enerģijas saturs šķīdumā, kurā ir viens mols amonjaka ūdenī, ir  $G_{NH_{3aq}}=91,1$  kJ/mol

$$G_{NH_{3aq}}=G_{NH_4^+}+G_{OH^-}-(\Delta G_{beq}+G_{H_2O})=50,81+77,36-(37,07+0)=91,1 \text{ kJ/mol.}$$

Endoerģiska amonjaka protolīze akumulē enerģiju produktos  $G_{NH_4^+}+G_{OH^-}=50,81+77,36=128,17$  kJ/mol.

Vājas skābes  $G_{NH_4^+}=50,81$  kJ/mol  $NH_4^++H_2O=NH_{3aq}+H_3O^+$  protolīze  $pK_{eq}=10,99$  uzrāda endoerģiskās enerģijas izmaiņu  $\Delta G_{aeq}=-R \cdot T \cdot \ln(K_{aeq})=-8,3144 \cdot 298,15 \cdot \ln(10^{(-10,99)})=G_{NH_{3Hydration}}+G_{H_3O^+}-G_{NH_4^+}-G_{H_2O}=62,73$  kJ/mol.

Amonija brīvās enerģijas saturs uz molu ir

$$G_{NH_4^+}=G_{NH_{3aq}}+G_{H_3O^+}-(\Delta G_{aeq}+G_{H_2O})=91,1+22,44-(62,73+0)=50,81 \text{ kJ/mol.}$$

Šķīdība  $NH_{3gas}+H_2O=NH_{3aq}$ ;  $G_{NH_{3aq}}=91,1$  kJ/mol; amonjakam pie pH=7,36 [8];

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

$$S_{Hydration}=\Delta S^{\circ}_{NH_{3aqua}}-\Delta S^{\circ}_{NH_{3gas}}-\Delta S^{\circ}_{H_2O}=-739,2922-192,77-69,9565=-1002 \text{ J/mol/K;}$$

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

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

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:

$$G_{NH_{3gas}}=G_{NH_{3aq}}-(\Delta G_{Hydration}+G_{H_2O})=91,1056-(-74,5537+0)=165,7 \text{ kJ/mol;}$$

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

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  $NH_4^+=H^++NH_{3aqua}$   $pK_a=9,25$ ;

Veidošanās no elementiem  $\text{HNO}_2$   $\Delta G^\circ_{\text{HNO}_2} = -46 \text{ kJ/mol}$  un  $\text{HNO}_3$   $\Delta G^\circ_{\text{HNO}_3} = -250,53 \text{ kJ/mol}$  Wikipedia:  
 Formation  $G_{\text{HNO}_3\text{Form}} = \Delta G^\circ_{\text{HNO}_3} + (0,5G_{\text{N}_2\text{gas}} + 1,5G_{\text{O}_2\text{gas}} + 0,5G_{\text{H}_2\text{gas}}) = -250,53 + (0,5 \cdot -9,55 + 1,5 \cdot 303) = 199,195 \text{ kJ/mol}$   
 $G_{\text{HNO}_2} = \Delta G^\circ_{\text{HNO}_2} + 0,5G_{\text{N}_2\text{gas}} + G_{\text{O}_2\text{gas}} + 0,5G_{\text{H}_2\text{gas}} = -46 + (0,5 \cdot -9,55 + 303 + 0,5 \cdot 85,6) = 295,025 \text{ kJ/mol}$  ;  
 $G_{\text{N}_2\text{gas}} = G_{\text{N}_2\text{aq}} - (\Delta G_{\text{Hess, šķ. N}_2\text{aq}} + G_{\text{H}_2\text{O}}) = 18,7 - (28,25 + 0) = -9,55 \text{ kJ/mol}$  ;  $G_{\text{H}_2\text{gas}} = 85,6 \text{ kJ/mol}$  ;  $G_{\text{O}_2\text{gas}} = 303 \text{ kJ/mol}$  ; [8]  
 $G_{\text{NO}_2\text{-Form}} = \Delta G^\circ_{\text{NO}_2} + 0,5G_{\text{N}_2\text{gas}} + G_{\text{O}_2\text{gas}} = -33,01 + 0,5 \cdot -9,55 + 1 \cdot 303 = 265,2 \text{ kJ/mol}$  ;  
 $G_{\text{NO}_2\text{-Form}} = \Delta G^\circ_{\text{NO}_2} + 0,5G_{\text{N}_2\text{aq}} + G_{\text{O}_2\text{aq}} = -33,01 + 0,5 \cdot 18,7 + 1 \cdot 330 + 0 = 306,34 \text{ kJ/mol}$  ;

Skābes un protolīzes līdzsvars  $K_{\text{eq}} = K_a / [\text{H}_2\text{O}]$  aprēķina dalot skābes konstanti ar ūdeni  $[\text{H}_2\text{O}] = 55,3 \text{ M}$ .

1.  $\text{HNO}_2 + \text{H}_2\text{O} = \text{NO}_2^- + \text{H}_3\text{O}^+$ ;  $pK_a = 3,15$ ;  $K_{\text{eq}} = K_a / [\text{H}_2\text{O}] = 10^{-(3,15)} / 55,3 = 0,00001280$ ;

$$\Delta G_{\text{eqHNO}_2} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(0,0000128) = G_{\text{NO}_2^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{HNO}_2} + G_{\text{H}_2\text{O}}) = 27,927 \text{ kJ/mol}$$

$$\Delta G_{\text{eqHNO}_2} = G_{\text{NO}_2^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{HNO}_2} + G_{\text{H}_2\text{O}}) = 82,618 + 22,44 - (77,131 + 0) = 27,927 \text{ kJ/mol}$$

$$G_{\text{NO}_2^-} = \Delta G_{\text{eqHNO}_2} - G_{\text{H}_3\text{O}^+} + (G_{\text{HNO}_2} + G_{\text{H}_2\text{O}}) = 27,927 - 22,44 + (77,131 + 0) = 82,618 \text{ kJ/mol}$$

$$G_{\text{HNO}_2} = G_{\text{NO}_2^-} - G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqHNO}_2} + G_{\text{H}_2\text{O}}) = 82,618 + 22,44 - (27,927 + 0) = 77,131 \text{ kJ/mol}$$

2.  $\text{HNO}_3 + \text{H}_2\text{O} = \text{NO}_3^- + \text{H}_3\text{O}^+$ ;  $pK_a = -1,4$ ;  $K_{\text{eq}} = K_a / [\text{H}_2\text{O}] = 10^{(1,4)} / 55,3 = 0,4542$ ;

$$\Delta G_{\text{eqHNO}_3} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(0,4542) = G_{\text{NO}_3^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{HNO}_3} + G_{\text{H}_2\text{O}}) = 1,956 \text{ kJ/mol}$$

$$\Delta G_{\text{eqHNO}_3} = G_{\text{NO}_3^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{HNO}_3} + G_{\text{H}_2\text{O}}) = 178,711 + 22,44 - (199,195 + 0) = 1,956 \text{ kJ/mol}$$

$$G_{\text{HNO}_3} = G_{\text{NO}_3^-} + G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqHNO}_3} + G_{\text{H}_2\text{O}}) = 178,711 + 22,44 - (1,956 + 0) = 199,195 \text{ kJ/mol}$$

$$G_{\text{NO}_3^-} = \Delta G_{\text{eqHNO}_3} - G_{\text{H}_3\text{O}^+} + (G_{\text{HNO}_3} + G_{\text{H}_2\text{O}}) = 1,956 - 22,44 + (199,195 + 0) = 178,711 \text{ kJ/mol}$$

Viela	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol	
$\text{HNO}_2$	$E^\circ_{\text{NO}_3^-/\text{H}_3\text{O}^+} = 0,8753 \text{ V}$		<b>77,131</b>	$G_{\text{HNO}_2} = G_{\text{NO}_3^-} + 3G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqNO}_3} + 4G_{\text{H}_2\text{O}}) = 77,131 \text{ kJ/mol}$
$\text{HNO}_2$	-	$pK_a = 3,15$	<b>238,42</b>	$G_{\text{HNO}_2} = G_{\text{NO}_2^-} - G_{\text{H}_3\text{O}^+} + (\Delta G_{\text{eqHNO}_2} + G_{\text{H}_2\text{O}}) = 238,42 \text{ kJ/mol}$
$\text{HNO}_2$	-79,5	254,1	-46,0	CRC [1]
$\text{HNO}_2$	-	formation	<b>295,025</b>	$G_{\text{HNO}_2\text{gas}} = \Delta G^\circ_{\text{HNO}_2\text{gas}} + 0,5G_{\text{N}_2\text{gas}} + G_{\text{O}_2\text{gas}} + 0,5G_{\text{H}_2\text{gas}} = 295,025 \text{ kJ/mol}$
$\text{pH}=7,36\text{NO}_2^-$	<b>-104,19</b>	<b>-238,7</b>	<b>-33,01</b>	<b>Biochem. Thermodynamic 2006 Massachusetts Technology Inst.</b>
$\text{NO}_2^-$	$0,5G_{\text{N}_2\text{gas}} + G_{\text{O}_2\text{gas}}$		<b>265,2</b>	$G_{\text{NO}_2\text{-form}} = \Delta G^\circ_{\text{NO}_2\text{aq}} + 0,5G_{\text{N}_2\text{gas}} + G_{\text{O}_2\text{gas}} = 265,2 \text{ kJ/mol}$
$\text{NO}_2^-$	$0,5G_{\text{N}_2\text{aq}} + G_{\text{O}_2\text{aq}}$		<b>306,34</b>	$G_{\text{NO}_2\text{-Form}} = \Delta G^\circ_{\text{NO}_2} + 0,5G_{\text{N}_2\text{aq}} + G_{\text{O}_2\text{aq}} = 306,34 \text{ kJ/mol}$
$\text{NO}_2^-$	$E^\circ_{\text{NO}_3^-/\text{OH}^-} = -0,3122 \text{ V}$		<b>84,236</b>	$G_{\text{NO}_2^-} = G_{\text{NO}_3^-} + G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqNO}_3\text{-OH}} + 2G_{\text{OH}^-}) = 84,236 \text{ kJ/mol}$
$\text{NO}_2^-$	$E^\circ_{\text{NO}_2^-} = 0,7188 \text{ V}$		<b>84,446</b>	$G_{\text{NO}_2^-} = G_{\text{NO}_3^-} + 3G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqNO}_2^-} + 3G_{\text{H}_2\text{O}}) = 84,446 \text{ kJ/mol}$
$\text{NO}_2^-$		$pK_a = 3,15$	<b>82,618</b>	$G_{\text{NO}_2^-} = \Delta G_{\text{eqHNO}_2} - G_{\text{H}_3\text{O}^+} + (G_{\text{HNO}_2} + G_{\text{H}_2\text{O}}) = 82,618 \text{ kJ/mol}$
$\text{HNO}_3$	-207	146	-250,53	[1] $G^\circ_{\text{NO}_3^-} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -207 - 298,15 \cdot 0,146 = -250,5886 \text{ kJ/mol}$ ; [1]
$\text{HNO}_3$	-	formation	<b>199,195</b>	$G_{\text{HNO}_3\text{Form}} = \Delta G^\circ_{\text{HNO}_3} + (0,5G_{\text{N}_2\text{gas}} + 1,5G_{\text{O}_2\text{gas}} + 0,5G_{\text{H}_2\text{gas}}) = 199,195 \text{ kJ/mol}$
$\text{HNO}_3$	-	$pK_a = -1,4$	<b>199,195</b>	$G_{\text{HNO}_3} = G_{\text{NO}_3^-} + G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqHNO}_3} + G_{\text{H}_2\text{O}}) = 199,195 \text{ kJ/mol}$
$\text{pH}=7,36\text{NO}_3^-$	<b>-204,59</b>	<b>-318,8</b>	<b>-109,55</b>	<b>Biochem. Thermodynamic 2006 Massachusetts Technology Inst.</b>
$\text{NO}_3^-$	$E^\circ_{\text{NO}_3^-/\text{H}_3\text{O}^+} = 0,8753 \text{ V}$		<b>178,711</b>	$G_{\text{NO}_3^-} = \Delta G_{\text{eqNO}_3} - 3G_{\text{H}_3\text{O}^+} + (G_{\text{HNO}_2} + 4G_{\text{H}_2\text{O}}) = 178,711 \text{ kJ/mol}$
$\text{NO}_3^-$	$E^\circ_{\text{NO}_2^-} = 0,7188 \text{ V}$		<b>155,83</b>	$G_{\text{NO}_3^-} = \Delta G_{\text{eqNO}_2^-} - 3G_{\text{H}_3\text{O}^+} + (G_{\text{NO}_2^-} + 3G_{\text{H}_2\text{O}}) = 155,833 \text{ kJ/mol}$
$\text{NO}_3^-$	$E^\circ_{\text{NH}_4^+/\text{H}_2\text{O}} = 0,7677 \text{ V}$		<b>601,06</b>	$G_{\text{NO}_3^-} = \Delta G_{\text{eqNH}_4^+/\text{H}_2\text{O}} - 10G_{\text{H}_3\text{O}^+} + (G_{\text{NH}_4^+} - 13G_{\text{H}_2\text{O}}) = 601,06 \text{ kJ/mol}$
$\text{NO}_3^-$	-206,85	146,7	-250,5886	$\Delta G^\circ_{\text{NO}_3^-} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -206,85 - 298,15 \cdot 0,1467 = -250,5886 \text{ kJ/mol}$ ; [1]
$\text{NO}_3^-$	-	$pK_a = -1,4$	<b>178,711</b>	$G_{\text{NO}_3^-} = \Delta G_{\text{eqHNO}_3} - G_{\text{H}_3\text{O}^+} + (G_{\text{HNO}_3} + G_{\text{H}_2\text{O}}) = 178,711 \text{ kJ/mol}$ ;
$\text{NO}_3^-$	$E^\circ_{\text{NO}_3^-/\text{OH}^-} = -0,3122 \text{ V}$		<b>178,711</b>	$G_{\text{NO}_3^-} = \Delta G_{\text{eqNO}_3\text{-OH}} - G_{\text{H}_2\text{O}} + (G_{\text{NO}_2^-} + 2G_{\text{OH}^-}) = 178,711 \text{ kJ/mol}$ ,
$\text{NO}_{\text{gas}}$	91,3	210,8	87,6	CRC [1]
$\text{NO}_{\text{aq}}$	Solubility product -		<b>61,024</b>	$G_{\text{NO}_{\text{gas}}} = G_{\text{H}_2\text{O}} + G_{\text{NO}_{\text{aq}}} - (\Delta G_{\text{sp}}) = 0 + 86,55 - (25,526) = 61,024 \text{ kJ/mol}$ ;
$\text{NO}_{\text{aq}}$	-	$\text{pH}=7,36$	<b>86,55</b>	<b>Biochem. Thermodynamic 2006 Massachusetts Technology Inst.</b>
$\text{NO}_{\text{aq}}$	$E^\circ_{\text{NO(g)}/\text{H}_3\text{O}^+} = 0,8266$		<b>49,695</b>	$G_{\text{NO}_{\text{aq}}} = G_{\text{HNO}_3} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqNO(g)}/\text{H}_3\text{O}^+} + 5G_{\text{H}_2\text{O}}) = 49,695 \text{ kJ/mol}$ , $\text{pH} < 1,4$

**Nernsta potenciāla  $\text{NO}_3^-/\text{NO}_2^-$  red-oks sistēmas īpašības skābā  $\text{H}_3\text{O}^+$  ūdens un bāziskā  $\text{OH}^-$  vidē**

$\text{HNO}_2 + 4\text{H}_2\text{O} = \text{NO}_3^- + 3\text{H}_3\text{O}^+ + 2\text{e}^-$ ;  $\text{pH} < 3,15$ ; Absolūtais aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = 0,94 \text{ V}$  [18], ūdens logaritmu un  $\Delta E^\circ$ :  $E^\circ_{\text{NO}_3^-} = E^\circ_{\text{klasisko}} - 0,0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^4) + \Delta E^\circ = 0,94 + 0,206 + 0,10166 - 0,37239 = 0,8753 \text{ V}$ ;

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

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

$$\Delta G_{\text{eqNO}_3} = G_{\text{NO}_3^-} + 3G_{\text{H}_3\text{O}^+} - (G_{\text{HNO}_2} + 4G_{\text{H}_2\text{O}}) = 178,711 + 3 \cdot 22,44 - (77,131 + 4 \cdot 0) = 168,9 \text{ kJ/mol}$$

$$G_{\text{HNO}_2} = G_{\text{NO}_3^-} + 3G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqNO}_3} + 4G_{\text{H}_2\text{O}}) = 178,711 + 3 \cdot 22,44 - (168,9 + 4 \cdot 0) = 77,131 \text{ kJ/mol}$$

$$G_{\text{NO}_3^-} = \Delta G_{\text{eqNO}_3} - 3G_{\text{H}_3\text{O}^+} + (G_{\text{HNO}_2} + 4G_{\text{H}_2\text{O}}) = 168,9 - 3 \cdot 22,44 + (77,131 + 4 \cdot 0) = 178,711 \text{ kJ/mol}$$



$\text{NO}_2^- + 2\text{OH}^- = \text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^-$ ;  $\text{pH} > 7$  Absolūtais aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = 0,01 \text{ V}$  [17], ūdens logaritmu un  $\Delta E^\circ$ :  $E^\circ_{\text{NO}_3-\text{OH}} = E^\circ_{\text{klasisko}} - 0,0591/2 \cdot \lg([\text{H}_2\text{O}]) + \Delta E^\circ = 0,01 - 0,0515 + 0,10166 - 0,37239 = -0,3122 \text{ V}$ ;

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

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

$$\Delta G_{\text{eqNO}_3-\text{OH}} = G_{\text{NO}_3^-} + G_{\text{H}_2\text{O}} - (G_{\text{NO}_2^-} + 2G_{\text{OH}^-}) = 178,711 + 0 - (84,446 + 2 \cdot 77,36) = -60,245 \text{ kJ/mol},$$

$$G_{\text{NO}_3^-} = \Delta G_{\text{eqNO}_3-\text{OH}} - G_{\text{H}_2\text{O}} + (G_{\text{NO}_2^-} + 2G_{\text{OH}^-}) = -60,2455 - 0 + (84,446 + 2 \cdot 77,36) = 178,711 \text{ kJ/mol},$$

$$G_{\text{NO}_2^-} = G_{\text{NO}_3^-} + G_{\text{H}_2\text{O}} - (\Delta G_{\text{eqNO}_3-\text{OH}} + 2G_{\text{OH}^-}) = 178,711 + 0 - (-60,245 + 2 \cdot 77,36) = 84,236 \text{ kJ/mol};$$

$\text{NO}_2^- + 3\text{H}_2\text{O} = \text{NO}_3^- + 2\text{H}_3\text{O}^+ + 2\text{e}^-$ ;  $\text{pH} > 3,15$  Absolūtais aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = 0,835 \text{ V}$  [21], ūdens logaritmu un  $\Delta E^\circ$ :  $E^\circ_{\text{NO}_2} = E^\circ - 0,0591/2 \cdot \lg(1/[\text{H}_2\text{O}]^3) + \Delta E^\circ = 0,835 + 0,1545 + 0,10166 - 0,37239 = 0,7188 \text{ V}$

$$\Delta G_{\text{eqNO}_2} = E^\circ_{\text{NO}_2} \cdot F \cdot 2 = 0,7188 \cdot 96485 \cdot 2 = 138,707 \text{ kJ/mol},$$

$$\Delta G_{\text{eqNO}_2} = G_{\text{NO}_3^-} + 3G_{\text{H}_3\text{O}^+} - (G_{\text{NO}_2^-} + 3G_{\text{H}_2\text{O}}) = 155,833 + 3 \cdot 22,44 - (84,446 + 3 \cdot 0) = 138,707 \text{ kJ/mol},$$

$$G_{\text{NO}_3^-} = \Delta G_{\text{eqNO}_2} - 3G_{\text{H}_3\text{O}^+} + (G_{\text{NO}_2^-} + 3G_{\text{H}_2\text{O}}) = 138,707 - 3 \cdot 22,44 + (84,446 + 3 \cdot 0) = 155,833 \text{ kJ/mol},$$

$$G_{\text{NO}_2^-} = G_{\text{NO}_3^-} + 3G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqNO}_2} + 3G_{\text{H}_2\text{O}}) = 155,833 + 3 \cdot 22,44 - (138,707 + 3 \cdot 0) = 84,446 \text{ kJ/mol},$$

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

$[\text{NO}_{\text{aq}}] = (0,00562 / 100 \cdot 996) / 30,006 = 0,001865 \text{ M}$ , ja tīras 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  $K_{\text{eq}} = [\text{NO}_{\text{aq}}] / [\text{NO}^{(\text{g})}] / [\text{H}_2\text{O}] = 0,001865 / 1 / 55,3 = 10^{(-4,472)}$ .

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

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

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

Gāzes  $\text{NO}_{\text{gas}}$  šķīdība kompensē vienu ūdens molekulu izteiksmē no  $6\text{H}_2\text{O}$  uz  $5\text{H}_2\text{O}$  un no  $5\text{H}_2\text{O}$  uz  $4\text{H}_2\text{O}$ :

$\text{NO}_{\text{aq}} + 5\text{H}_2\text{O} = \text{NO}_3^- + 4\text{H}_3\text{O}^+ + 3\text{e}^-$ ;  $\text{pH} > 1,4$  Aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = 0,96 \text{ V}$  [18], ūdens logaritmu un  $\Delta E^\circ$ :  $E^\circ_{\text{NO}^{(\text{g})}\text{H}_3\text{O}^+} = E^\circ_{\text{klasisko}} - 0,0591/3 \cdot \lg(1/[\text{H}_2\text{O}]^5) + \Delta E^\circ = 0,96 + 0,1717 + 0,10166 - 0,37239 = 0,8609 \text{ V}$ ;

$$E_{\text{NO}^{(\text{g})}\text{H}_3\text{O}^+} = E^\circ_{\text{NO}^{(\text{g})}\text{H}_3\text{O}^+} + 0,0591/3 \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{NO}_{\text{aq}}] \cdot [\text{H}_2\text{O}]^5} = 0,8609 \text{ V} + 0,0197 \cdot \log \frac{[\text{NO}_3^-] \cdot [\text{H}_3\text{O}^+]^4}{[\text{NO}_{\text{aq}}] \cdot [\text{H}_2\text{O}]^5}$$

$$\Delta G_{\text{eqNO}^{(\text{g})}\text{H}_3\text{O}^+} = E^\circ_{\text{NO}^{(\text{g})}\text{H}_3\text{O}^+} \cdot F \cdot 3 = 0,86093 \cdot 96485 \cdot 3 = 249,20 \text{ kJ/mol},$$

$$\Delta G_{\text{eqNO}^{(\text{g})}\text{H}_3\text{O}^+} = G_{\text{NO}_3^-} + 4G_{\text{H}_3\text{O}^+} - (G_{\text{NO}_{\text{aq}}} + 5G_{\text{H}_2\text{O}}) = 178,711 + 4 \cdot 22,44 - (19,271 + 5 \cdot 0) = 249,20 \text{ kJ/mol},$$

$$G_{\text{NO}_{\text{aq}}} = G_{\text{NO}_3^-} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqNO}^{(\text{g})}\text{H}_3\text{O}^+} + 5G_{\text{H}_2\text{O}}) = 178,711 + 4 \cdot 22,44 - (249,20 + 5 \cdot 0) = 19,271 \text{ kJ/mol},$$

$\text{NO}_{\text{aq}} + 4\text{H}_2\text{O} = \text{HNO}_3^- + 3\text{H}_3\text{O}^+ + 3\text{e}^-$ ;  $\text{pH} < 1,4$  Aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = 0,96 \text{ V}$  [18], ūdens logaritmu un  $\Delta E^\circ$ :  $E^\circ_{\text{NO}^{(\text{g})}\text{H}_3\text{O}^+} = E^\circ_{\text{klasisko}} - 0,0591/3 \cdot \lg(1/[\text{H}_2\text{O}]^4) + \Delta E^\circ = 0,96 + 0,1373 + 0,10166 - 0,37239 = 0,8266 \text{ V}$ ;

$$E_{\text{NO}^{(\text{g})}\text{H}_3\text{O}^+} = E^\circ_{\text{NO}^{(\text{g})}\text{H}_3\text{O}^+} + 0,0591/3 \cdot \log \frac{[\text{HNO}_3^-] \cdot [\text{H}_3\text{O}^+]^3}{[\text{NO}_{\text{aq}}] \cdot [\text{H}_2\text{O}]^4} = 0,8266 \text{ V} + 0,0197 \cdot \log \frac{[\text{HNO}_3^-] \cdot [\text{H}_3\text{O}^+]^3}{[\text{NO}_{\text{aq}}] \cdot [\text{H}_2\text{O}]^4}$$

$$\Delta G_{\text{eqNO}^{(\text{g})}\text{H}_3\text{O}^+} = E^\circ_{\text{NO}^{(\text{g})}\text{H}_3\text{O}^+} \cdot F \cdot 3 = 0,8266 \cdot 96485 \cdot 3 = 239,26 \text{ kJ/mol},$$

$$\Delta G_{\text{eqNO}^{(\text{g})}\text{H}_3\text{O}^+} = G_{\text{HNO}_3^-} + 4G_{\text{H}_3\text{O}^+} - (G_{\text{NO}_{\text{aq}}} + 5G_{\text{H}_2\text{O}}) = 199,195 + 4 \cdot 22,44 - (49,695 + 5 \cdot 0) = 239,26 \text{ kJ/mol},$$

$$G_{\text{NO}_{\text{aq}}} = G_{\text{HNO}_3^-} + 4G_{\text{H}_3\text{O}^+} - (\Delta G_{\text{eqNO}^{(\text{g})}\text{H}_3\text{O}^+} + 5G_{\text{H}_2\text{O}}) = 199,195 + 4 \cdot 22,44 - (239,26 + 5 \cdot 0) = 49,695 \text{ kJ/mol},$$

$\text{NH}_3_{\text{gas}} + \text{H}_2\text{O} = \text{NH}_3_{\text{aq}}$  brīvā enerģija  $G_{\text{NH}_3_{\text{aq}}} = 91,1 \text{ kJ/mol}$ ;  $\text{NH}_3_{\text{aq}} + \text{H}_2\text{O} = \text{NH}_4^+ + \text{OH}^-$ ;

$\text{NH}_4^+ + 13\text{H}_2\text{O} + \text{OH}^- = \text{NO}_3^- + 10\text{H}_3\text{O}^+ + \text{OH}^- + 8\text{e}^-$ ;  $\text{H}_3\text{O}^+ + \text{OH}^- = 2\text{H}_2\text{O}$ ;

$\text{NH}_4^+ + 11\text{H}_2\text{O} + \text{OH}^- = \text{NO}_3^- + 9\text{H}_3\text{O}^+ + 8\text{e}^-$ ;  $\text{H}_3\text{O}^+ + \text{OH}^- = 2\text{H}_2\text{O}$ ;

$\text{NH}_4^+ + 13\text{H}_2\text{O} = \text{NO}_3^- + 10\text{H}_3\text{O}^+ + 8\text{e}^-$ ; Absolūtais aprēķins satur standarta potenciālu  $E^\circ_{\text{klasisko}} = 0,87 \text{ V}$  [17], ūdens logaritmu un  $\Delta E^\circ$ :  $E^\circ_{\text{NH}_4+\text{H}_2\text{O}} = E^\circ_{\text{klasisko}} - 0,0591/8 \cdot \lg(1/[\text{H}_2\text{O}]^{13}) + \Delta E^\circ = 0,87 + 0,16737 + 0,10166 - 0,37239 = 0,7667 \text{ V}$ ;

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

$$\Delta G_{\text{eqNH}_4+\text{H}_2\text{O}} = E^\circ_{\text{NH}_4+\text{H}_2\text{O}} \cdot F \cdot 8 = 0,76669 \cdot 96485 \cdot 8 = 591,8 \text{ kJ/mol},$$

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

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

**Nernsta potenciāla studijas  $5(\text{Pt})\text{H}+\text{MnO}_4^-$  uzskaitot hidroksioniju  $\text{H}_3\text{O}^+$  un ūdeni  $\text{H}_2\text{O}$ .**

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

Divpadsmit ūdens molekulu uzskaitē  $[\text{H}_2\text{O}]=55,3\text{ M}=(996\text{ g/L})/(18\text{ g/mol})$  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:  $5(\text{Pt})\text{H}+5\text{H}_2\text{O}=5\text{H}_3\text{O}^++5e^-$ ;  $E^\circ_{\text{H}}=-0,27073\text{ V}$

$$E_{\text{MnO}_4^-}=-1,4865\text{ V}+0,0591/5\cdot\log([\text{H}_2\text{O}]^{12}\cdot[\text{Mn}^{2+}]/[\text{MnO}_4^-]/[\text{H}_3\text{O}^+]^8);$$

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

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

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

$$\Delta G_{\text{HessCRC}}=\Delta G^\circ_{\text{Mn}^{2+}}+7\Delta G^\circ_{\text{H}_2\text{O}}-(\Delta G^\circ_{\text{MnO}_4^-}+3\Delta G^\circ_{\text{H}_3\text{O}^+}+5/2\Delta G^\circ_{\text{H}_2})=-228,1+7\cdot-237,191-(3\cdot-213,2746-447,2+5\cdot99,13/2)=-1049\text{ kJ/mol};$$

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

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

CRC Handbook of Chemistry and Physics, 2010, D.Lide [1]

Biochem. Thermodyn., Massachusetts Technology Inst. [8] pH=7,36

RC [1]

RC [1]

Biochem. Thermodyn., Massachusetts Technology Inst. [8] pH=7,36

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

CRC [1]

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

Biochem. Thermodyn., Massachusetts Technology Inst. [8] pH=7,36

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

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

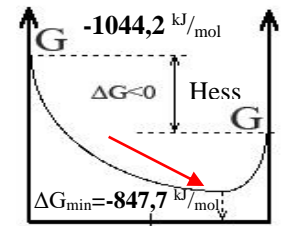
Eksotermiska un eksoergiska  $\text{MnO}_4^-$  reducēšanas ar metālisku  $5(\text{Pt})\text{H}$  Hesa brīvās enerģijas izmaiņa negatīva  $\Delta G_{\text{Hess}}=\Delta G_{\text{OxRed}}=-1043,7\text{ kJ/mol}$ , bet minimizējas sasniedzot

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

Brīvās enerģijas izmaiņas minimums  $\Delta G_{\text{min}}$  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  $\text{Mn}^{2+}+7\text{H}_2\text{O}$



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

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

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

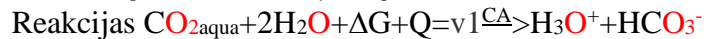
$$E^\circ_{\text{MnO}_4^{2-}/\text{MnO}_4^-}=E^\circ-0,0591/3\cdot\log([\text{H}_2\text{O}]^0)+0,10166-0,37239=0,558-0,0591/3\cdot\log(55,3^0)+0,10166-0,37239=\mathbf{0,2883\text{ V}};$$

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:

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

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



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

$\text{CO}_2$  nereaģē ar ūdeni  $\text{H}_2\text{O}$  bez CA klātbūtnes.  $\text{CO}_2$  ir mazšķīstošs un lēni reaģē ar  $\text{OH}^-$ .

[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  $\text{OH}^-$  joniem reizes  $10^{16,54}$  lēnāk par bikarbonāta  $\text{HCO}_3^-$  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  $\text{OH}^-$  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  $\text{H}_3\text{O}^+$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_{2\text{aqua}}$  un  $\text{O}_{2\text{aqua}}$ ,  $\text{H}_2\text{O}$  osmozei cauri akvaporīnu kanāliem. [9]

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

$\text{CO}_{2\text{aqua}}+2\text{H}_2\text{O}+\Delta G+Q=v_1\overset{\text{CA}}{\text{H}_3\text{O}^++\text{HCO}_3^-}$ , 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  $\text{pH}=7,36$ :

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

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

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

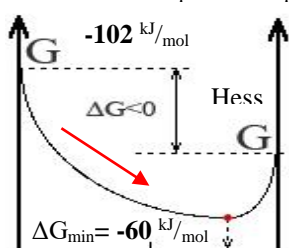
$$\Delta G_{\text{Absolute}}=2G_{\text{H}_2\text{O}}+G_{\text{CO}_{2\text{aqua}}}-G_{\text{H}_3\text{O}^+}-G_{\text{HCO}_3^-}=2\cdot 0+18,38-22,44-56,08=-60,14 \text{ kJ/mol}$$
 un

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:

$$\Delta G_{\text{eqNeitralizācija}}=-R\cdot T\cdot \ln(K_{\text{eqNeitralizācija}})=-8,3144\cdot 298,15\cdot \ln(34407299853)=-60,14 \text{ kJ/mol}$$
, bet  $\text{CO}_{2\text{aqua}}$  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  $\text{CO}_{2\text{aqua}}+2\text{H}_2\text{O}$ .

2CO<sub>2</sub> / H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> / CH<sub>4gas</sub> šķīdība un protolīze iekļauj hidroksjonija H<sub>3</sub>O<sup>+</sup> un ūdens H<sub>2</sub>O uzskaiti.

Standarta brīvās enerģijas izmaiņas oglekļa dioksīda veidošanai no brīvajiem elementiem C<sub>gr</sub>+O<sub>2gas</sub>=CO<sub>2gas</sub> ir negatīva ΔG<sup>o</sup><sub>Hess\_CO2gas</sub>=G<sub>CO2gas</sub>-(G<sub>gr</sub>+G<sub>O2gas</sub>)=-394,36 kJ/mol. [1] Ja bioķīmijas absolūtās enerģijas skalas fona līmenis ir nulle G<sub>CO2gas</sub>=0 kJ/mol, tad pēc Hesa likuma absolūtās brīvās enerģijas saturs vienā molā grafīta ir

$$G_{gr}=G_{CO2gas}-(\Delta G^o_{Hess\_CO2gas}+G_{O2gas})=0-(-394,36+303,1)=91,26 \text{ kJ/mol.}$$

Standarta brīvās enerģijas izmaiņas metāna veidošanai no brīvajiem elementiem C<sub>gr</sub>+2H<sub>2gas</sub>>CH<sub>4gas</sub> [1,8] ir

$$\Delta G^o_{Hess\_CH4gas}=G_{CH4gas}-(G_{Cgr}+2*G_{H2})=G_{CH4gas}-(91,26+2*85,64)=-50,5 \text{ kJ/mol un}$$

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

$$G_{CH4gas}=\Delta G^o_{Hess\_CH4gas}+(G_{Cgr}+2*G_{H2})=-50,5+(91,26+2*85,64)=212,04 \text{ kJ/mol.}$$

Tas ļauj mums aprēķināt absolūto brīvo enerģiju uz vienu grafīta molu absolūtajā brīvās enerģijas skalā:

$$G_{CgrCH4gas}=G_{CH4gas}-\Delta G^o_{Hess\_CH4gas}-2*G_{H2gas}=212,04-(-50,5+2*85,64)=91,26 \text{ kJ/mol ,}$$

kas sakrīt ar gāzes un ūdens nulli G<sub>CO2gas</sub>=G<sub>H2O</sub>=0 kJ/mol bioķīmijas absolūtās enerģijas skalā.



ir 22,7 mg/L un metāna mol masa ir M<sub>CH4</sub>=16,043 g/mol. Ūdens uzskaitē [H<sub>2</sub>O]=996/18=55,3 M aprēķina konstanti K<sub>eq</sub>=K<sub>sp</sub>/[H<sub>2</sub>O]=0,001414947 M/55,3 M=10<sup>-(4,592)</sup>.

Metāna šķīdības [CH<sub>4</sub>]=0,0227/16,043=0,001414947 M līdzsvaram absolūtā brīvās enerģijas izmaiņa ir

$$\Delta G_{eq}=-R\cdot T\cdot \ln(K_{eq})=-8,3144\cdot 298,15\cdot \ln(10^{-(4,592)})=-8,3144\cdot 298,15\cdot -10,573=26,21 \text{ kJ/mol .}$$

Albertija dati aprēķina šķīdības enerģijas izmaiņu ΔG<sub>eqCH4gas</sub>=26,21 kJ/mol .

Līdzsvara enerģijas izmaiņa ΔG<sub>eqCH4</sub>=G<sub>CH4aq</sub>-(G<sub>H2O</sub>+G<sub>CH4gas</sub>)=G<sub>CH4aq</sub>-(0+212,04)=26,21 kJ/mol ļauj aprēķināt absolūto brīvās enerģijas saturu metānam ūdenī (aqua): G<sub>CH4aq</sub>=G<sub>CH4gas</sub>+G<sub>CH4sp</sub>=212,04+26,21=238,25 kJ/mol;

Viela	ΔH <sup>o</sup> <sub>H</sub> kJ/mol	ΔS <sup>o</sup> <sub>H</sub> J/mol/K	ΔG <sup>o</sup> <sub>H</sub> kJ/mol	ΔG <sub>H2C2O4</sub> =ΔH <sub>H</sub> -T*ΔS <sub>H</sub> =-829,9-298,15*-0,1098=-747,75 kJ/mol;
H <sub>2</sub> O	-285,85	69,9565	-237,191	CRC [1]
H <sub>3</sub> O <sup>+</sup>	-285,81	-3,854	-213,2746	CRC [1] Mischenko 1972, Himia, Leningrad [26]
H <sub>2</sub> C <sub>2</sub> O <sub>4cr</sub>	-829,9	-109,8	-797,16	CRC [1]
H <sub>2</sub> C <sub>2</sub> O <sub>4cr</sub>	formation	-797,16	76,96	G <sub>H2C2O4cr</sub> =ΔG <sup>o</sup> <sub>H2C2O4crForm</sub> +(2G <sub>Cgr</sub> +2G <sub>O2gas</sub> +G <sub>H2gas</sub> )=76,96 kJ/mol;
H <sub>2</sub> C <sub>2</sub> O <sub>4sq</sub>	ΔG <sub>eq_sp</sub> = 9,0161		85,976	G <sub>H2C2O4aq</sub> =ΔG <sub>eq_sp</sub> +(G <sub>H2O</sub> +G <sub>H2C2O4cr</sub> )=85,976 kJ/mol;
H <sub>2</sub> C <sub>2</sub> O <sub>4sq</sub>	E <sup>o</sup> <sub>H2C2O4</sub> = -0,6577 V		171,78	G <sub>H2C2O4</sub> =2G <sub>CO2</sub> +2G <sub>H3O</sub> -(ΔG <sub>eqH2C2O4</sub> +2G <sub>H2O</sub> )=171,78 kJ/mol;
HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	17,08 pK <sub>a2</sub> =1,25		80,618	G <sub>HC2O4</sub> =ΔG <sub>eq1H2C2O4</sub> -G <sub>H3O</sub> +(G <sub>H2C2O4</sub> +ΔG <sub>H2O</sub> )=80,618 kJ/mol ;
HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	E <sup>o</sup> <sub>HC2O4</sub> = -0,7092 V		159,028	G <sub>HC2O4</sub> =2G <sub>CO2</sub> +G <sub>H3O</sub> -(ΔG <sub>eqHC2O4</sub> +G <sub>H2O</sub> )=159,028 kJ/mol;
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	-	-pH=7,36	-677,14	Alberty 2006 Biochem.Thermodyn Massachusetts Techn. Inst.
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	33,578 pK <sub>a2</sub> =4,14		91,756	G <sub>C2O4</sub> =ΔG <sub>eq2HC2O4</sub> -G <sub>H3O</sub> +(G <sub>HC2O4</sub> +G <sub>H2O</sub> )=91,756 kJ/mol ;
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	E <sup>o</sup> <sub>C2O4</sub> = -0,7607 V		146,79	G <sub>C2O4</sub> =2G <sub>CO2</sub> -(ΔG <sub>eqC2O4</sub> )=2*0-(-146,79)=146,79 kJ/mol;
CH <sub>4gas</sub>	-74,6	186,3	-50,5	=ΔG <sup>o</sup> <sub>Hess_CO2gas</sub> =G <sub>CO2gas</sub> -(G <sub>gr</sub> +G <sub>O2gas</sub> ) Wikipedia CRC [1]
CH <sub>4gas</sub>	formation	-50,5	212,04	G <sub>CH4gas</sub> =ΔG <sup>o</sup> <sub>Hess_CH4gas</sub> +(G <sub>Cgr</sub> +2*G <sub>H2</sub> )=212,04 kJ/mol;
CH <sub>4gas</sub>	pH=7,36 Albertijs [8]		120,56	Alberty 2006 Biochem.Thermodyn Massachusetts Techn. Inst.
CH <sub>4aq</sub>	Solubility 26,21		238,25	G <sub>CH4aq</sub> = G <sub>CH4gas</sub> + G <sub>CH4sp</sub> =212,04+26,21=238,25 kJ/mol;
CH <sub>4aq</sub>	[8] pH=7,36		136,95	Alberty 2006 Biochem.Thermodyn Massachusetts Techn. Inst.
C <sub>gr</sub>	background Biochemistry		91,26	G <sub>gr</sub> =G <sub>CO2gas</sub> -(ΔG <sup>o</sup> <sub>Hess_CO2gas</sub> +G <sub>O2gas</sub> )=91,26 kJ/mol; pH=7.36
CO <sub>2gas</sub>	-393,509	213,74	-394,359	CRC [1]
CO <sub>2aq</sub>	-413,798	117,5704	-385,98	CRC [1]
CO <sub>2aq</sub>	E <sup>o</sup> <sub>H2C2O4</sub> = -0,6577 V		-42,90	2G <sub>CO2</sub> = ΔG <sub>eqH2C2O4</sub> -2G <sub>H3O</sub> +(G <sub>H2C2O4</sub> +2G <sub>H2O</sub> )=2*-42,902 kJ/mol;
CO <sub>2aq</sub>	E <sup>o</sup> <sub>HC2O4</sub> = -0,7092 V		-97,514	2G <sub>CO2</sub> = ΔG <sub>eqHC2O4</sub> -G <sub>H3O</sub> +(G <sub>HC2O4</sub> +G <sub>H2O</sub> )=2*-97,514 kJ/mol;
CO <sub>2aq</sub>	E <sup>o</sup> <sub>C2O4</sub> = -0,7607 V		-27,517	2G <sub>CO2</sub> =ΔG <sub>eqC2O4</sub> +(G <sub>C2O4</sub> )=-27,517 kJ/mol;
CO <sub>2aq</sub>	K <sub>eqCO2aqua</sub> šķīdība		18,38	G <sub>CO2aqua</sub> =ΔG <sub>eqCO2aqua</sub> +(G <sub>CO2gas</sub> +G <sub>H2O</sub> )=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 [1,29] datiem ar blīvumu  $1,072$  g/mL :

$$K_{eq\_sp}=[H_2C_2O_{4aq}]/[H_2C_2O_4^{cr}]/[H_2O]=1,3106/1/49,77=0,026329.$$

Mola masa  $M_{H_2C_2O_4}=90,034$  g/mol; koncentrācijas  $[H_2O]=982/18=49,777$  M;  $[H_2C_2O_4]=118/90,034=1,3106$  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  $K_{eq\_sp}=0,026329$ :

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

Hesa izteiksmē  $\Delta G_{eq\_sp}=G_{H_2C_2O_{4aq}}-(G_{H_2O}+G_{H_2C_2O_4^{cr}})=G_{H_2C_2O_{4aq}}-(0+76,96)=9,0161$  kJ/mol tika aprēķināts viena molā brīvās enerģijas saturu  $G_{H_2C_2O_{4aq}}=\Delta G_{eq\_sp}+(G_{H_2O}+G_{H_2C_2O_4^{cr}})=9,0161+(0+76,96)=85,976$  kJ/mol [29].

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;

$pH\leq 1,25$   $H_2C_2O_4+2H_2O=2CO_2+2H_3O^++2e^-$ ; Absolūtais aprēķins satur standarta potenciālu  $E^\circ_{klasisko}=-0,49$  V [17], ūdens logaritmu  $-0,0591/2*\lg(1/[H_2O]^2)=0,103$  un  $\Delta E^\circ=0,10166-0,37239$ :

$$E^\circ_{H_2C_2O_4}=E^\circ_{klasisko}-0,0591/2*\lg(1/[H_2O]^2)+\Delta E^\circ=-0,49+0,103+0,10166-0,37239=-0,6577$$
 V;

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

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

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

$$\Delta G_{eqH_2C_2O_4}=2G_{CO_2}+2G_{H_3O}-(G_{H_2C_2O_4}+2G_{H_2O})=2*0+2*22,44-(80,618+2*0)=-126,9$$
 kJ/mol ;

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

$1,25 < pH \leq 4,14$ ;  $HC_2O_4^-+H_2O=2CO_2+H_3O^++2e^-$ ; Aprēķins satur standarta potenciālu  $E^\circ_{klasisko}=-0,49$  V [17], ūdens logaritmu  $-0,0591/2*\lg(1/[H_2O])=0,0515$  un  $\Delta E^\circ=0,10166-0,37239$ :

$$E^\circ_{HC_2O_4}=E^\circ_{klasisko}-0,0591/2*\lg(1/[H_2O]^1)+\Delta E^\circ=-0,49+0,0515+0,10166-0,37239=-0,7092$$
 V;

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

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

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

$4,14 < pH$ ;  $C_2O_4^{2-}=2CO_2+2e^-$ ; Aprēķins satur standarta potenciālu  $E^\circ_{klasisko}=-0,49$  V [17], ūdens nulli 0 un  $\Delta E^\circ=0,10166-0,37239$ :

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

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

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

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

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



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

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

$\text{NAD}^++\text{H}(\text{H}^++2\text{e}^-)=\text{NADH}$ ; Absolūtais aprēķins satur inverso standarta potenciālu  $-E^{\circ}_{\text{klasisko}}=0,113 \text{ V}$  [22], ūdens nulli +0 un  $\Delta E^{\circ}=0,10166-0,37239$ :  $-E^{\circ}_{\text{NADH}}=-E^{\circ}_{\text{klasisko}}+0+\Delta E^{\circ}=0,113+0+0,10166-0,37239=0,38373 \text{ V}$ ;

$\text{CH}_3\text{CH}_2\text{OH}+\text{H}_2\text{O}=\text{CH}_3\text{CHO}+\text{H}_3\text{O}^++\text{H}(\text{H}^++2\text{e}^-)$ ; Absolūtais aprēķins satur standarta potenciālu  $E^{\circ}_{\text{klasisko}}=0,19 \text{ V}$  [19], ūdens  $-0,0591/2\cdot\log(1/[\text{H}_2\text{O}]^1)=0,0515$  logaritmu un  $\Delta E^{\circ}=0,10166-0,37239$ :

$$E^{\circ}_{\text{C}_2\text{H}_5\text{OH}}=E^{\circ}_{\text{klasisko}}-0,0591/2\cdot\log(1/[\text{H}_2\text{O}]^1)+\Delta E^{\circ}=0,19+0,0515+0,10166-0,37239=-0,02923 \text{ V};$$

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

Novērtētajā balansā  $n=2=m$  ar elektronu skaitu  $2\text{e}^-$  donors  $E^{\circ}_{\text{C}_2\text{H}_5\text{OH}}=-0,02923 \text{ V}$  plus elektronu akceptors  $-E^{\circ}_{\text{NAD}^+}=0,38373 \text{ V}$ , jo  $-E^{\circ}_{\text{NAD}^+}=0,38373 \text{ V}$  akceptē elektronus no etanola  $E^{\circ}_{\text{C}_2\text{H}_5\text{OH}}=0,02923 \text{ V}$ :

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



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

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

Red  $\text{NADH}=\text{NAD}^++\text{H}(\text{H}^++2\text{e}^-)$ ; Absolūtais aprēķins satur standarta potenciālu  $E^{\circ}_{\text{klasisko}}=-0,113 \text{ V}$  [22], ūdens nulli 0 un  $\Delta E^{\circ}=0,10166-0,37239$ :  $E^{\circ}_{\text{NADH}}=E^{\circ}_{\text{klasisko}}+0+\Delta E^{\circ}=-0,113+0+0,10166-0,37239=-0,38373 \text{ V}$ ;

Ox  $\text{CH}_3\text{CHO}+2\text{H}_3\text{O}^++\text{H}(2\text{e}^-)=\text{CH}_3\text{CH}_2\text{OH}+2 \text{H}_2\text{O}$ ; inversais standarta potenciāls  $-E^{\circ}_{\text{CH}_3\text{CHO}}=0,02923 \text{ V}$ ; [19]; Summa:

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

Novērtētajā balansā  $n=2=m$  ar elektronu skaitu  $2\text{e}^-$  donors  $E^{\circ}_{\text{NADH}}=-0,38373 \text{ V}$  plus elektronu akceptors  $-E^{\circ}_{\text{CH}_3\text{CHO}}=0,02923 \text{ V}$ , jo  $-E^{\circ}_{\text{CH}_3\text{CHO}}=0,02923 \text{ V}$  akceptē elektronus no B3 vitamīna  $E^{\circ}_{\text{NADH}}=-0,38373 \text{ V}$ .

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

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

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

Aerobi ja attiecība ir  $[\text{NAD}^+]/[\text{NADH}]=10^3$ ;  $\Delta\text{G}_{\text{Homeostāze}}=68,408-69,08=-0,674 \text{ kJ/mol}$ .

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

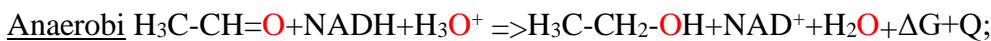
sasniedzot līdzsvaru  $\Delta\text{G}_{\text{min}}=\Delta\text{G}_{\text{eq}}=68,4 \text{ kJ/mol}$  aerobi un inversi

simetriski anaerobi  $\Delta\text{G}_{\text{min}}=\Delta\text{G}_{\text{eq}}=-68,4 \text{ kJ/mol}$  sasniedzot līdzsvara

maisījumu ar inversi simetriskām 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

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



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

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  $\text{D}+\text{E}+\text{F}$  50%  $\text{A}+\text{B}+\text{C}$

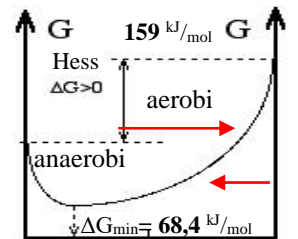
NADH reduktāzes enzīmu negatīva brīvās enerģijas izmaiņa  $\Delta\text{G}_{\text{Homeostāze}}=-27,86 \text{ kJ/mol}$   $\text{NADH}+\text{H}_3\text{CCH}=\text{O}+\text{H}_3\text{O}^+$

Anaerobā attiecība  $[\text{NADH}]/[\text{NAD}^+]=10$  virs  $[\text{NAD}^+]$  labvēlīga reducēšanai:  $\text{NAD}^++\text{H}_3\text{CCH}_2\text{OH}+\text{H}_2\text{O}$

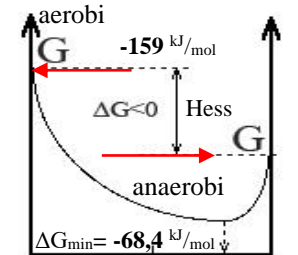
$$\Delta\text{G}_{\text{Anaerobā}}=-68,41+8,3144\cdot 298,15\cdot\ln(1\cdot 1\cdot 55,3/10/10/10^{(-7,36)})=-27,86 \text{ kJ/mol};$$

Aerobā homeostāzes  $\text{K}_{\text{Aerobā}}=\frac{[\text{NADH}]\cdot[\text{CH}_3\text{CHO}]\cdot[\text{H}_3\text{O}^+]}{[\text{NAD}^+]\cdot[\text{CH}_3\text{CH}_2\text{OH}]\cdot[\text{H}_2\text{O}]}$  oksidēšanas attiecība ir  $[\text{NADH}]/[\text{NAD}^+]=1/770$ ;

$$\Delta\text{G}_{\text{Homeostāze}}=68,408+8,3144\cdot 298,15\cdot\ln(1/770\cdot 1/1\cdot 10^{(-7,36)}/55,3)=-0,026 \text{ kJ/mol}.$$



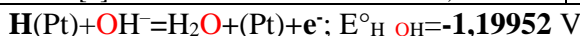
$\text{A}+\text{B}+\text{C}$  50%  $\text{D}+\text{E}+\text{F}$   
izejvielas  $\text{NAD}^++\text{H}_3\text{CCH}_2\text{OH}+\text{H}_2\text{O}$   
produkti  $\text{NADH}+\text{H}_3\text{CCH}=\text{O}+\text{H}_3\text{O}^+$



$\text{D}+\text{E}+\text{F}$  50%  $\text{A}+\text{B}+\text{C}$   
 $\text{NADH}+\text{H}_3\text{CCH}=\text{O}+\text{H}_3\text{O}^+$   
 $\text{NAD}^++\text{H}_3\text{CCH}_2\text{OH}+\text{H}_2\text{O}$

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

	Reducētā forma = Oksidētā forma + n e <sup>-</sup> ;	H <sub>2</sub> O atlaide klasiskā nulle E <sub>o</sub>	Termodinamiskā skala 0,10166 V	Absolūtā skala -0,37239
H	$\underline{\text{H}}(\text{Pt}) + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + (\text{Pt}) + \text{e}^-$ ; skalas atskaites potenciāls [1] $\underline{\text{H}}(\text{Pt}) + \text{OH}^- = \text{H}_2\text{O} + (\text{Pt}) + \text{e}^-$ ; klasika CRC [1]	klasiskā nulle 0 -0,8277	<b>0,10166</b> -0,8282	-0,27072 -1,200576
	$\underline{\text{H}}(\text{Pt}) + \text{OH}^- = \text{H}_2\text{O} + (\text{Pt}) + \text{e}^-$ ; korekcija -0,10449 klasikai [1]	-0,93219	-0,9326	-1,30507
	$\text{H}_{2\text{aq}} + \text{H}_2\text{O} = 2\text{H}_3\text{O}^+ + 2\text{e}^-$ ; grafitā elektrods	0,4687	0,6733	0,302
O	$5\text{H}_2\text{O} = \text{O}_{2\text{aq}} + 4\text{H}_3\text{O}^+ + 4\text{e}^-$ ; $\text{H}_2\text{O}_2 + 2\text{H}_2\text{O} = \text{O}_{2\text{aqua}} + 2\text{H}_3\text{O}^+ + \text{e}^-$ ; David Harris [21] $4\text{H}_2\text{O} = \text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^-$ ; Suchotina [17] $\text{H}_2\text{O}_{2\text{aqua}} + 2\text{H}_2\text{O} = \text{O}_{2\text{aqua}} + 2\text{H}_3\text{O}^+ + 2\text{e}^-$ University Alberta [19]	1,2288 1,2764 1,776 0,6945	1,4592 1,4811 2,0837 0,8992	1,0868 1,1087 1,7113 0,5268
CHO	$\text{C}_6\text{H}_{12}\text{O}_6 + 42\text{H}_2\text{O} = 24\text{H}_3\text{O}^+ + 6\text{H}_3\text{O}^+ + 6\text{HCO}_3^- + 24\text{e}^-$ $\text{HOO}^- + \text{H}_2\text{O} = \text{O}_{2\text{aqua}} + \text{H}_3\text{O}^+ + 2\text{e}^-$ ; Kaksis	-0,04909 0,3155	0,2328 0,4686	-0,13958 0,09625
N	$\text{NO}_2^- + 2\text{OH}^- = \text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^-$ ; pH>3,15 Suchotina [17] $\text{HNO}_2 + 4\text{H}_2\text{O} = \text{NO}_3^- + 3\text{H}_3\text{O}^+ + 2\text{e}^-$ ; pH<3,15 Kortly, Shucha [18] $\text{NO}_{\text{aq}} + 4\text{H}_2\text{O} = \text{HNO}_3^- + 3\text{H}_3\text{O}^+ + 3\text{e}^-$ ; pH<1,4 Kortly, Shucha [18] $\text{NH}_4^+ + 13\text{H}_2\text{O} = \text{NO}_3^- + 10\text{H}_3\text{O}^+ + 8\text{e}^-$ ; Suchotina [17]	0,01 0,94 0,96 0,87	0,0602 1,2477 1,19899 1,1390	-0,3122 0,8753 0,8266 0,7666
Br	$2\text{Br}^- = \text{Br}_2(\text{aq}) + 2\text{e}^-$ ; CRC [1]	1,0873	1,18896	0,8176
Bi	$\text{BiO}^+ + 6\text{H}_2\text{O} = \text{BiO}_3^- + 4\text{H}_3\text{O}^+ + 2\text{e}^-$ ; Suchotina [17]	1,80	2,21065	1,83826
Mn H <sup>+</sup>	$\text{Mn}^{2+} + 12\text{H}_2\text{O} = \text{MnO}_4^- + 8\text{H}_3\text{O}^+ + 5\text{e}^-$ ; Kortly, Shucha [18]	1,51	1,85885	1,4865
H <sub>2</sub> O	$\text{MnO}_2 \downarrow + 4\text{OH}^- = \text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^-$ ; Suchotina [17]	0,603	0,6360	0,2636
OH <sup>-</sup>	$\text{MnO}_4^{2-} = \text{MnO}_4^- + \text{e}^-$ ; Suchotina [17]	0,558	0,65966	0,2873
Pb	$\text{Pb}^{2+} + 6\text{H}_2\text{O} = \text{PbO}_2(\text{s}) + 4\text{H}_3\text{O}^+ + 2\text{e}^-$ ; Kortly, Shucha [18] $\text{Pb} + \text{H}_2\text{O} = \text{Pb}^{2+} + 2\text{e}^-$ ; pH<7 Kortly, Shucha [18]	1,455 -0,126	1,86565 0,02716	1,4933 -0,3452
S	$\text{H}_2\text{SO}_{3\text{aq}} + 4\text{H}_2\text{O} = \text{HSO}_4^- + 3\text{H}_3\text{O}^+ + 2\text{e}^-$ ; pH<2 Suchotina [17] $\text{HSO}_3^- + 4\text{H}_2\text{O} = \text{SO}_4^{2-} + 3\text{H}_3\text{O}^+ + 2\text{e}^-$ ; Suchotina [17] 2=<pH<7 $\text{SO}_3^{2-} + 2\text{OH}^- = \text{SO}_4^{2-} + \text{H}_2\text{O} + 2\text{e}^-$ ; Suchotina [17] pH > 7 $\text{S}^{2-} = \text{S}_{\text{rombisks}} + \text{H}_2\text{O} + 2\text{e}^-$ ; CRC 2010 [1] $\text{HS}^- + \text{OH}^- = \text{S}_{\text{rombisks}} + 2\text{H}_2\text{O} + 2\text{e}^-$ ; CRC 2010 [1] $\text{H}_2\text{S}_{\text{aq}} + 2\text{H}_2\text{O} = \text{S}_{\text{rombisks}} + 2\text{H}_3\text{O}^+ + 2\text{e}^-$ ; CRC [1]; Suchotina [17] $2\text{S}_2\text{O}_3^{2-} = \text{S}_4\text{O}_6^{2-} + 2\text{e}^-$ ; Suchotina [17]	0,172 0,172 -0,93 -0,4763 -0,478 0,142 0,08	0,47965 0,47965 -0,87984 -0,4261 -0,4793 0,3467 0,1817	0,10726 0,10726 -1,2522 -0,7985 -0,8517 -0,025735 -0,1907
Fe	$\text{Fe}^{2+} = \text{Fe}^{3+} + \text{e}^-$ ; Suchotina [17] $\text{Fe}_{(\text{s})} + \text{H}_2\text{O} = \text{Fe}^{2+} + 2\text{e}^-$ ; Suchotina [17]	0,769 -0,4402	0,8707 -0,2870	0,4983 -0,6594
Ag	$\text{Ag} + \text{H}_2\text{O} = \text{Ag}^+ + \text{e}^-$ ; Kortly, Shucha [18] $\text{Ag}(\text{s}) + \text{Cl}^- = \text{AgCl}(\text{s}) + \text{H}_2\text{O} + \text{e}^-$ ; Kortly, Shucha [18] $\text{Ag} + 2\text{NH}_3(\text{aq}) = \text{Ag}(\text{NH}_3)_2^+ + \text{e}^-$ ; Suchotina [17] $2\text{Ag} + 2\text{OH}^- = \text{Ag}_2\text{O}(\text{s}) + \text{H}_2\text{O} + 2\text{e}^-$ ; Suchotina [17]	0,7994 0,2223 0,373 0,345	1,00406 0,2210 0,57766 0,39516	0,6327 -0,1514 0,2053 0,02277
Hg	$2\text{Hg} + \text{H}_2\text{O} = \text{Hg}_2^{2+} + 2\text{e}^-$ ; Kortly, Shucha [18] $2\text{Hg} + 2\text{Cl}^- = \text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{H}_2\text{O} + 2\text{e}^-$ ; Suchotina ; [17] $2\text{Hg} + \text{SO}_4^{2-} = \text{Hg}_2\text{SO}_4(\text{s}) + \text{H}_2\text{O} + 2\text{e}^-$ ; Kortly, Shucha ; [18] $\text{Hg} + 2\text{OH}^- = \text{HgO} + \text{H}_2\text{O} + 2\text{e}^-$ ; Suchotina ; [17]	0,907 0,2676 0,614 0,098	1,0602 0,2663 0,6642 0,1482	0,6888 -0,1059 0,2918 -0,2242
I	$3\text{I}^- = \text{I}_3^- + 2\text{e}^-$ ; Kortly, Shucha [18]	0,6276	0,72926	0,35687
Cu	$\text{Cu}(\text{Hg}) + \text{H}_2\text{O} = \text{Cu}^{2+} + (\text{Hg}) + 2\text{e}^-$ ; Kortly, Shucha [18]	0,3435	0,4967	0,1243
F	$2\text{F}^- = \text{F}_2(\text{g}) + 2\text{e}^-$ ; Kortly, Shucha [18]	2,87	2,97166	2,5993
Cl	$2\text{Cl}^- = \text{Cl}_2(\text{g}) + 2\text{e}^-$ ; Kortly, Shucha [18]	1,358	1,45966	1,0873
Cl	$\text{Cl}_2(\text{g}) + 4\text{H}_2\text{O} = 2\text{HOCl} + 2\text{H}_3\text{O}^+ + 2\text{e}^-$ ; Kortly, Shucha [18]	1,63	1,93765	1,5653
Cr	$2\text{Cr}^{3+} + 21\text{H}_2\text{O} = \text{Cr}_2\text{O}_7^{2-} + 14\text{H}_3\text{O}^+ + 6\text{e}^-$ ; Kortly, Shucha [18] $\text{Cr}^{3+} + 11\text{H}_2\text{O} = \text{HCrO}_4^- + 7\text{H}_3\text{O}^+ + 3\text{e}^-$ ; Kortly, Shucha [18] $\text{Cr}(\text{OH})_3 \downarrow + 5\text{OH}^- = \text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^-$ ; pH>9 ; Suchotina [17]	1,33 1,20 -0,13	1,7921 1,6793 -0,1657	1,41975 1,30692 -0,53806
C	$\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} = 2\text{CO}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^-$ ; Suchotina [17]	-0,49	-0,2853	-0,6577
Cr	$\text{Cr} + \text{H}_2\text{O} = \text{Cr}^{3+} + 3\text{e}^-$ ; Suchotina [17]	-0,744	-0,60801	-0,97935
Zn	$\text{Zn} + \text{H}_2\text{O} = \text{Zn}^{2+} + 2\text{e}^-$ ; Kortly, Shucha [18]	-0,7628	-0,6096	-0,98098
Al	$\underline{\text{Al}} + \text{H}_2\text{O} = \text{Al}^{3+} + 3\text{e}^-$ ; CRC [1] $\underline{\text{Al}} + 4\text{OH}^- = \text{H}_2\text{AlO}_3^- + \text{H}_2\text{O} + 3\text{e}^-$ ; CRC [1]	-1,662 -2,35	-1,52601 -2,28267	-1,8984 -2,63506



Absolūtais potenciāls tiek koriģēts ar hidroksīda G<sub>OH</sub> = 77,36 kJ/mol brīvās enerģijas uzskaiti Hesa aprēķinā:

$$\Delta G_{\text{AlbertyH,OH}} = G_{\text{H}_2\text{O}} - (G_{\text{H}(\text{Pt})} + G_{\text{OH}}) = 0 - (48,56025 + 77,36) = -125,92 \text{ kJ/mol un aprēķina izteiksmē izlaboto absolūto potenciālu: } E_{\text{H}}^{\circ} = \Delta G_{\text{eq}} / F = -125920 / 96485 = -1,30508 \text{ V.}$$

Ūdens daudzuma atlaide [H<sub>2</sub>O] = 963/18 = 53,5 M litrā sērskābes [H<sub>2</sub>SO<sub>4</sub>] = [H<sub>3</sub>O<sup>+</sup>] = 1 M šķīdumam ar 1,061 g/mL blīvumu **ūdenražā elektrodam** ir klasiska E<sub>o,classic</sub> = -0,8277 V un absolūtā standarta potenciāls ir:

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

$$\text{dati koriģē } \Delta G_{\text{eqH,OH}} = E_{\text{H,OH}}^{\circ} \cdot F \cdot 1 = -1,30508 * 96485 * 1 = -125,92 \text{ kJ/mol uz } E_{\text{H}}^{\circ} = -0,8277 - 0,10449 = -0,9322 \text{ V.}$$

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

<b>Tabula 1.</b> Nernsta un <b>inversās</b> pus-reakcijas	Standart potenciāli E° dati no [1-24]	Ūdens atlaide klasika E° <sub>H=0</sub>	Termodinamiskā skala 0,10166 V	<b>Absolūtā</b> -0,37239
$\text{OH}^- = \text{HO} + e^-$	CRC	2,020	2,1217	1,750321
$4 \text{H}_2\text{O} = \text{H}_2\text{O}_{2\text{aqua}} + 2 \text{H}_3\text{O}^+ + 2 e^-$	Suchotina	1,776	2,0837	1,7113
$\text{H}_2\text{O}_2 + 2 \text{H}_2\text{O} = \text{O}^-_{2\text{aqua}} + 2 \text{H}_3\text{O}^+ + e^-$	David Harris	1,276	1,4811	1,1087
$5\text{H}_2\text{O} = \text{O}_{2\text{aq}} + 4\text{H}_3\text{O}^+ + 4 e^-$ ; $\text{HNO}_2 + 4\text{H}_2\text{O} = \text{NO}_3^- + 3\text{H}_3\text{O}^+ + 2e^-$	University Alberta	1,2288	1,45920	1,0868
$\text{NO}_2 + 3 \text{H}_2\text{O} = \text{NO}_3^- + 2 \text{H}_3\text{O}^+ + 2e^-$	David Harris	0,94	1,24765	0,87631
Hydroquinone + 2H <sub>2</sub> O = p-quinone + 2H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup>		0,699	0,9041	0,5327
$\text{H}_2\text{O}_{2\text{aqua}} + 2\text{H}_2\text{O} = \text{O}_{2\text{aqua}} + 2\text{H}_3\text{O}^+ + 2e^-$	University Alberta	0,695	0,8992	0,5268
$\text{Fe}^{2+} = \text{Fe}^{3+} + e^-$	University Alberta	0,769	0,8707	0,4983
Ubiquinol + 2H <sub>2</sub> O = Ubiquinone + 2H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup>		0,459	0,6638	0,2924
Succinate <sup>2-</sup> + 2H <sub>2</sub> O = Fumarate <sup>2-</sup> + 2H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup> pH=7 E <sub>0</sub> =0,031 V		0,4447	0,6494	0,2780
ButyrylCoA + 2H <sub>2</sub> O = CrotonylCoA + 2H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup>		0,399	0,6038	0,2056
AscorbicAcid + 2H <sub>2</sub> O = C <sub>6</sub> H <sub>6</sub> O <sub>6</sub> + 2H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup> DC, Harris		0,390	0,5947	0,1965
glycolate + 2H <sub>2</sub> O = Glyoxylate + H <sup>+</sup> (H <sup>+</sup> + 2e <sup>-</sup> ) + H <sub>3</sub> O <sup>+</sup> ; D.C.Harris		0,324	0,5287	0,1305
$\text{C}_6\text{H}_{12}\text{O}_6 + 42\text{H}_2\text{O} = 24\text{H}_3\text{O}^+ + 6\text{H}_3\text{O}^+ + 6\text{HCO}_3^- + 24e^-$ <a href="#">6. lapa</a> Kaksis		-0,0491	0,2328	-0,1396
$\text{HOO}^- + \text{H}_2\text{O} = \text{O}_{2\text{aqua}} + \text{H}_3\text{O}^+ + 2e^-$	Aris Kaksis	0,3155	0,4686	0,09625
$\text{Fe}^{2+} = \text{Cytochrome F Fe}^{3+} + e^-$	David Harris	0,365	0,4667	0,0953
$[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-} = [\text{Fe}^{\text{III}}(\text{CN})_6]^{3-} + e^-$	University Alberta	0,356	0,4574	0,0860
Malate <sup>2-</sup> + 2H <sub>2</sub> O = Oxalo-acetate <sup>2-</sup> + 2H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup>		0,248	0,4528	0,0814
$\text{Fe}^{2+} = \text{Cytochrome a3 Fe}^{3+} + e^-$		0,350	0,4517	0,0803
Lactate <sup>-</sup> + H <sub>2</sub> O = Pyruvate <sup>-</sup> + H <sub>3</sub> O <sup>+</sup> + H <sup>+</sup> (H <sup>+</sup> + 2e <sup>-</sup> ) <sup>-</sup>		0,229	0,3823	0,0109
$\text{FADH}_2 + 2\text{H}_2\text{O} = \text{FADfree} + 2\text{H}_3\text{O}^+ + 2e^-$		0,195	0,3998	0,0284
$\text{CH}_3\text{COO}^- + \text{H}_2\text{O} = \text{glycolate} + \text{H}^+ (\text{H}^+ + 2e^-) + \text{H}_3\text{O}^+$ ; D.C.Harris		0,1605	0,3652	-0,00618
$\text{H}_2\text{S}_{\text{aq}} + 2\text{H}_2\text{O} = \text{S}_{\text{rombisks}} + 2\text{H}_3\text{O}^+ + 2e^-$ ; CRC 2010		0,142	0,3467	-0,0247
$\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} = \text{CH}_3\text{CHO} + \text{H}_3\text{O}^+ + \text{H}^+ (\text{H}^+ + 2e^-)$ [17]		0,19	0,3432	-0,02923
$\text{Fe}^{2+} = \text{Cytochrome a Fe}^{3+} + e^-$		0,2900	0,3917	0,02032
$2\text{GlutathSH} + 2\text{H}_2\text{O} = \text{GlutaS-Sthione} + 2\text{H}_3\text{O}^+ + 2e^-$		0,1841	0,3888	0,01742
$\text{Fe}^{2+} = \text{Cytochrome c Fe}^{3+} + e^-$		0,2540	0,3557	-0,01568
$\text{LipSHSH} + 2\text{H}_2\text{O} = \text{LipoicAcidS-S} + 2\text{H}_3\text{O}^+ + 2e^-$		0,1241	0,3288	-0,04258
$\text{Fe}^{2+} = \text{Cytochrome c1 Fe}^{3+} + e^-$		0,2200	0,3217	-0,04968
$\beta\text{-OH Butyrate}^- + 2\text{H}_2\text{O} = \text{AcetoAcetate}^- + 2\text{H}_3\text{O}^+ + 2e^-$		0,0681	0,2728	-0,09858
$\text{isocitrate}^{2-} + 2\text{H}_2\text{O} = \alpha\text{-Ketoglutarate}^{2-} + \text{CO}_2 + 2\text{H}_3\text{O}^+ + 2e^-$		0,0341	0,2388	-0,13258
Nernst's $\text{H}_{2\text{aq}} + \text{H}_2\text{O} = 2\text{H}_3\text{O}^+ + 2e^-$ $\Delta G_{\text{Hess, H}_3\text{O}^+} = -58,12$ kJ/mol			<b>H<sub>2aq</sub> Oxidē ar grafiņa elektrodu</b>	-0,302
Inverse: $2\text{H}_3\text{O}^+ + 2e^- = \text{H}_{2\text{aq}} + \text{H}_2\text{O}$ ; $\Delta G_{\text{Hess, H}_{2\text{aq}}} = 58,12$ kJ/mol			<b>Reducēšana ar grafiņa elektrīdu</b>	0,302
$2\text{H}(\text{Pt}) + \text{H}_2\text{O} = \text{H}_{2\text{aq}}$ $\Delta G_{\text{šķ, H}(\text{Pt})} = G_{\text{H}_{2\text{aq}}} - 2G_{\text{H}(\text{Pt})} - G_{\text{H}_2\text{O}} = 1,14$ kJ/mol			<b>K<sub>šķ, H(Pt)</sub> = [H(Pt)]<sup>2</sup> * [H<sub>2</sub>O] / [H<sub>2aq</sub>] = 11,8</b>	
$\text{H}(\text{Pt}) + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + (\text{Pt}) + e^-$ ; [H <sub>3</sub> O <sup>+</sup> ] = 1 M pH=0 classic zero		0,0000	0,10166	<b>-0,27072</b>
<b>Luciferin</b> + OH <sup>-</sup> = ? <b>luciferin</b> + CO <sub>2</sub> aqua + OH <sup>-</sup> + 3H(3H <sup>+</sup> + 3e <sup>-</sup> ) + e <sup>-</sup> ;		0	0,1017	-0,27073
$\text{Fe}^{2+} = \text{Cytochrome b Fe}^{3+} + e^-$		0,0770	0,1787	-0,1937
$\text{CH}_3\text{CHO} + 3\text{H}_2\text{O} = \text{CH}_3\text{COOH} + 2\text{H}_3\text{O}^+ + 2e^-$ Suchotina		-0,1180	0,1382	-0,2342
$\text{Glycaldehy3P}^{2-} + \text{H}_2\text{O} + \text{HPO}_4^{2-} = 13\text{PGlycerate}^{4-} + \text{H}_3\text{O}^+ + \text{H}^+$		-0,1314	0,0218	-0,3506
$\text{NADPH} = \text{NADP}^+ + \text{H}^+ (\text{H}^+ + 2e^-)$ ;		-0,1170	-0,0153	-0,3877
$\text{NADH} = \text{NAD}^+ + \text{H}^+ (\text{H}^+ + 2e^-)$ ;	David Harris	-0,1130	-0,0113	-0,3837
$\text{O}^-_{2\text{aqua}} = \text{O}_{2\text{aqua}} + e^-$	Suchotina	-0,2450	-0,1433	-0,5157
$\text{Ferredoxin Fe}^{2+} = \text{Ferredoxin Fe}^{3+} + e^-$		-0,4320	-0,3303	-0,7027
$\text{C}_6\text{H}_{12}\text{O}_6 + 4\text{H}_2\text{O} = 2\text{C}_3\text{H}_4\text{O}_3 + 4\text{H}_3\text{O}^+ + 4e^-$ Stryer		-0,5427	-0,3380	-0,7104
$\text{S}^{2-} = \text{S}_{\text{rombisks}} + 2 e^-$ ; CRC 2010		-0,4763	-0,3746	-0,7470
$\text{HS}^- + \text{OH}^- = \text{S}_{\text{rombisks}} + \text{H}_2\text{O} + 2e^-$ ; CRC 2010		-0,4780	-0,4278	-0,8002
$\text{H}(\text{Pt}) + \text{OH}^- = \text{H}_2\text{O} + (\text{Pt}) + e^-$ ; corrected (-0,8277 + -0,10449) =		-0,9322	-0,9335	-1,3059
Ubiquinol6 + 2H <sub>2</sub> O = Ubiquinone6 + 2H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup> CRC 2012		-1,0500	-0,8453	-1,2177

$\Delta G_{\text{Alberty H-OH}} = G_{\text{H}_2\text{O}} - (G_{\text{H}(\text{Pt})} + G_{\text{OH}^-}) = \mathbf{0 - (48,56 + 77,36) = -125,92}$  kJ/mol,  $E^\circ_{\text{H}} = \Delta G_{\text{eq}} / F / 1 = \mathbf{-125920 / 96485 / 1 = -1,30508}$  V  
dati koriģē  $\Delta G_{\text{eqH-OH}} = E^\circ_{\text{H-OH}} \cdot F \cdot 1 = \mathbf{-1,30508 * 96485 * 1 = -125,92}$  kJ/mol uz  $E^\circ_{\text{H}} = -0,8277 - 0,10449 = -0,9322$  V.

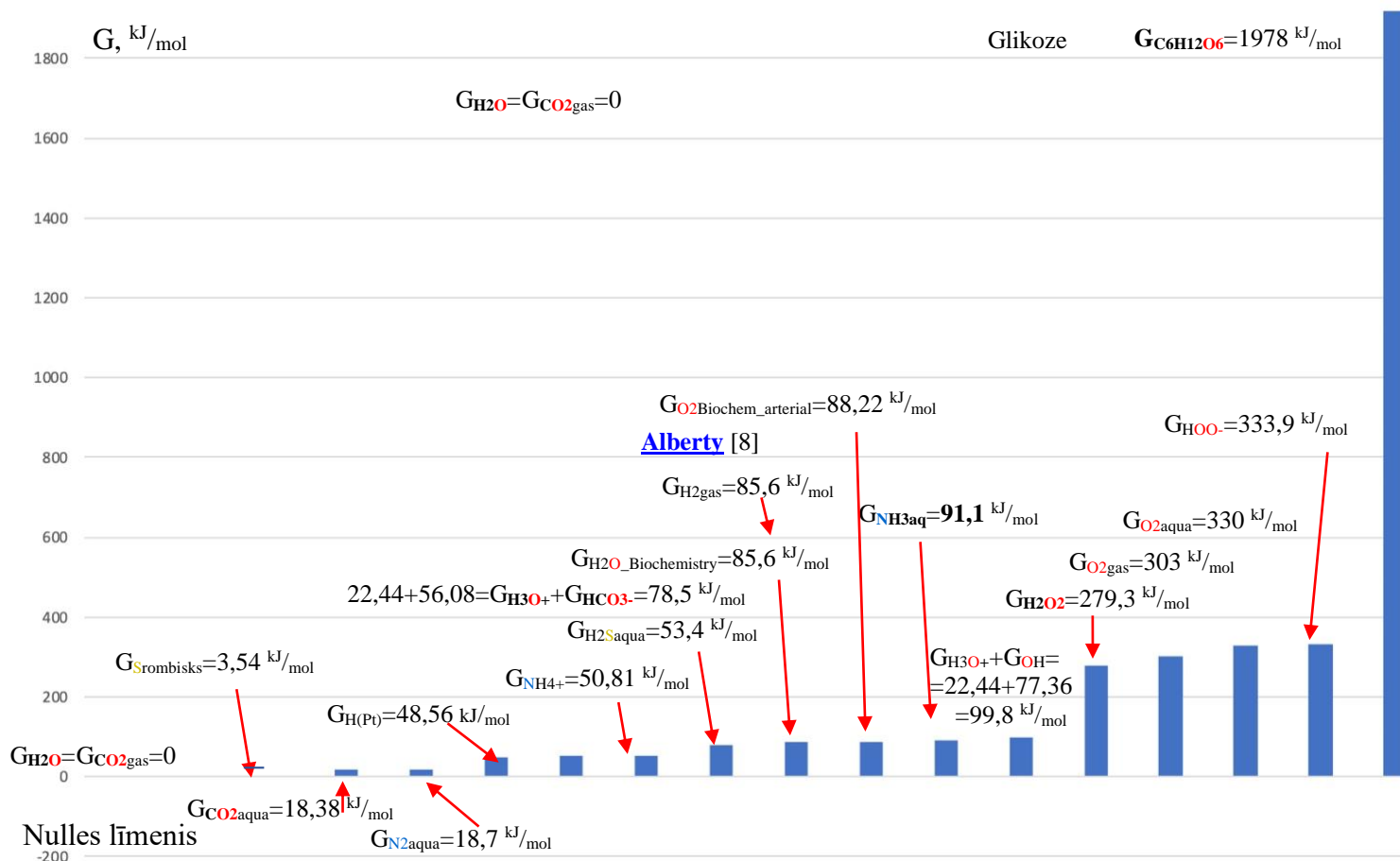


**Tabula 2. Nernsta pus reakciju Standarta Electrodu Potenciāli klssikais, termodinamiskais absolūtais V.**

	Reducētā forma = Oksidētā forma	H <sub>2</sub> O atlaide klasika nulle E°=0	Termodinamiskais. E°=0,10166 V	Absolūtā skala E° -0,37239 V
<b>H</b>	<u>H</u> (Pt)+H <sub>2</sub> O=H <sub>3</sub> O <sup>+</sup> +(Pt)+e <sup>-</sup> ; skalas atskaites potenciāls [1]	classic zero <b>0</b>	<b>0,10166</b>	-0,27072
<b>N</b>	NO <sub>2</sub> <sup>-</sup> +2OH <sup>-</sup> =NO <sub>3</sub> <sup>-</sup> +H <sub>2</sub> O+2e <sup>-</sup> ; pH>3.15 Suchotina [17]	0,01	0,0602	-0,3112
	HNO <sub>2</sub> +4H <sub>2</sub> O=NO <sub>3</sub> <sup>-</sup> +3H <sub>3</sub> O <sup>+</sup> +2e <sup>-</sup> ; pH<3.15 Kortly, Shucha	0,94	1,2477	0,8763
	NO <sub>aq</sub> +4H <sub>2</sub> O=HNO <sub>3</sub> <sup>-</sup> +3H <sub>3</sub> O <sup>+</sup> +3e <sup>-</sup> ; pH<1,4 Kortly, Shucha	0,96	1,19899	0,8266
	NH <sub>4</sub> <sup>+</sup> +13H <sub>2</sub> O=NO <sub>3</sub> <sup>-</sup> +10H <sub>3</sub> O <sup>+</sup> +8e <sup>-</sup> ; Suchotina [17]	0,87	1,4180	1,0466
<b>Br</b>	2Br <sup>-</sup> =Br <sub>2</sub> (aq)+2e <sup>-</sup> ; CRC	1,0873	1,18896	0,8176
<b>Bi</b>	BiO <sup>+</sup> +6H <sub>2</sub> O=BiO <sub>3</sub> <sup>-</sup> +4H <sub>3</sub> O <sup>+</sup> +2e <sup>-</sup> ; 1<pH<7 Suchotina [17]	1,80	2,21065	1,8383
<b>Mn H<sup>+</sup></b>	Mn <sup>2+</sup> +12H <sub>2</sub> O=MnO <sub>4</sub> <sup>-</sup> +8H <sub>3</sub> O <sup>+</sup> +5e <sup>-</sup> ; Kortly, Shucha [18]	1,51	1,85885	1,4865
<b>H<sub>2</sub>O</b>	MnO <sub>2</sub> ↓+4OH <sup>-</sup> =MnO <sub>4</sub> <sup>-</sup> +2H <sub>2</sub> O+3e <sup>-</sup> ; Suchotina	0,603	0,6360	0,2636
<b>OH<sup>-</sup></b>	MnO <sub>4</sub> <sup>2-</sup> =MnO <sub>4</sub> <sup>-</sup> +e <sup>-</sup> ; Suchotina	0,558	0,65966	0,2873
<b>Pb</b>	Pb <sup>2+</sup> +6H <sub>2</sub> O=PbO <sub>2</sub> (s)+4H <sub>3</sub> O <sup>+</sup> +2e <sup>-</sup> ; Kortly, Shucha	1,455	1,86565	1,4933
<b>S</b>	H <sub>2</sub> SO <sub>3aq</sub> +3H <sub>2</sub> O=HSO <sub>4</sub> <sup>-</sup> +3H <sub>3</sub> O <sup>+</sup> +2e <sup>-</sup> ;	0,172	0,47965	0,10726
	HSO <sub>3</sub> <sup>-</sup> +4H <sub>2</sub> O=SO <sub>4</sub> <sup>2-</sup> +3H <sub>3</sub> O <sup>+</sup> +2e <sup>-</sup> ; Suchotina 2=<pH<7	0,172	0,47965	0,10726
	SO <sub>3</sub> <sup>2-</sup> +2OH <sup>-</sup> =SO <sub>4</sub> <sup>2-</sup> +H <sub>2</sub> O+2e <sup>-</sup> ; Suchotina pH > 7	-0,93	-0,87984	-1,2522
	S <sup>2-</sup> =S <sub>rombic</sub> +H <sub>2</sub> O + 2 e <sup>-</sup> ; CRC2010	-0,4763	-0,4261	-0,7985
	H <sub>2</sub> S <sub>aq</sub> +2H <sub>2</sub> O=S <sub>rombic</sub> +2H <sub>3</sub> O <sup>+</sup> +2e <sup>-</sup> ; CRC 2010: Suchotina	0,142	-0,4793	-0,8517
2S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> =S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> +2e <sup>-</sup> ; Suchotina	0,08	0,3467	-0,025735	
<b>Fe</b>	Fe <sup>2+</sup> =Fe <sup>3+</sup> +e <sup>-</sup> ; Suchotina [17]	0,769	0,8707	0,4983
	Fe(s)+H <sub>2</sub> O=Fe <sup>2+</sup> +2e <sup>-</sup> ; Suchotina	-0,4402	-0,2870	-0,6594
<b>Ag</b>	Ag+H <sub>2</sub> O=Ag <sup>+</sup> +e <sup>-</sup> ; Kortly, Shucha [18]	0,7994	1,00406	0,6327
	Ag(s)+Cl <sup>-</sup> =AgCl(s)+H <sub>2</sub> O+e <sup>-</sup> ; Kortly, Shucha	0,2223	0,2210	-0,1514
	Ag+2NH <sub>3aq</sub> =Ag(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup> +H <sub>2</sub> O+e <sup>-</sup> ; Suchotina	0,373	0,57766	0,2053
	2Ag+2OH <sup>-</sup> =Ag <sub>2</sub> O(s)+H <sub>2</sub> O+2e <sup>-</sup> ; Suchotina	0,345	0,39516	0,02277
<b>I</b>	3I <sup>-</sup> =I <sub>3</sub> <sup>-</sup> +2e <sup>-</sup> ; Kortly, Shucha	0,6276	0,72926	0,35687
<b>Cu</b>	Cu(Hg)+H <sub>2</sub> O=Cu <sup>2+</sup> +(Hg)+2e <sup>-</sup> ; Kortly, Shucha	0,3435	0,4967	0,1243
<b>F</b>	2F <sup>-</sup> =F <sub>2</sub> (g)+2e <sup>-</sup> ; Kortly, Shucha	2,87	2,97166	2,5993
<b>Cl</b>	2Cl <sup>-</sup> =Cl <sub>2</sub> (g)+2e <sup>-</sup> ; Kortly, Shucha	1,358	1,45966	1,0873
<b>Cl</b>	Cl <sub>2</sub> (g)+4H <sub>2</sub> O=2HOCl+2H <sub>3</sub> O <sup>+</sup> +2e <sup>-</sup> ; Kortly, Shucha	1,63	1,93765	1,5653
<b>Cr</b>	2Cr <sup>3+</sup> +21H <sub>2</sub> O=Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> +14H <sub>3</sub> O <sup>+</sup> +6e <sup>-</sup> ; 1<pH<7 [18]	1,33	1,7921	1,41975
	Cr <sup>3+</sup> +11H <sub>2</sub> O=HCrO <sub>4</sub> <sup>-</sup> +7H <sub>3</sub> O <sup>+</sup> +3e <sup>-</sup> ; pH>7 Kortly, Shucha	1,20	1,6793	1,30692
	Cr(OH) <sub>3</sub> ↓+5OH <sup>-</sup> =CrO <sub>4</sub> <sup>2-</sup> +4H <sub>2</sub> O+3e <sup>-</sup> ; pH>9; Suchotina	-0,13	-0,1657	-0,53806
<b>C</b>	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> +2H <sub>2</sub> O=2CO <sub>2</sub> +2H <sub>3</sub> O <sup>+</sup> +2e <sup>-</sup> ; pH<1,25 Suchotina [17]	-0,49	-0,2853	-0,6577
<b>Cr</b>	Cr+H <sub>2</sub> O=Cr <sup>3+</sup> +3e <sup>-</sup> ; Suchotina	-0,744	-0,60801	-0,97935
<b>Zn</b>	Zn+H <sub>2</sub> O=Zn <sup>2+</sup> +2e <sup>-</sup> ; Kortly, Shucha	-0,7628	-0,6096	-0,98098
<b>H</b>	<u>H</u> (Pt)+OH <sup>-</sup> =H <sub>2</sub> O+(Pt)+e <sup>-</sup> ; corrected (-0.8277+-0.10449)=	-0,9322	-0,93375	-1,30508

Hesa brīvo elementu **nulles** standarta vērtības absolūtajā bioķīmijas brīvās enerģijas skalā patiesībā ir pozitīvas  $G_{H_2gas}=85,6 \text{ kJ/mol}$  [Alberty](#) attiecinātas uz homeostāzes produktu ūdens un  $CO_2gas$  nulli  $G_{H_2O}=G_{CO_2gas}=0 \text{ kJ/mol}$ . Uzrādīto metabolītu brīvās enerģijas saturi homeostāzē  $pH=7,36$ , kas attiecas uz ūdens un  $CO_2gas$  gāzes nulles vērtībām enerģijas mērogā ir:

Glikoze  $G_{C_6H_{12}O_6}=1978 \text{ kJ/mol} > \text{deprotonēts peroksīda anjons } G_{HO_2}=333,9 \text{ kJ/mol} > G_{O_2aqua}=330 \text{ kJ/mol} > G_{O_2gas}=303 \text{ kJ/mol} > \text{peroksīds } G_{H_2O_2}=279,3 \text{ kJ/mol} > \text{ūdens protolīzes } pH=pOH=7 \text{ } G_{H_3O^++OH^-}=G_{H_3O^+}+G_{OH^-}=22,44+77,36=99,8 \text{ kJ/mol} > G_{NH_3aq}=91,1 \text{ kJ/mol} > G_{O_2Biochem\_arterial}=88,22 \text{ kJ/mol} > G_{H_2gas}=85,6 \text{ kJ/mol} \equiv G_{H_2O\_Biochemistry}=85,6 \text{ kJ/mol} > CO_2aqua \text{ šķīduma protolīze ar karbo anhidrāzi } G_{H_3O^+}+G_{HCO_3^-}=G_{H_3O^+}+G_{HCO_3^-}=22,44+56,08=78,5 \text{ kJ/mol} > G_{H_2Saq}=53,4 \text{ kJ/mol} > G_{NH_4^+}=50,81 \text{ kJ/mol} > G_{H(Pt)}=48,56 \text{ kJ/mol} > G_{N_2aqua}=18,7 \text{ kJ/mol} > G_{CO_2aqua}=18,38 \text{ kJ/mol} > G_{Srombisks}=3,54 \text{ kJ/mol} > \text{homeostāzes produktu nulles vērtības } G_{H_2O}=G_{CO_2gas}=0 \text{ kJ/mol} > G_{N_2gas}=-9,55 \text{ kJ/mol};$



Grafiks 1. Augoša **absolūtās** brīvā enerģija metabolītiem attiecināta uz  $G_{H_2O}=G_{CO_2gas}=0 \text{ kJ/mol}$  nulles vērtību. Atklājums zinātnē par **Absolūto potenciālu skalu** ir sakrītošs ar **absolūtās** brīvās enerģijas nozīmīgi.

Ūdens un hidroksionija atlaide reakcijās ieskaitot protolīzi un elektroķīmiju Nernsta pus reakcijās ierobežo zinātniskās studijas termodinamikā, fizikālā ķīmijā un bioķīmijā. [8,14,15]

**Inversijas simetrijas** termodinamiskā īpašība ir tieša reakcija starp reaģentiem un produktiem, kas apgriežas pretējā virzienā, sākotnēji nozīmējot produktus kā reaģentus un atstājot reaģentus kā galaproduktus. Ūdeni par skābekli oksidēšanas reducēšanas  $5H_2O=O_{2aqua}+4H_3O^++4e^-$  Nernsta pus reakcijā ir **absolūtais standarta potenciāls**:  $E^{\circ}_{O_2Absolute}=1.0868 \text{ V}$ . Par  $O_{2aqua}+4H_3O^++4e^-=5H_2O$  iesaistīšanos **inversajā** reakcijā **absolūtam potenciālam** ir vienāds skaitlis ar pretēju zīmi  $E^{\circ}_{O_2Absolute}=-1.0868 \text{ V}$  negatīvs.

Atklātā **absolūtā potenciāla skala** Nernsta vai **inversajām** reakcijām sakrīt ar **absolūtās** brīvās enerģijas īpašību **inversajā simetrijā**. [8, 14, 15] Nernsta vai **inverso** reakciju **inversās simetrijas** īpašība ar identiskām vērtībām, bet ar **pretēju zīmi**, kas izpaužas **absolūtā potenciāla skalā** ar **absolūto** brīvo enerģiju, ir sakrītīga termodinamiskā īpašība protolīzes reakcijai, Nernsta pus reakcijai vai **inversajai** reakcijai.

Koriģētā metāla ūdeņraža termodinamiskā standarta potenciāla atskaite 0,10166 Volti dažu gadu laikā dod impulsu zinātnēm iegūt **absolūtās** termodinamiskās vērtības elementu un molekulu brīvajai enerģijai.

Pateicoties Alberty dotajiem datiem par ūdeņraža **absolūto** brīvo enerģiju gāzei  $G_{H_2gas}=85,6 \text{ kJ/mol}$  un  $G_{H_2aqua}=103 \text{ kJ/mol}$  šķīdumā ir noteikti **absolūtie** standarta potenciāli metāla ūdeņraža vispārīgā atskaite  $\Delta G^{\circ}_{H_2O}=G_{H_2O}-(G_{H_2aq}+0,5G_{O_2})=0-(103,24+88,04/2)=-147,26 \text{ kJ/mol}$ .

$E^\circ_{\text{H}} = -0.27073$  Volto. Tabulā 1. tiek publicētas 50 bioķīmijā lietotas Nernsta oksidēšanas pus vai reducēšanas **inversās** reakcijas.

Trijos stabiņos mēs varam novērot attīstību ūdeņraža vispārīgai atskaites skalai no klasiskās nulles  $E^\circ_{\text{H}} = 0$  V ar ūdens atlaidi. Ūdens un hidroksionija katjona uzskaitē koriģē vispārīgo ūdeņraža termodinamisko standarta skalas atskaites potenciālu uz  $E^\circ_{\text{H}} = 0.10166$  Voltiem. Trešajā stabiņā Alberty dati beidzot noved pie **absolūtās** standarta **potenciāla** vērtības  $E^\circ_{\text{H}} = -0.27073$  Volti ūdeņraža elektrodam.

**H<sub>2</sub>O<sub>2</sub> veidošanās** 41. lapa **H<sub>2</sub>gas + O<sub>2</sub>gas => H<sub>2</sub>O<sub>2</sub>**;  $\Delta G^\circ_{\text{UnivAlberta}} = -134,03$  kJ/mol;  $\Delta G^\circ_{\text{Alberty}} = -48,39$  kJ/mol;

$\Delta G_{\text{Alberty}} = G_{\text{H}_2\text{O}_2} - (G_{\text{O}_2\text{gas}} + G_{\text{H}_2\text{gas}}) = 284,25 - (85,64 + 303) = -104,64$  kJ/mol (-134,03 kJ/mol); (= -48,39 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
<b>H<sub>2</sub>O<sub>2</sub>aq</b>	<b>-191,99</b>	<b>-481,688</b>	<b>-48,39</b>
H <sub>2</sub> O <sub>2</sub> aq	-191,17	143,9	-134,03
<b>Succinat<sup>2-</sup></b>	<b>-908,69</b>	<b>-1295,576</b>	<b>-522,414</b>
<b>Fumarate<sup>2-</sup></b>	<b>-776,56</b>	<b>-862,288</b>	<b>-519,4688</b>

Alberty nulles  $G_{\text{H}_2\text{O}} = 0$  kJ/mol; atskaitē bāzēti **G<sub>H<sub>2</sub>O<sub>2</sub></sub> = 284,25** kJ/mol  
University Alberta

$G_{\text{SuccinatFor}} = -522,4 + (4 * 91,26 + 2 * 85,6 + 2 * 303) = 619,8$  kJ/mol;  $G_{\text{Succinat}} = 650,8$  kJ/mol;

$G_{\text{FumaricFor}} = -519,5 + (4 * 91,26 + 85,6 + 2 * 303) = 537,1$  kJ/mol;  $G_{\text{Fumarat}} = 554,75$  kJ/mol;

**Succinat<sup>2-</sup> veidošanās** **4C + 2H<sub>2</sub>gas + 2O<sub>2</sub>gas => (CH<sub>2</sub>)<sub>2</sub>(CO<sub>2</sub><sup>-</sup>)(CO<sub>2</sub><sup>-</sup>)**;  $\Delta G_{\text{Succinat}} = -522,4$  kJ/mol Alberty;

$\Delta G_{\text{SuccinatFor}} = G_{\text{SuccinatFor}} - (4G_{\text{Cgraph}} + 2 * G_{\text{H}_2\text{gas}} + 2 * G_{\text{O}_2\text{gas}}) = -522,4$  kJ/mol;

$G_{\text{SuccinatFor}} = -522,4 + (4 * 91,26 + 2 * 85,6 + 2 * 303) = 619,8$  kJ/mol;

**Fumarate<sup>2-</sup> veidošanās** **4C + H<sub>2</sub>gas + 2O<sub>2</sub>gas => (CH)<sub>2</sub>(CO<sub>2</sub><sup>-</sup>)(CO<sub>2</sub><sup>-</sup>)**;  $\Delta G_{\text{Fumarat}} = -519,5$  kJ/mol Alberty;

$\Delta G_{\text{Fumarat}} = G_{\text{FumaratFor}} - (4G_{\text{Cgraph}} + G_{\text{H}_2\text{gas}} + 2 * G_{\text{O}_2\text{gas}}) = -519,5$  kJ/mol;

$G_{\text{FumaratFor}} = -519,5 + (4 * 91,26 + 85,6 + 2 * 303) = 537,1$  kJ/mol; ; [veidošanās](#) 73. lapa

**Inversais O<sub>2</sub>aq + 2H<sub>3</sub>O<sup>+</sup> + 2e<sup>-</sup> = H<sub>2</sub>O<sub>2</sub>aq + 2H<sub>2</sub>O**; standarta potenciāls  $E^\circ_{\text{OxO}_2\text{H}_2\text{O}_2} = -0,5278$ V University Alberta ;

$\Delta G_{\text{AlbertyOxO}_2\text{H}_2\text{O}_2} = G_{\text{H}_2\text{O}_2} + 2 * G_{\text{H}_2\text{O}} - (G_{\text{O}_2\text{aq}} + 2 * G_{\text{H}_3\text{O}^+}) = 279,29 + 2 * 0 - (330 + 2 * 22,44) = -95,59$  kJ/mol ;

$\Delta G_{\text{eqAlbertyAbsoluteOxO}_2\text{H}_2\text{O}_2} = E^\circ_{\text{eqOxO}_2\text{H}_2\text{O}_2} * F * 1 * 2 = -0,5278 * 96485 * 2 = -101,85$  kJ/mol;

**Succinat<sup>2-</sup> + O<sub>2</sub>aq => fumarate<sup>2-</sup> + H<sub>2</sub>O<sub>2</sub>aq + Q + ΔG**;  $\Delta G_{\text{min}} = \Delta G_{\text{eqSuccinat}_\text{H}_2\text{O}_2} = -38,3$  kJ/mol;

$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{H}_2\text{O}_2} + \Delta G^\circ_{\text{fumarat}} - \Delta G^\circ_{\text{O}_2} - \Delta G^\circ_{\text{Succinat}} = -48,39 - 519,4688 - (16,4 - 522,414) = -61,845$  kJ/mol;

$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = (E^\circ_{\text{RedSuccinate}} - E^\circ_{\text{OxO}_2}) * F * n = (0,2512 - 0,4495) * 96485 * 2 = (-0,1983) * 96485 * 2 = -38,3$  kJ/mol;

Alberty Hesa  $\Delta G_{\text{Succinat}_\text{H}_2\text{O}_2} = G_{\text{Fumarat}} + G_{\text{H}_2\text{O}_2} - (G_{\text{Succinat}} + G_{\text{O}_2\text{aq}}) = 537,1 + 284,24 - (619,8 + 330) = -128,5$  kJ/mol ;

$K_{\text{eq}} = \exp(-\Delta G_{\text{eq}}/R/T) = \exp(38270/8,3144/298,15) = 5065991$  [veidošanās](#) 58. Lapa.

**Absolūto** termodinamisko parametru jēdzieni temperatūra, brīvā enerģija un potenciāls ir **absolūti** savstarpēji instrumenti, lai atklātu paralēlu un secīgu komplekso reakciju strukturālās detaļas, izmantojot inversijas simetrijas īpašības.

1. **Absolūtā** temperatūra T Kelvina grādos ir standarta vērtībā 298.15 K (25 ° C),

Lord Kelvin



2. Uz Alberty bāzētais absolūtais brīvās enerģijas saturs

$G_{\text{H}_2\text{gas}} = 85,6$  kJ/mol ūdeņraža gāzei, tās šķīdumam ūdenī  $G_{\text{H}_2\text{aq}} = 103$  kJ/mol un

[metālam](#) ūdeņradim  $G_{\text{H(Pt)}} = 48,46$  kJ/mol

atsaucoties uz nulles atskaites vērtību  $G_{\text{H}_2\text{O}} = G_{\text{CO}_2\text{gas}} = 0$  kJ/mol kā fonu

ūdenī un oglekļa dioksīda gāzē **CO<sub>2</sub>gas**.

Alberty Robert

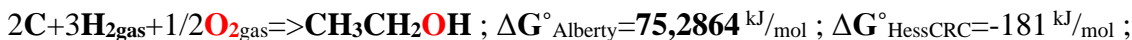


3. Atklājums **Absolūtā potenciālu** skala.

**Absolūtā potenciāla** skala, pamatojas uz vispārīgu atsauci

metāla ūdeņraža absolūto standarta Potenciālu  $E^\circ_{\text{H}} = -0.2965$  Volti. [8, 14, 15]

**CH<sub>3</sub>CH<sub>2</sub>OH** etanola veidošanās no elementiem:



$$\Delta G^\circ_{\text{Alberty}}=G_{\text{CH}_3\text{CH}_2\text{OH}}-(2G_{\text{Cgraph}}+3*G_{\text{H}_2\text{gas}}+1/2*G_{\text{O}_2\text{gas}})=75,2864 \text{ kJ/mol};$$

$$\Delta G^\circ_{\text{CRC}}=G_{\text{CH}_3\text{CH}_2\text{OH}}-(2G_{\text{Cgraph}}+3*G_{\text{H}_2\text{gas}}+1/2*G_{\text{O}_2\text{gas}})=-181 \text{ kJ/mol};$$

$$\Delta G^\circ_{\text{Alberty}}+(2G_{\text{Cgraph}}+3*G_{\text{H}_2\text{gas}}+1/2*G_{\text{O}_2\text{gas}})=75,2864+(2*91,26+3*85,6+1/2*303)=G_{\text{CH}_3\text{CH}_2\text{OH}}=666,106 \text{ kJ/mol};$$

$$\Delta G^\circ_{\text{CRC}}+(2G_{\text{Cgraph}}+3*G_{\text{H}_2\text{gas}}+1/2*G_{\text{O}_2\text{gas}})=-181+(2*91,26+3*85,6+1/2*303)=G_{\text{CH}_3\text{CH}_2\text{OH}}=409,82 \text{ kJ/mol};$$

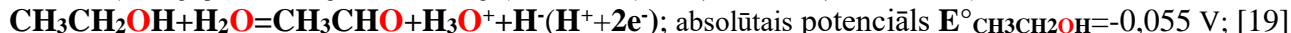
**CH<sub>3</sub>CHO** acetaldehīda veidošanās no elementiem:  $2\text{C}+2\text{H}_{2\text{gas}}+1/2\text{O}_{2\text{gas}}\Rightarrow\text{CH}_3\text{CHO}$ ;

$$\Delta G^\circ_{\text{Alberty}}=G_{\text{CH}_3\text{CHO}}-(2G_{\text{Cgraph}}+2*G_{\text{H}_2\text{gas}}+1/2*G_{\text{O}_2\text{gas}})=32,282 \text{ kJ/mol};$$

$$\Delta G^\circ_{\text{CRC}}=G_{\text{CH}_3\text{CHO}}-(2G_{\text{Cgraph}}+2*G_{\text{H}_2\text{gas}}+1/2*G_{\text{O}_2\text{gas}})=24,06 \text{ kJ/mol};$$

$$\Delta G^\circ_{\text{Alberty}}+(2G_{\text{Cgraph}}+2*G_{\text{H}_2\text{gas}}+1/2*G_{\text{O}_2\text{gas}})=32,282+(2*91,26+2*85,6+1/2*303)=G_{\text{CH}_3\text{CHO}}=537,5 \text{ kJ/mol};$$

$$\Delta G^\circ_{\text{CRC}}+(2G_{\text{Cgraph}}+2*G_{\text{H}_2\text{gas}}+1/2*G_{\text{O}_2\text{gas}})=24,06+(2*91,26+2*85,6+1/2*303)=G_{\text{CH}_3\text{CHO}}=529,28 \text{ kJ/mol};$$



$$\Delta G_{\text{eqCH}_3\text{CH}_2\text{OH}}=E^\circ_{\text{eqNernsCH}_3\text{CH}_2\text{OH}}*F*2=-0,055*96485*2=-10,6 \text{ kJ/mol};$$

$$\Delta G_{\text{HessCH}_3\text{CH}_2\text{OH}}=G_{\text{CH}_3\text{CHO}}+G_{\text{H}_3\text{O}^+}+G_{\text{H}^-}-(G_{\text{CH}_3\text{CH}_2\text{OH}}+G_{\text{H}_2\text{O}})=537,5+22,44+G_{\text{H}^-}-(409,82+0)=-10,6 \text{ kJ/mol}.$$

$$\Delta G_{\text{HessCH}_3\text{CH}_2\text{OH}}=G_{\text{CH}_3\text{CHO}}+G_{\text{H}_3\text{O}^+}+G_{\text{H}^-}-(G_{\text{CH}_3\text{CH}_2\text{OH}}+G_{\text{H}_2\text{O}_{\text{Biochem}}})=537,5+22,44+G_{\text{H}^-}-(409,82+85,64)=-10,6 \text{ kJ/mol}.$$

$$\Delta G_{\text{HessCH}_3\text{CH}_2\text{OH}}-G_{\text{CH}_3\text{CHO}}-G_{\text{H}_3\text{O}^+}+(G_{\text{CH}_3\text{CH}_2\text{OH}}+G_{\text{H}_2\text{O}})=G_{\text{H}^-}=-10,6-537,5-22,44+(409,82+0)=-160,7 \text{ kJ/mol}.$$

$$\Delta G_{\text{HessCH}_3\text{CH}_2\text{OH}}-G_{\text{CH}_3\text{CHO}}-G_{\text{H}_3\text{O}^+}+(G_{\text{CH}_3\text{CH}_2\text{OH}}+G_{\text{H}_2\text{O}_{\text{Biochem}}})=G_{\text{H}^-}=-10,6-537,5-22,44+(409,82+85,64)=-75,08 \text{ kJ/mol}.$$

Viela	$\Delta H^\circ_{\text{H}}/\text{kJ/mol}$	$\Delta S^\circ_{\text{H}}/\text{J/mol/K}$	$\Delta G^\circ_{\text{H}}/\text{kJ/mol}$
H <sub>3</sub> C-CH=O	-212,23	-281,84	24,06
H <sub>3</sub> C-CH=O	-213,88	-825,64	32,2824
NADH	-41,41	-4465,708	1175,5732
NADH	-1036,66	-140,50	1120,09
H <sub>3</sub> O <sup>+</sup>	-285,81	-3,854	-213,275
NAD <sup>+</sup>	-10,30	-3766,008	1112,534
NAD <sup>+</sup>	-1007,48	-183	1059,11
H <sub>3</sub> CCH <sub>2</sub> OH	-290,77	-1227,764	75,2864
H <sub>3</sub> CCH <sub>2</sub> OH <sub>a</sub> q	-288,3	-357,7394	-181,64
H <sub>2</sub> O	-285,85	69,9565	-237,191
H <sub>2</sub> O	-286,65	-453,188	-151,549

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$$G_{\text{CH}_3\text{CHO}}=529,28 \text{ kJ/mol};$$

$$G_{\text{CH}_3\text{CHO}}=537,5 \text{ kJ/mol};$$

BioThermodynam06;

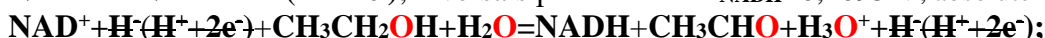
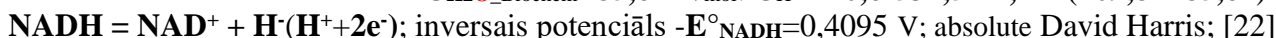
BioThermodynamic,2006,Massachusetts Tecnology Institute

$$\text{Alberty } G_{\text{CH}_3\text{CH}_2\text{OH}}=666,106 \text{ kJ/mol};$$

$$\text{CRC } G_{\text{CH}_3\text{CH}_2\text{OH}}=409,82 \text{ kJ/mol};$$

$$G_{\text{H}_2\text{O}}=0 \text{ kJ/mol}; G_{\text{H}^-}=-10,6-537,5-22,44+(409,82+0)=-160,7 \text{ kJ/mol}.$$

$$G_{\text{H}_2\text{O}_{\text{Biochem}}}=85,64 \text{ kJ/mol}. G_{\text{H}^-}=-10,6-537,5-22,44+(409,82+85,64)=-75,08 \text{ kJ/mol};$$



$$\text{summa: } E^\circ_{\text{eqNernsCH}_3\text{CH}_2\text{OH}}-E^\circ_{\text{NAD}^+}=-0,055+0,4095=0,4562;$$

$$\Delta G_{\text{min}}=\Delta G_{\text{eq}}=(E^\circ_{\text{eqNernsCH}_3\text{CH}_2\text{OH}}-E^\circ_{\text{NAD}^+})*F*n=(-0,055+0,4095)*96485*2=0,4562*96485*2=68,408 \text{ kJ/mol};$$

$$\Delta G_{\text{HessAlbertyCH}_3\text{CH}_2\text{OH}}=G_{\text{NADH}}+G_{\text{H}_3\text{O}^+}+G_{\text{CH}_3\text{CHO}}-(G_{\text{NAD}^+}+G_{\text{CH}_3\text{CH}_2\text{OH}}+G_{\text{H}_2\text{O}})=68,02 \text{ kJ/mol}.$$

$$=1112,534+22,44+32,282-(1175,5+75,2864-151,549)=68,02 \text{ kJ/mol}.$$



$$\Delta G_{\text{eqH}_3\text{CHC}(\text{OH})\text{COO}^-} = E^\circ_{\text{eqH}_3\text{CHC}(\text{OH})\text{COO}^-} \cdot F \cdot 2 = -0,0159 \cdot 96485 \cdot 2 = -3,068 \text{ kJ/mol};$$

$$\Delta G_{\text{HessCH}_3\text{CH}_2\text{OH}} = G_{\text{H}_3\text{CC}=\text{OCOO}^-} + G_{\text{H}_3\text{O}^+} + G_{\text{H}^-} - (G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} + G_{\text{H}_2\text{O}}) = 534,2 + 22,44 + G_{\text{H}^-} - (668,8 + 0) = -3,068 \text{ kJ/mol}.$$

$$\Delta G_{\text{HessCH}_3\text{CH}_2\text{OH}} = G_{\text{H}_3\text{CC}=\text{OCOO}^-} + G_{\text{H}_3\text{O}^+} + G_{\text{H}^-} - (G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} + G_{\text{H}_2\text{O}_{\text{Biochem}}}) = 534,2 + 22,44 + G_{\text{H}^-} - (668,8 + 85,64) = -3,068 \text{ kJ/mol}.$$

$$\Delta G_{\text{HessCH}_3\text{CH}_2\text{OH}} - G_{\text{H}_3\text{CC}=\text{OCOO}^-} - G_{\text{H}_3\text{O}^+} + (G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} + G_{\text{H}_2\text{O}}) = G_{\text{H}^-} = -3,068 - 534,2 - 22,44 + (668,8 + 0) = 109,092 \text{ kJ/mol}.$$

$$\Delta G_{\text{HessCH}_3\text{CH}_2\text{OH}} - G_{\text{H}_3\text{CC}=\text{OCOO}^-} - G_{\text{H}_3\text{O}^+} + (G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} + G_{\text{H}_2\text{O}_{\text{Biochem}}}) = G_{\text{H}^-} = -3,068 - 534,2 - 22,44 + (668,8 + 85,64) = 194,7 \text{ kJ/mol}.$$

$$I = 0,25 \text{ M, BioTherm06, pH} = 7,36, \Delta G_{\text{H}} = G^\circ_{\text{H}_3\text{CC}=\text{OCOO}^-} + G^\circ_{\text{H}_3\text{O}^+} + G_{\text{H}^-} - G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} - G_{\text{H}_2\text{O}} = \text{kJ/mol};$$

Viela  $\Delta H^\circ_{\text{H}} \text{ kJ/mol}$   $\Delta S^\circ_{\text{H}} \text{ J/mol/K}$   $\Delta G^\circ_{\text{H}} \text{ kJ/mol}$ ;

PyruvEnolP <sup>3-</sup>	-1400	-1100	-1189,73	$G_{\text{H}_2\text{O}} = 0 \text{ kJ/mol}; G_{\text{H}^-} = -3,068 - 534,2 - 22,44 + (668,8 + 0) = 109,092 \text{ kJ/mol}$
H <sub>3</sub> CC=OCOO <sup>-</sup>	-597,4	-850	-350,78	$G_{\text{H}_2\text{O}_{\text{Biochem}}} = 85,64 \text{ kJ/mol}; G_{\text{H}^-} = -3,068 - 534,2 - 22,44 + (668,8 + 85,64) = 194,7 \text{ kJ/mol}$
H <sub>3</sub> CC=OCOO <sup>-</sup>	-603,7	-433,54	-474,44	
H <sub>3</sub> CC=OCOO <sup>-</sup>	<b>-597,04</b>	<b>-846,66</b>	<b>-344,62</b>	$G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} = 534,2 \text{ kJ/mol}; pK_a = 2,5;$
H <sub>3</sub> O <sup>+</sup>	-285,81	-3,854	-213,275	
H <sub>2</sub> O	-285,85	69,9565	-237,191	
H <sub>2</sub> O	<b>-286,65</b>	<b>-453,188</b>	<b>-151,549</b>	
H <sub>3</sub> CHC(OH)COO <sup>-</sup>	<b>-688,29</b>	<b>-1290,9</b>	<b>-303,4</b>	$G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} = 668,8 \text{ kJ/mol}; pK_a = 3,86;$

$$pK_a = 3,86; \Delta H_c^\circ = 1361,9 \text{ kJ/mol}; G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} = 2271 \text{ kJ/mol}; \text{H}_3\text{CHC}(\text{OH})\text{COOH} + 3\text{O}_2\text{gas} = 3\text{CO}_2\text{gas} + 3\text{H}_2\text{O};$$

$$\Delta H_c^\circ = 3G_{\text{CO}_2\text{gas}} + 3G_{\text{H}_2\text{O}} - (G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} + 3G_{\text{O}_2\text{gas}}) = 3 \cdot 0 + 3 \cdot 0 - (G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} + 3 \cdot 303) = 1361,9 \text{ kJ/mol};$$

$$G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} = 3G_{\text{CO}_2\text{gas}} + 3G_{\text{H}_2\text{O}} - (3G_{\text{O}_2\text{gas}}) = 3 \cdot 0 + 3 \cdot 0 - (3 \cdot 303) - 1361,9 = G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} = 2271 \text{ kJ/mol};$$

**Lactic acid** Formation 71<sup>st</sup> page  $3\text{C} + 3\text{H}_2\text{gas} + 1,5\text{O}_2\text{gas} \Rightarrow \text{H}_3\text{CHC}(\text{OH})\text{COOH}$ ;  $G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} = -303,4 \text{ kJ/mol}$  [8];

$$\Delta G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} = G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} - (3G_{\text{Cgraph}} + 3 \cdot G_{\text{H}_2\text{gas}} + 1,5 \cdot G_{\text{O}_2\text{gas}}) = -303,4 \text{ kJ/mol};$$

$$G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} = -303,4 + (3 \cdot 91,26 + 3 \cdot 85,6 + 1,5 \cdot 303) = 681,7 \text{ kJ/mol};$$

Lactic acid  $\text{H}_3\text{CHC}(\text{OH})\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{CHC}(\text{OH})\text{COO}^- + \text{H}_3\text{O}^+$ ;  $pK_a = 3,86$ ;

$$K_{\text{eq}} = [\text{H}_3\text{CHC}(\text{OH})\text{COO}^-] \cdot [\text{H}_3\text{O}^+] / [\text{H}_3\text{CHC}(\text{OH})\text{COOH}] \cdot [\text{H}_2\text{O}] = K_a / [\text{H}_2\text{O}] = 10^{-(3,86)} / 55,3 = 10^{-(5,603)};$$

$$\Delta G_{\text{eqH}_3\text{CHC}(\text{OH})\text{COOH}} = -R \cdot T \cdot \ln(K_{\text{aq}}) = -8,3144 \cdot 298,15 \cdot \ln(10^{-(5,603)}) / 1000 = 31,98 \text{ kJ/mol}.$$

$$\Delta G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} = G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} + 2G_{\text{H}_3\text{O}^+} - (G_{\text{LacticAc}} + 2G_{\text{H}_2\text{O}}) = G_{\text{Succinat}} + 2 \cdot 22,44 - (681,7 + 2 \cdot 0) = 31,98 \text{ kJ/mol};$$

$$G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} = \Delta G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} - 2G_{\text{H}_3\text{O}^+} + (G_{\text{LacticAc}} + 2G_{\text{H}_2\text{O}}) = 31,98 - 2 \cdot 22,44 + (681,7 + 2 \cdot 0) = 668,8 \text{ kJ/mol};$$

**Pyruvic acid** Formation 71<sup>st</sup> page  $3\text{C} + 2\text{H}_2\text{gas} + 1,5\text{O}_2\text{gas} \Rightarrow \text{H}_3\text{CC}=\text{OCOOH}$ ;  $\Delta G_{\text{Succinat}} = -344,62 \text{ kJ/mol}$  Alberty;

$$\Delta G_{\text{Fumarat}} = G_{\text{Fumarat}} - (3G_{\text{Cgraph}} + 2G_{\text{H}_2\text{gas}} + 1,5 \cdot G_{\text{O}_2\text{gas}}) = -344,62 \text{ kJ/mol};$$

$$G_{\text{Fumarat}} = -344,62 + (3 \cdot 91,26 + 2 \cdot 85,6 + 1,5 \cdot 303) = 554,86 \text{ kJ/mol};$$

**Pyruvic acid**  $\text{H}_3\text{CC}=\text{OCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{CHC}(\text{OH})\text{COO}^- + \text{H}_3\text{O}^+$ ;  $pK_a = 2,5$ ;

$$K_{\text{eq}} = [\text{H}_3\text{CHC}(\text{OH})\text{COO}^-] \cdot [\text{H}_3\text{O}^+] / [\text{H}_3\text{CC}=\text{OCOOH}] \cdot [\text{H}_2\text{O}] = K_a / [\text{H}_2\text{O}] = 10^{-(2,5)} / 55,3 = 2,5 \cdot 10^{-(6)} = 10^{-(4,243)};$$

$$\Delta G_{\text{eqH}_3\text{CC}=\text{OCOOH}} = -R \cdot T \cdot \ln(K_{\text{aq}}) = -8,3144 \cdot 298,15 \cdot \ln(10^{-(4,243)}) / 1000 = 24,22 \text{ kJ/mol}.$$

$$\Delta G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} = G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} + 2G_{\text{H}_3\text{O}^+} - (G_{\text{LacticAc}} + 2G_{\text{H}_2\text{O}}) = G_{\text{Succinat}} + 2 \cdot 22,44 - (554,86 + 2 \cdot 0) = 24,22 \text{ kJ/mol};$$

$$G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} = \Delta G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} - 2G_{\text{H}_3\text{O}^+} + (G_{\text{LacticAc}} + 2G_{\text{H}_2\text{O}}) = 24,22 - 2 \cdot 22,44 + (554,86 + 2 \cdot 0) = 534,2 \text{ kJ/mol};$$

**NADH** =  $\text{NAD}^+ + \text{H}^-(\text{H}^+ + 2\text{e}^-)$ ;  $E^\circ_{\text{NADH}} = -0,4095 \text{ V}$ ; absolute Lehninger; [6]

**Red lactate** +  $\text{H}_2\text{O} \rightleftharpoons \text{pyruvate}^- + \text{H}_3\text{O}^+ + \text{H}^-(\text{H}^+ + 2\text{e}^-)$ ; absolute potential  $E^\circ_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} = -0,0159 \text{ V}$ ;

**Ox**  $\text{NAD}^+ + \text{H}^-(2\text{e}^-) = \text{NADH}$ ;  $E^\circ = -0,4095 \text{ V}$ ; OksRed  $\text{NAD}^+ + \text{lactate}^- + \text{H}_2\text{O} = \text{NADH} + \text{pyruvate}^- + \text{H}_3\text{O}^+$ ;

Balanced  $n=2=m$  with  $2\text{e}^-$  electrons  $\Delta E^\circ_{\text{NAD}^+}$  accept electrons from lactate:

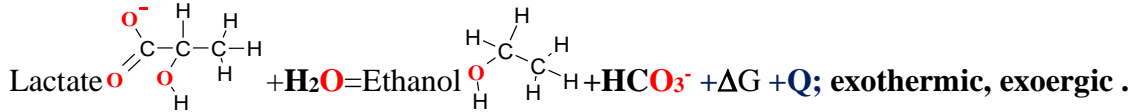
$$\Delta G_{\text{eqAerobic}} = \Delta E^\circ \cdot F \cdot n = (E^\circ_{\text{Red}} - E^\circ_{\text{Ox}}) \cdot F \cdot n = (-0,0159 - 0,4095) \cdot 96485 \cdot 2 = (0,3936) \cdot 2 = 75,95 \text{ kJ/mol}$$

$$K_{\text{eqAerobic}} = \text{EXP}(-\Delta G_{\text{eqAerobic}} / R/T) = \text{EXP}(-75950 / 8,3144 / 298,15) = 10^{-13,3};$$

$$K_{\text{eqAerobic}} = \frac{[\text{NADH}] \cdot [\text{pyruvate}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{NAD}^+] \cdot [\text{lactate}^-] \cdot [\text{H}_2\text{O}]} = e^{-\frac{\Delta G_{\text{eqAerobic}}}{R \cdot T}} = e^{-\frac{75950}{8,314 \cdot 298,15}} = 10^{-13,3};$$

$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = 45,764 - 298,15 \cdot -0,5479605 = 209,14 \dots \text{ kJ/mol}$  endoergic; [formation](#) 62<sup>nd</sup>, 75<sup>th</sup> pages

Pyruvate  $\text{H}_3\text{CC}=\text{O}\text{COO}^-$  decarboxylation  $\text{H}_3\text{CCHO}+\text{HCO}_3^-$ ;  $\text{H}_3\text{CC}=\text{O}\text{COO}^-+\text{H}_2\text{O}\Delta\text{G}+\text{Q}\Rightarrow\text{H}_3\text{CCHO}+\text{HCO}_3^-$



$$\Delta\text{G}_{\text{Hess}}=\Delta\text{G}^{\circ}_{\text{H}_3\text{CCH}_2\text{OH}}+\Delta\text{G}^{\circ}_{\text{HCO}_3^-}-\Delta\text{G}^{\circ}_{\text{H}_2\text{O}}-\Delta\text{G}^{\circ}_{\text{H}_3\text{CCH}_2\text{OHCoo}}=\underline{75,2864-544,9688-(-151,549-303,4256)}=-14,71 \text{ kJ/mol}$$

$$\Delta\text{G}_{\text{Alberty}}=\Delta\text{G}_{\text{H}_3\text{CCH}_2\text{OH}}+\Delta\text{G}_{\text{HCO}_3^-}-\Delta\text{G}_{\text{H}_2\text{O}}-\Delta\text{G}_{\text{H}_3\text{CCH}_2\text{OHCoo}}=\underline{666,1+46,08-(0+668,8)}=43,38 \text{ kJ/mol}$$

$$\Delta\text{G}_{\text{Alberty\_Biochem}}=\Delta\text{G}_{\text{H}_3\text{CCH}_2\text{OH}}+\Delta\text{G}_{\text{HCO}_3^-}-\text{G}_{\text{H}_2\text{O\_Biochem}}-\Delta\text{G}_{\text{H}_3\text{CCH}_2\text{OHCoo}}=\underline{666,1+46,08-(85,64+668,8)}=-42,26 \text{ kJ/mol}$$

$$\Delta\text{H}_{\text{Hess}}=\Delta\text{H}^{\circ}_{\text{H}_3\text{CCH}_2\text{OH}}+\Delta\text{H}^{\circ}_{\text{HCO}_3^-}-\Delta\text{H}^{\circ}_{\text{H}_2\text{O}}-\Delta\text{H}^{\circ}_{\text{H}_3\text{CCH}_2\text{OHCoo}}=-\underline{290,77-692,4948-(-286,65-688,29)}=-8,325 \text{ kJ/mol}$$

$$\Delta\text{S}_{\text{izkliedes}}=-\Delta\text{H}_{\text{Hess}}/\text{T}=\underline{8,325/298,15}=27,9 \text{ J/K/mol};$$

$$\Delta\text{S}_{\text{Hess}}=\Delta\text{S}^{\circ}_{\text{H}_3\text{CCH}_2\text{OH}}+\Delta\text{S}^{\circ}_{\text{HCO}_3^-}-\Delta\text{S}^{\circ}_{\text{H}_2\text{O}}-\Delta\text{S}^{\circ}_{\text{H}_3\text{CCH}_2\text{OHCoo}}=21,51 \text{ J/mol/K};$$

$$=-\underline{1227,764-494,768-(-453,188-1290,852)}=21,51 \text{ J/mol/K} \dots$$

$$\Delta\text{S}_{\text{kopējs}}=\Delta\text{S}_{\text{Hess}}+\Delta\text{S}_{\text{izkliedes}}=\underline{21,51+27,9}=49,41 \text{ J/mol/K};$$

$$\Delta\text{G}_{\text{Hess}}=\Delta\text{H}_{\text{Hess}}-\text{T}\cdot\Delta\text{S}_{\text{Hess}}=-\underline{8,325-298,15\cdot 0,02151}=-\underline{14,738} \text{ kJ/mol exoergic} \dots$$

$$\text{T}\cdot\Delta\text{S}_{\text{kopējs}}=\underline{0,04941}\cdot 298,15 \text{ K}=\underline{14,73} \text{ kJ/mol}; \text{bound T}\Delta\text{Sn}; \text{izkliedes-lost energy patvalīga}$$

Lactic acid Formation 71<sup>st</sup> page  $3\text{C}+3\text{H}_2\text{gas}+1,5\text{O}_2\text{gas}\Rightarrow\text{H}_3\text{CHC}(\text{OH})\text{COOH}$ ;  $\text{G}_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}}=-303,4 \text{ kJ/mol}$  [8];

$$\Delta\text{G}_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}}=\text{G}_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}}-(3\text{G}_{\text{Cgraph}}+3\cdot\text{G}_{\text{H}_2\text{gas}}+1,5\cdot\text{G}_{\text{O}_2\text{gas}})=-\underline{303,4} \text{ kJ/mol};$$

$$\text{G}_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}}=-\underline{303,4}+(3\cdot 91,26+3\cdot 85,6+1,5\cdot 303)=\underline{681,7} \text{ kJ/mol};$$

Lactic acid  $\text{H}_3\text{CHC}(\text{OH})\text{COOH}+\text{H}_2\text{O}\rightleftharpoons\text{H}_3\text{CHC}(\text{OH})\text{COO}^-+\text{H}_3\text{O}^+$ ;  $\text{pK}_a=3,86$ ;

$$\text{K}_{\text{eq}}=[\text{H}_3\text{CHC}(\text{OH})\text{COO}^-]\cdot[\text{H}_3\text{O}^+]/[\text{H}_3\text{CHC}(\text{OH})\text{COOH}][\text{H}_2\text{O}]=\text{K}_a/[\text{H}_2\text{O}]=10^{(-3,86)}/55,3=10^{(-5,603)};$$

$$\Delta\text{G}_{\text{eqH}_3\text{CHC}(\text{OH})\text{COOH}}=-\text{R}\cdot\text{T}\cdot\ln(\text{K}_{\text{aq}})=-8,3144\cdot 298,15\cdot\ln(10^{(-5,603)})/1000=\underline{31,98} \text{ kJ/mol} .$$

$$\Delta\text{G}_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-}=\text{G}_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-}+2\text{G}_{\text{H}_3\text{O}^+}-(\text{G}_{\text{LacticAc}}+2\text{G}_{\text{H}_2\text{O}})=\text{G}_{\text{Succinat}}+2\cdot 22,44-(\underline{681,7}+2\cdot 0)=\underline{31,98} \text{ kJ/mol};$$

$$\text{G}_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-}=\Delta\text{G}_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-}-2\text{G}_{\text{H}_3\text{O}^+}+(\text{G}_{\text{LacticAc}}+2\text{G}_{\text{H}_2\text{O}})=\underline{31,98}-2\cdot 22,44+(\underline{681,7}+2\cdot 0)=\underline{668,8} \text{ kJ/mol};$$

$\text{CH}_3\text{CH}_2\text{OH}$  ethanol formation from elements:

$$2\text{C}+3\text{H}_2\text{gas}+1/2\text{O}_2\text{gas}\Rightarrow\text{CH}_3\text{CH}_2\text{OH}; \Delta\text{G}^{\circ}_{\text{Alberty}}=\underline{75,2864} \text{ kJ/mol}; \Delta\text{G}^{\circ}_{\text{HessCRC}}=-181 \text{ kJ/mol};$$

$$\Delta\text{G}^{\circ}_{\text{Alberty}}=\text{G}_{\text{CH}_3\text{CH}_2\text{OH}}-(2\text{G}_{\text{Cgraph}}+3\cdot\text{G}_{\text{H}_2\text{gas}}+1/2\cdot\text{G}_{\text{O}_2\text{gas}})=\underline{75,2864} \text{ kJ/mol};$$

$$\Delta\text{G}^{\circ}_{\text{CRC}}=\text{G}_{\text{CH}_3\text{CH}_2\text{OH}}-(2\text{G}_{\text{Cgraph}}+3\cdot\text{G}_{\text{H}_2\text{gas}}+1/2\cdot\text{G}_{\text{O}_2\text{gas}})=-181 \text{ kJ/mol};$$

$$\Delta\text{G}^{\circ}_{\text{Alberty}}+(2\text{G}_{\text{Cgraph}}+3\cdot\text{G}_{\text{H}_2\text{gas}}+1/2\cdot\text{G}_{\text{O}_2\text{gas}})=\underline{75,2864}+(2\cdot 91,26+3\cdot 85,6+1/2\cdot 303)=\text{G}_{\text{CH}_3\text{CH}_2\text{OH}}=\underline{666,106} \text{ kJ/mol};$$

$$\Delta\text{G}^{\circ}_{\text{CRC}}+(2\text{G}_{\text{Cgraph}}+3\cdot\text{G}_{\text{H}_2\text{gas}}+1/2\cdot\text{G}_{\text{O}_2\text{gas}})=-181+(2\cdot 91,26+3\cdot 85,6+1/2\cdot 303)=\text{G}_{\text{CH}_3\text{CH}_2\text{OH}}=\underline{409,82} \text{ kJ/mol};$$

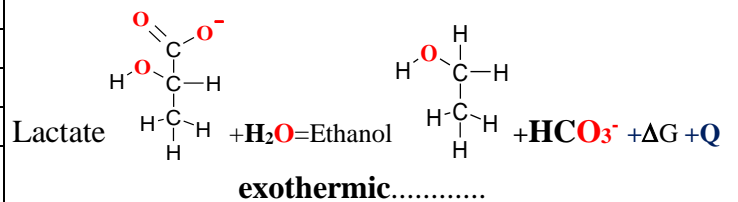
Substance	$\Delta\text{H}^{\circ}_{\text{H}}$ kJ/mol	$\Delta\text{S}^{\circ}_{\text{H}}$ J/mol/K	$\Delta\text{G}^{\circ}_{\text{H}}$ kJ/mol
$\text{H}_3\text{CCH}(\text{OH})\text{COO}^-$	-688,29	1290,852	303,4256
$\text{H}_3\text{CCH}(\text{OH})\text{COO}^-$	-686,2	-557,71	-313,70
$\text{H}_3\text{CCH}_2\text{OH}_{\text{aq}}$	-290,77	1227,764	75,2864
$\text{H}_3\text{CCH}_2\text{OH}_{\text{l}}$	-277,6	160,7	62,96
$\text{H}_2\text{O}$	-285,85	69,9565	-237,191
$\text{H}_2\text{O}$	-286,65	-453,188	-151,549
$\text{HCO}_3^-$	-689,93	98,324	-586,94
$\text{HCO}_3^-$	692,4948	-494,768	544,9688

BioThermodynamics06;  $\text{G}_{\text{H}_2\text{O\_Biochem}}=85,64 \text{ kJ/mol}$ ;

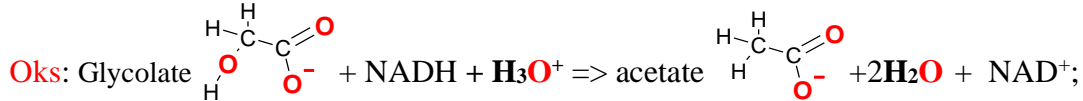
$$(\text{G}_{\text{H}_3\text{O}^+}+\text{G}_{\text{HCO}_3^-})=\underline{22,44+46,08} \text{ kJ/mol};$$

CRC 2010;

$$\Delta\text{S}_{\text{Hess}}=\Sigma\Delta\text{S}^{\circ}_{\text{products}}-\Sigma\Delta\text{S}^{\circ}_{\text{reactants}};\Delta\text{G}_{\text{Hess}}=\Delta\text{H}_{\text{Hess}}-\text{T}\cdot\Delta\text{S}_{\text{Hess}}$$

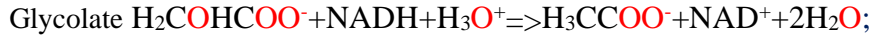


Oks:  $\text{H}_2\text{COHCOO}^- + \text{H}^+(\text{H}^+ + 2\text{e}^-) + \text{H}_3\text{O}^+ \Rightarrow \text{H}_3\text{CCOO}^- + 2\text{H}_2\text{O}$ ;  $E^\circ_{\text{OxH}_2\text{COHCOO}} = -0,033 \text{ V}$  absolute; [23]



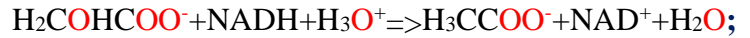
$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{CH}_3\text{COO}} + \Delta G^\circ_{\text{NAD}^+} + 2\Delta G^\circ_{\text{H}_2\text{O}} - \Delta G^\circ_{\text{H}_2\text{COHCOO}} - \Delta G^\circ_{\text{NADH}} - \Delta G^\circ_{\text{H}_3\text{O}^+} = -161,8 \text{ kJ/mol};$$

$$= -240,963 + 1112,534 - 2 \cdot 237,191 - (-403,2968 + 1175,5732 - 213,2746) = -161,8 \text{ kJ/mol}$$
 **exoergic**.....



$$\Delta G_{\text{eq}} = (E^\circ_{\text{Red}} - E^\circ_{\text{OxH}_2\text{COHCOO}}) \cdot F \cdot n = (-0,4095 - (-0,033)) \cdot 96485 \cdot 2 = (-0,38) \cdot 96485 \cdot 2 = -72,65 \text{ kJ/mol};$$

Substance	$\Delta H^\circ_{\text{Hess}}$ kJ/mol	$\Delta S^\circ_{\text{Hess}}$ J/mol/K	$\Delta G^\circ_{\text{Hess}}$ kJ/mol
Glyoxylate			
$\text{OHCCOOH}$	-	-	-
$\text{OHCCOO}^-$	-	-	-426,588
$\text{H}_2\text{COHCOO}^-$	-	-	-403,2968
$\text{H}_2\text{COHCOOH}$	- 651	318,6	-
$\text{NADH}(aq)$	-1036,66	-140,5	-
$\text{NAD}^+(aq)$	-1041,41	-4081,784	1175,5732
$\text{H}_3\text{O}^+(aq)$	-285,81	-3,854	-213,2746
$\text{NAD}^+(aq)$	-1007,48	-183	-
$\text{NAD}^+(aq)$	-1010,3	-3766,008	1112,534
$\text{H}_3\text{CCOOH}$	-484,09	159,83	-531,743
$\text{H}_3\text{CCOO}^-$	-486,84	82,23	-247,83
$\text{H}_3\text{CCOO}^-$	-486	85,3	-240,963
$\text{H}_2\text{O}$	-285,85	69,9565	-237,191
$\text{H}_2\text{O}$	,65	-453,188	-151,549



$$G_{\text{OHCCOOH}} = -426,588 + (2 \cdot 91,26 + 85,6 + 1,5 \cdot 303) = 296,032 \text{ kJ/mol}$$

$$G_{\text{OHCCOO}^-} = \Delta G_{\text{eq}}_{\text{OHCCOOH}} - G_{\text{H}_3\text{O}^+} + (G_{\text{OHCCOOH}} + G_{\text{H}_2\text{O}}) = 305,6 \text{ kJ/mol}$$

$$G_{\text{H}_2\text{COHCOO}^-} = \Delta G_{\text{eq}}_{\text{H}_2\text{COHCOO}^-} - G_{\text{H}_3\text{O}^+} + (G_{\text{H}_2\text{COHCOO}^-} + G_{\text{H}_2\text{O}}) = 414,3 \text{ kJ/mol}$$

$$G_{\text{H}_2\text{COHCOOH}} = -403,2968 + (2 \cdot 91,26 + 2 \cdot 85,6 + 1,5 \cdot 303) = 404,9232 \text{ kJ/mol}$$

Exothermic, exoergic reduction  
Hess free energy change -161,8

negative, but minimized

reaching  $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -72,65$

or

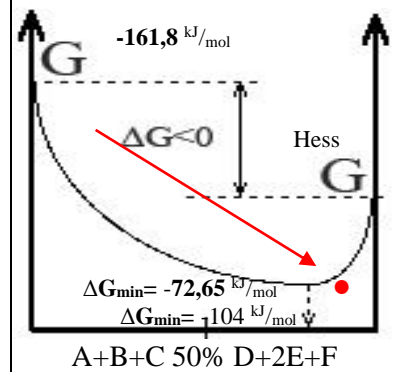
-104 kJ/mol equilibrium mixture.

Le Chatelier principle is

Prigogine attractor free energy

change minimum  $\Delta G_{\text{min}}$

reaching.



Glyoxylic acid Formation 61<sup>st</sup> page  $2\text{C} + \text{H}_2\text{gas} + 1,5\text{O}_2\text{gas} \Rightarrow \text{OHCCOOH}$ ;  $\Delta G_{\text{OHCCOOH}} = -426,588 \text{ kJ/mol}$  [8];

$$\Delta G_{\text{OHCCOOH}} = G_{\text{OHCCOOH}} - (2G_{\text{Cgraph}} + G_{\text{H}_2\text{gas}} + 1,5 \cdot G_{\text{O}_2\text{gas}}) = -426,588 \text{ kJ/mol};$$

$$G_{\text{OHCCOOH}} = -426,588 + (2 \cdot 91,26 + 85,6 + 1,5 \cdot 303) = 296,032 \text{ kJ/mol};$$

Glyoxylic acid  $\text{OHCCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{OHCCOO}^- + \text{H}_3\text{O}^+$ ;  $pK_{a1} = 3,32$ ; Wikipedia

$$K_{\text{eq}} = \frac{[\text{OHCCOO}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{OHCCOOH}] \cdot [\text{H}_2\text{O}]} = K_a / [\text{H}_2\text{O}] = 10^{-(3,32)} / 55,3 = 8,655 \cdot 10^{-(6)} = 10^{-(5,063)};$$

$$\Delta G_{\text{eq}}_{\text{OHCCOOH}} = -R \cdot T \cdot \ln(K_{\text{aeq}}) = -8,3144 \cdot 298,15 \cdot \ln(10^{-(5,063)}) / 1000 = 31,98 \text{ kJ/mol}.$$

$$\Delta G_{\text{eq}}_{\text{OHCCOOH}} = G_{\text{OHCCOO}^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{OHCCOOH}} + G_{\text{H}_2\text{O}}) = G_{\text{OHCCOO}^-} + 22,44 - (296,032 + 0) = 31,98 \text{ kJ/mol};$$

$$G_{\text{OHCCOO}^-} = \Delta G_{\text{eq}}_{\text{OHCCOOH}} - G_{\text{H}_3\text{O}^+} + (G_{\text{OHCCOOH}} + G_{\text{H}_2\text{O}}) = 31,98 - 22,44 + (296,032 + 0) = 305,6 \text{ kJ/mol};$$

Glycolic acid Formation 61<sup>st</sup> page  $2\text{C} + 2 \cdot \text{H}_2\text{gas} + 1,5\text{O}_2\text{gas} \Rightarrow \text{H}_2\text{COHCOOH}$ ;  $\Delta G_{\text{H}_2\text{COHCOOH}} = -403,2968 \text{ kJ/mol}$  [8];

$$\Delta G_{\text{H}_2\text{COHCOOH}} = G_{\text{H}_2\text{COHCOOH}} - (2G_{\text{Cgraph}} + 2G_{\text{H}_2\text{gas}} + 1,5 \cdot G_{\text{O}_2\text{gas}}) = -403,2968 \text{ kJ/mol};$$

$$G_{\text{H}_2\text{COHCOOH}} = -403,2968 + (2 \cdot 91,26 + 2 \cdot 85,6 + 1,5 \cdot 303) = 404,9232 \text{ kJ/mol};$$

Glycolic acid  $\text{H}_2\text{COHCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{COHCOO}^- + \text{H}_3\text{O}^+$ ;  $pK_{a1} = 3,83$ ; Wikipedia

$$K_{\text{eq}} = \frac{[\text{H}_2\text{COHCOO}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{COHCOOH}] \cdot [\text{H}_2\text{O}]} = K_a / [\text{H}_2\text{O}] = 10^{-(3,83)} / 55,3 = 2,675 \cdot 10^{-(6)} = 10^{-(5,573)};$$

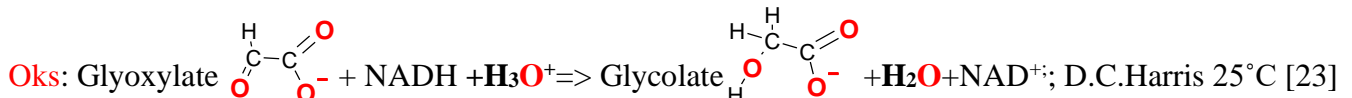
$$\Delta G_{\text{eq}}_{\text{H}_2\text{COHCOOH}} = -R \cdot T \cdot \ln(K_{\text{aeq}}) = -8,3144 \cdot 298,15 \cdot \ln(10^{-(5,573)}) / 1000 = 31,81 \text{ kJ/mol}.$$

$$\Delta G_{\text{eq}}_{\text{H}_2\text{COHCOOH}} = G_{\text{H}_2\text{COHCOO}^-} + G_{\text{H}_3\text{O}^+} - (G_{\text{H}_2\text{COHCOOH}} + G_{\text{H}_2\text{O}}) = G_{\text{H}_2\text{COHCOO}^-} + 22,44 - (404,9232 + 0) = 31,81 \text{ kJ/mol};$$

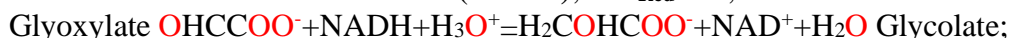
$$G_{\text{H}_2\text{COHCOO}^-} = \Delta G_{\text{eq}}_{\text{H}_2\text{COHCOOH}} - G_{\text{H}_3\text{O}^+} + (G_{\text{H}_2\text{COHCOOH}} + G_{\text{H}_2\text{O}}) = 31,81 - 22,44 + (404,9232 + 0) = 414,3 \text{ kJ/mol};$$

Nernst's half reaction **glycolate** +  $\text{H}_2\text{O} =$  **Glyoxylate** +  $\text{H}^+(\text{H}^+ + 2\text{e}^-) + \text{H}_3\text{O}^+$ ; D.C.Harris 25°C [23]

Oks:  $\text{OHCCOO}^- + \text{H}^+(\text{H}^+ + 2\text{e}^-) + \text{H}_3\text{O}^+ \Rightarrow \text{H}_2\text{COHCOO}^- + \text{H}_2\text{O}$ ;  $E^\circ_{\text{H}_2\text{COHCOO}} = 0,1305 \text{ V}$  absolute; [23]



Nernst's half reaction **Red**:  $\text{NADH} = \text{NAD}^+ + \text{H}^+(\text{H}^+ + 2\text{e}^-)$ ;  $E^\circ_{\text{Red}} = -0,4095 \text{ V}$  David Harris absolute [22]



$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{H}_2\text{COHCOOH}} + \Delta G^\circ_{\text{NAD}^+} + \Delta G^\circ_{\text{H}_2\text{O}} - \Delta G^\circ_{\text{H}_2\text{COHCOO}^-} - \Delta G^\circ_{\text{NADH}} - \Delta G^\circ_{\text{H}_3\text{O}^+} = -63,66 \text{ kJ/mol};$$

$$= -403,2968 + 1112,534 - 237,191 - (-426,588 + 1175,5732 - 213,2746) = -63,66 \text{ kJ/mol}$$
 **exoergic**.....;

$$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = (E^\circ_{\text{eqNernst\_NADH}} - E^\circ_{\text{H}_2\text{COHCOO}}) \cdot F \cdot n = (-0,4095 - 0,1305) \cdot 96485 \cdot 2 = (-0,54) \cdot 96485 \cdot 2 = -104,2 \text{ kJ/mol};$$

## Abstrakts.

Uz Alberti bāzēts absolūtās brīvās enerģijas saturs  $G_{H_2\text{gas}}=85.6$  kJ/mol gāzei,  $G_{H_2\text{aqua}}=103$  kJ/mol ūdenim un  $G_{H(Pt)}=48,56$  kJ/mol [metālam](#) ūdeņradim pie nulles atskaites  $G_{H_2O}=G_{CO_2\text{gas}}=0$  kJ/mol fona enerģijas ūdenim un oglekļa dioksīda  $CO_2\text{gas}$  gāzei. [8,15] Metāla ūdeņraža nulles klasiskā standarta potenciāla atskaite tiek izmantota tā hidroksoniya katjona  $[H_3O^+]=1.01$  M koncentrācija sērskābes  $[H_2SO_4]=1$  M šķīdumā ar blīvumu 1.061 g/mL.

Kopš 1920. gada Nernsta Nobela prēmijas ķīmijā saņemšanas visas elektroķīmijas sērijas reducētāju oksidēšanas pus reakciju standarta potenciāli ir noteikti attiecībā pret ūdeņraža metāla pus reakcijas klasisko standarta potenciālu  $E^{\circ}_H$  nulle. [1,15] Skābekļa, oglekļa dioksīda un ūdens protolīzes funkcionālās aktivitātes kvantitatīvie pētījumi atklāj ģenerētus daudzveidīgus Dzīvības pašorganizējošus atraktoros: ūdens  $[H_2O]=55.3$  mol/Litrā koncentrāciju, pH=7,36, enzīma karbo anhidrāzes (CA) reaktivitāte, gaisa skābekļa līmenis 20,95 %, osmolārā koncentrācija 0,305 M, jonu spēks 0,25 M, temperatūra 310,15 K grādi utt. . [1,15]

Liela ātruma protolīze ūdenī padara skābekli ugundrošu, CA funkcionāli aktivizē oglekļa dioksīdu, reaģējot ar divām ūdens molekulām, veidojot  $H_3O^++HCO_3^-$  koncentrācijas gradientus abpus membrānei osmozei pretēji koncentrācijas gradientiem bet protonu un bikarbonāta jonu transportēšanai lejup cauri protonu un bikarbonātu jonu kanāliem.

Iepriekšējās publikācijas atklāj neizstājamu ūdens un hidroksoniya uzskaiti līdzsvara reakciju termodinamiskajās izpausmēs, ieskaitot protolīzi un elektroķīmijas Nernsta pus reakcijas. [8,14,15] Pētījumi sasniedz metāla ūdeņraža termodinamiskā standarta potenciāla atsauces vērtību 0.10166 Volti. Alberty vārdā sniegtie dati par ūdeņraža brīvo enerģiju  $G_{H_2\text{gas}}=85.6$  kJ/mol ,  $G_{H_2\text{aqua}}=103$  kJ/mol ir atklājies **absolūtais** standarta **potenciāls**  $E^{\circ}_H=-0.27073$  Volts kā elektroda termodinamiskā atskaites vērtība ar absolūtās brīvās enerģijas izmaiņas vērtību  $\Delta G_{eq}=-26,12$  kJ/mol.

*Atslēgas vārdi: Fizikālā ķīmija; Elektroķīmija; Termodinamika; Atraktori; Bioķīmija.*



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