

TERMODINAMIKA **VINGRINĀJUMS** 1. gāzveida **6CO₂** foto sintēze par **6O₂aq** un **C₆H₁₂O₆**

Aprēķināt ΔH_H ΔS_H ΔG_H. Reakcija ir **eksotermiska**, **atermiska**, **endotermiska**? Foto sintētiskajā reakcijas centrā PRC+h•v gāzveida **CO₂** asimilācijas reakcija ūdenī zaļajos augos ar zilo un sarkano fotonu **E=h•v** enerģiju, foto sintezējot **6O₂aq** un **C₆H₁₂O₆** standarta apstākļos (25° C) 298.15 K, pielietojiet tabulas datus!

Miniet vai reakcija būs **eksoerģiska** vai **endoerģiska**! **Izejvielas => produkti** glikoze + skābeklis



Substance	ΔH ^o _H kJ/mol	ΔS ^o _H J/mol/K	ΔG ^o _H kJ/mol
C₆H₁₂O₆aq	-1263,78	269,45	-919,96
Glc	-1267,13	-2901,49	-402,05
O₂aq	-11,715	110,876	16,4
O₂aq	-11,7	-94,2	16,4
O₂↑_{gas}	0	205,152	-61,166
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549
H₃O⁺	-285,81	-3,854	-213,275
CO₂↑_{gas}	-393,509	213,74	-394,359
CO₂aq	-413,798	117,5704	-385,98
CO₂aq	-413,26	-119,36	-
HCO₃⁻	-689,93	98,324	-586,93988
HCO₃⁻	-692,4948	-494,768	-544,9688

ΔG_H=ΔG^o_{C₆H₁₂O₆}+6ΔG^o_{O₂}+6ΔG^o_{H₂O}-6ΔG^o_{H₃O⁺}-6ΔG^o_{HCO₃⁻}=**3336,5** kJ/mol
 =-402,05+6*16,4+6*-151,549-(6*-544,9688+6*-213,274599)=**3336,5** kJ/mol
Biothermodynamic 2006; data recalculate for pH=7,36. [8]
 ΔH_H=ΔH^o_{C₆H₁₂O₆}+6ΔH^o_{O₂}+6ΔH^o_{H₂O}-6ΔH^o_{H₃O⁺}-6ΔH^o_{HCO₃⁻}=kJ/mol
 =-1267,13+6*-11,7+6*-286,65-(6*-692,4948+6*-285,81)=**2812,6**
 ΔS_H=ΔS^o_{C₆H₁₂O₆}+6ΔS^o_{O₂}+6ΔS^o_{H₂O}-6ΔS^o_{H₃O⁺}-6ΔS^o_{HCO₃⁻}=-3194,1 J/mol/K
 =-2901,49+6*-94,2+6*-453,188-(6*-494,768+6*-3,854)=-**3194,1** J/mol/K
 ΔG_{Hess}=ΔH_H-T*ΔS_H=2812,6-298,15*-3,1941=**3764,92** kJ/mol
 CRC102. ΔS_{izkļiedēta}=-ΔH_H/T=-2812,6/298,15=**9433,5** J/mol/K;
 ΔS_{kopēja}=ΔS_H+ΔS_{izkļiedēta}=**3194,1+9433,5=12627,6** J/mol/K;
 T*ΔS_{kopēja}=**12,6276*298,15=-3764,9** kJ/mol **akumulētā enerģija**

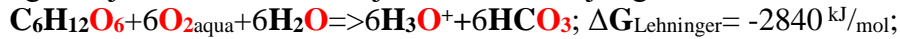
ΔG_{Heas}=**3764,92** kJ/mol > ΔG_{Lehninger}=2840 kJ/mol

[lapas puse 3.](#) Fotosintēzē produktos akumulētā

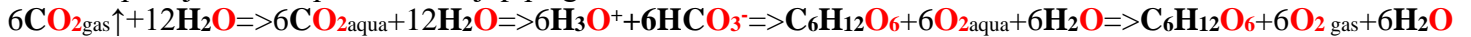
C₆H₁₂O₆+6H₂O un skābeklī **6O₂aq** Bio-degvielas enerģija :



tiek izlietoti oksidēšanā ģenerējot **6HCO₃⁻+6H₃O⁺** jonu koncentrācijas gradientus :



osmozei pretēji un transportēšanai lejup pa gradientiem cauri membrānu kanāliem..



ΔG_H=ΔG^o_{C₆H₁₂O₆}+6ΔG^o_{O₂}+6ΔG^o_{H₂O}-6ΔG^o_{CO₂aq}-12ΔG^o_{H₂O}= **2921,5** kJ/mol;

=-402,05+6*16,4+6*-151,549-(6*-385,98+12*-151,549)=**2921,5**;

ΔG_H=ΔG^o_{C₆H₁₂O₆}+6ΔG^o_{O₂}+6ΔG^o_{H₂O}-6ΔG^o_{CO₂gas}-12ΔG^o_{H₂O} = **2971,8** kJ/mol;

=-402,05+6*16,4+6*-151,549-(6*-394,359+12*-151,549)=**2971,8** kJ/mol;

ΔG_H=ΔG^o_{C₆H₁₂O₆}+6ΔG^o_{O₂gas}+6ΔG^o_{H₂O}-6ΔG^o_{CO₂gas}-12ΔG^o_{H₂O} = **2873,4** kJ/mol;

=-402,05+6*0+6*-151,549-(6*-394,359+12*-151,549)=**2873,4**; ΔG_{BioChem}=**2873,4** kJ/mol;

ΔG_{Hess}=ΔH_H-T*ΔS_H=2812,6-298,15*-3,1941=**3764,92** kJ/mol;

ΔG_{Heas}=**3764,92** kJ/mol > ΔG_{Lehninger}=2840 kJ/mol;

ΔG_{Lehninger}=ΔG_{eq}=-R•T•ln(K_{eq})=-8,3144•298,15•ln(10^{-497,55})=2840 kJ/mol;

Endotermiskā un endoerģiskā fotosintēzē Hesa brīvās enerģijas izmaiņa pozitīva

gāzveida **6O₂** un **6CO₂** ΔG_{fotosintēze}=**2873** kJ/mol , tad ΔG_{fotosintēze}=**2971,8** kJ/mol vairāk

pozitīva aqua **6O₂aq**, **6CO₂aq** abiem un ΔG_{fotosintēze}=**2921,5** kJ/mol **6O₂aq** & **6CO₂gas**,

pozitīva CA karbo anhidrāzes virzīta ΔG_{fotosintēze}=**3336,5** kJ/mol **6O₂aq**, **6H₃O⁺**, **6HCO₃⁻**;

bet minimizējas ΔG_{min}=ΔG_{eq}=2840 kJ/mol sasniežot kvazi līdzsvara maisījumu

reaģentiem.

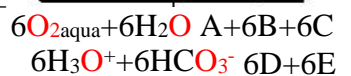
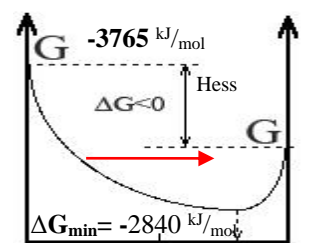
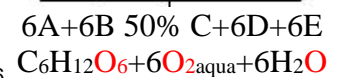
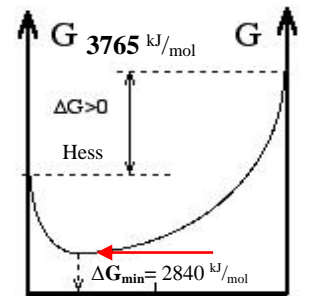
12 izejvielām **6H₃O⁺+6HCO₃⁻** un 13 produktiem

$$K_{eq1} = \text{EXP}(-\Delta G_{Lehninger1}/R/T) = \text{EXP}(-2840/8,3144/298,15) = 10^{-498} = \frac{[C_6H_{12}O_6] \cdot [O_2aq]^6 \cdot [H_2O]^6}{[HCO_3^-]_{\text{aq}}^6 \cdot [H_3O^+]^6}$$

$$K_{eq2} = \text{EXP}(-\Delta G_{Lehninger1}/R/T) = \text{EXP}(2840/8,3144/298,15) = 10^{498} = \frac{[HCO_3^-]_{\text{aq}}^6 \cdot [H_3O^+]^6}{[C_6H_{12}O_6] \cdot [O_2aq]^6 \cdot [H_2O]^6}$$

Homeostazes kvazi līdzsvars Prigožina atraktors ir brīvās enerģijas minimums ΔG_{min}.

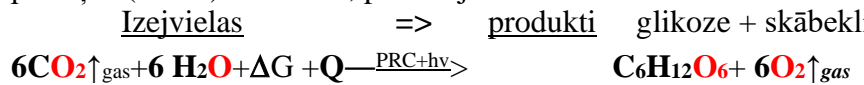
Brīvās enerģijas izmaiņas minimums stabilizē homestāzes kvazi līdzsvaru **K_{eq}. C₆H₁₂O₆+6O₂aq+6H₂O**



TERMODINAMIKA VINGRINĀJUMS 1a. gāzveida 6CO_2 foto sintēze par $\text{C}_6\text{H}_{12}\text{O}_6$ un gāzveida $6\text{O}_2\uparrow_{\text{gas}}$

Aprēķināt ΔH_H ΔS_H ΔG_H . Reakcija ir **eksotermiska**, **atermiska**, **endotermiska**? Foto sintētiskajā reakcijas centrā $\text{PRC}+\mathbf{h}\cdot\mathbf{v}$ gāzveida CO_2 asimilācijas reakcija ūdenī zaļajos augos ar zilo un sarkano fotonu $\mathbf{E}=\mathbf{h}\cdot\mathbf{v}$ enerģiju, foto sintezējot $6\text{O}_2\uparrow_{\text{gas}}$ un $\text{C}_6\text{H}_{12}\text{O}_6$ standarta apstākļos (25°C) 298.15K , pielietojiet tabulas datus! Miniet vai reakcija būs **eksoerģiska** vai **endoerģiska**!

Viela	$\Delta H^\circ_{\text{H}} \text{ kJ/mol}$	$\Delta S^\circ_{\text{H}} \text{ J/mol/K}$
$\text{O}_2\uparrow_{\text{gas}}$	0	205,04



$$1. \Delta H_H=\Delta H^\circ_{\text{C}_6\text{H}_{12}\text{O}_6}+6\Delta H^\circ_{\text{O}_2}-6\Delta H^\circ_{\text{H}_2\text{O}}-6\Delta H^\circ_{\text{CO}_2}=\dots\dots\dots\text{kJ/mol}$$

$$\dots\dots\dots=-1263,78-6\cdot 0-(6\cdot -285,85+6\cdot -393,509)=-1263,78+4076,154=+2812,37\text{ kJ/mol endotermiska}\dots\dots$$

$$2. \Delta S_{\text{izkļiedēta}}=-\Delta H_H/T=-2812,37/298,15=-9432,59\dots\dots\text{J/mol/K}$$

$$\Delta S_H=\Delta S^\circ_{\text{C}_6\text{H}_{12}\text{O}_6}+6\Delta S^\circ_{\text{O}_2}-6\Delta S^\circ_{\text{H}_2\text{O}}-6\Delta S^\circ_{\text{CO}_2}=269,45+6\cdot 205,04-(6\cdot 69,9565+6\cdot 213,74)=-202,489\dots\dots\text{J/mol/K};$$

$$\Delta S_{\text{kopēja}}=\Delta S_H+\Delta S_{\text{izkļiedēta}}=-202,489-9432,59=-9635,079\text{J/mol/K};$$

$$\Delta G_H=\Delta H_H-T\cdot\Delta S_H=2812,37-298,15\cdot -0,202489=2872,74\text{ kJ/mol endoerģiska}.$$

$$T\cdot\Delta S_{\text{kopēja}}=-9635,079\cdot 298,15=-2872,7\text{ kJ/mol saistīta } T\Delta S_n\leftarrow\text{uzkrātā enerģija}$$



$$1. \Delta H_H=6\Delta H^\circ_{\text{H}_2\text{O}}+6\Delta H^\circ_{\text{CO}_2}-\Delta H^\circ_{\text{C}_6\text{H}_{12}\text{O}_6}-6\Delta H^\circ_{\text{O}_2}=6\cdot -285,85+6\cdot -393,509-(-1263,78-6\cdot 0)=-2812,37\text{ kJ/mol};$$

$$2. \Delta S_{\text{izkļiedēta}}=-\Delta H_H/T=-2812,37/298,15=9432,59\dots\dots\text{J/mol/K};$$

$$\Delta S_H=6\Delta S^\circ_{\text{H}_2\text{O}}+6\Delta S^\circ_{\text{CO}_2}-\Delta S^\circ_{\text{C}_6\text{H}_{12}\text{O}_6}-6\Delta S^\circ_{\text{O}_2}=6\cdot 69,9565+6\cdot 213,74-(269,45+6\cdot 205,04)=+202,489\dots\dots\text{J/mol/K};$$

$$3. \Delta S_{\text{kopēja}}=\Delta S_H+\Delta S_{\text{izkļiedēta}}=202,489+9432,59=9635,079\dots\dots\text{J/mol/K};$$

$$\Delta G_H=\Delta H_H-T\cdot\Delta S_H=-2812,37-298,15\cdot 0,202489=-2812,37-60,3721=-2872,74\dots\dots\text{kJ/mol eksoerģiska}\dots\dots\dots$$

$$T\cdot\Delta S_{\text{kopēja}}=9635,079\cdot 298,15=+2872,7\dots\dots\text{kJ/mol saistīta } T\Delta S_n\leftarrow\text{izkļiedētā enerģija}$$

Molekulu O_2 , CO_2 , $2\text{H}_2\text{O}$ protolītiskā funkcionāla aktivācija bioķīmijā.

$$G_{\text{O}_2\text{Biochem_arterial}}=G_{\text{O}_2\text{gas}}+G_{\text{O}_2\text{sp}}+\Delta G_{\text{arterial}}=303,1+26,58-251,6=78,08\text{ kJ/mol samazinās};$$

$$\text{Skābekļa } \text{O}_{2\text{aqua}} \text{ brīvās enerģijas saturs ūdenī } G_{\text{O}_{2\text{aqua}}}=330\text{ kJ/mol samazina uz } G_{\text{O}_2\text{Biochem}}=78,08\text{ kJ/mol}.$$

$$\frac{[\text{O}_{2\text{aqua}}]}{[\text{O}_{2\text{gas}}]\cdot[\text{H}_2\text{O}]}=\text{Šķīdības } \text{O}_{2\text{gas AIR}}+\text{H}_2\text{O}+\Delta G_{\text{Akvaporīni}}\Rightarrow\text{O}_{2\text{aqua-Blood}}+\text{Q konstante}:$$

$$=K_{\text{šk}}=2.205\cdot 10^{-5}. G_{\text{O}_{2\text{aqua}}}=-R\cdot T\cdot\ln(K_{\text{šk}})=-8.3144\cdot 298.15\cdot\ln(2.205\cdot 10^{-5})=26.58\text{ kJ/mol}.$$

$$\text{O}_{2\text{aqua}}+4\text{H}_3\text{O}^++4\text{e}^-=5\text{H}_2\text{O}; -E^\circ=-1,0868\text{ V inversais absolūtais standarta potenciāls}.$$

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

$$\Delta E_{\text{H}_2\text{O}}=-E^\circ-E_o=-1,0868+0,46068=-0,62612\text{ Volti}; \Delta G_{\text{arterial}}=\Delta E_{\text{H}_2\text{O}}\cdot F\cdot n=-0,62612\cdot 96485\cdot 4/1000=-251,6\text{ kJ/mol}.$$

$$G_{\text{O}_2\text{Biochem_arterial}}=G_{\text{O}_2\text{gas}}+G_{\text{O}_2\text{sp}}+\Delta G_{\text{arterial}}=303,1+26,58-241,6448=88,04\text{ kJ/mol};$$

$$\text{Karbo anhidrāze CA akumulē brīvo enerģiju uz } G_{\text{H}_3\text{O}^++\text{HCO}_3^-}=G_{\text{H}_3\text{O}^+}+G_{\text{HCO}_3^-}=22,44+46,08=68,52\text{ kJ/mol}$$

$$\text{pret nulli ūdenim un } \text{CO}_{2\text{gas}} G_{\text{CO}_2+2\text{H}_2\text{O}}=0\text{ kJ/mol}. \text{ Šķīdības } \text{CO}_{2\text{gas}}+\text{H}_2\text{O}+\Delta G\rightleftharpoons\text{CO}_{2\text{aqua}}+\text{Q konstante:}$$

$$K_{\text{škCO}_{2\text{aqua}}}=[\text{CO}_{2\text{aqua}}]/[\text{CO}_{2\text{gas}}]\cdot[\text{H}_2\text{O}]=\text{EXP}(-\Delta G_{\text{šk}}/R/T)=\text{EXP}(-8379/8,3144/298,15)=0,034045.$$

$$\Delta G_{\text{škCO}_{2\text{aqua}}}=-R\cdot T\cdot\ln(K_{\text{škCO}_{2\text{aqua}}})=-8.3144\cdot 298.15\cdot\ln(0.034045)/1000=8.379\text{ kJ/mol}.$$

$$\frac{[\text{HCO}_3^-]_{\text{aqua}}\cdot[\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}}\cdot[\text{H}_2\text{O}]^2}=\text{CO}_{2\text{aqua}}+2\text{H}_2\text{O}+\Delta G+\text{Q}=\mathbf{v1}^{\text{CA}}\text{H}_3\text{O}^++\text{HCO}_3^- \text{ ātruma konstante } k_{1\text{CO}_{2\text{aqua}}}=1.5\cdot 10^8\text{ M}^{-1}\text{s}^{-1}. [9]$$

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

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

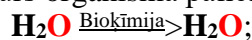
$$G_{\text{H}_3\text{O}^+}+G_{\text{HCO}_3^-}=22,44+46,08=G_{\text{H}_3\text{O}^++\text{HCO}_3^-}=\Delta G_{\text{spCO}_{2\text{aqua}}}+\Delta G_{\text{eqCO}_{2\text{aqua}}}=8,379+60,14=68,52\text{ kJ/mol}.$$

$$\text{Ūdens protolīze palielina brīvās enerģijas saturu no nulles } G_{2\text{H}_2\text{O}}=0\text{ kJ/mol uz } G_{\text{H}_3\text{O}^++\text{OH}^-}=99,8\text{ kJ/mol}.$$

$$\frac{[\text{OH}^-]\cdot[\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]\cdot[\text{H}_2\text{O}]}=K_{\text{H}_3\text{O}^++\text{OH}^-}=[\text{H}_3\text{O}^+]\cdot[\text{OH}^-]/[\text{H}_2\text{O}]^2=3,26\cdot 10^{-18};$$

$$\Delta G_{\text{H}_3\text{O}^++\text{OH}^-}=-R\cdot T\cdot\ln(K_{\text{H}_3\text{O}^++\text{OH}^-})=-8,3144\cdot 298,15\cdot\ln(3,26\cdot 10^{-(18)})/1000=99,8\text{ kJ/mol}.$$

$$\text{Destilēta protolītiskā ūdens brīvās enerģijas saturs organismā palielinās no nulles uz } G_{\text{H}_2\text{O_Bioīmija}}=\mathbf{85,65}\text{ kJ/mol}. [1,8].$$

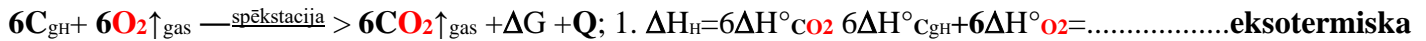


$$G_{\text{H}_2\text{O_Bioīmija}}=\Delta G^\circ_{\text{H}_2\text{O_Bioīmija}}-\Delta G^\circ_{\text{H}_2\text{O_destilēts}}=-151,549-(-237,191)=\mathbf{85,64}\text{ kJ/mol}.$$

Endotermiska un endoerģiska brīvās enerģijas akumulēšana bioķīmiskā vidē:

osmolāra koncentrācija $C_{\text{osm}}=0,305\text{ M}$, jonu spēks $I=0,2\text{ M}$, temperatūra $298,15\text{ K}$

ūdenī rada pozitīvu $G_{\text{H}_2\text{O_Bioīmija}}=\mathbf{85,64}\text{ kJ/mol}$ aktivāciju kā pašorganizējoša homeostāze.



Viela	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
C_{gr}	0	5.74	0
C_{gr}	716.7	158.1	671.3

$= 6 \cdot -393,509 - (6 \cdot 0 - 6 \cdot 0) = 2361,05 - 0 = -2361,05 \dots \text{kJ/mol}$
 2. $\Delta S_{izklydēta} = -\Delta H_H / T = -2361,05 / 298,15 = 7919 \dots \text{J/K/mol}$
 3. $\Delta S_{kopēja} = \Delta S_H + \Delta S_{izklydēta} = 17,76 + 7919 = 7936,76 \dots \text{J/mol/K}$

$\Delta S_H = 6\Delta S^\circ_{CO_2} - 6\Delta S^\circ_{C_{gr}} - 6\Delta S^\circ_{O_2} = 6 \cdot 213,74 - (6 \cdot 5,74 + 6 \cdot 205,04) = 17,76 \dots \text{J/mol/K}$;

$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -2361,05 - 298,15 \cdot 0,01776 = -2366,35 \dots \text{kJ/mol}$ **eksotermiska**

$T \cdot \Delta S_{kopēja} = 7936,76 \cdot 298,15 = 2366,35 \dots \text{kJ/mol}$ saistīta $T\Delta S_n \leftarrow$ izklydētā enerģija

$C_{gas} + O_2 \uparrow_{gas} \rightarrow CO_2 \uparrow_{gas}$. $\Delta G_H = \Delta G^\circ_{CO_2 \uparrow_{gas}} - (\Delta G^\circ_{C_{gas}} + \Delta G^\circ_{O_2}) = -394,4 - (671,3 + 0) = -1065,7 \text{ kJ/mol}$

$C_{gr} + O_2 \uparrow_{gas} \rightarrow CO_2 \uparrow_{gas}$. $\Delta G_H = G^\circ_{CO_2 \uparrow_{gas}} - (G^\circ_{C_{gr}} + G^\circ_{O_2}) = G^\circ_{CO_2 \uparrow_{gas}} - (-671,3 + 237,19) = -394,5 \text{ kJ/mol}$;

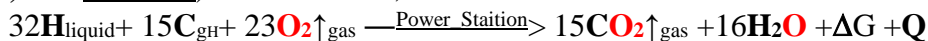
$G^\circ_{CO_2 \uparrow_{gas}} = -394,4 + (-671,3 + 237,19) = -828,51 \text{ kJ/mol}$; $G_{O_2 \text{Air}} = 237,19 \text{ kJ/mol}$.

$\Delta H_H = \Delta H^\circ_{CO_2 \uparrow_{gas}} - \Delta H^\circ_{C_{gr}} + \Delta H^\circ_{O_2} = -393,509 - (0 + 716,7) = -1110,209 \text{ kJ/mol}$ **exothermic**.

$O_2 \text{gas AIR} + H_2O_{\text{Aquaporins}} \rightarrow O_2 \text{Blood}$; $G_{O_2 \text{aqua}} = G_{O_2 \text{Air}} + G_{O_2 \text{sp}} = 237,19 + 26,58 = 263,77 \text{ kJ/mol}$.

$C_{gr} + 2H_2 \uparrow_{gas} \rightarrow CH_4 \uparrow_{gas}$; $\Delta G_H = G^\circ_{CH_4 \uparrow_{gas}} - (G^\circ_{C_{gr}} + 2G^\circ_{H_2}) = G^\circ_{CH_4 \uparrow_{gas}} - (-671,3 + 2 \cdot 237,19/2) = -50,5 \text{ kJ/mol}$;

$G^\circ_{CH_4 \uparrow_{gas}} = -50,5 + (-671,3 + 2 \cdot 237,19/2) = -484,61 \text{ kJ/mol}$;



Viela	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
H_{atom}	218.0	114.7	203.3

1. $\Delta H_H = 15\Delta H^\circ_{CO_2} + 16\Delta H^\circ_{H_2O} - 32\Delta H^\circ_H - 15\Delta H^\circ_{C_{gr}} - 23\Delta H^\circ_{O_2} = -17452,2$
 $= 15 \cdot -393,509 + 16 \cdot -285,85 - (32 \cdot 218 + 15 \cdot 0 + 23 \cdot 0) = -10476 - 6976 = \dots \text{kJ/mol}$

$\Delta S_H = 15\Delta S^\circ_{CO_2} + 16\Delta S^\circ_{H_2O} - 32\Delta S^\circ_H - 15\Delta S^\circ_{C_{gr}} - 23\Delta S^\circ_{O_2} = \dots \text{J/mol/K}$;

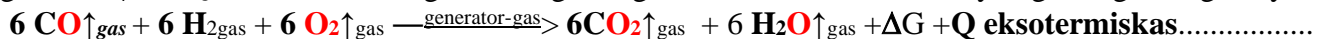
$= 15 \cdot 213,74 + 16 \cdot 69,9565 - (32 \cdot 114,7 + 15 \cdot 5,74 + 23 \cdot 205,04) = 4325,4 - 8472,42 = -4147 \dots \text{J/mol/K}$;

$\Delta S_{\text{dispersed}} = -\Delta H_H / T = -17452,2 / 298,15 = 58535 \dots \text{J/K/mol}$; $\Delta S_{\text{total}} = \Delta S_H + \Delta S_{\text{dispersed}} = 58535 - 4147 = 54388 \dots \text{J/mol/K}$;

$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -17452,2 - 298,15 \cdot -4,147 = -17452,2 + 1236,43 = -16215,8 \dots \text{kJ/mol}$ **exoergic**

$T \cdot \Delta S_{\text{total}} = 54388 \cdot 298,15 = 16215,8 \dots \text{kJ/mol}$ bound $T\Delta S_n \leftarrow$ lost free energy

Generator gas $6CO \uparrow + 6H_2 \uparrow_{gas}$ is home heating, street lightning fuel of 19th as 20th century beginning in Riga city.



Substance	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
$CO \uparrow_{gas}$	-110,525	197,674	-137,2
$H_2 \uparrow_{gas}$	0	130,68	-
$-O_2 \uparrow_{gas}$	0	205,152	-
$H_2O \uparrow_{gas}$	-241,8352	188,74024	-228,6

$\Delta H_H = 6\Delta H^\circ_{CO_2} + 6\Delta H^\circ_{H_2O} - 6\Delta H^\circ_{H_2 \uparrow_{gas}} - 6\Delta H^\circ_{CO \uparrow_{gas}} - 6\Delta H^\circ_{O_2 \uparrow_{gas}} = \text{kJ/mol}$

$= 6 \cdot -393,509 + 6 \cdot -241,8352 - (6 \cdot -110,53 + 6 \cdot 0 + 6 \cdot 0) = \text{kJ/mol}$

$= -3812,07 + 663,18 = -3148,89$ **eksotermiskas** $\dots \text{kJ/mol}$

2. $\Delta S_{izklydēta} = -\Delta H_H / T = 3148,89 / 298,15 = 10561,4 \dots \text{J/K/mol}$

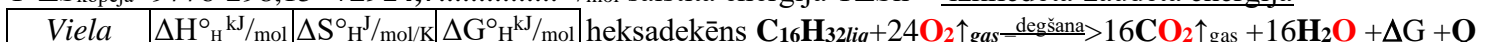
$\Delta S_H = 6\Delta S^\circ_{CO_2} + 6\Delta S^\circ_{H_2O} - 6\Delta S^\circ_{H_2 \uparrow_{gas}} - 6\Delta S^\circ_{CO \uparrow_{gas}} - 6\Delta S^\circ_{O_2 \uparrow_{gas}} = \text{J/mol/K}$

$\dots = 6 \cdot 213,74 + 6 \cdot 188,74024 - (6 \cdot 130,68 + 6 \cdot 197,66 + 6 \cdot 205,04) = 2414,88 - 3200,28 = -785,399 \text{ J/mol/K} \dots$

3. $\Delta S_{kopēja} = \Delta S_H + \Delta S_{izklydēta} = -785,399 + 10561,4 = 9776 \dots \text{J/mol/K}$

$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -3148,89 - 298,15 \cdot -0,785399 = -3148,89 + 234,16 = -2914,72 \dots \text{kJ/mol}$ **eksotermiskas**

$T \cdot \Delta S_{kopēja} = 9776 \cdot 298,15 = 2914,7 \dots \text{kJ/mol}$ saistīta enerģija $T\Delta S_n \leftarrow$ izklydēta-zaudēta enerģija



$\Delta H_{\text{Hess}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{Reactants}}$; 2. $\Delta S_{\text{Hess}} = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{Reactants}}$

$\Delta H_H = 16\Delta H^\circ_{CO_2} + 16\Delta H^\circ_{H_2O} - \Delta H^\circ_{C_{16}H_{32}} - 24\Delta H^\circ_{O_2} = \dots \text{kJ/mol}$

$= 16 \cdot -393,509 + 16 \cdot -285,85 - (24 \cdot 0 - 328,7) = -10541 \text{ kJ/mol}$ **exothermic**

$\Delta S_{\text{dispersed}} = -\Delta H_H / T = -10541 / 298,15 = 33050 \dots \text{J/mol/K}$.

2. $\Delta S_H = 16\Delta S^\circ_{CO_2} + 16\Delta S^\circ_{H_2O} - \Delta S^\circ_{C_{16}H_{32}} - 24\Delta S^\circ_{O_2} = -969,716 \dots \text{J/mol/K}$

$= 16 \cdot 213,74 + 16 \cdot 69,9565 - (24 \cdot 205,04 + 587,9) = 4539,14 - 5508,86 = -969,716 \dots \text{J/mol/K}$;

3. $\Delta S_{\text{total}} = \Delta S_H + \Delta S_{\text{dispersed}} = 33050 - 969,716 = 32080,7 \dots \text{J/mol/K}$;

3. $\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -10541 - 298,15 \cdot -0,969716 = -10541 + 289,121 = -10251,9 \dots \text{kJ/mol}$ **exoergic**

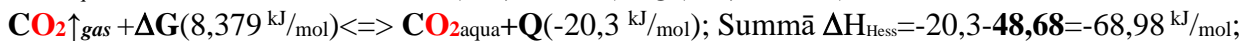
$T \cdot \Delta S_{\text{total}} = 34385 \cdot 298,15 = 10251,9 \dots \text{kJ/mol}$ bound $T\Delta S_n \leftarrow$ lost free energy

$C_{16}H_{32} \text{liq}$ kJ/mol/C/12 = 10251,9/16/12 = 53,4 kJ/gC; C 12 g/mol 1 Gt = $1 \cdot 10^9 \cdot 10^6 \text{ g} = 1 \cdot 10^{15} \text{ g}$;

9,55 Gt = $9,55 \cdot 10^9 \cdot 10^6 \text{ g} = 9,55 \cdot 10^{15} \text{ g}$; 9,55 Gt/12 Gkmol = $9,55 / 12 \cdot 10^9 \cdot 10^6 \text{ mol} = 9,55 / 12 \cdot 10^{15} \text{ mol}$ C;

$G_{\text{Hess}} = 53,4 \text{ kJ/gC} \cdot 9,55 \cdot 10^{15} \text{ gC} = 53,4 \cdot 9,55 \cdot 10^{15} = 510 \cdot 10^{15} \text{ kJ}$

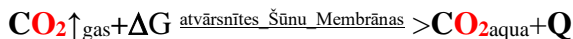
Reakcija ir lēna pie $pOH = 5,9$ okeānā ar hidroksīda anjonu



TERMODINAMIKA VINGRINĀJUMS II. GAISA CO₂ izšķīšanas reakcija ūdenī CO_{2(aqu)}

CO_{2(gas)} + ΔG + Q <=> CO_{2(aqua)}; E3 klases enzīma CA hidrolīzes-protolīzes līdzsvars 2H₂O^{CA}/CO₂/H₃O⁺+HCO₃⁻ CO_{2(gas)} nereaģē ar H₂O bet šķīst ūdenī. (298.15 K). Reakcija ir eksotermiska, atermiska, endotermiska? Enzīma karbo anhidrāzes (CA) protolīze 2H₂O^{CA}/CO₂/H₃O⁺+HCO₃⁻ virza CO_{2(aqua)} ūdenī 2H₂O! Būs eksoerģiska vai endoerģiska! CO_{2(gas)} + ΔG <=> CO_{2(aqua)} + Q; CO_{2(aqua)} + 2H₂O + ΔG + Q =^{CA}> H₃O⁺ + HCO₃⁻.....

Viela	ΔH ^o _H kJ/mol	ΔS ^o _H J/mol/K	ΔG ^o _H kJ/mol
CO _{2(gas)}	-393,509	213,74	-394,359
H ₂ O	-285,85	69,9565	-237,191
CO _{2(aqua)}	413,7976	117,5704	-385,98



ΔH_{hydration} = -17,9 kJ/mol; hidratācija

ΔG_{šķ} = ΔG^oCO_{2(aqua)} - ΔG^oCO_{2(gas)} = -385,98 - (-394,359) = +8,379 kJ/mol

= -385,98 - (-394,359) = 8,379 kJ/mol endoerģiska.....

1. ΔH_{Hess} = ΔH^oCO_{2(aqua)} - ΔH^oCO_{2(gas)} = -413,7976 - (-393,509) = -20,2886..... kJ/mol eksotermiska....

ΔS_{izkliedēta} = -ΔH_{Hess}/T = 20,2886/298,15 = 68,048 J/mol/K; ΔS_{izkliedētaHydration} = -ΔH_{hydration}/T = 17,9/298,15 = 60,037 J/mol/K

2. ΔS_{Hess} = ΔS^oCO_{2(aqua)} - ΔS^oCO_{2(gas)} = 117,57 - (213,74) = -96,17..... J/mol/K

ΔS_{kopēja} = ΔS_{Hess} + ΔS_{izkliedēta} = -96,17 + 68,046 = -28,124..... J/mol/K

ΔS_{kopēja} = ΔS_{Hydration} + ΔS_{izkliedētaHydration} = -96,17 + 60,037 = -36,13..... J/mol/K

3. ΔG_{Hess} = ΔH_{Hess} - T * ΔS_{Hess} = -20,1986 - 298,15 * -96,17 = 8,3845..... kJ/mol endoerģiska.....

3. ΔG_{hydrationHess} = ΔH_{hydrationHess} - T * ΔS_{hydrationHess} = -17,9 - 298,15 * -0,09617 = 10,77..... kJ/mol hidratācija.....

T * ΔS_{kopēja} = -28,124 * 298,15 K = -8,385..... kJ/mol; T * ΔS_{kopēja} = -36,13 * 298,15 K = -10,77..... kJ/mol

saistīta TΔSn ← uzkrātā enerģija produktos nav patvaļīga ΔG_{Hess} = +8,3845 kJ/mol. Mol daļās X^{CO_{2(aqua)}}:

šķīdība K_{šķ} = $\frac{X_{CO_2}}{[CO_2]_{gas}} = \frac{[CO_2]_{aqua}}{[CO_2]_{gas} \cdot [H_2O]}$ = EXP(-ΔG_{šķ}/R/T) = EXP(-8379/8,3144/298,15) = 0,034045 = 1/29,375

Nelabvēlīga šķīdība ΔG_{šķ} = -R * T * ln(K_{šķ}) = -8,3144 * 298,15 * ln(0,034045) = 8,379 kJ/mol.

Eksotermiska un endoerģiska [CO_{2(gas)}] = 1 moldaļās 100% gāzes izšķīdināšanas ūdenī

CO_{2(aqua)} Hesa brīvās enerģijas izmaiņa pozitīva ΔG_{hidratēšanaHess} = 10,77..... kJ/mol, bet

minimizējas ΔG_{min} = ΔG_{šķ} = 8,379..... kJ/mol sasniedzot līdzsvara maisījumu

Tīra 100% [CO_{2(gas)}] gāze; [CO_{2(aqua)}] = K_{šķ} * 1 * [H₂O] = 0,034045 * 55,3 = 1,882 M;

Līdzsvara sasniegšana ir Prigožina atraktors brīvās enerģijas izmaiņas minimums ΔG_{min}.

Gaisa 0,04% mol daļās [CO_{2(air)}] = 0,0004 kā 400 ppm vienības uz miljonu izšķīst

ūdenī [CO_{2(aqua)}] veidojot molaritāti [CO_{2(aqua)}] = 0,00075125 M;

[CO_{2(aqua)}] = K_{šķ} * [CO_{2(air)}] * [H₂O] = 0,034045 * 0,0004 * 55,346 = 0,00075125..... M;

CA karbo anhidrāze veic neatgriezeniski izšķīdušā oglekļa dioksīda reakciju ar divām ūdens molekulām

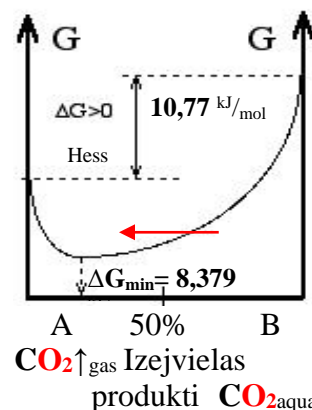


$\frac{[HCO_3^-]_{aqua} \cdot [H_3O^+]}{[CO_2]_{aqua} \cdot [H_2O]^2} = K_{eqCAHCO3aqua} = K_a \cdot CO_2(aqua) / [H_2O]^2 = 10^{-7,0512} / 55,3^2 = 2,906 \cdot 10^{-11}$. CA equilibrium constant

accumulate energy: ΔG_{eqCO_{2(aqua)}} = -R * T * ln(K_{eqCO_{2(aqua)}}) = -8,3144 * 298,15 * ln(2,906 * 10⁻¹¹) / 1000 = 60,14 kJ/mol.

G_{H3O+HCO3} = G_{H3O+} + G_{HCO3} = 22,44 + 46,08 = ΔG_{spCO_{2(aqua)}} + ΔG_{eqCO_{2(aqua)}} = 8,379 + 60,14 = 68,52 kJ/mol. [1,8,14]

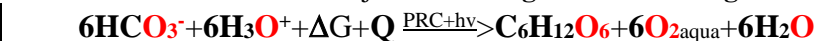
K_{CO_{2(aqua)}} = [CO_{2(aqua)} + HCO₃⁻] / [CO_{2(air)}] = 0,023 M / 0,00075125 M = 30,6 reizes. Kaļķakmens, dolomīta, krīta kalnu un marmora klinšu apjomīga veidošanās iespējama vienīgi ja CO_{2(air)} oglekļa dioksīds (no gaisa 0,04%) reaģē ar ūdeni. Uz Zemes šo reakciju realizē E3 hidrolāzes klases enzīms karbo anhidrāze CA (Carbonic Anhydrase).



TERMODINAMIKA VINGRINĀJUMS III. Bikarbonāta $6\text{HCO}_3^- + 6\text{H}_3\text{O}^+$ pārvēršana foto sintēze 6O_2 un $\text{C}_6\text{H}_{12}\text{O}_6$

Aprēķināt ΔH_H ΔS_H ΔG_H . Reakcija ir **eksotermiska**, **atermiska**, **endotermiska**? Bikarbonāta asimilācijas ūdenī zaļajos augos ar zilo un sarkano fotonu $E=h\nu$ enerģijas absorbciju foto sintētiskajā reakcijas centrā $\text{PRC}+h\nu$ producē $6\text{O}_{2\text{aqua}}$ un $\text{C}_6\text{H}_{12}\text{O}_6$ standarta apstākļos 298.15 K. Lietojiet tabulas datus! Miniet vai reakcija būs **eksoergiska** vai **endoergiska**!

Viela	ΔH_H° kJ/mol	ΔS_H° J/mol/K	ΔH_H° kJ/mol
$\text{C}_6\text{H}_{12}\text{O}_{6\text{aq}}$	-1263,78	269,45	-919,96
Glc	-1267,13	-2901,49	-402,05
$\text{O}_{2\text{aqua}}$	-11,715	110,876	16,4
$\text{O}_{2\text{aqua}}$	-11,7	-94,2	16,4
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
H_3O^+	-285,81	-3,854	-213,275
HCO_3^-	-689,93	98,324	-586,94
HCO_3^-	-692,4948	-494,768	-544,9688



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2006, Maschusetts's Technology Inst. Alberty [8]

$\Delta H_H = \Delta H^{\circ}_{\text{C}_6\text{H}_{12}\text{O}_6} + 6\Delta H^{\circ}_{\text{O}_2} + 6\Delta H^{\circ}_{\text{H}_2\text{O}} - 6\Delta H^{\circ}_{\text{H}_3\text{O}^+} - 6\Delta H^{\circ}_{\text{HCO}_3^-} = 2812,6 \text{ kJ/mol}$
 $= -1267,13 + 6 \cdot (-11,7) + 6 \cdot (-286,65) - (6 \cdot (-692,4948) + 6 \cdot (-285,81)) = 2812,6 \text{ kJ/mol}$
 $\Delta G_H = \Delta G^{\circ}_{\text{C}_6\text{H}_{12}\text{O}_6} + 6\Delta G^{\circ}_{\text{O}_2} + 6\Delta G^{\circ}_{\text{H}_2\text{O}} - 6\Delta G^{\circ}_{\text{H}_3\text{O}^+} - 6\Delta G^{\circ}_{\text{HCO}_3^-} = 3336,52 \text{ kJ/mol}$
 $= -402,05 + 6 \cdot 16,4 + 6 \cdot (-151,549) - (6 \cdot (-544,9688) + 6 \cdot (-213,275)) = 3336,5 \text{ kJ/mol}$
 $\Delta S_H = \Delta S^{\circ}_{\text{C}_6\text{H}_{12}\text{O}_6} + 6\Delta S^{\circ}_{\text{O}_2} + 6\Delta S^{\circ}_{\text{H}_2\text{O}} - 6\Delta S^{\circ}_{\text{H}_3\text{O}^+} + 6\Delta S^{\circ}_{\text{HCO}_3^-} = 3194,1 \text{ J/mol/K}$
 $= -2901,49 + 6 \cdot (-94,2) + 6 \cdot (-453,188) - (6 \cdot (-494,768) + 6 \cdot (-3,854)) = -3194,1 \text{ J/mol/K}$
 $\Delta G_H = \Delta H_H - T \cdot \Delta S_H = 2812,6 - 298,15 \cdot (-3,1941) = 3765 \text{ kJ/mol}$ **endoergiska**

$\Delta S_{\text{izkļiedēta}} = -\Delta H_H/T = -2812,6/298,15 = -9433,51 \text{ J/mol/K}$; $\Delta S_{\text{kopēja}} = \Delta S_H + \Delta S_{\text{izkļiedēta}} = -3194,1 - 9433,51 = -12627,6 \text{ J/mol/K}$;
 $T \cdot \Delta S_{\text{kopēja}} = -12627,6 \cdot 298,15 \text{ K} = -3764,9 \text{ kJ/mol}$; saistīta $T\Delta S_n$ uzkrātā enerģija produkto.

[Lapas puse](#).3.: nav patvaļīga, nelabvēlīga.

Uzkrātā enerģija $T\Delta S_{\text{kopēja}} = -3764,9 \text{ kJ/mol}$ ir saistīta produkto: $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_{2\text{aqua}} + 6\text{H}_2\text{O}$

Biodegviela $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} + 6\text{O}_{2\text{aqua}}$! $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_{2\text{aqua}} + 6\text{H}_2\text{O} \xrightarrow{\text{biooksidēšana}} 6\text{HCO}_3^- + 6\text{H}_3\text{O}^+ + \Delta G + Q$

$\Delta H_H = 6\Delta H^{\circ}_{\text{H}_3\text{O}^+} + 6\Delta H^{\circ}_{\text{HCO}_3^-} - \Delta H^{\circ}_{\text{C}_6\text{H}_{12}\text{O}_6} - 6\Delta H^{\circ}_{\text{O}_2} - 6\Delta H^{\circ}_{\text{H}_2\text{O}} = 6 \cdot (-692,4948) + 6 \cdot (-285,81) - (-1267,13 + 6 \cdot (-11,7) + 6 \cdot (-286,65)) = -2812,6 \text{ kJ/mol}$
 $\Delta G_H = 6\Delta G^{\circ}_{\text{H}_3\text{O}^+} + 6\Delta G^{\circ}_{\text{HCO}_3^-} - \Delta G^{\circ}_{\text{C}_6\text{H}_{12}\text{O}_6} - 6\Delta G^{\circ}_{\text{O}_2} - 6\Delta G^{\circ}_{\text{H}_2\text{O}} = 6 \cdot (-544,9688) + 6 \cdot (-213,275) - (-402,05 + 6 \cdot 16,4 + 6 \cdot (-151,549)) = -3336,5 \text{ kJ/mol}$
 $\Delta S_H = 6\Delta S^{\circ}_{\text{H}_3\text{O}^+} + 6\Delta S^{\circ}_{\text{HCO}_3^-} - \Delta S^{\circ}_{\text{C}_6\text{H}_{12}\text{O}_6} - 6\Delta S^{\circ}_{\text{O}_2} - 6\Delta S^{\circ}_{\text{H}_2\text{O}} = 6 \cdot (-494,768) + 6 \cdot (-3,854) - (-2901,49 + 6 \cdot (-94,2) + 6 \cdot (-453,188)) = 3194,1 \text{ J/mol/K}$

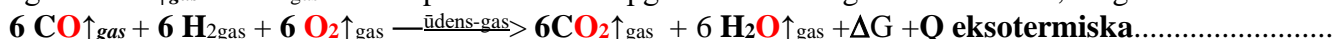
$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -2812,6 - 298,15 \cdot (-3,1941) = -3765 \text{ kJ/mol}$ **exoergic....**

$\Delta S_{\text{izkļiedēta}} = -\Delta H_H/T = 2812,6 \cdot 1000/298,15 = 9433,51 \text{ J/mol/K}$; $\Delta S_{\text{total}} = \Delta S_H + \Delta S_{\text{izkļiedēta}} = 3194,1 + 9433,51 = 12627,6 \text{ J/mol/K}$;

$T \cdot \Delta S_{\text{kopēja}} = 12627,6 \cdot 298,15 \text{ K} = 3764,9 \text{ kJ/mol}$; saistīta $T\Delta S_n \leftarrow$ izkļiedēta enerģija **patvaļīga**.

[Lapas puse](#).3.: Bio-degviela $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_{2\text{aqua}} + 6\text{H}_2\text{O}$ izkļiedētā brīvā enerģija $T\Delta S_{\text{kopēja}} = 3764,9 \text{ kJ/mol}$ iztērēta generētajās $6\text{HCO}_3^- + 6\text{H}_3\text{O}^+$ produktu koncentrācijās.

Ūdens gāze $6\text{CO}\uparrow_{\text{gas}} + 6\text{H}_2\text{gas}$ ir ēku apkures un ielu apgaismošanas degviela lietota 19.,20. gadsimta sākumā Rīgā



Viela	ΔH_H° kJ/mol	ΔS_H° J/mol/K	ΔG_H° kJ/mol
$\text{CO}\uparrow_{\text{gas}}$	-110,525	197,674	-
H_2gas	0	130,68	0
$\text{O}_2\uparrow_{\text{gas}}$	0	205,04	-61.166
$\text{H}_2\text{O}\uparrow_{\text{gas}}$	-241,8352	188,74024	-

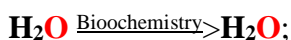
1. $\Delta H_H = 6\Delta H^{\circ}_{\text{CO}_2} + 6\Delta H^{\circ}_{\text{H}_2\text{O}} - 6\Delta H^{\circ}_{\text{H}_2\text{gas}} - 6\Delta H^{\circ}_{\text{COgas}} - 6\Delta H^{\circ}_{\text{O}_2\text{gas}} = \dots \text{ kJ/mol}$
 $= 6 \cdot (-393,509) + 6 \cdot (-241,8352) - (6 \cdot (-110,53) + 6 \cdot 0 + 6 \cdot 0) = \dots \text{ kJ/mol}$
 $= -3812,07 + 663,18 = -3148,89$ **eksotermiska**..... kJ/mol
 2. $\Delta S_{\text{izkļiedēta}} = -\Delta H_H/T = -3148,89/298,15 = 10561,4 \dots \text{ J/K/mol}$
 2. $\Delta S_H = 6\Delta S^{\circ}_{\text{CO}_2} + 6\Delta S^{\circ}_{\text{H}_2\text{O}} - 6\Delta S^{\circ}_{\text{H}_2\text{gas}} - 6\Delta S^{\circ}_{\text{COgas}} - 6\Delta S^{\circ}_{\text{O}_2\text{gas}} = \dots \text{ J/K/mol}$

$\dots = 6 \cdot 213,74 + 6 \cdot 188,74024 - (6 \cdot 130,68 + 6 \cdot 197,66 + 6 \cdot 205,04) = -785,399 \dots \text{ J/mol/K}$;

3. $\Delta S_{\text{kopēja}} = \Delta S_H + \Delta S_{\text{izkļiedēta}} = -785,399 + 10561,4 = 9776 \dots \text{ J/mol/K}$

$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -3148,89 - 298,15 \cdot (-0,785399) = -3148,89 + 234,16 = -2914,72 \dots \text{ kJ/mol}$ **eksoergiska**....

$T \cdot \Delta S_{\text{kopēja}} = 9776 \cdot 298,15 = +2914,7 \dots \text{ kJ/mol}$ saistīta $T\Delta S_n \leftarrow$ izkļiedētā, izlietotā enerģija



$G_{\text{H}_2\text{O}_{\text{Biochemistry}}} = \Delta G^{\circ}_{\text{H}_2\text{O}_{\text{Biochemistry}}} - \Delta G^{\circ}_{\text{H}_2\text{O}_{\text{distilled}}} = -151,549 - (-237,191) = 85,64 \text{ kJ/mol}$.

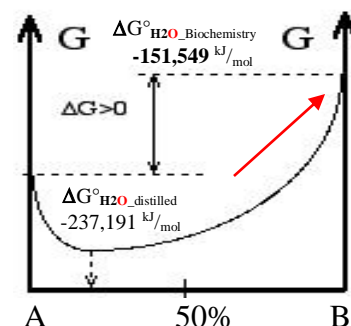
Endotermiska un endoergiska brīvās enerģijas uzkrāšana no bioķīmiskās vides:

osmolārā koncentrācija $C_{\text{osm}} = 0.305 \text{ M}$, jonu spēks $I = 0,2 \text{ M}$, temperatūra 298.15 K

ūdenim ir pozitīva $G_{\text{H}_2\text{O}_{\text{Biochemistry}}} = 85,64 \text{ kJ/mol}$ aktivācija kā pašorganizācija

homeostāzē.

reaktanti $\text{H}_2\text{O} \Rightarrow$ produkts H_2O .

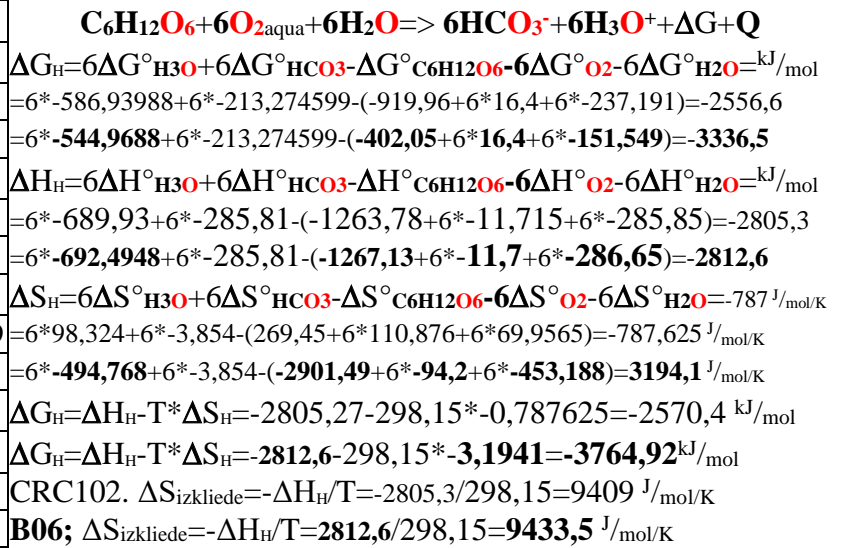


TERMODINAMIKA VINGRINĀJUMS III B Glikozes $C_6H_{12}O_6$ oksidēšana ar $6O_{2(aqua)}$ par $6HCO_3^- + 6H_3O^+$

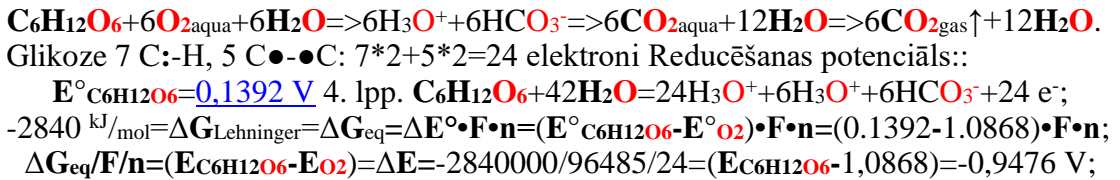
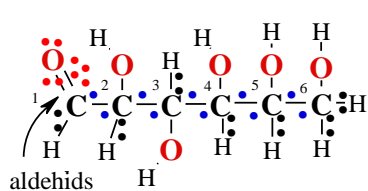
Aprēķināt ΔH_H ΔS_H ΔG_H . Reakcija ir **eksotermiska**, **atermiska**, **endotermiska**? Glikozes $C_6H_{12}O_6$ oksidēšana ar $6O_{2(aqua)}$ par $6HCO_3^- + 6H_3O^+$ 298.15 K. Lietojot tabulas datus! Vai reakcija būs **eksoerģiskas** or **endoerģiska**!



Viela	$\Delta H^\circ_H \text{ kJ/mol}$	$\Delta S^\circ_H \text{ J/mol/K}$	$\Delta G^\circ_H \text{ kJ/mol}$
$C_6H_{12}O_{6(aq)}$	-1263,78	269,45	-919,96
Glc	-1267,13	-2901,49	-402,05
$O_{2(aqua)}$	-11,715	110,876	16,4
$O_{2(aqua)}$	-11,7	-94,2	16,4
$O_2 \uparrow_{gas}$	0	205,152	-61,166
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
H_3O^+	-285,81	-3,854	-213,274599
$CO_2 \uparrow_{gas}$	-393,509	213,74	-394,359
$CO_{2(aq)}$	-413,798	117,5704	-385,98
$CO_{2(aq)}$	-413,26	-119,36	-
HCO_3^-	-6 89,93	98,324	-586,93988
HCO_3^-	-692,4948	-494,768	-544,9688



lpp. 3.: Bio-degvielal ($C_6H_{12}O_6 + 6H_2O$) + $6O_{2(aqua)}$ akumulētā saistītā enerģija $T\Delta S_{kopējā} = +2570,4 \text{ kJ/mol}$ producē dzīvības resursus $C_6H_{12}O_6 + 6H_2O + 6O_{2(aqua)}$ un tiek izlietoti oksidēšanā ģenerējot $6HCO_3^- + 6H_3O^+$ jonu koncentrācijas gradientus osmozei pretēji un transportēšanai lejup pa gradientiem cauri membrānu kanāliem.



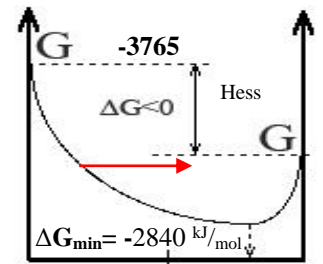
Atraktoru pH=7,36 un $[O_{2(aqua)}] = 6 \cdot 10^{-5} \text{ M}$ reducētāja potenciāls ir $E_{C_6H_{12}O_6} = \Delta E + E_{O_2} = -0,9476 + 1,0868 = 0,1392 \text{ V}$;
 $[H_3O^+] = 10^{-7,36} \text{ M}$, $[O_{2(aq)}] = 6 \cdot 10^{-5} \text{ M}$; $E_{O_2} = E^\circ + 0,0591/4 \cdot \log([O_{2(aqua)}] \cdot [H_3O^+]^4 / [H_2O]^5) =$
 $= 0,1392 + 0,0591/24 \cdot \log(6 \cdot 10^{-5} \cdot 10^{(-7,36 \cdot 4)} / 55,3^{15}) = 0,03485 \text{ V}$

Oxidised form: $6 \cdot (O_{2(aqua)} + 4H_3O^+ + 4e^- = 5H_2O)$ Suchotinas absolūtais standarta potenciāls $-E^\circ_{O_2} = -1,0868 \text{ V}$;
 $\Delta G_{Hess} = \Delta H_H - T \cdot \Delta S_H = -2812,6 - 298,15 \cdot 3,1941 = -3764,92 \text{ kJ/mol}$;
 $|\Delta G_{Hess} = -3764,92 \text{ kJ/mol}| > |\Delta G_{Lehninger} = -2840 \text{ kJ/mol}|$;
 $\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = -8,3144 \cdot 298,15 \cdot \ln(10^{497,55}) = -2840 \text{ kJ/mol}$

Eksotermiskā un eksoerģiskā oksidēšanas Hesa brīvās enerģijas gāzēm $6O_{2(gas)}$, $6CO_2$
 $\Delta G_{oksidēšana} = -2873 \text{ kJ/mol}$ tad $\Delta G_{oksidēšana} = -2921,5 \text{ kJ/mol}$ vairāk ūdenī $6O_{2(aqua)}$, $6CO_{2(aqua)}$,
 $\Delta G_{oksidēšana} = -2971,8 \text{ kJ/mol}$ $6O_{2(aqua)}$, $6CO_{2(gas)}$, $\Delta G_{oksidēšana} = -3765 \text{ kJ/mol}$ $6H_3O^+$, $6HCO_3^-$, bet
 minimizējas $\Delta G_{min} = \Delta G_{eq} = -2840 \text{ kJ/mol}$ sasniedzot kvazi līdzsvara maisījumu.

Reaģentiem 13 izejvielām $C_6H_{12}O_6 +$ un 12 produkti $6O_{2(aqua)} + 6H_2O$

$$\text{EXP}(-\Delta G_{Lehninger} / R / T) = \text{EXP}(2840 / 8,3144 / 298,15) = 10^{498} = K_{eq} = \frac{[HCO_3^-]_{aq}^6 \cdot [H_3O^+]^6}{[C_6H_{12}O_6] \cdot [O_{2(aqua)}]^6 \cdot [H_2O]^6}$$



A + 6B + 6C 50% 6D + 6E
 $C_6H_{12}O_6 + 6O_{2(aq)} + 6H_2O$
 reaktanti produkti
 $6H_3O^+ + 6HCO_3^-$

Homeostazes kvazi līdzsvars Prigožina atraktors ir brīvās enerģijas minimums ΔG_{min} .

Brīvās enerģijas izmaiņas minimums stabilizē homestāzes kvazi līdzsvara maisījumu K_{eq} .

Fotosintēze 1. lpp. akumulē brīvo enerģiju dzīvības resursos $C_6H_{12}O_6 + 6O_{2(aqua)} + 6H_2O$ $\Delta G_{Lehninger} = 2840 \text{ kJ/mol}$; no izejas līmeņa $6 \cdot G_{H_3O} + G_{HCO_3} = 6 \cdot 68,38 \text{ kJ/mol} = 411,12 \text{ kJ/mol}$ ar protolītiski aktivētiem sasniedz kvazi līdzsvaru un $\Delta G_{Lehninger} = G_{C_6H_{12}O_6} + 6G_{O_2(Biochem_arterial)} + 6G_{H_2O(Bioķīmija)} - 6G_{H_3O} + G_{HCO_3} = 2840 \text{ kJ/mol}$ ģenerē glikozes brīvās enerģijas saturu $G_{C_6H_{12}O_6} = 2840 - 6 \cdot 78,08 - 6 \cdot 85,64 + 6 \cdot 68,52 = 2840 - 468,48 - 513,84 + 411,12 = 2268,8 \text{ kJ/mol}$ līdz glikozei ar reducēšanas absolūto potenciālu $E_{C_6H_{12}O_6} = -0,884 \text{ V}$ pie atraktoru vērtībām $[H_3O^+] = 10^{-7,36} \text{ M}$, $[O_{2(aq)}] = 6 \cdot 10^{-5} \text{ M}$.

Aprēķināt ΔH_H ΔS_H ΔG_H . Reakcija ir **eksotermiska**, **atermiska**, **endotermiska**? Beta oksidēšana mitohondrijā, peroksi somā palmitīnskābei ar $O_{2\text{aqua}}$ standarta apstākļos (25° C) 298.15 K, pielietojiet tabulas datus! Miniet vai reakcija būs **eksoerģiska** vai **endoerģiska**!



Viela	ΔH_H° kJ/mol	ΔS_H° J/mol/K	ΔG_H° kJ/mol
$C_{16}H_{32}O_2$	-	-	1067,2384
$C_{16}H_{32}O_{2s}$	-891,5	452,4	-
$C_{16}H_{32}O_{2\text{liq}}$	-838,1	-	1003,54
$O_{2\text{aqua}}$	-11,715	110,876	16,4
$O_{2\text{aqua}}$	-11,7	-94,2	16,4
$O_2 \uparrow_{\text{gas}}$	0	205,152	0
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
H_3O^+	-285,81	-3,854	-213,2746
$CO_2 \uparrow_{\text{gas}}$	-393,509	213,74	-394,359
$CO_{2\text{aq}}$	-413,798	117,5704	-385,98
$CO_{2\text{aq}}$	-413,26	-119,36	-
HCO_3^-	-689,93	98,324	-586,93988
HCO_3^-	-692,4948	-494,768	-544,9688

biooksidēšana (mitohondrijā un peroksisomā)

$$1. \Delta H_{\text{Hess}} = \sum \Delta H^\circ_{\text{produkti}} - \sum \Delta H^\circ_{\text{izejvielas}}$$

$$2. \Delta S_{\text{Hess}} = \sum \Delta S^\circ_{\text{produkti}} - \sum \Delta S^\circ_{\text{izejvielas}}; 3. \Delta G_H = \Delta H_H - T \cdot \Delta S_H$$

$$2. \Delta S_{\text{izkļiedēta}} = -\Delta H_H / T = 9930,7 / 298,15 = 3337,7 \text{ J/mol/K}; \mathbf{33224,5}$$

$$\Delta S_{\text{kopēja}} = \Delta S_H + \Delta S_{\text{izkļiedēta}} = 33307,7 - 2610,33 = 30697,47 \text{ J/mol/K};$$

$$\Delta S_{\text{kopēja}} = \Delta S_H + \Delta S_{\text{izkļiedēta}} = \mathbf{33224,5 + 987,26 = 34211,76 \text{ J/mol/K}};$$

$$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = 9930,7 - 298,15 \cdot -2,61933 = -9152,5 \text{ kJ/mol};$$

$$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = \mathbf{-9905,9 - 298,15 \cdot 0,987256 = -10200,2 \text{ kJ/mol}};$$

$$T \cdot \Delta S_{\text{kopēja}} = 30,69747 \cdot 298,15 = 9152,5 \text{ kJ/mol}$$

$$T \cdot \Delta S_{\text{kopēja}} = \mathbf{34,21173 \cdot 298,15 = 10200,2 \text{ kJ/mol}}$$

izkļiedētā enerģija

CRC102.

B06;

$$\Delta G_H = 16\Delta G^\circ_{HCO_3} + 16\Delta G^\circ_{H_3O} - \Delta G^\circ_{C_{16}H_{32}O_2} - 16\Delta G^\circ_{H_2O} - 23\Delta G^\circ_{O_2} = \text{kJ/mol};$$

$$= 16 \cdot -586,93988 + 16 \cdot -213,2746 - (16 \cdot -237,191 + 23 \cdot 16,4 + 1003,54) = -10389 \text{ kJ/mol};$$

$$= 16 \cdot \mathbf{-544,9688} + 16 \cdot -213,2746 - (16 \cdot \mathbf{-151,549} + 23 \cdot \mathbf{16,4} + \mathbf{1067,2384}) = \mathbf{-11151,55 \text{ kJ/mol}};$$

$$\Delta G_H = 16\Delta G^\circ_{CO_{2\text{aqua}}} + 32\Delta G^\circ_{H_2O} - \Delta G^\circ_{C_{16}H_{32}O_2} - 16\Delta G^\circ_{H_2O} - 23\Delta G^\circ_{O_2} = \text{kJ/mol};$$

$$= 16 \cdot -385,98 + 32 \cdot -213,2746 - (16 \cdot -237,191 + 23 \cdot 16,4 + 1003,54) = -10386 \text{ kJ/mol};$$

$$= 16 \cdot -385,98 + 32 \cdot -213,2746 - (16 \cdot \mathbf{-151,549} + 23 \cdot \mathbf{16,4} + \mathbf{1067,2384}) = \mathbf{-12020 \text{ kJ/mol}};$$

$$\Delta G_H = 16\Delta G^\circ_{CO_{2\text{gas}}} + 32\Delta G^\circ_{H_2O} - \Delta G^\circ_{C_{16}H_{32}O_2} - 16\Delta G^\circ_{H_2O} - 23\Delta G^\circ_{O_2} = \text{kJ/mol};$$

$$= 16 \cdot -394,359 + 32 \cdot -213,2746 - (16 \cdot -237,191 + 23 \cdot 16,4 + 1003,54) = -10720 \text{ kJ/mol};$$

$$= 16 \cdot -394,359 + 32 \cdot -213,2746 - (16 \cdot \mathbf{-151,549} + 23 \cdot \mathbf{16,4} + \mathbf{1067,2384}) = \mathbf{-12154 \text{ kJ/mol}};$$

$$\Delta H_H = 16\Delta H^\circ_{HCO_3} + 16\Delta H^\circ_{H_3O} - \Delta H^\circ_{C_{16}H_{32}O_2} - 16\Delta H^\circ_{H_2O} - 23\Delta H^\circ_{O_2} = \text{kJ/mol};$$

$$= 16 \cdot -689,93 + 16 \cdot -285,81 - (16 \cdot -285,85 + 23 \cdot -11,715 - 838,1) = -9930,7 \text{ kJ/mol}$$

$$= 16 \cdot \mathbf{-692,4948} + 16 \cdot -285,81 - (16 \cdot \mathbf{-286,65} + 23 \cdot \mathbf{-11,7} - 891,5) = \mathbf{-9905,9 \text{ kJ/mol}}$$

$$\Delta S_H = 16\Delta S^\circ_{HCO_3} + 16\Delta S^\circ_{H_3O} - \Delta S^\circ_{C_{16}H_{32}O_2} - 16\Delta S^\circ_{H_2O} - 23\Delta S^\circ_{O_2} = \text{J/mol/K};$$

$$= 16 \cdot 98,324 + 16 \cdot -3,854 - (16 \cdot 69,9565 + 23 \cdot 110,876 + 452,4) = -2619,33 \text{ J/mol/K};$$

$$= 16 \cdot \mathbf{-494,768} + 16 \cdot -3,854 - (16 \cdot \mathbf{-453,188} + 23 \cdot \mathbf{-94,2} + 452,4) = \mathbf{987,256 \text{ J/mol/K}};$$

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(10^{1711,6428}) = -9770 \text{ kJ/mol}$$

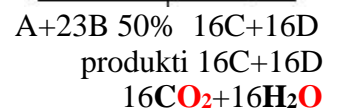
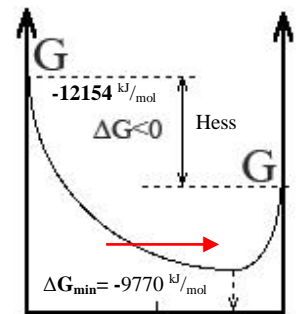
Eksotermiska un eksoerģiska palmitāta oksidēšanas Hesa brīvās enerģijas izmaiņa

negatīva akva $O_{2\text{aqua}} >$ un gāzveida $CO_{2\text{gas}} \uparrow$ $\Delta G_{\text{oksidēšana}} = -12154 \text{ kJ/mol}$ vai

$\Delta G_{\text{oksidēšana}} = -12020 \text{ kJ/mol}$ abiem ūdens šķīdumā $O_{2\text{aqua}}$ un $CO_{2\text{aqua}}$, bet minimizējas

$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -9770 \text{ kJ/mol}$ sasniedzot līdzsvara maisījumu

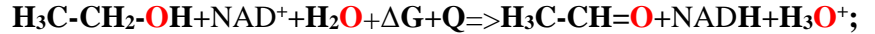
$$\text{EXP}(-\Delta G_{\text{Lehninger}}/R/T) = \text{EXP}(9770/8,3144/298,15) = 10^{1711,6428} = K_{\text{eq}} = \frac{[CO_{2\text{aqua}}]^{16} \cdot [H_2O]^{16}}{[C_{16}H_{32}O_6] \cdot [O_{2\text{aqua}}]^{23}}$$



Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara

maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

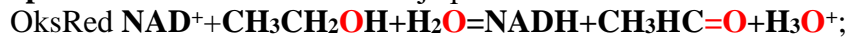
TERMODINAMIKA VINGRINĀJUMS IV. vitamīns B₃ oksidē H₃CCH₂OH etanolu par etanālu H₃CCH=O
Aprēķināt ΔH_H ΔS_H ΔG_H. Reakcija ir **eksotermiska**, **atermiska**, **endotermiska**? Reakcija standarta apstākļos
298,15 K. Vitamīn 3 B₃ oksidē etanolu alkohola dehidrogenāzes enzīmā par etanālu! Miniet vai reakcija būs
eksoerģiska vai **endoerģiska**!



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

CRC Handbook of Chemistry un Physics 2010 90th David R. Lide
 $\Delta H_{\text{Hess}} = \Delta H^{\circ}_{\text{H}_3\text{O}^+} + \Delta H^{\circ}_{\text{CH}_3\text{CHO}} + \Delta H^{\circ}_{\text{NADH}} - \Delta H^{\circ}_{\text{CH}_3\text{CH}_2\text{OH}} - \Delta H^{\circ}_{\text{H}_2\text{O}} - \Delta H^{\circ}_{\text{NAD}^+} =$
 $= -213,88 - 1036,66 - 285,81 - (-288,3 - 1007,48 - 285,85) = 45,28 \text{ kJ/mol}$
 BioThermodynam06; $\Delta S_{\text{izklienēta}} = -\Delta H_{\text{H}}/T = -45,28/298,15 = -151,9 \text{ J/mol/K}$
 $\Delta S_{\text{Hess}} = \Delta S^{\circ}_{\text{H}_3\text{O}^+} + \Delta S^{\circ}_{\text{CH}_3\text{CHO}} + \Delta S^{\circ}_{\text{NADH}} - \Delta S^{\circ}_{\text{CH}_3\text{CH}_2\text{OH}} - \Delta S^{\circ}_{\text{H}_2\text{O}} - \Delta S^{\circ}_{\text{NAD}^+} =$
 $= -825,64 - 140,50 - 3,854 - (-357,7394 - 183 + 69,9565) = -499,211 \text{ J/mol/K}$
 BioThermodynamic, 2006, Massachusetts Tecnology Institute, Albany
 $\Delta S_{\text{kopēja}} = \Delta S_{\text{H}} + \Delta S_{\text{izklienēta}} = -151,9 - 499,211 = -651,111 \text{ J/mol/K}$
 $\Delta G_{\text{H}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = 45,28 - 298,15 \cdot (-0,4992) = -194,12 \text{ kJ/mol}$ endoerģiski
 pH=7,36 $T \cdot \Delta S_{\text{kopēja}} = -0,651111 \cdot 298,15 = -194,1 \text{ kJ/mol}$
 $\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{H}_3\text{O}^+} + \Delta G^{\circ}_{\text{CH}_3\text{CHO}} + \Delta G^{\circ}_{\text{NADH}} - \Delta G^{\circ}_{\text{CH}_3\text{CH}_2\text{OH}} - \Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{NAD}^+} =$
 Standarta potenciāli E^o voltos David Harris; KortlyShucha datos

$\Delta G_{\text{Hess}} = 32,2824 + 1175,5732 - 151,549 - (75,2864 + 1059,11 - 237,191) = 159,1 \text{ kJ/mol}$ eksoerģiskas;
Red NADH <=> NAD⁺ + H⁺(2e⁻); absolute potential E^o_{NADH} = -0,4095 V; David Harris; [22];
Ox CH₃CHO + 2H₃O⁺ + H⁺(2e⁻) <=> CH₃CH₂OH + 2H₂O; E^o_{CH₃CH₂OH} = -0,055 V; [19];
 Novērtētajā balansā n=2=m ar elektronu skaitu 2e⁻ ΔE^o izteiksmē E^o_{H₂O} elektronu donors mīnus E^o₁ elektronu akceptors, jo NAD⁺ akceptē elektronus no etanola dotajā piemērā:



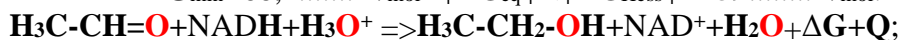
$$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = (E^{\circ}_{\text{NAD}^+} - E^{\circ}_{\text{eqNernsCH}_3\text{CH}_2\text{OH}}) \cdot F \cdot n = (-0,4095 + 0,055) \cdot 96485 \cdot 2 = (-0,3545) \cdot 96485 \cdot 2 = -68,408 \text{ kJ/mol};$$

$$\frac{[\text{NADH}] \cdot [\text{CH}_3\text{CHO}] \cdot [\text{H}_3\text{O}^+]}{[\text{NAD}^+] \cdot [\text{CH}_3\text{CH}_2\text{OH}] \cdot [\text{H}_2\text{O}]} = K_{\text{eqAerobiOx}} = \text{EXP}(-\Delta G_{\text{eq}}/R/T) = \text{EXP}(-68408/8,3144/298,15) = 19,65 \cdot 10^{11} = 10^{-12};$$

O₂ aqua attiecība [NADH]/[NAD⁺] = 10⁻⁶ pie pH=7,36 brīvās enerģijas izmaiņa negatīva:
 $\Delta G_{\text{Aerobi}} = 68,4 + 8,3144 \cdot 298,15 \cdot \ln(1/10^6 \cdot 1/1 \cdot 10^{-7,36}/55,3)/1000 = -17,8 \text{ kJ/mol};$
 $\Delta G_{\text{Hom}} = 68,4 - 86,21 = -17,8 \text{ kJ/mol},$ [NAD⁺]/[NADH] = 10⁵; $\Delta G_{\text{Hom}} = 68,4 - 80,5 = -12,14 \text{ kJ/mol}.$
 Aeroba endotermiska un endoerģiska H₃CCH₂OH etanola oksidēšanas Hesa brīvā enerģija pozitīva ΔG_{Hess} = 159..... kJ/mol inversi H₃CCH=O etanāla anaeroba reducēšana negatīva ΔG_{Hess} = -159..... kJ/mol, bet minimizējas inversi aerobā oksidēšanā

$\Delta G_{\text{min}} = \Delta G_{\text{eqAerobiOx}} = 68,4 \text{ kJ/mol}$ un $\Delta G_{\text{min}} = \Delta G_{\text{eqAnaerobiRed}} = -68,4 \text{ kJ/mol}$ reducēšanā
 sasniedzot līdzsvara maisījuma konstantes 10⁻¹² = K_{eqAerobiOx} < 1 etanola oksidēšanai un etanāla reducēšanai anaerobi 10¹² = K_{eqAnaerobi} > 1.

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



Anaerobi labvēlīgi ΔG_{eq} = ΔE^o · F · n = -0,3545 V · 2 mol · 96485 C/mol = -68,4 kJ/mol.

Niecīgā O₂ aqua koncentrācijā hipoksijā anaerobi spirta oksidēšana nelabvēlīga, bet etanāla reducēšana par etanolu labvēlīga attiecībai [H₃CCH₂OH]/[H₃CCH=O] = 1/10

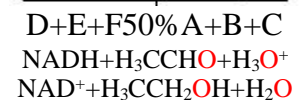
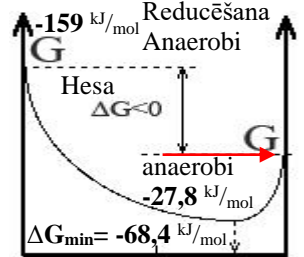
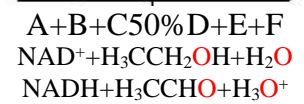
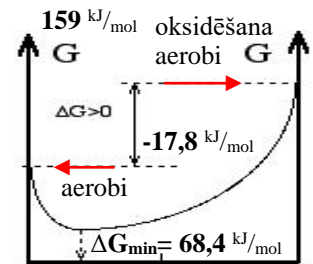
homeostāzē anaerobi attiecība [NAD⁺]/[NADH] = 1/10 labvēlīga reducēšanai kopā ar NADH reduktāzes enzīmu kā negatīva brīvās enerģijas izmaiņa

$$\Delta G_{\text{anaerobiRed}} = -68,4 + 8,3144 \cdot 298,15 \cdot \ln(1/10 \cdot 1/10 \cdot 55,3457/10^{-7,36})/1000 = -27,8 \text{ kJ/mol}.$$

$$\Delta G_{\text{AnaerobiRed}} = -68,4 + 8,3144 \cdot 298,15 \cdot \ln\left(\frac{1}{10} \cdot \frac{10}{1} \cdot \frac{55,333}{10^{-7,36}}\right) = -16,4 \text{ kJ/mol};$$

$$K_{\text{AnaerobiRed}} = 10^{12} = \frac{[\text{NAD}^+] \cdot [\text{CH}_3\text{CH}_2\text{OH}] \cdot [\text{H}_2\text{O}]}{[\text{NADH}] \cdot [\text{CH}_3\text{CHO}] \cdot [\text{H}_3\text{O}^+]}; \quad K_{\text{AerobiOx}} = 10^{-12} = \frac{[\text{NADH}] \cdot [\text{CH}_3\text{CHO}] \cdot [\text{H}_3\text{O}^+]}{[\text{NAD}^+] \cdot [\text{CH}_3\text{CH}_2\text{OH}] \cdot [\text{H}_2\text{O}]};$$

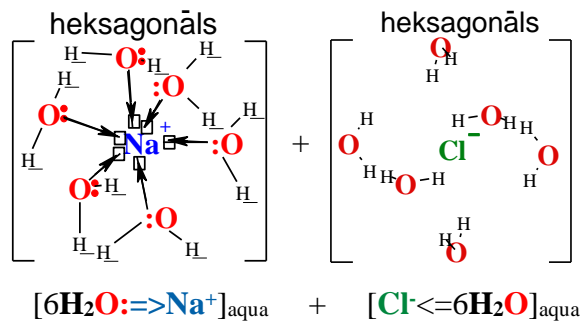
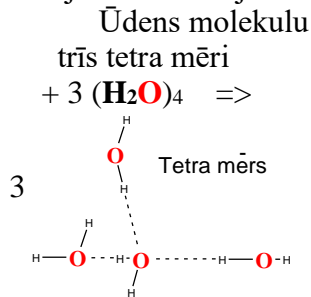
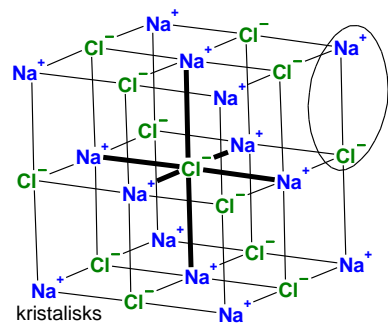
$$[\text{NADH}]/[\text{NAD}^+] = 1/7700; \quad \Delta G_{\text{AerobiRed}} = 68,4 + 8,3144 \cdot 298,15 \cdot \ln(1/7700 \cdot 1/10 \cdot 10^{-7,36}/55,3457)/1000 = -11,5 \text{ kJ/mol}.$$



TERMODINAMIKA VINGRINĀJUMS V sāls Na^+Cl^- kristāliem reakcija ar ūdeni

Sāls Na^+Cl^- kristāliem hidratācijas reakcijā ar ūdeni 36 g/100g šķīdība 100 g ūdens, blīvums šķīdumam 1,203 g/mL; w%=26,4706 %: $\text{Na}^+\text{Cl}^- + 3(\text{H}_2\text{O})_4 \Rightarrow [6\text{H}_2\text{O} \Rightarrow \text{Na}^+] + [\text{Cl}^- \Leftarrow 6\text{H}_2\text{O}]$ resursu skaits $n_c=49,142/12=4,0952$ M.

1. Pirais faktors koordinēšanās ap nātrija un hlorīda joniem patērē 12 ūdens molekulas: produkti $\text{Na}^+_{\text{aq}} + \text{Cl}^-_{\text{aq}}$



- $\text{Na}^+\text{Cl}^- \Rightarrow \text{Na}^+ + \text{Cl}^-$; enerģija $\Delta G_{\text{Na}^+\text{Cl}^-} = 700$ kJ/mol; Jonu kristāla noārdīšana.
- $3(\text{H}_2\text{O})_4 \Rightarrow 12\text{H}_2\text{O}$; enerģija $3 * \Delta G_{(\text{H}_2\text{O})_4} = 3 * 90 = 270$ kJ/mol; Tetra mēru noārdīšana.
- $\text{Na}^+ + 6\text{H}_2\text{O} \Rightarrow [6(\text{H}_2\text{O} \rightarrow \square) - \text{Na}^+]$ enerģija $6 * \Delta G_{[6\text{H}_2\text{O} \Rightarrow \text{Na}^+]} = 6 * -400 = -2400$ kJ/mol; Koordinatīvs heksagonāls.
- $\text{Cl}^- + 6\text{H}_2\text{O} \Rightarrow [\text{Cl}^- (...6\text{H}_2\text{O})]$ enerģija $6 * \Delta G_{[\text{Cl}^- (...6\text{H}_2\text{O})]} = 6 * -30 = -180$ kJ/mol; sešām ūdenražā saitēm.

$$\Delta G_{\text{reakcijās}} = \Delta G_{\text{Na}^+\text{Cl}^-} + 3 * \Delta G_{(\text{H}_2\text{O})_4} + 6 * \Delta G_{[6\text{H}_2\text{O} \Rightarrow \text{Na}^+]} + 6 * \Delta G_{[\text{Cl}^- (...6\text{H}_2\text{O})]} = 700 + 270 - 2400 - 180 = -1610$$
 kJ/mol;

Disociācijas pakāpe $\alpha = 4,0952/5,4434 = 75,2$ % kristāliskam $\text{NaCl}_{\text{aqua}} + \text{Q} \Rightarrow \text{Na}^+_{\text{aqua}} + \text{Cl}^-_{\text{aqua}} + \Delta G$; šķīdības konstante: $K_{\text{šķ}} = K_{\text{eq}} = [\text{Na}^+_{\text{aq}}] * [\text{Cl}^-_{\text{aq}}] / [\text{NaCl}_{\text{aq}}] = 4,0952 * 4,0952 / 1,3482 = 12,4393$ pārvērtoties izejvielu un produktu maisījumā: $\Delta G_{\text{šķ}} = -R * T * \ln(K_{\text{šķ}}) = -8,3144 * 298,15 * \ln(12,44) = -6,25$ kJ/mol, $\alpha = 0,752 = 4,0952/5,4434$; 75,2%.

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T * \Delta S_{\text{Hess}} = 3,82 - 298,15 * 0,0435 = -9,15 \dots \dots \text{kJ/mol}$$
 eksoerģiska..

Vielā	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol
Na^+Cl^-	-411,12	72,00	-
$\text{Na}^+_{\text{aqua}}$	-240,10	59,00	-261,9
$\text{Cl}^-_{\text{aqua}}$	-167,2	56,50	-
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
H_3O^+	-285,81	-3,854	-213,275
HCl_{gas}	-92,31	186,902	-95,3
HCl_{aqua}	-167,2	56,5	-131,2



- $\Delta H_{\text{H}} = \Delta H^\circ_{\text{Na}^+} + \Delta H^\circ_{\text{Cl}^-} - \Delta H^\circ_{\text{NaCl}} = \dots \dots \text{kJ/mol}$. **endotermiska**.....
 $= -240,1 - 167,2 - (-411,12) = -407,3 + 411,12 = +3,82 \dots \dots \text{kJ/mol}$
- $\Delta S_{\text{izkļiedēta}} = -\Delta H_{\text{H}} / T = -3,82 / 298,15 = -12,812 \dots \dots \text{J/(mol K)}$
 $\Delta S_{\text{H}} = \Delta S^\circ_{\text{Na}^+} + \Delta S^\circ_{\text{Cl}^-} - \Delta S^\circ_{\text{NaCl}} = 59 + 56,5 - 72 = 43,5 \dots \dots \text{J/mol K}$
 $\Delta S_{\text{kopēja}} = \Delta S_{\text{H}} + \Delta S_{\text{izkļiedēta}} = -12,812 + 43,5 = +30,688 \dots \dots \text{J/mol K}$

$$\Delta G_{\text{H}} = \Delta H_{\text{H}} - T * \Delta S_{\text{H}} = 3,82 - 298,15 * 0,0435 = -9,15 \dots \dots \text{kJ/mol}$$
 eksoerģiska....

$$T * \Delta S_{\text{kopēja}} = 30,688 * 298,15 = 9,15 \dots \dots \text{kJ/mol}$$
 saistīta brīvā enerģija

Nedisociēta sāls neitrālas molekulas veidojas divos veidos:

1. **Elektrostatiski** pievelkoties joniem Debaja Hikeļa fizioloģisko 0,9% šķīdumu veido osmolāru koncentrāciju $C_{\text{osm}} = 0,305$ M ar nātrija, hlorīda joniem un sāls neitrālām molekulām: $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$ vienā litrā 1000 mL. $C_{\text{osm}} = [\text{Na}^+] + [\text{Cl}^-] + [\text{NaCl}] = i * C_M = 0,305$ M. $m_{\text{NaCl}} / m_{\text{šķ}} = m_{\text{NaCl}} / 1000 * 100\% = w\% = 0,9\%$, jo blīvums ir 1 g/mL. Nātrija hlorīda masa $m_{\text{NaCl}} = 0,9\% * 1000 / 100\% = 9$ g/L un molu skaits $n_{\text{NaCl}} = m_{\text{NaCl}} / M_{\text{NaCl}} = 9 / 58,5 = 0,15385$ mol/L; $C_{\text{osm}} = [\text{Na}^+] + [\text{Cl}^-] + [\text{NaCl}] = i * C_M = (1 + \alpha(m-1)) * C_M = (1 + \alpha(2-1)) * 0,15385 = 0,305$ M. Disociācijas pakāpe alfa ir: $\alpha = (0,305 / 0,15385 - 1) = 0,98245$ un nedisociētā daļa $[\text{NaCl}_{\text{aq}}] = C_M - C_M * \alpha = 0,15385 - 0,15385 * 0,98245 = 0,0027$ M Fizioloģiskās šķīdības konstante $K_{0,9\%} = [\text{Na}^+_{\text{aq}}] * [\text{Cl}^-_{\text{aq}}] / [\text{NaCl}_{\text{aq}}] = 0,15115 * 0,15115 / 0,0027 = 8,4616$;

$$\Delta G_{0,9\%} = -R * T * \ln(K_{0,9\%}) = -8,3144 * 298,15 * \ln(8,4616) = -5,294$$
 kJ/mol,

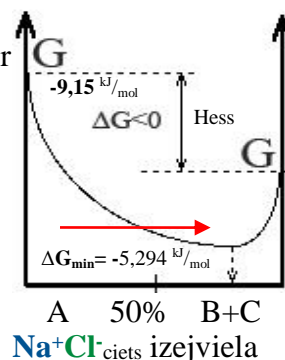
Endotermiskas un eksoerģiskas šķīdības Hesa brīvās enerģijas izmaiņa $\Delta G_{\text{Hess}} = -9,15$ kJ/mol ir

negatīva, bet minimizējas $\Delta G_{\text{min}} = \Delta G_{0,9\%} = -5,294$ kJ/mol fizioloģiskā 0,9 % maisījumā sasniedzot līdzsvaru $K_{0,9\%} = [\text{Na}^+_{\text{aq}}] * [\text{Cl}^-_{\text{aq}}] / [\text{NaCl}_{\text{aq}}] = 8,46$ vai kristāla nātrija hlorīda Na^+Cl^- šķīšanas līdzsvaru $\Delta G_{\text{šķ}} = -6,25$ kJ/mol ar $K_{\text{šķ}} = K_{\text{eq}} = 12,44$. Šķīšanas Reakcijas Prigožina atraktors ir brīvās enerģijas izmaiņas minimums ΔG_{min} .

Piezīme: Stiprie elektrolīti ir šķīstoši ar negatīvu $\Delta G < 0$ un par vienu lielāki $K_{\text{eq}} \gg 1$;

Vājie elektrolīti ar pozitīvu $\Delta G_{\text{eq}} > 0$ un $0 < K_{\text{eq}} < 1$ **endoerģiski** ir ūdenī nešķīstošie.

Kristāls šķīst ūdenī: $\text{Na}^+\text{Cl}^- + 3(\text{H}_2\text{O})_4 \Rightarrow [6\text{H}_2\text{O} \Rightarrow \text{Na}^+]_{\text{aqua}} + [\text{Cl}^- \Leftarrow 6\text{H}_2\text{O}]_{\text{aqua}}$.



TERMODINAMIKA VINGRINĀJUMS V sāls Na^+OH^- kristāliem reakcija ar ūdeni

100 g/100g šķīdība 200 g ūdens šķīduma blīvums 1,5217 g/mL ; w%=50 %

$M_{\text{NaOH}} = \text{Na} + \text{O} + \text{H} = 23 + 16 + 1 = 40 \text{ g/mol}$; $n_{\text{NaOH}} = m_{\text{NaOH}} / M_{\text{NaOH}} = 760,85 / 40 = 19,02 \text{ mol}$;

$n_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}} / M_{\text{H}_2\text{O}} = 760,85 / 18 = 42,27 \text{ mol}$; $n_c = 42,27 \cdot 2 = 19,02 = 4,23 \text{ M}$ M; Ūdens molu divkārtšais skaits ir pietiekams nātrija jonu koordinācijai . Hidroksīda joni atgrūžas no ūdens molekulām un nestrukturējas.

Viela	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol
NaOH_{aq}	-44,51	šķīd.-	-
$\text{NaOH} \cdot \text{H}_2\text{O}$	-21,41	šķīd.	-
$\text{NaOH}_{\text{lattice}}$	-	lattice	-887
$\text{NaOH}_{\text{Cryst}}$	-425,8	64,4	-379,7
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
H_3O^+	-285,81	-3,854	-213,275
$\text{Na}^+_{\text{aqua}}$	-240,10	59,00	-261,9
OH^-	-230,00	-10,539	-157,2

$$\Delta H_{\text{Hes}} = \Delta H^\circ_{\text{Na}} + \Delta H^\circ_{\text{OH}} - \Delta H^\circ_{\text{NaOH}} - 2 \cdot \Delta H^\circ_{\text{H}_2\text{O}} = 527,4 \text{ kJ/mol};$$

$$= -240,1 - 230 - (-425,8 - 2 \cdot 285,85) = 527,4 \text{ kJ/mol};$$

$$\Delta S_{\text{dispersed}} = -\Delta H_{\text{H}} / T = -527,4 / 298,15 = -1768,908 \text{ J/(mol K)}$$

$$\Delta S_{\text{H}} = \Delta S^\circ_{\text{Na}} + \Delta S^\circ_{\text{OH}} - \Delta S^\circ_{\text{NaOH}} - 2 \cdot \Delta S^\circ_{\text{H}_2\text{O}} = 59 - 10,539 - 64,4 - 2 \cdot 69,9565 = -155,852 \text{ J/mol/K}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{Hes}} + \Delta S_{\text{dispersed}} = -155,852 - 1768,908 = -1924,76 \text{ J/mol/K}$$

$$\Delta G_{\text{Hes}} = \Delta H_{\text{Hes}} - T \cdot \Delta S_{\text{Hes}} = 527,4 - 298,15 \cdot (-0,155852) = 573,867 \text{ kJ/mol};$$

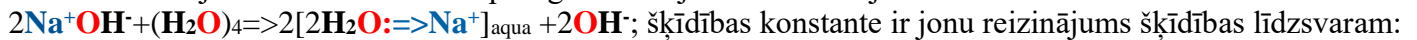
$$T \cdot \Delta S_{\text{total}} = -1,92476 \cdot 298,15 = -573,867 \text{ kJ/mol bound free energy}$$

$$\Delta G_{\text{H}} = \Delta G^\circ_{\text{Na}} + \Delta G^\circ_{\text{OH}} - \Delta G^\circ_{\text{NaOH}} = 467,9 \text{ kJ/mol. eksoergiska.}$$

$$= -261,9 - 157,2 - (-887) = 467,9 \text{ kJ/mol}$$

Nedisociēts hidroksīds neitrālas molekulas neveidojas:

I) **Kristālisks** nātrija hidroksīds Na^+OH^- pilnīgi disociē jonus koordinējot divas ūdens molekulas H_2O w%=50 %.



kristālisks nātrija hidroksīda šķīdība $\text{Na}^+\text{OH}^- + 2\text{H}_2\text{O} \Rightarrow [1,0469\text{H}_2\text{O} \Rightarrow \text{Na}^+]_{\text{aqua}} + \text{OH}^-; w\%=50 \%$.

$$\Delta G_{\text{Hes}} = \Delta G^\circ_{\text{Na}} + \Delta G^\circ_{\text{OH}} - \Delta G^\circ_{\text{NaOH}} - 2 \cdot \Delta G^\circ_{\text{H}_2\text{O}} = -261,9 - 157,2 - (-379,7 - 2 \cdot 237,191) = 435 \text{ kJ/mol};$$

$$\text{Kopējā koncentrācija } n_{\text{kopā}} = [\text{H}_2\text{O}] + [2\text{H}_2\text{O} \Rightarrow \text{Na}^+]_{\text{aqua}} + [\text{OH}^-] = 4,23 + 19,02 + 19,02 = 42,27 \text{ M};$$

$$\text{Šķīdība mola daļās } K_{\text{šk}} = [\text{Na}^+_{\text{aqua}}] \cdot [\text{OH}^-]_{\text{aqua}} / [\text{Na}^+\text{OH}^-] / n_{\text{kopā}}^2 = 19,02 \cdot 19,02 / 42,27^2 = 0,2025.$$

$$\Delta G_{\text{min}} = \Delta G_{\text{sp}} = -R \cdot T \cdot \ln(K_{\text{šk}}) = -8,3144 \cdot 298,15 \cdot \ln(0,2025) = 3,959 \text{ kJ/mol};$$

Šķīdība 100 g/100g ūdens blīvums 1,5217 g/mL ; w%=50 %; Viens litrs šķīduma satur

$$n_{\text{NaOH}} = m_{\text{NaOH}} / M_{\text{NaOH}} = 760,85 / 40 = 19,02 \text{ mol}; n_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}} / M_{\text{H}_2\text{O}} = 760,85 / 18 = 42,27 \text{ mol}.$$

Divas 2 ūdens molekulas koordinējas lineāri pie Na^+ jona, bet OH^- jons atgrūž ūdeni.

Hesa izmaiņa pozitīva $\Delta G_{\text{Hes}} = \Delta G_{\text{NaOH}} + \Delta G_{(\text{H}_2\text{O})_4/2} + 2 \cdot \Delta G_{[2\text{H}_2\text{O} \Rightarrow \text{Na}^+]} = 887 + 45 - 800 = 132 \text{ kJ/mol}$ endoergiski, bet

minizējas: $\Delta G_{\text{eq}} = \Delta G_{\text{šk}} = -8,3144 \cdot 298,15 \cdot \ln(0,1984) = 4,01 \text{ kJ/mol}$ maisījumā sasniedzot šķīdības

līdzsvaru. Līdzsvars ir Prigožina atraktors brīvās enerģijas izmaiņas minimums ΔG_{min} .

Brīvās enerģijas izmaiņas minimumā ir **kristālisks** nātrija hidroksīda Na^+OH^- līdzsvars.

1. jonu kristāla noārdīšanas: $\text{NaOH} \Rightarrow \text{Na}^+ + \text{OH}^-$ enerģija: $\Delta G_{\text{NaOH}} = 887 \text{ kJ/mol}$.

2. Tetramēra noārdīšanas: $(\text{H}_2\text{O})_4 \Rightarrow 4\text{H}_2\text{O}$ enerģija $\Delta G_{(\text{H}_2\text{O})_4} = 90 \text{ kJ/mol}$. 3.a w%=50 %;

3.a Divu H_2O koordinēšanas katjonā enerģija $2 \cdot \Delta G_{[2\text{H}_2\text{O} \Rightarrow \text{Na}^+]} = 2 \cdot -400 = -800 \text{ kJ/mol}$:

$$\Delta G_{\text{Hes}} = \Delta G_{\text{NaOH}} + \Delta G_{(\text{H}_2\text{O})_4/2} + 2 \cdot \Delta G_{[2\text{H}_2\text{O} \Rightarrow \text{Na}^+]} = 887 + 45 - 800 = 132 \text{ kJ/mol}.$$

Piezīme: **Stipri elektrolīti** ir šķīstoši **eksoergiski** ar negatīvu $\Delta G_{\text{šk}} < 0$ un

konstanti lielāku par vienu $K_{\text{šk}} \gg 1$

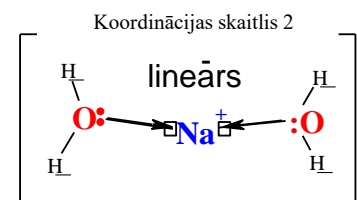
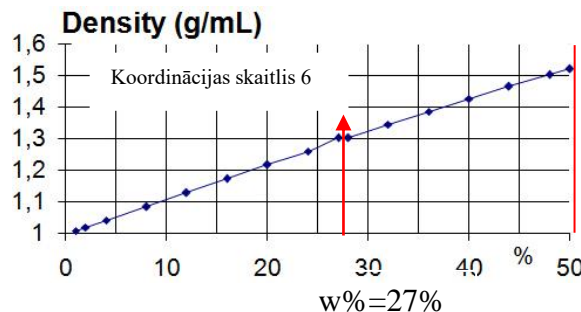
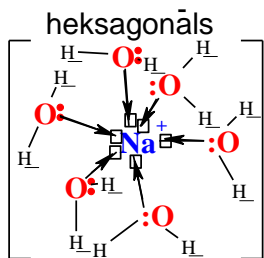
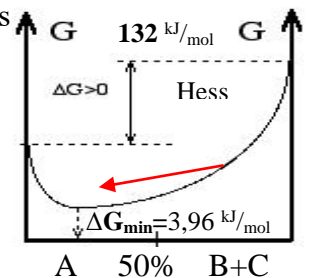
; $\text{Na}^+\text{OH}^-_{\text{Cryst}} \Rightarrow$ produkti $\text{Na}^+ + \text{OH}^-$

Vāji elektrolīti ar pozitīvu $\Delta G_{\text{šk}} > 0$ and $0 < K_{\text{eq}} < 1$ ir **ūdenī nešķīstoši endoergiski**.

Pie $0\% < w\% < 27\%$ $\text{NaOH}_{\text{Cryst}}$ šķīduma blīvums 1,301 g/mL $2\text{Na}^+\text{OH}^- + 3(\text{H}_2\text{O})_4 \Rightarrow 2[6\text{H}_2\text{O} \Rightarrow \text{Na}^+]_{\text{aqua}} + 2\text{OH}^-;$

3.b Sešas H_2O molekulas koordinējas simetriski heksagonāli ap katjonu $6 \cdot \Delta G_{[2\text{H}_2\text{O} \Rightarrow \text{Na}^+]} = 6 \cdot -400 = -2400 \text{ kJ/mol}$:

$$\Delta G_{\text{reactions}} = \Delta G_{\text{NaOH}} + 3/2 \cdot \Delta G_{(\text{H}_2\text{O})_4} + 6 \cdot \Delta G_{[2\text{H}_2\text{O} \Rightarrow \text{Na}^+]} = 887 + 270/2 - 2400 = -1378 \text{ kJ/mol}.$$



TERMODINAMIKA VINGRINĀJUMS Va hlorūdeņraža **HCl** šķīdība un reakcija ar ūdeni

$\Delta H_{\text{hidratācija HCl}} = \Delta H^{\circ} \text{HCl}_{\text{aq}} - \Delta H^{\circ} \text{HCl}_{\text{gas}} = -167,2 - (-92,31) = -74,89 \dots \text{kJ/mol}$ **eksotermiska**.....

CRC 2010 Eksotermiska, endotermiska vai atermiska un eksoergiska vai endoergiska! $? \text{HCl}_{\text{gas}} \Rightarrow \text{HCl}_{\text{aq}} + \Delta G + Q;$

Viela	$\Delta H^{\circ}_{\text{H}} \text{ kJ/mol}$	$\Delta S^{\circ}_{\text{H}} \text{ J/mol/K}$	$\Delta G^{\circ}_{\text{H}} \text{ kJ/mol}$
Na⁺Cl⁻	-411,12	72,00	-
Na⁺aq	-240,10	59,00	-
Cl⁻aq	-167,08	56,50	-
H₂O_{aq}	-285,85	69,956	-237,191
H₂O	-286,65	-453,188	-151,549
H₃O⁺	-285,81	-3,854	-213,275
HCl_{gas}	-92,31	186,902	-95,3
HCl_{aq}	-167,2	56,5	-131,2

$\Delta G_{\text{H}} = \Delta G^{\circ} \text{HCl}_{\text{aq}} - \Delta G^{\circ} \text{HCl}_{\text{gas}} = -131,2 - (-95,3) = -36,59 \dots \text{kJ/mol}$

1. $\Delta H_{\text{Hess}} = \Sigma \Delta H^{\circ}_{\text{produkti}} - \Sigma \Delta H^{\circ}_{\text{izejvielas}}$; **eksoergiska**.....

$\Delta H_{\text{hidratācija HCl}} = \Delta H^{\circ} \text{HCl}_{\text{aq}} - \Delta H^{\circ} \text{HCl}_{\text{gas}} = -167,2 - (-92,31) = -74,89 \dots \text{kJ/mol}$

2. $\Delta S_{\text{Hess}} = \Sigma \Delta S^{\circ}_{\text{produkti}} - \Sigma \Delta S^{\circ}_{\text{izejvielas}}$; **eksotermiska**.....

$\Delta S_{\text{kopēja}} = \Delta S_{\text{H}} + \Delta S_{\text{izkļiedēta}} = 251,182 - 130,4 = 120,78 \dots \text{J/mol/K}$;

$\Delta S_{\text{Hess}} = \Delta S^{\circ} \text{HCl}_{\text{aq}} - \Delta S^{\circ} \text{HCl}_{\text{gas}} = 56,5 - 186,902 = -130,402 \dots \text{J/mol/K}$;

$\Delta S_{\text{izkļiedēta}} = -\Delta H_{\text{Hess}} / T = 74,89 / 298,15 = 251,182 \dots \text{J/mol/K}$;

$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = -74,89 - 298,15 \cdot (-0,130) = -36,01 \dots \text{kJ/mol}$

$T \cdot \Delta S_{\text{kopēja}} = 120,78 \text{ J/K/mol} \cdot 298,15 \text{ K} = \mathbf{36,01} \dots \text{kJ/mol}$; **eksoergiska**.....

37%, 1,180 g/mL, 436,6 g/36,45=11,978 mol/L, 1180-436,6=743,4; 743,4/18=41,3 mol/L, 41,3-0,25236=41,048 mol/L



$\Delta H_{\text{Hess}} = \Delta H^{\circ} \text{H}_3\text{O} + \Delta H^{\circ} \text{Cl}^- - \Delta H^{\circ} \text{HCl}_{\text{aq}} - \Delta H^{\circ} \text{H}_2\text{O} = -285,81 - 167,08 - (-167,2 - 285,85) = 0,16 \dots \text{kJ/mol}$; **atermiska**.....

2. $\Delta S_{\text{izkļiedēta}} = -\Delta H_{\text{Hess}} / T = -0,16 / 298,15 = -0,537 \dots \text{J/mol/K}$

$\Delta S_{\text{Hess}} = \Delta S^{\circ} \text{H}_3\text{O} + \Delta S^{\circ} \text{Cl}^- - \Delta S^{\circ} \text{HCl} - \Delta S^{\circ} \text{H}_2\text{O} = -3,854 + 56,60 - (69,96 + 56,5) = -73,714 \dots \text{J/mol/K}$

$\Delta S_{\text{kopēja}} = \Delta S_{\text{Hess}} + \Delta S_{\text{izkļiedēta}} = -0,537 - 73,714 = -74,251 \dots \text{J/mol/K}$;

$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = 0,16 - 298,15 \cdot (-0,073714) = 22,1378 \dots \text{kJ/mol}$ **endoergiska**.....

$T \cdot \Delta S_{\text{kopēja}} = -74,251 \text{ J/K/mol} \cdot 298,15 \text{ K} = \mathbf{-22,14} \dots \text{kJ/mol}$;

$m_{\text{H}_2\text{O}} = 1180 - 436,6 = 743,4 \text{ g}$; $n_{\text{H}_2\text{O}} = 743,4 / 18 = 41,3 \text{ mol/L}$, Pirmais tuvinājums.

$[\text{H}_2\text{O}] = 41,3 - [\text{H}_3\text{O}^+] = 41,3 - 0,25235 = 41,04765 \text{ mol/L}$; $C_{\text{HCl}} = [\text{HCl}_{\text{aq}}] + [\text{Cl}^-] = 11,978 \text{ M}$;

$[\text{HCl}_{\text{aq}}] = (11,978 - [\text{Cl}^-]) = (11,978 - 0,25235) = 11,725664 \text{ mol/L}$; $[\text{HCl}_{\text{aq}}] [\text{H}_2\text{O}] \cdot K_{\text{dis}} = [\text{H}_3\text{O}^+_{\text{aq}}] \cdot [\text{Cl}^-_{\text{aq}}]$;

Tā kā $[\text{Cl}^-_{\text{aq}}] = [\text{H}_3\text{O}^+]$ un aizvietojojot $[\text{Cl}^-_{\text{aq}}]$ ar $[\text{H}_3\text{O}^+]$ iegūst kvadrātviņnādojumu: $ax^2 + bx + c = 0$.

$(11,978 - [\text{Cl}^-]) [\text{H}_2\text{O}] \cdot K_{\text{dis}} = [\text{H}_3\text{O}^+] \cdot [\text{Cl}^-_{\text{aq}}]$; $(11,978 - [\text{H}_3\text{O}^+]) [\text{H}_2\text{O}] \cdot K_{\text{dis}} = [\text{H}_3\text{O}^+] \cdot [\text{H}_3\text{O}^+]$;

$[\text{H}_3\text{O}^+]^2 + [\text{H}_2\text{O}] \cdot K_{\text{dis}} \cdot [\text{H}_3\text{O}^+] - K_{\text{dis}} \cdot [\text{H}_2\text{O}] \cdot 11,978 = 0$

Kvadrātviņnādojuma $ax^2 + bx + c = 0$ reālā sakne no divām matemātiskajām ir $x = \left(\frac{-b + \sqrt{b^2 - 4ac}}{2a} \right)$;

$[\text{Cl}^-_{\text{aq}}] = [\text{H}_3\text{O}^+] = \frac{-K_{\text{dis}} \cdot [\text{H}_2\text{O}] + \sqrt{(K_{\text{dis}} \cdot [\text{H}_2\text{O}])^2 - 4 \cdot K_{\text{dis}} \cdot [\text{H}_2\text{O}] \cdot 11,7257}}{2} = 0,25235 \text{ M}$

$[\text{Cl}^-_{\text{aq}}] = [\text{H}_3\text{O}^+] = (-K_{\text{dis}} \cdot 41,04765 + \text{SQRT}((K_{\text{dis}} \cdot 41,04765)^2 - 4 \cdot K_{\text{dis}} \cdot 41,04765 \cdot 11,978)) / 2 = 0,25235 \dots \text{M}$

Disociācijas pakāpe $\alpha = 0,021 = C_{\text{dis}} / C_{\text{M}} = 0,25235 / 11,978$; $C_{\text{M}} = C_{\text{dis}} + C_{\text{nedis}} = 0,25235 + 11,725664 = 11,978 \text{ mol/L}$;

Disociācijas pakāpe $\alpha\% = 2,1\%$; pH=0,6; Līdzsvara konstante: $K_{\text{dis1}} = 0,000132306$;

$\frac{[\text{H}_3\text{O}^+] \cdot [\text{Cl}^-]_{\text{aq}}}{[\text{HCl}]_{\text{aq}} \cdot [\text{H}_2\text{O}]} = K_{\text{eq}} = (0,25235 \cdot 0,25235) / (41,04765 \cdot 11,725664) = 0,000132306 = 10^{-3,878}$;

$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(0,000132306) / 1000 = 22,137 \text{ kJ/mol}$

Ja sālskābes koncentrācija ir $C_{\text{HCl}} = [\text{HCl}_{\text{aq}}] + [\text{Cl}^-] = 0,1 \text{ M}$; $[\text{H}_2\text{O}] = 55,33 - [\text{H}_3\text{O}^+] = 55,33 - 0,1 = 55,23 \text{ mol/L}$

$0,04728863 \text{ M} = [\text{Cl}^-_{\text{aq}}] = [\text{H}_3\text{O}^+] = (-K_{\text{dis1}} \cdot 55,23 + \text{SQRT}((K_{\text{dis1}} \cdot 55,23)^2 - 4 \cdot K_{\text{dis1}} \cdot 55,23 \cdot 0,1)) / 2$;

$\frac{[\text{H}_3\text{O}^+] \cdot [\text{Cl}^-]_{\text{aq}}}{[\text{HCl}]_{\text{aq}} \cdot [\text{H}_2\text{O}]} = K_{\text{eq}} = (0,04728863 \cdot 0,04728863) / (55,23 \cdot 0,05271137) = 0,000768129 = K_{\text{dis1}}$; $C_{\text{M}} = 0,1 \text{ M}$

$[\text{HCl}_{\text{aq}}] = 0,1 - 0,04728863 = 0,05271137 \text{ M}$;

$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(0,000768129) / 1000 = 17,8 \text{ kJ/mol}$

Protolīze nelabvēlīga Hesa likumā pozitīva 22,138 kJ/mol, bet minimizējas sasniedzot līdzsvaru 17,8 kJ/mol.

$0,04728863 \text{ M} = [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-1,325}$; $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0,04728863) = 1,325 = \text{pH}$;

Disociācijas pakāpe $\alpha_{0,1} = C_{\text{dis}} / C_{\text{M}} = 0,0472886 / 0,1 = 0,047$, $\alpha\% = 4,7\%$; $\alpha_{0,01} = 0,008343 / 0,01 = 0,8343$, $\alpha\% = 83,43\%$;

$K_{\text{eq}} = (0,008343 \cdot 0,008343) / (55,32 \cdot (0,01 - 0,008343)) = 0,000759346 = K_{\text{dis2}}$; $C_{\text{M}} = 0,01 \text{ M}$; $\text{pH} = 2,08$;

$0,008343 \text{ M} = [\text{Cl}^-_{\text{aq}}] = [\text{H}_3\text{O}^+] = (-K_{\text{dis2}} \cdot 55,32 + \text{SQRT}((K_{\text{dis2}} \cdot 55,32)^2 - 4 \cdot K_{\text{dis2}} \cdot 55,32 \cdot 0,01)) / 2$;

$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(0,000759346) / 1000 = 17,8 \text{ kJ/mol}$; $0,008343 / 0,01 = 0,834$, $\alpha\% = \mathbf{83,4\%}$

$\Delta G_{\text{Hess}} = 22,138 \dots \text{kJ/mol}$ **endoergiska**..... Prigožina minimums $\Delta G_{\text{eq}} = 17,8 \dots \text{kJ/mol}$,

TERMODINAMIKA VINGRINĀJUMS V b. $\text{CH}_3\text{COO}^-\text{Na}^+$ kristālu šķīdība un reakcija



Šķīdība 50,4 g/100g H_2O , blīvums 1,26 g/mL, $C_{\text{CH}_3\text{COONa}} = 5,1493 \text{ mol/L}$; $w\% = 36,1 \%$

Viena litra šķīduma masa ar blīvumu 1,26 g/mL ir $m_{\text{šķ}} = 1260 \text{ g/L}$.

Cik reizes 150,4 g ietilpst 1260 gramos šķīdumā $1260/150,4 = 8,7766 \dots$ reizes

Nātrija acetāta masa litrā $m_{\text{CH}_3\text{COONa}} = 8,7766 * 50,4 \text{ g/100g} = 442,34 \dots \text{ g/L}$.

Mola masu aprēķina kā summu no atoma masām: $M_{\text{CH}_3\text{COONa}} = M_{\text{Na}} + M_{\text{CH}_3\text{COO}} = 23 + 24 + 32 + 3 = 82 \text{ g/mol}$.

Sāls molu skaits vienā litrā ir masa sālīm dalīta ar tās mol masu:

$$n_{\text{CH}_3\text{COONa}} = m_{\text{CH}_3\text{COONa}} / M_{\text{CH}_3\text{COONa}} = 442,34 / 82 = 5,1493 \text{ mol/L}; C_{\text{CH}_3\text{COONa}} = 5,1493 \text{ mol/L};$$

Ūdens $m_{\text{H}_2\text{O}} = m_{\text{šķ}} - m_{\text{CH}_3\text{COONa}} = 1260 - 442,34 = 817,76 \text{ g}$ $n_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}} / M_{\text{H}_2\text{O}} = 817,76 / 18 = 45,431 \text{ mol}$.

Masas daļu procentos aprēķina masu sālīm dalot ar šķīduma masu

$$m_{\text{CH}_3\text{COONa}} / m_{\text{šķ}} = 442,34 / 1260 * 100\% = w\% = 36,1;$$

Pilnīgi disociējot jonus ideālā šķīdumā koordinējot 6 H_2O un 2 H_2O nātrija joniem un acetāta joniem kristālisks

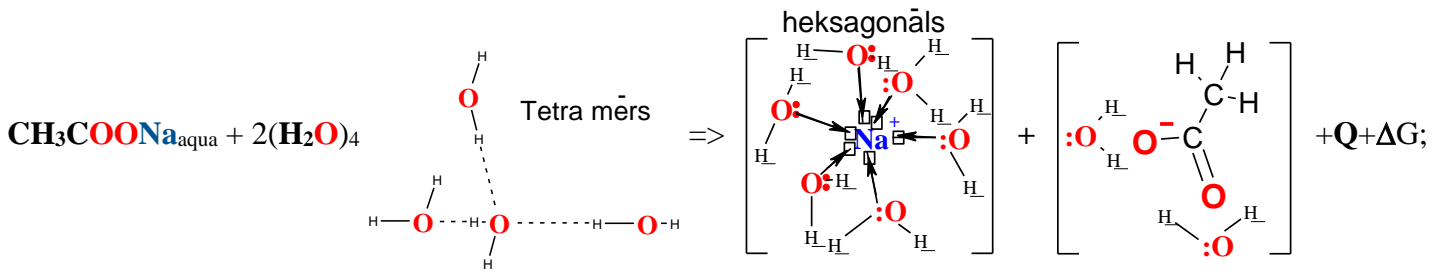
$\text{CH}_3\text{COONa}_s \rightleftharpoons \text{Na}^+ + \text{CH}_3\text{COO}^-$ cietas tīras vielas mol daļa ir viens $[\text{CH}_3\text{COONa}]_{\text{ciets}} = 1$ un šķīdības konstante:

$K_{\text{šķ}} = K_{\text{eq}} = [\text{Na}^+] * [\text{CH}_3\text{COO}^-] = 5,1493 * 5,1493 = 26,515$ ir jonu reizinājums sasniedzot Prigožina atraktoru līdzsvara brīvās enerģijas izmaiņas minimumu negatīvu:

Termodinamiski labvēlīgā šķīdības konstante: termodinamiski labvēlīgam līdzsvaram

$$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(26,515) = -8,125 \text{ kJ/mol},$$

Piesātināta šķīduma ūdens koordinācijas resursi 8 ir pietiekoši: $n_c = n_{\text{H}_2\text{O}} / 8 = 45,431 / 8 = 5,6789 \dots$ moli.

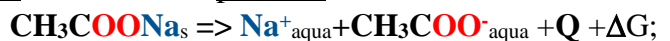


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Izejvielas

produkti

Viela	$\Delta H^{\circ}_{\text{Hess}}$, kJ/mol	$\Delta S^{\circ}_{\text{Hess}}$, J/mol/K	$\Delta G^{\circ}_{\text{Hess}}$, kJ/mol
$\text{Na}^+_{\text{aqua}}$	-240,1	59	-
$\text{CH}_3\text{COO}^-_{\text{aq}}$	-486	85,3	-247,83
$\text{CH}_3\text{COO}^-_{\text{aq}}$	-486,836	-822,3	-241,663
$\text{CH}_3\text{COONa}_s$	-708,8	123,0-	-607,7-



$$1. \Delta H_{\text{Hess}} = \sum \Delta H^{\circ}_{\text{produkti}} - \sum \Delta H^{\circ}_{\text{izejvielas}}$$

$$2. \Delta S_{\text{Hess}} = \sum \Delta S^{\circ}_{\text{produkti}} - \sum \Delta S^{\circ}_{\text{izejvielas}}; 3. \Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}}$$

$$2. \Delta S_{\text{izkļiedēta}} = -\Delta H_{\text{Hess}} / T = 17,3 / 298,15 = 58,02448 \dots \text{ J/mol/K};$$

$$\Delta S_{\text{kopēja}} = \Delta S_{\text{Hess}} + \Delta S_{\text{izkļiedēta}} = 58,02448 + 21,3 = 79,32448 \dots \text{ J/mol/K};$$

$$1. \Delta H_{\text{Hess}} = \Delta H^{\circ}_{\text{H}_3\text{CCOO}^-} + \Delta H^{\circ}_{\text{Na}^+} - \Delta H^{\circ}_{\text{H}_3\text{CCOO Na}} = -486 - 240,1 - (-708,8) = -17,3 \text{ kJ/mol}$$
 eksotermiska.....

$$2. \Delta S_{\text{Hess}} = \Delta S^{\circ}_{\text{H}_3\text{CCOO}^-} + \Delta S^{\circ}_{\text{Na}^+_{\text{aqua}}} - \Delta S^{\circ}_{\text{H}_3\text{CCOO Na}} = 59 + 85,3 - 123 = 144,3 - 123 = 21,3 \dots \text{ J/mol/K}$$
 eksoerģiska.....

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = -17,3 - 298,15 * 0,0213 = -23,65 \dots \text{ kJ/mol}; T \cdot \Delta S_{\text{kopēja}} = 79,32448 * 298,15 = 23,65 \dots \text{ kJ/mol};$$

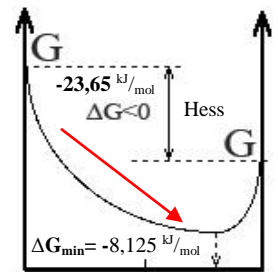
Eksotermiskas un eksoerģiskas $\text{CH}_3\text{COONa}_s$ šķīdības reakcijas Hesa brīvās enerģijas

izmaiņa ΔG_{Hess} negatīva $-23,65 \text{ kJ/mol}$, bet minimizējas līdz $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -8,125 \text{ kJ/mol}$

piesātinājumā ar ūdens koordināciju 8 maisījumā sasniedzot līdzsvara konstanti $K_{\text{eq}} = 26,515$.

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min}

sasniegšana maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



Maisījumā izejviela kristāliska $\text{CH}_3\text{COONa}_s$ un produkti $\text{Na}^+_{\text{aq}} + \text{CH}_3\text{COO}^-_{\text{aq}}$

TERMODINAMIKA VINGRINĀJUMS Vaa. $\text{NH}_4\text{Cl}_{(s)}$ kristālu šķīdība ūdenī

Dati tabulās: Šķīdība 39,5 g/100g H_2O , blīvums 1,3536 g/mL,

Viena litra šķīduma masa ar blīvumu 1,3536 g/mL ir $m_{\text{šķ}} = 1353,6$ g/L.

Cik reizes 139,5 g ietilpst 1353,6 gramos šķīdumā $1353,6/139,5 = 9,7032$reizes

Amonija hlorīda masa litrā $m_{\text{NH}_4\text{Cl}} = 9,7032 * 39,5 \text{ g/100g} = 383,2764$g/L..

Mola masu aprēķina kā summu no atoma masām: $M_{\text{NH}_4\text{Cl}} = M_{\text{NH}_4} + M_{\text{Cl}} = 16 + 24 + 35,5 = 75,5$g/mol .

Sāls molu skaits vienā litrā ir masa sālīm dalīta ar tās mol masu:

$$n_{\text{NH}_4\text{Cl}} = m_{\text{NH}_4\text{Cl}} / M_{\text{NH}_4\text{Cl}} = 383,2764 / 75,5 = 5,07651 \text{ mol/L} ; C_{\text{NH}_4\text{Cl}} = 5,07651 \text{ mol/L} ;$$

Ūdens $m_{\text{H}_2\text{O}} = m_{\text{šķ}} - m_{\text{NH}_4\text{Cl}} = 1353,6 - 383,2764 = 970,32 \text{ g}$ $n_{\text{H}_2\text{O}} = m_{\text{H}_2\text{O}} / M_{\text{H}_2\text{O}} = 970,32/18 = 53,907$moli.

Masas daļu procentos aprēķina masu sālīm dalot ar šķīduma masu

$$m_{\text{NH}_4\text{Cl}}/m_{\text{šķ}} = 383,2764/1353,6 * 100\% = w\% = 28,32 \text{.....}\%$$

Termodinamiski labvēlīgs Hesa likums un šķīdības konstante: ir termodinamiski labvēlīga reakcija

Viela	$\Delta H^\circ_{\text{Hess}}$ kJ/mol	$\Delta S^\circ_{\text{Hess}}$ J/mol/K	$\Delta G^\circ_{\text{Hess}}$ kJ/mol
$\text{Cl}^-_{\text{aqua}}$	-167,2	56,50	-
$\text{NH}_4^+_{\text{(aq)}}$	-132,5	113,4	-
$\text{NH}_4\text{Cl}_{(s)}$	-314,4	94,6-	-202,97

izejvielas $\text{NH}_4\text{Cl}_{(s)} + \text{Q} \Rightarrow \text{NH}_4^+ + \text{Cl}^-_{\text{aqua}} + \Delta G$ produkti;

$$1. \Delta H_{\text{Hess}} = \sum \Delta H^\circ_{\text{produkti}} - \sum \Delta H^\circ_{\text{izejvielas}}$$

$$2. \Delta S_{\text{Hess}} = \sum \Delta S^\circ_{\text{produkti}} - \sum \Delta S^\circ_{\text{izejvielas}}$$

$$3. \Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}}$$

$$1. \Delta H_{\text{Hess}} = \Delta H^\circ_{\text{NH}_4^+} + \Delta H^\circ_{\text{Cl}^-} - \Delta H^\circ_{\text{NH}_4\text{Cl}_{(s)}} = -132,5 - 167,2 - (-314,4) = -299,7 + 314,4 = 14,7 \text{.....kJ/mol}$$
 endotermiska.....

$$2. \Delta S_{\text{izkliedēta}} = -\Delta H_{\text{Hess}}/T = -14,7/298,15 = -49,3 \text{.....J/mol/K};$$

$$2. \Delta S_{\text{Hess}} = \Delta S^\circ_{\text{NH}_4^+} + \Delta S^\circ_{\text{Cl}^-} - \Delta S^\circ_{\text{NH}_4\text{Cl}} = 113,4 + 56,50 - (94,6) = 169,9 - 94,6 = 75,3 \text{.....J/mol/K}$$

$$3. \Delta S_{\text{kopēja}} = \Delta S_{\text{Hess}} + \Delta S_{\text{izkliedēta}} = -49,3 + 75,3 = 26 \text{.....J/mol/K};$$

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = 14,7 - 298,15 * 0,0753 = -7,75 \text{.....kJ/mol};$$
 eksoergiska.....

$$T \cdot \Delta S_{\text{kopēja}} = 26 \text{ J/mol} \cdot 298,15 \text{ K} = 7,75 \text{.....kJ/mol};$$

$$\frac{[\text{NH}_4^+]_{\text{aqua}} \cdot [\text{Cl}^-]_{\text{aqua}}}{[\text{NH}_4\text{Cl}]_{\text{aqua}}} = K_{\text{šk_Hess}} = \exp(-\Delta G_{\text{Hess}}/R/T) = \exp(7,75/8,3144/298,15) = 22,8 \text{.....}$$

Termodinamiski labvēlīgs Hesa šķīdība ūdenī .

Pilnīgi disociēta šķīdības konstante ir $K_{\text{dis}} = [\text{NH}_4^+] \cdot [\text{Cl}^-]_{\text{aqua}} = 5,07651 * 5,07651 = 25,771$

Amonija hlorīda $K_{\text{šk_Hess}} = 22,8$ nedisociētā koncentrācija ir termodinamiski aprēķināma izteiksmē:

$$[\text{NH}_4\text{Cl}]_{\text{aqua}} = [\text{NH}_4^+] \cdot [\text{Cl}^-]_{\text{aqua}} / K_{\text{šk_Hess}} = 25,771/22,8 = 1,13 \text{.....mol/L} ,$$

iekļaujot vienādu disociēto jonu koncentrācijas kā starpību šķīdības koncentrācijai mīnus nedisociētās sāls koncentrācija:

$$[\text{NH}_4^+] = [\text{Cl}^-]_{\text{aqua}} = 5,07651 - 1,13 = 3,97651 \text{.....mol/L} ,$$

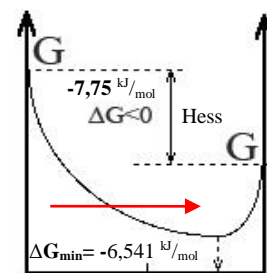
$$\text{Labvēlīgā šķīdības konstantes vērtība ir: } K_{\text{eq}} = \frac{[\text{NH}_4^+]_{\text{aqua}} \cdot [\text{Cl}^-]_{\text{aqua}}}{[\text{NH}_4\text{Cl}]_{\text{aqua}}} = 3,97651 * 3,97651 / 1,13 = 13,9935 \text{.....}$$

$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 * 298,15 * \ln(13,9935) = -6,541 \text{ kJ/mol}$, Endotermiskas un eksoergiskas $\text{NH}_4\text{Cl}_{(s)}$ disociācijas $\Delta G_{\text{disociācijaHess}} = -7,75$ kJ/mol Hesa brīvās enerģijas

izmaiņa negatīva, bet minimizējas $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -6,541$kJ/mol

$$\text{maisījumā sasniedzot līdzsvaru } K_{\text{eq}} = \frac{[\text{NH}_4^+]_{\text{aqua}} \cdot [\text{Cl}^-]_{\text{aqua}}}{[\text{NH}_4\text{Cl}]_{\text{aqua}}} = 13,9935 \text{.....}$$

Maisījumā izejviela ir nedisociētais amonija hlorīds $\text{NH}_4\text{Cl}_{\text{aqua}}$ – produkti ir $\text{NH}_4^+ + \text{Cl}^-_{\text{aqua}}$



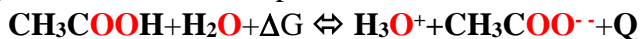
Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

TERMODINAMIKA VINGRINĀJUMS V.b etiķskābes **CH₃COOH** protolīzes reakcija

Aprēķināt ΔH_H ΔS_H ΔG_H . Reakcija ir **eksotermiska**, **atermiska**, **endotermiska**? Reakcija standarta apstākļos 298,15 K **CH₃COOH** protolīzes reakcijā ar ūdeni pielietojiet tabulas datus! Miniet vai reakcija būs **eksoerģiska** vai **endoerģiska**!

Viela	ΔH_H° kJ/mol	ΔS_H° J/mol/K	ΔG_H° kJ/mol
H₃O⁺	-285.81	-3.854	-213,275
H₃CCOO⁻	-486	85.3	85.3
CH₃COO⁻_{aq}	-486,836	-822,3	-241,663
H₂O	-285.85	69.9565	69.9565
H₂O	-286,65	-453,188	-151,549
H₃C-COOH	-484,09	159,83	-531,743

Izejvielas => produkti



- $\Delta H_{\text{Hess}} = \sum \Delta H^\circ_{\text{produkti}} - \sum \Delta H^\circ_{\text{izejvielas}}$
- $\Delta S_{\text{Hess}} = \sum \Delta S^\circ_{\text{produkti}} - \sum \Delta S^\circ_{\text{izejvielas}}$; 3. $\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}}$

1. $\Delta H_H = \Delta H^\circ_{\text{H}_3\text{CCOO}^-} + \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{H}_3\text{CCOOH}} = -486 - 285,81 - (-285,85 - 484,09) = -1,87 \text{ kJ/mol}$ **eksotermiska**.....

2. $\Delta S_{\text{izkļiedāta}} = -\Delta H_H / T = 1,87 / 298,15 = 6,272011 \text{ J/(mol K)}$

2. $\Delta S_H = \Delta S^\circ_{\text{H}_3\text{CCOO}^-} + \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{H}_3\text{CCOOH}} = 85,3 - 3,854 - (69,9565 + 159,83) = -148,3405 \text{ J/mol K}$

3. $\Delta S_{\text{kopēja}} = \Delta S_H + \Delta S_{\text{izkļiedāta}} = -148,3405 + 6,272011 = -142,0685 \text{ J/(mol K)}$

$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -1,87 + 298,15 \cdot 0,1483405 = 42,3577 \text{ kJ/mol}$ **endoerģiska**.....

$T \cdot \Delta S_{\text{kopēja}} = -142,0685 \text{ J/K/mol} \cdot 298,15 \text{ K} = -42,3577 \text{ kJ/mol}$ saistīta TΔSn ← akumulētā enerģija..... **nepatvaļīga**

Līdzsvarā tiek sasniegts brīvās enerģijas starpības minimums atbilstoši vielu maisījuma sastāvam izteiksmē:

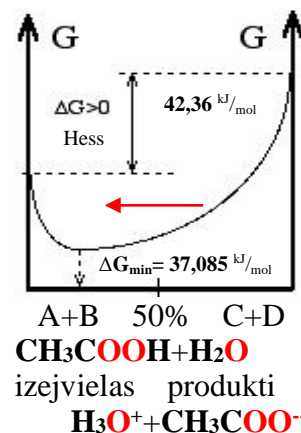
$$\text{Termodinamiski nelabvēlīgs } K_{\text{eq}} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{H}_2\text{O}][\text{CH}_3\text{COOH}]_{\text{nedis}}} = K_a / [\text{H}_2\text{O}] = 1,76 \cdot 10^{-5} / 55,3 = 10^{-6,497}$$

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(10^{-6,497}) = 37,085 \text{ kJ/mol},$$

Eksotermiskas un endoerģiskas etiķskābes protolīzes reakcijas Hesa brīvās enerģijas izmaiņa $\Delta G_{\text{jonizācijaHess}} = 42,36 \text{ kJ/mol}$ pozitīva, bet minimizējas līdz

$$\Delta G_{\text{eq}} = 37,085 \text{ kJ/mol}$$

$$\text{maisījumā sasniedzot līdzsvaru } K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{H}_2\text{O}][\text{CH}_3\text{COOH}]_{\text{nedis}}} = 10^{-6,497}$$



Klasiskā protolīzes konstante $K_a = K_{\text{eq}}[\text{H}_2\text{O}] = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]_{\text{nedis}}} = 10^{-6,497} \cdot 55,3 = 10^{-4,76}$; ir termodinamiski

nelabvēlīgās konstantes K_{eq} reizinājums ar ūdens konstanto koncentrāciju $[\text{H}_2\text{O}] = 55,3 \text{ M}$

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara

maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

$$[\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-] = C \cdot \alpha = 0,2 \cdot 0,00931 = 10^{-2,73} \text{ M} = 1,862 \cdot 10^{-3} \text{ M}; \alpha = 10^{-2,73} / 0,2 = 0,00931 ;$$

TERMODINAMIKA VINGRINĀJUMS V.c H_2O Ūdens jonizācijas un neutralizācijas inversie atraktori reakcijā

Ūdens H_2O protolīzes līdzsvāri $\text{H}_2\text{O} + \text{H}_2\text{O} + \Delta G + Q \Leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$; $\text{H}_3\text{O}^+ + \text{OH}^- \Leftrightarrow \text{H}_2\text{O} + \text{H}_2\text{O} + \Delta G + Q$;

Viela	$\Delta H^\circ_{\text{H}}$, kJ/mol	$\Delta S^\circ_{\text{H}}$, J/mol/K	$\Delta G^\circ_{\text{H}}$, kJ/mol
H_3O^+	-285,81	-3,854	-213,275
OH^-	-230,00	-10,539	-157,2
H_2O	-285,85	69,9565	-237,191
$\text{H}_2\text{O}_{\uparrow\text{gas}}$	-241,8352	188,7402	-228,6

$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{OH}} + \Delta G^\circ_{\text{H}_3\text{O}} - 2\Delta G^\circ_{\text{H}_2\text{O}} = -157,2 - 213,275 - 2 \cdot (-237,191) = 103,907 \text{ kJ/mol};$$

$$\Delta H_{\text{H}} = \Delta H^\circ_{\text{OH}} + \Delta H^\circ_{\text{H}_3\text{O}} - 2\Delta H^\circ_{\text{H}_2\text{O}} = 55,89 \text{ kJ/mol}; \text{ endotermiska}$$

$$= -285,81 - 230 - (2 \cdot (-285,85)) = -515,81 + 571,7 = 55,89 \text{ kJ/mol}$$

$$\Delta S_{\text{izkļiedēta}} = -\Delta H_{\text{H}}/T = -55,89/298,15 = -187,456 \dots \text{ J/(mol K)}$$

$$\Delta S_{\text{H}} = \Delta S^\circ_{\text{OH}} + \Delta S^\circ_{\text{H}_3\text{O}} - 2\Delta S^\circ_{\text{H}_2\text{O}} = -3,854 - 10,539 - 2 \cdot 69,956 = 14,393 - 139,912 = -154,305 \dots \text{ J/mol/K}$$

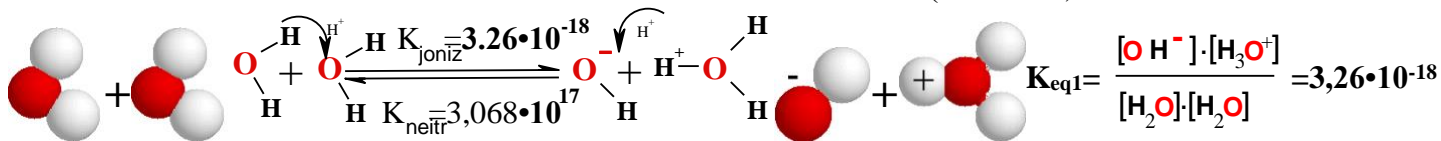
$$\Delta S_{\text{kopēja}} = \Delta S_{\text{H}} + \Delta S_{\text{izkļiedēta}} = -187,456 - 154,305 = -341,761 \text{ J/(mol K)}$$

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = 55,89 + 298,15 \cdot 0,154305 = 101,8967 \text{ kJ/mol} \text{ endoerģiska.}$$

$$T \cdot \Delta S_{\text{kopēja}} = -341,761 \text{ J/mol} \cdot 298,15 \text{ K} = -101,896 \text{ kJ/mol}; \text{ saistīta } T\Delta S_{\text{H}} \leftarrow \text{akumulētā enerģija nepatvaļīga} \dots$$

Līdzsvarā tiek sasniegts brīvās enerģijas starpības minimums atbilstoši vielu maisījuma sastāvam izteiksmē:

$$G_{\text{H}_3\text{O}^+ + \text{OH}^-} = G_{\text{H}_3\text{O}^+} + G_{\text{OH}^-} = 22,44 + 77,36 = G_{\text{H}_3\text{O}^+} + G_{\text{OH}^-} - G_{2\text{H}_2\text{O}} = -R \cdot T \cdot \ln(K_{\text{H}_3\text{O}^+ + \text{OH}^-}) + 2 \cdot 0 = 99,8 \text{ kJ/mol} \quad [1,8,14]$$



$$\Delta G_{\text{eq1}} = -R \cdot T \cdot \ln(K_{\text{eq1}}) = -R \cdot T \cdot \ln\left(\frac{[\text{OH}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2}\right) = 99,8 \text{ kJ/mol},$$

Endotermiskas un endoerģiskas ūdens jonizācijas reakcijas Hesa brīvās enerģijas izmaiņa $\Delta G_{\text{Hess}} = \Delta G_{\text{jonizācija}} = 101,9 \text{ kJ/mol}$ pozitīva, bet minimizējas maisījumā sasniedzot

$$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = 99,8 \text{ kJ/mol} \text{ līdzsvaru } K_{\text{eq1}} = \frac{[\text{OH}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2} = 3,26 \cdot 10^{-18};$$

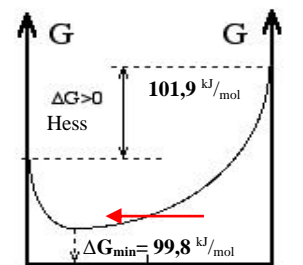
vielu maisījumā brīvās enerģijas izmaiņa minimizējas

$$99,8 \text{ kJ/mol} = |\Delta G_{\text{eq2}}| < |\Delta G_{\text{Hess2}}| = 101,9 \text{ kJ/mol};$$

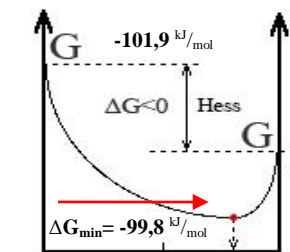
Visas reakcija tiecas uz līdzsvara maisījumu Prigožina atraktoru brīvās enerģijas izmaiņas minimumu $\Delta G_{\text{min}} = \Delta G_{\text{eq}}$ ar darbīgo masu inverso reakciju konstantēm

$$3,26 \cdot 10^{-18} = \frac{[\text{OH}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2} = K_{\text{eq1}} = \frac{1}{K_{\text{eq2}}} = \frac{1}{\frac{[\text{H}_2\text{O}]^2}{[\text{OH}^-] \cdot [\text{H}_3\text{O}^+]}} = \frac{1}{3,068 \cdot 10^{17}}$$

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



A+B 50% C+D
 $\text{H}_2\text{O} + \text{H}_2\text{O}$ izejvielas
produkti $\text{H}_3\text{O}^+ + \text{OH}^-$



C+D 50% A+B
 $\text{H}_3\text{O}^+ + \text{OH}^-$ izejvielas
produkti $\text{H}_2\text{O} + \text{H}_2\text{O}$

Pareizinot ar ūdens konstanto koncentrācijas kvadrātu $K_{\text{eq1}} \cdot [\text{H}_2\text{O}]^2 = 3,26 \cdot 10^{-18} \cdot 55,33^2 = 10^{-14} = K_w$ aprēķina ūdens jonu reizinājuma konstanti $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$, Atraktori nosaka, ka visums ir perfekts un precīzi parāda, ka katrs process tiecas uz atraktoru - enerģijas izmaiņas minimumu reaģējošo vielu maisījumā.

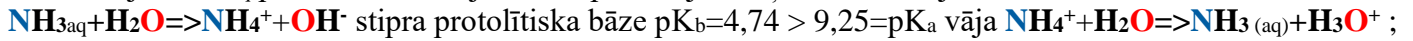
Protolīze $\Delta G_{\text{H}_3\text{O}^+ + \text{OH}^-} = G_{\text{H}_3\text{O}^+} + G_{\text{OH}^-} = 22,44 + 77,36 = 99,8 \text{ kJ/mol}$ akumulē vienādi skābu un bāzisku pH = pOH = 7.

$\text{H}_2\text{O} + Q \Leftrightarrow \text{H}_2\text{O}_{\text{gas}} + \Delta G$; $\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{H}_2\text{O}_{\text{gas}}} - \Delta H^\circ_{\text{H}_2\text{O}} = -241,8352 - (-285,85) = 44,0148 \text{ kJ/mol}$ endotermiska iztvaikošana ir $\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{H}_2\text{O}_{\text{gas}}} - \Delta G^\circ_{\text{H}_2\text{O}} = -228,6 - (-237,191) = G_{\text{gasH}_2\text{O}} + G_{\text{H}_2\text{O}} = 8,59 + 0 \text{ kJ/mol}$ endoerģiska; 101,3 kPa parciālā spiedienā $p_o = 3,1699 \text{ kPa}$ endoerģiska šķīdības konstante $K_{\text{šķ}} = X_{\text{H}_2\text{O}}/X_{\text{H}_2\text{O}_{\text{gas}}} = 1/0,03129 = 31,959$, jo tvaika mola daļa ir $X_{\text{H}_2\text{O}_{\text{gas}}} = 3,1699/101,3 = 0,03129$, bet tīra ūdens mola daļa ir viens $X_{\text{H}_2\text{O}} = 1$. Iztvaikošana akumulē enerģiju

$$\Delta G_{\text{evaporation}} = -R \cdot T \cdot \ln(K_{\text{sp}}) = -8,3144 \cdot 298,15 \cdot \ln(0,03129) = 8,588 \text{ kJ/mol} \text{ vienā molā.}$$

TERMODINAMIKA VINGRINĀJUMS V d šķīdība NH_3gas , NH_4^+ protolīzes reakcija un NH_3aq protonēšana

Amonija NH_4^+aq protolīzes reakcija notiek protonējot izšķīdušās amonjaka molekulas ūdenī.



$G_{\text{NH}_3\text{gas}} = \Delta G^\circ_{\text{NH}_3\text{aq}} - \Delta G_{\text{Hess-sp-NH}_3\text{gas}} - G^\circ_{\text{H}_2\text{O}} = 91,1056 - (-74,5537) - (-0) = 165,7 \text{ kJ/mol}$; **Alberty**

$\text{NH}_3\text{gas} + \text{H}_2\text{O} \Rightarrow \text{NH}_3\text{aq}$; $\Delta H_{\text{hidratācija}} = \Delta H^\circ_{\text{NH}_3\text{aq}} - \Delta H^\circ_{\text{NH}_3\text{gas}} - \Delta H^\circ_{\text{H}_2\text{O}} = -132,5608 + 45,94 - 286,65 = -373,3 \text{ kJ/mol}$;

$G_{\text{Hydration}} + G_{\text{NH}_3\text{gas}} + \Delta G_{\text{H}_2\text{O}} = G_{\text{NH}_3\text{aq}} = 107,5 + 165,7 + 0 = 273,2 \text{ kJ/mol}$;

$\Delta G_{\text{Hydration}} = \Delta G_{\text{NH}_3\text{aq}} - \Delta G_{\text{NH}_3\text{gas}} - \Delta G_{\text{H}_2\text{O}} = 91,1056 - (-16,4 - 0) = 107,5 \text{ kJ/mol}$;

$\Delta S_{\text{Hydration}} = \Delta S^\circ_{\text{NH}_3\text{aq}} - \Delta S^\circ_{\text{NH}_3\text{gas}} - \Delta S^\circ_{\text{H}_2\text{O}} = -739,2922 - 192,77 - 69,9565 = -1002 \text{ J/mol/K}$;

$\Delta G_{\text{Hess-sp-NH}_3\text{gas}} = \Delta H_{\text{Hydrations}} - T \cdot \Delta S_{\text{Hydration}} = -373,3 - 298,15 \cdot (-1,002) = -74,5537 \text{ kJ/mol}$;

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

Amonjaka NH_3aq protonēšana:

2. $K_{\text{eq}2}$; Amonjaka ūdens $\text{NH}_3\text{aq} + \text{H}_2\text{O} + \text{Q} \Rightarrow \text{NH}_4^+ + \text{OH}^- + \Delta G$ stipra protolītiska bāze;

$\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{NH}_4^+} + \Delta H^\circ_{\text{OH}^-} - \Delta H^\circ_{\text{NH}_3} - \Delta H^\circ_{\text{H}_2\text{O}} = 55,8 \text{ kJ/mol}$ endotermiska

$\Delta H_{\text{Hess}} = -132,5608 - 230,015 - (-132,5 - 285,85) = 55,8 \text{ kJ/mol}$; $\Delta S_{\text{dispersed}} = -\Delta H_{\text{H}}/T = -55,77/298,15 \cdot 1000 = -187 \text{ J/(mol K)}$;

Viela	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol
H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
NH_4^+	-132,5	113,4	-79,3
NH_3aq	-132,5608	-739,2922	91,1056
NH_3gas	-45,94	192,77	-16,4
OH^-	-230,015	-10,9	-157,2

2. $\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{NH}_4^+} + \Delta S^\circ_{\text{OH}^-} - \Delta S^\circ_{\text{NH}_3} - \Delta S^\circ_{\text{H}_2\text{O}} = 771,8 \text{ J/mol/K}$;

CRC 2010; $= 113,4 - 10,9 - (-739,2922 + 69,9565) = 771,8 \text{ J/mol/K}$

3. $\Delta S_{\text{kopēja}} = \Delta S_{\text{H}} + \Delta S_{\text{izkliedēta}} = -187 + 771,8 = 584,8 \text{ J/(mol K)}$;

$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = 55,77 - 298,15 \cdot 0,7718 = -174,3 \text{ kJ/mol}$;

$T \cdot \Delta S_{\text{kopēja}} = 0,5848 \cdot 298,15 = 174,4 \text{ kJ/mol}$; saistīta enerģija;

BioTherm2006; $\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{NH}_4^+} + \Delta G^\circ_{\text{OH}^-} - \Delta G^\circ_{\text{NH}_3} - \Delta G^\circ_{\text{H}_2\text{O}} = -90,415 \text{ kJ/mol}$

$= -79,3 - 157,2 - (91,1056 - 237,191) = -90,4146 \text{ kJ/mol}$ eksoerģiska.

$K_{\text{eq}2} = \exp(-\Delta G_{\text{min}}/R/T) = \exp(90414,6/8,3144/298,15) = 10^{15,84}$; stipra

Hessa izmaiņa negatīva $\Delta G_{\text{Hess}} = -174,3 \text{ kJ/mol}$ minimizējas līdzsvara maisījumā $\Delta G_{\text{min}} = -R \cdot T \cdot \ln(K_{\text{eq}2}) = -90,415 \text{ kJ/mol}$;

3. $K_{\text{eq}3}$; protolīze $\text{NH}_4^+ + \text{H}_2\text{O} + \Delta G + \text{Q} \Rightarrow \text{NH}_3\text{aq} + \text{H}_3\text{O}^+$; $\text{p}K_{\text{eq}} = 10,9944$; $\text{NH}_4^+ = \text{H}^+ + \text{NH}_3\text{aq}$; $\text{p}K_a = 9,25$;

1. $\Delta H_{\text{H}} = \Delta H^\circ_{\text{NH}_3} + \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{NH}_4^+} - \Delta H^\circ_{\text{H}_2\text{O}} = -132,5 - 285,81 - (-132,5608 - 286,65) = 0,901 \text{ kJ/mol}$ atermiska

2. $\Delta S_{\text{izkliedēta}} = -\Delta H_{\text{H}}/T = -0,901/298,15 = -3,02 \text{ J/(mol K)}$; $\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{NH}_3} + \Delta G^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{\text{NH}_4^+} - \Delta G^\circ_{\text{H}_2\text{O}} = 108,7 \text{ kJ/mol}$

2. $\Delta S_{\text{H}} = \Delta S^\circ_{\text{NH}_3} + \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{NH}_4^+} - \Delta S^\circ_{\text{H}_2\text{O}} = -739,2922 - 3,854 - (113,4 - 453,188) = -403,4 \text{ J/mol/K}$

$\Delta G_{\text{H}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = 0,9008 - 298,15 \cdot (-0,4033582) = 121,2 \text{ kJ/mol}$ endoerģiska.....

$\Delta S_{\text{kopēja}} = \Delta S_{\text{H}} + \Delta S_{\text{izkliedēta}} = -3,021 - 403,358 = -406,4 \text{ J/(mol K)}$ $T \cdot \Delta S_{\text{kopēja}} = -406,4 \cdot 298,15 = -121,2 \text{ kJ/mol}$;

$K_{\text{eq}2} = \frac{[\text{OH}^-] \cdot [\text{NH}_4^+]}{[\text{NH}_3]_{\text{aq}} \cdot [\text{H}_2\text{O}]} = 10^{15,84}$; $K_{\text{eq}3} = \frac{[\text{NH}_3]_{\text{aq}} \cdot [\text{H}_3\text{O}^+]}{[\text{NH}_4^+] \cdot [\text{H}_2\text{O}]} = [\text{H}_2\text{O}] \cdot K_{\text{H}_2\text{O}} / K_{\text{NH}_4\text{OH}} = [\text{H}_2\text{O}] \cdot \frac{3,26 \cdot 10^{-18}}{1,78 \cdot 10^{-5}} = 1,014 \cdot 10^{(-11)}$;

Skābes konstante $K_a = \frac{[\text{H}^+][\text{NH}_3]_{\text{aq}}}{[\text{NH}_4^+]} = [\text{H}_2\text{O}] \cdot K_{\text{eq}3} = 55,3 \cdot 1,014 \cdot 10^{-11} = 5,6025 \cdot 10^{-10} = 10^{-9,25} = 10^{\text{p}K_a}$; $\text{p}K_a = 9,25$;

$\Delta G_{\text{eq}3} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(1,01395 \cdot 10^{(-11)}) = 62,75 \text{ kJ/mol}$, Endotermiska un eksoerģiska NH_4^+ protolītiskā Hesa brīvās enerģijas izmaiņa $\Delta G_{\text{protolīzeHess}3} = 108,7 \text{ kJ/mol}$ ir pozitīva, bet minimizējas līdz $\Delta G_{\text{eq}3} = 62,75 \text{ kJ/mol}$ sasniedzot līdzsvara maisījumu:

$K_{\text{eq}3} = \frac{[\text{NH}_3]_{\text{aq}} \cdot [\text{H}_3\text{O}^+]}{[\text{NH}_4^+] \cdot [\text{H}_2\text{O}]} = 10^{-10,994}$. Endotermiskas un eksoerģiskas NH_3aq un H_2O

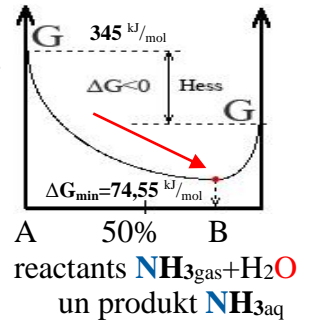
protolīzes brīvā enerģijas izmaiņa $\Delta G_{\text{protolīzeHess}}$ negatīva $-174,3 \text{ kJ/mol}$ bet minimizējas līdz $\Delta G_{\text{eq}2} = \Delta G_{\text{min}} = -90,4 \text{ kJ/mol}$ sasniedzot stipras bāzes līdzsvara maisījumu $K_{\text{eq}2} = 10^{15,84}$; izejvielas Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} produkti sasniegšana maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

$\Delta G_{\text{eq}} = G_{\text{NH}_3\text{aq}} + G_{\text{H}_3\text{O}^+} - G_{\text{NH}_4^+} - G_{\text{H}_2\text{O}} = 273,2 + 22,44 - 232,89 - 0 = 62,76 \text{ kJ/mol}$;

$G_{\text{NH}_4^+} = G_{\text{NH}_3\text{aq}} + G_{\text{H}_3\text{O}^+} - \Delta G_{\text{eq}} - G_{\text{H}_2\text{O}} = 273,2 + 22,44 - 62,75 - 0 = 232,9 \text{ kJ/mol}$;

Amonjaka šķīduma koncentrācija $C = 0,001 \text{ M}$; : [ax²-bx-c-0NH4-CH3COO](#)

$[\text{OH}^-] = [\text{NH}_4^+] = C \cdot \alpha = 0,001 \cdot 0,1259 = 10^{-3,9} \text{ M} = 1,259 \cdot 10^{-4} \text{ M}$; $\text{pOH} = 3,9$; $\alpha = 10^{-3,9}/0,001 = 0,1259$;



TERMODINAMIKA VINGRINĀJUMS V.e dihidrogenfosfāta H_2PO_4^- aq protolīze ūdenī

Aprēķināt ΔH_H ΔS_H ΔG_H standarta apstākļos 298,15 K. Vai reakcija ir **eksotermiska**, **atermiska**, **endotermiska**? Dihidrogenfosfāta H_2PO_4^- aq protolīze ar ūdeni! Būs **eksoerģiska** vai **endoerģiska**!

Dati $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ šķīdība 94,9 g/100g H_2O , blīvums 1,32 g/mL, Na_2HPO_4 s 11,8 g/100g H_2O , blīvums 1,1 g/mL, CRC 2010; **BioThermodynamic2006** $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} + \Delta G + \text{Q} \Rightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$ CRC2020; pH=7,36; I=0,25 M;

Viela	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H , kJ/mol
H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
$\text{H}_3\text{PO}_4(\text{aq})$	-1271,7	150,8	-1123,6
H_2PO_4^-	-1302,6	92,5	-1137,3
HPO_4^{2-}	-1292,14	-33,47	-1089,28
HPO_4^{2-}	-1298,89	-810,792	-1057,143
PO_4^{3-}	-1277,4	-220,5	-1018,7

1. $\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{produkti}} - \Delta H^\circ_{\text{reaktanti}}$; 2. $\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{produkti}} - \Delta S^\circ_{\text{reaktanti}}$

CRC 2010; 3. $\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}}$
 $= -1057,143 - 213,275 - (-1137,3 - 151,549) = 18,43$ kJ/mol

BioTherm2006; $\Delta G_H = \Delta G^\circ_{\text{HPO}_4^{2-}} + \Delta G^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{\text{H}_2\text{PO}_4^-} - \Delta G^\circ_{\text{H}_2\text{O}}$
 $= -1089,28 - 213,275 - (-1137,3 - 237,191) = 71,936$ kJ/mol

1. $\Delta H_H = \Delta H^\circ_{\text{HPO}_4^{2-}} + \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{H}_2\text{PO}_4^-} - \Delta H^\circ_{\text{H}_2\text{O}} = 10,5$ kJ/mol endot
 $= -1292,14 - 285,81 - (-1302,6 - 285,85) = -1577,95 - (-1588,45) = 10,5$ kJ/mol

2. $\Delta S_{\text{izkļiede}} = -\Delta H_H / T = -10,52 / 298,15 = -35,3$ J/(mol K);

3. $\Delta S_{\text{kopējā}} = \Delta S_H + \Delta S_{\text{izkļiede}} = -199,784 - 35,3 = -234,984$ J/(mol K);

2. $\Delta S_H = \Delta S^\circ_{\text{HPO}_4^{2-}} + \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{H}_2\text{PO}_4^-} - \Delta S^\circ_{\text{H}_2\text{O}} = -33,47 - 3,854 - (92,5 + 69,96) = -199,784$ J/mol/K;

$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = 10,5 - 298,15 \cdot (-0,199784) = 70,0$ kJ/mol; endoerģiska.....

3. $T \cdot \Delta S_{\text{kopējā}} = -234,984 \text{ J/mol/K} \cdot 298,15 \text{ K} = -70,0$ kJ/mol saistītā $T \Delta S_n$ **akumulētā enerģija** nepatvaļīga.

Līdzsvara sasniegšana brīvās enerģijas izmaiņas minimumā vielu reizinājumu attiecības izteiksmē ir Prigožina

atraktors produkti dalīti ar izejvielām: $\frac{[\text{HPO}_4^{2-}] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-] \cdot [\text{H}_2\text{O}]} = K_{\text{eq}2} = K_a / [\text{H}_2\text{O}] = 10^{-7,199} / 55,3 = 1,143 \cdot 10^{-9}$; $\text{p}K_{a2} = 7,199$

$\Delta G_{\text{eq}2} = -R \cdot T \cdot \ln(K_{\text{eq}2}) = -8,3144 \cdot 298,15 \cdot \ln(1,143 \cdot 10^{-9}) = 51,04$ kJ/mol;

Dihidrogenfosfāts H_2PO_4^- aq vāja skābe $\text{p}K_a = 7,199$ nelabvēlīga protolīze $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \Rightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$.

$K_a = \frac{[\text{HPO}_4^{2-}] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]} = [\text{H}_2\text{O}] K_{\text{eq}} = 55,3 \cdot 1,144 \cdot 10^{-9} = 10^{-7,199} = 10^{-\text{p}K_a}$; $\text{p}K_a = 7,199$;

$\text{HPO}_4^{2-} + \text{H}_2\text{O} \Rightarrow \text{PO}_4^{3-} + \text{H}_3\text{O}^+ = K_{\text{eq}3} = K_{\text{HPO}_4^{2-}} / [\text{H}_2\text{O}] = 10^{-12,35} / 55,3 = 8,07 \cdot 10^{-15}$; $\text{p}K_{a3} = 12,35$

$\Delta G_H = \Delta G^\circ_{\text{PO}_4^{3-}} + \Delta G^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{\text{HPO}_4^{2-}} - \Delta G^\circ_{\text{H}_2\text{O}} = -1018,7 - 213,275 - (-1089,28 - 237,191) = 94,5$ kJ/mol;

$\Delta G_{\text{eq}3} = -R \cdot T \cdot \ln(K_{\text{eq}3}) = -8,3144 \cdot 298,15 \cdot \ln(8,07 \cdot 10^{-15}) = 80,44$ kJ/mol;

$\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \Rightarrow \text{H}_2\text{PO}_4^- + \text{H}_3\text{O}^+$; $K_{\text{eq}1} = K_{\text{H}_3\text{PO}_4} / [\text{H}_2\text{O}] = 10^{-2,147975} / 55,3 = 7,113 \cdot 10^{-3}$; $\text{p}K_{a1} = 2,148$

$\Delta G_H = \Delta G^\circ_{\text{H}_2\text{PO}_4^-} + \Delta G^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{\text{H}_3\text{PO}_4} - \Delta G^\circ_{\text{H}_2\text{O}} = -1089,28 - 213,275 - (-1123,6 - 237,191) = 58,24$ kJ/mol;

$\Delta G_{\text{eq}1} = -R \cdot T \cdot \ln(K_{\text{eq}1}) = -8,3144 \cdot 298,15 \cdot \ln(7,113 \cdot 10^{-3}) = 22,21$ kJ/mol;

Endotermiska, endoerģiska HPO_4^{2-} , H_2PO_4^- , H_3PO_4 protolīzes Hess brīvās enerģijas

izmaiņa pozitīva $\Delta G_{\text{Hess}} = \Delta G_{\text{protolīze}} = 94,5$, $70,0$ un $58,24$ kJ/mol, bet minimizējas līdz

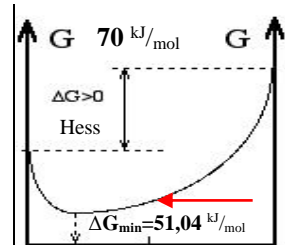
$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = 80,44$, $51,04$ un $22,21$ kJ/mol sasniedzot līdzsvaru



$\frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]_{\text{aqua}} \cdot [\text{H}_2\text{O}]} = K_{\text{eq}1} = K_{\text{H}_3\text{PO}_4} / [\text{H}_2\text{O}] = 10^{-2,148} / 55,3 = 0,0001285$;

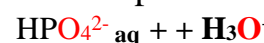
$\Delta G_{\text{eq}3} = -R \cdot T \cdot \ln(K_{\text{eq}3}) = -8,3144 \cdot 298,15 \cdot \ln(7,113 \cdot 10^{-3}) = 80,44$ kJ/mol,

$\frac{[\text{PO}_4^{3-}] \cdot [\text{H}_3\text{O}^+]}{[\text{HPO}_4^{2-}] \cdot [\text{H}_2\text{O}]} = K_{\text{eq}3} = K_{\text{HPO}_4^{2-}} / [\text{H}_2\text{O}] = 10^{-12,35} / 55,3 = 8,07 \cdot 10^{-15}$;



A+B 50% C+D

H_2PO_4^- aq + H_2O
reaktanti produkti



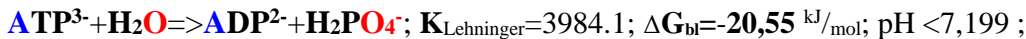
Lešatēle princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

TERMODINAMIKA VINGRINĀJUMS V f **ATP⁴⁻** adenoziņa trifosfāta hidrolīzes reakcija

Aprēķināt ΔH_H ΔS_H ΔG_H standarta apstākļos 298,15 K vai ir **eksotermiska**, **atermiska**, **endotermiska**? **ATP⁴⁻** adenoziņa trifosfāta hidrolīzes reakcijā ar ūdeni! Būs **eksoerģiska** vai **endoerģiska**!



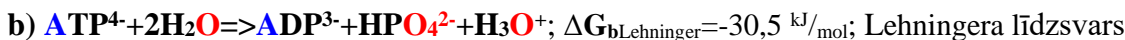
$K_{H_2PO_4} = K_{KortlyShuh} / [H_2O] = 10^{-7,199} / 55,3457 = 1,143 \cdot 10^{-9} = \frac{[HPO_4^{2-}] \cdot [H_3O^+]}{[H_2PO_4^-] \cdot [H_2O]}$; $[H_2PO_4^-] = \frac{[HPO_4^{2-}]_{\text{aqua}} \cdot [H_3O^+]}{1,143 \cdot 10^{-9} \cdot [H_2O]}$;



$\Delta G_{bLehninger} = -R \cdot T \cdot \ln(K_{Lehninger}) = -8,3144 \cdot 298,15 \cdot \ln(3984,1) / 1000 = -20,55 \text{ kJ/mol}$;

$K_{Lehninger} = K_{bLehninger} / [H_2O] = 220500,2 / 55,3457 = 3984,1 = \frac{[H_2PO_4^-] \cdot [ADP^{3-}]}{[H_2O] \cdot [ATP^{4-}]}$

$\Delta G_H = \Delta G^\circ_{ADP^{3-}} + \Delta G^\circ_{HPO_4^{2-}} - \Delta G^\circ_{ATP^{4-}} - \Delta G^\circ_{H_2O} = -1399,9 - 1137,3 - (-2267,64 - 237,191) = -32,4 \text{ kJ/mol}$;



$K_{bLehninger} = \exp(-\Delta G_{bLehninger} / R/T) = \exp(30500 / 8,3144 / 298,15) = \exp(12,304) = 220500,2 = \frac{[HPO_4^{2-}] \cdot [ADP^{3-}] \cdot [H_3O^+]}{[H_2O]^2 \cdot [ATP^{4-}]}$

$\Delta G_{Hess} = \Delta G^\circ_{ADP^{3-}} + \Delta G^\circ_{HPO_4^{2-}} + \Delta G^\circ_{H_3O^+} - \Delta G^\circ_{ATP^{4-}} - 2\Delta G^\circ_{H_2O} = -99,58 \text{ kJ/mol}$;

$= -1399,9 - 1057,143 - 213,275 - (-2267,64 + 2 \cdot -151,549) = -99,58 \text{ kJ/mol}$;

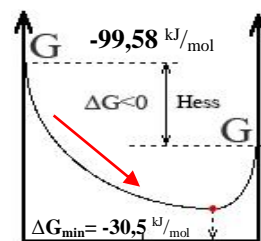
$K_{bLehninger} = \exp(-\Delta G_{bLehninger} / R/T) = \exp(30500 / 8,3144 / 310,15) = 136983,25$

Eksotermiskas un eksoerģiskas **ATP³⁻** hidrolīzes reakcijas Hesa brīvās enerģijas izmaiņa negatīva $\Delta G_{Hess} = -99,58 \text{ kJ/mol}$, bet minimizējas $\Delta G_{min} = \Delta G_{eqLehninger} = -30,5 \text{ kJ/mol}$

sasniedzot līdzsvara maisījumu 298,15 K temperatūrā $3984,05 = K_{eqLehninger}$

Līdzsvara sasniegšana ir Prigožina atraktors brīvās enerģijas izmaiņas minimums ΔG_{min} .

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



Reaktanti **ATP⁴⁻ + 2H₂O**

- produkti **ADP³⁻ + HPO₄²⁻ + H₃O⁺**

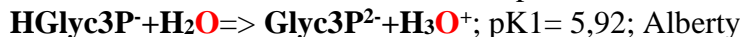
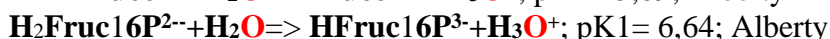
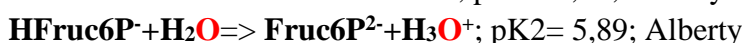
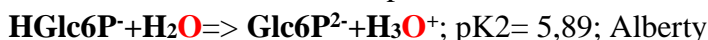
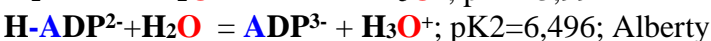
A+2B 50% C+D+E

1. $\Delta H_{\text{reaction}} = \Delta H^\circ_{\text{produkti}} - \Delta H^\circ_{\text{reaktanti}}$;

Viela $\Delta H^\circ_H \text{ kJ/mol}$ $\Delta S^\circ_H \text{ J/mol/K}$ $\Delta G^\circ_H \text{ kJ/mol}$; 2. $\Delta S_{Hess} = \Delta S^\circ_{\text{produkti}} - \Delta S^\circ_{\text{reaktanti}}$; 3. $\Delta G_{Hess} = \Delta H_{Hess} - T \cdot \Delta S_{Hess}$;

H₃O⁺	-285,81	-3,854	-213,275
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549
H₂PO₄⁻	-1296,3	90,4	-1130,2
H₂PO₄⁻	-1302,6	92,5	-1137,3
HPO₄²⁻	-1292,14	-33,47	-1089,28
HPO₄²⁻	-1298,89	-810,792	-1057,143
ADP³⁻	-2627,4	-4010	-1424,7
ATP⁴⁻	-3617,15	-4520	-2292,5
ADP³⁻	-2627,4	-4117,11	-1399,9
ATP⁴⁻	-3617,1	-4526,1	-2267,64

Miščenko; **H-ATP³⁻ + H₂O = ATP⁴⁻ + H₃O⁺**; pK₂=6,71; Alberty



Biochemistry Thermodynamic 2006 Massachusetts T.Institute, Alberty



$K_{bbLehninger} = \exp(-\Delta G_{bbLehninger} / R/T) = \exp(-30500 / 8,3144 / 298,15) = 4,54 \cdot 10^{(-6)}$;

$\Delta G_H = \Delta G^\circ_{ATP^{4-}} - 2\Delta G^\circ_{H_2O} - \Delta G^\circ_{ADP^{3-}} - \Delta G^\circ_{HPO_4^{2-}} - \Delta G^\circ_{H_3O^+} =$

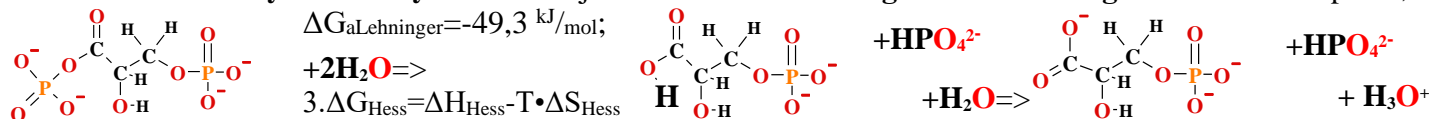
$= -2267,64 + 2 \cdot -151,549 - (-1399,9 - 1057,143 - 213,275) = 99,58 \text{ kJ/mol}$;

$K_{bbLehninger} = \exp(-\Delta G_{bbLehninger} / R/T) = \exp(-30500 / 8,3144 / 310,15) = 7,3 \cdot 10^{(-6)}$;

TERMODINAMIKA VINGRINĀJUMS V g **1,3-bis-fosfo-glicerāta** hidrolīze par **3-fosfo-glicerātu**

Aprēķinat ΔH_H ΔS_H ΔG_H standarta apstākļos 298.15 K vai ir **eksotermiska**, **atermiska**, **endotermiska**?

Fosfāta hidrolīzes **Glyc31P²⁻ => Glyc3P³⁻** reakcija ar ūdeni! Būs **eksoergiska** vai **endoergiska**! CRC 2010 pH=7,36 ;

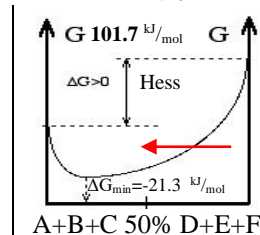


$K_{aLehninger} = \exp(49300/8,3144/298,15) = 433562158,5$; **Glycerat31P⁴⁻ + 2H₂O => Glycerat3P³⁻ + HPO₄²⁻ + H₃O⁺**;

Miščenko (**H₃O⁺**) $\Delta H^\circ_{Hess} = -285,81$ kJ/mol; $\Delta G_{Hess} = \Delta G^\circ_{H3O^+} + \Delta G^\circ_{Glyc3P} + \Delta G^\circ_{HP042} - \Delta G^\circ_{Glyc31P} - 2\Delta G^\circ_{H2O} = -107,75$ kJ/mol;

Viela ΔH°_H kJ/mol ΔS°_H J/mol/K ΔG°_H kJ/mol ; 1. $\Delta H_{Hess} = \Delta H^\circ_{\text{produkti}} - \Delta H^\circ_{\text{reaktanti}}$; 2. $\Delta S_{Hess} = \Delta S^\circ_{\text{produkti}} - \Delta S^\circ_{\text{reaktanti}}$;

H₃O⁺	-285,81	-3,854	-213,275	B06 ; = -213,275 - 1347,73 - 1057,143 - (-2207,30 + 2 * -151,549) = -107,75 kJ/mol;
H₂O	-285,85	69,9565	-237,191	CRC10 Glyc3P²⁻ + H₂O => Glycerol + HPO₄²⁻ + ΔG + Q ; $\Delta G_{Leninger} = -9,2$ kJ/mol;
H₂O	-286,65	-453,188	-151,549	CRC10 $\Delta G_{Hess} = \Delta G^\circ_{\text{Glycerol}} + \Delta G^\circ_{\text{HP042}} - \Delta G^\circ_{\text{Glyc3P}} - \Delta G^\circ_{\text{H2O}} = -46,43$ kJ/mol
H₂PO₄⁻	-1296,3	90,4	-1130,2	CRC10 = -171,35 - 1089,28 - (-1062,65 + (-151,549)) = -46,43 kJ/mol;
H₂PO₄⁻	-1302,6	92,5	-1137,3	$K_{aLeninger} = \exp(9200/8,3144/298,15) = 40,906$
HPO₄²⁻	-1292,14	-33,47	-1089,28	Glycerol1P⁻ + ADP²⁻ (+H₂O) => Glycerol + ATP³⁻ ; $\Delta G_{Leninger} = 11,35$ kJ/mol;
HPO₄²⁻	-1298,89	-810,792	-1057,143	$K_{aL} = K_{Lehninger} * [\text{H}_2\text{O}] = 0,000185513 * 55,3457339 = 0,0102673531329907$
Glyat3P³⁻	-1725,81	-2224,26	-1347,73	$\Delta G_H = \Delta G^\circ_{\text{Glyc}} + \Delta G^\circ_{\text{ATP3}} - \Delta G^\circ_{\text{Glyc3P}} - \Delta G^\circ_{\text{ADP2}} = 40$ kJ/mol;
Glyt31P⁴⁻	-1725,76	-2290,6	-2207,30	= -171,35 - 2267,64 - (-1062,65 - 1399,9) = 39,998 kJ/mol;
Glyat2P³⁻	-	-	-1341,79	abb) Glycerol1P²⁻ + ADP³⁻ + H₃O⁺ => Glycerol + ATP⁴⁻ + H₂O ; $\Delta G_{Leninger} = 21,3$ kJ/mol;
Glyat2P³⁻	-	-	-1333,2	$K_{abb} = K_a K_{bb} = 40,906 * 0,000004535142 = 0,000185513$
Glycerol	-	-	-171,35	$K_{abb} = \exp(-21300/8,3144/298,15) = 0,000185513$;
Glycerol	-679,85	-1760,65	-154,912	$\Delta G_H = \Delta G^\circ_{\text{Glyc}} + \Delta G^\circ_{\text{ATP4}} + \Delta G^\circ_{\text{H2O}} - \Delta G^\circ_{\text{Glyc3P}} - \Delta G^\circ_{\text{ADP3}} - \Delta G^\circ_{\text{H3O}} = 101,724$ kJ/mol;
Glycerate	Bio	Thermo	-452,31	= -154,912 - 2267,64 - 151,549 - (-1062,65 - 1399,9 - 213,275) = 101,724 kJ/mol ;
Glyol3P³⁻	dynamic	2006	-1077,13	$\Delta G_{abb} = \Delta G_a + \Delta G_{bb} = -9,2 + 30,5 = 21,3$ kJ/mol;
Glyo13P³⁻	-1725,8	-2224,26	-1062,65	Eksoergiska HPO₄²⁻ pārnese no Glycerola1P²⁻ uz ATP⁴⁻ pozitīva $\Delta G_{\text{transfer}} = 101,7$ kJ/mol, bet minimizējas sasniedzot $\Delta G_{abb} = \Delta G_a + \Delta G_{bb} = 21,3$ kJ/mol līdzsvaru
ADP³⁻	-2627,4	-4010	-1424,7	$K_{abb} = K_a K_{bb} = 40,906 * 0,000004535142 = 0,000185513$.
ATP⁴⁻	-3617,15	-4520	-2292,5	$\Delta G_{aL} = -8,3144 * 298,15 * \ln(0,010267353) = 11,35$ kJ/mol
ADP³⁻	-2627,4	-4117,11	-1399,9	
ATP⁴⁻	-3617,1	-4526,1	-2267,64	



$\Delta G_{abb} = \Delta G_a + \Delta G_{bb} = -9,2 + 30,5 = 21,3$ kJ/mol; Reaktanti **Glycerola1P²⁻ + ADP³⁻ + H₃O⁺**

$\frac{[\text{Glycerol}] \cdot [\text{HPO}_4^{2-}] \cdot [\text{ATP}^4]}{[\text{H}_2\text{O}] \cdot [\text{Glycerol1P}^{2-}] \cdot [\text{ADP}^3]} = K_{eqL} = K_{abb} = K_a K_{bb} = 0,000185513$ Produkti **Glycerol + ATP⁴⁻ + H₂O**;;
Glycerat31P²⁻ + H₂O => Glycerat3P³⁻ + H₂PO₄,

$\Delta G_{Hess} = \Delta G^\circ_{\text{Glyc3P}} + \Delta G^\circ_{\text{H2PO4}} - \Delta G^\circ_{\text{Glyc31P}} - \Delta G^\circ_{\text{H2O}} = -1347,73 - 1137,3 - (-2207,3 + (-237,191)) = -40,54$ kJ/mol ;

$\Delta G_{eal} = -R \cdot T \cdot \ln(K_{aL}) = -8,3144 \cdot 298,15 \cdot \ln(7833705) = -39,35$ kJ/mol ;

$K_{aL} = K_{Lehninger} / [\text{H}_2\text{O}] = 433562158,5 / 55,3457339 = 7833705 = \frac{[\text{Glycerat3P}^3] \cdot [\text{H}_2\text{PO}_4]}{[\text{H}_2\text{O}] \cdot [\text{Glycerat13P}^4]}$

$\Delta G_H = \Delta G^\circ_{\text{Glyc3P}} + \Delta G^\circ_{\text{HP042}} + \Delta G^\circ_{\text{H3O}} - \Delta G^\circ_{\text{Glyc31P}} - \Delta G^\circ_{\text{H2O}} = -1347,73 - 1057,143 - 213,275 - (-2207,3 + 2 * (-151,549)) = -107,75$ kJ/mol ;

Glycerat31P⁴⁻ + 2H₂O => Glycerat3P³⁻ + HPO₄²⁻ + H₃O⁺; pH=7,36 ; $\Delta G_{Lehninger} = -49,3$ kJ/mol,

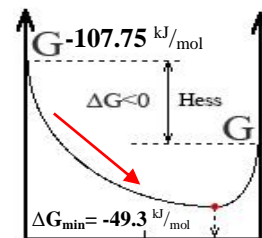
$K_{aLehninger} = \exp(-\Delta G_{Lehninger} / R/T) = \exp(49300/8,3144/298,15) = 433562158,5$;

Līdzsvars labvēlīgs. Eksotermiska un eksoergiska **1,3-bis-fosfo-glicerāta** hidrolīzes reakcijas brīvās enerģijas izmaiņa negatīva pH=7,36 $\Delta G_{\text{hidrolīze}} = -107,74$ kJ/mol , bet minimizējas sasniedzot $\Delta G_{eq} = -49,3$ kJ/mol līdzsvara maisījumu:

$K_{aLehninger} = \frac{[\text{HPO}_4^{2-}] \cdot [\text{H}_3\text{O}^+] \cdot [\text{Glycerat3P}^3]}{[\text{H}_2\text{O}]^2 \cdot [\text{Glycerat13P}^4]} = 433562158,5$; Līdzsvara sasniegšana ir Prigožina

atraktora brīvās enerģijas izmaiņas minimums ΔG_{min} vielu maisījumā.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



reaktanti **Glyc31P⁴⁻ + 2H₂O**
 produkti **Glyc3P³⁻ + HPO₄²⁻ + H₃O⁺**

$$\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{ATP3}} + \Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{H}_2\text{PO}_4} - \Delta G^{\circ}_{\text{ADP2}} = -2267,64 - 151,549 - (-1399,9 - 1057,143) = 37,85 \text{ kJ/mol};$$



$$K_{\text{bl}} = \frac{[\text{H}_2\text{O}][\text{ATP}^{3-}]}{[\text{ADP}^{2-}][\text{H}_2\text{PO}_4^-]} = 0,000004535142 * 55,34573393 = 0,000251001 = 10^{-3,6004}$$

$$\Delta G_{\text{blLehninger}} = -R \cdot T \cdot \ln(K_{\text{blLehninger}}) = -8,3144 \cdot 298,15 \cdot \ln(0,000251001) = 20,551 \text{ kJ/mol};$$



$$K_{\text{bb}} = K_{\text{Lehninger}} = \exp(-30,5/8,3144/298,15) = 0,000004535142 =$$

$$\frac{[\text{H}_2\text{O}] \cdot [\text{ATP}^{4-}]}{[\text{H}_2\text{PO}_4^-] \cdot [\text{ADP}^{3-}]} \\ \downarrow \\ \frac{[\text{H}_2\text{O}]^2 \cdot [\text{ATP}^{4-}]}{[\text{HPO}_4^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]}$$

$$\Delta G_{\text{H}} = \Delta G^{\circ}_{\text{ATP4}} + 2\Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{HPO}_4} - \Delta G^{\circ}_{\text{ADP3}} - \Delta G^{\circ}_{\text{H}_3\text{O}} = 46,015 \text{ kJ/mol};$$

$$= -2267,64 - 2 * 151,549 - (-1057,143 - 1399,9 - 213,275) = 46,015 \text{ kJ/mol};$$

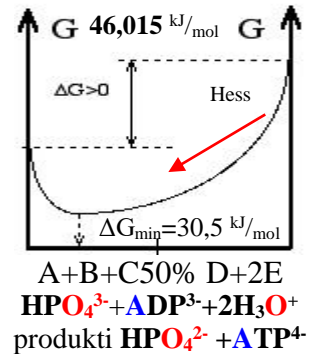
Biochemistry Thermodynamic 2006, Alberty Massachusetts; H_3O^+ Miščenko 213,275 kJ/mol;

Endotermiska un endoerģiska ADP^{3-} fosforilēšanas Hesa brīvās enerģijas izmaiņa pozitīva

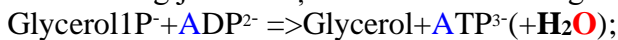
pie pH 7,36 $\Delta G_{\text{Hess}} = 46,015 \text{ kJ/mol}$, bet minimizējas $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = 30,5 \text{ kJ/mol}$ sasniedzot

$$\text{līdzsvara maisījumu: } 0,000004535142 = K_{\text{bb}} = \frac{[\text{H}_2\text{O}]^2 \cdot [\text{ATP}^{4-}]}{[\text{HPO}_4^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]}. \quad \text{re aktanti}_-$$

Līdzsvara sasniegšana ir Prigožina atraktors brīvās enerģijas izmaiņas minimums ΔG_{min} .



Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



$$\Delta G_{\text{H}} = \Delta G^{\circ}_{\text{Glyc}} + \Delta G^{\circ}_{\text{ATP3}} - \Delta G^{\circ}_{\text{Glyc3P}} - \Delta G^{\circ}_{\text{ADP2}} = -154,912 - 2267,64 - (-1062,65 - 1399,9) = 39,998 \text{ kJ/mol};$$

$$K_{\text{eqLehninger}} = K_{\text{Lehninger}} * [\text{H}_2\text{O}] = 0,000185512570561914 * 55,34573393 = 0,010267$$

$$\Delta G_{\text{eqLehninger}} = -R \cdot T \cdot \ln(K_{\text{eqLehninger}}) = -8,3144 * 298,15 * \ln(0,01026732937099) / 1000 = 11,351 \text{ kJ/mol};$$



$$\Delta G_{\text{H}} = \Delta G^{\circ}_{\text{Glyc}} + \Delta G^{\circ}_{\text{ATP4}} + 2\Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{Glyc3P2}} - \Delta G^{\circ}_{\text{ADP3}} - \Delta G^{\circ}_{\text{H}_3\text{O}} = 40 \text{ kJ/mol};$$

$$= -154,912 - 2267,64 + 2 * -151,549 - (-1062,65 - 1399,9 - 213,275) = 39,998 \text{ kJ/mol};$$

$$K_{\text{bb}} = K_{\text{Lehninger}} = \exp(-21300/8,3144/298,15) = 0,000185512570561914$$



$$K_{\text{Lehninger}} = K_{\text{eq}} = \exp(-\Delta G_{\text{Lehninger}}/R/T) = \exp(18800/8,3144/298,15) = \exp(7,58389) = 1,966266 = 10^{0,2936};$$

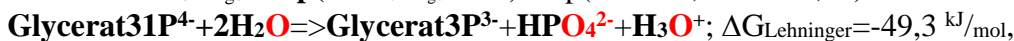


$$K_{\text{aLehninger}} = K_{\text{Lehninger}} / [\text{H}_2\text{O}] = 433562158,5 / 55,3457339 = 7833705,111 = \frac{[\text{Glycerat3P}^{3-}][\text{H}_2\text{PO}_4^-]}{[\text{H}_2\text{O}] \cdot [\text{Glycerat13P}^{4-}]}$$

$$\Delta G_{\text{aLehninger}} = -R \cdot T \cdot \ln(K_{\text{aLehninger}}) = -8,3144 \cdot 298,15 \cdot \ln(7833705,111) = -39,350534 \text{ kJ/mol};$$

$$K_{\text{abbLehninger}} = \exp(-\Delta G_{\text{abbLehninger}}/R/T) = \exp(18800/8,3144/298,15) = 1966,266$$

$$K_{\text{a}} = K_{\text{Lehninger}} = \exp(-\Delta G_{\text{Lehninger}}/R/T) = \exp(49300/8,3144/298,15) = 433562158,5 = \frac{[\text{HPO}_4^{2-}] \cdot [\text{H}_3\text{O}^+] \cdot [\text{Glycerat3P}^{3-}]}{[\text{H}_2\text{O}]^2 \cdot [\text{Glycerat13P}^{4-}]}$$



$$\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{H}_3\text{O}} + \Delta G^{\circ}_{\text{Glyc3P}} + \Delta G^{\circ}_{\text{HPO}_4} - \Delta G^{\circ}_{\text{Glyc3P}} - 2\Delta G^{\circ}_{\text{H}_2\text{O}} = -107,75 \text{ kJ/mol}; \text{exothermic}$$

$$= -213,275 - 1347,73 - 1057,143 - (-2207,30 + 2 * -151,549) = -107,75 \text{ kJ/mol};$$



$$\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{ATP4}} + \Delta G^{\circ}_{\text{Glyc3P3}} - \Delta G^{\circ}_{\text{Glyc3P4}} - \Delta G^{\circ}_{\text{ADP3}} = -33 \text{ kJ/mol}; = -2292,5 - 1347,73 - (-2207,3 - 1399,9) = -33 \text{ kJ/mol};$$

$$K_{\text{a}} K_{\text{bb}} = K_{\text{abb}} = 433562158,5 * 0,000004535142 = 1966,266 = \frac{[\text{Glycerat3P}^{3-}] \cdot [\text{ATP}^{4-}]}{[\text{Glycerat13P}^{4-}] \cdot [\text{ADP}^{3-}]}$$

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(1965,363914) = -18,8 \text{ kJ/mol} \quad \text{pH} = 7,36.$$

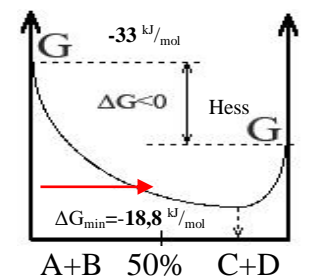
Eksotermiska un eksoerģiska Glycerat31P^{4-} fosfāta pārnese Hesa brīvās enerģijas izmaiņa ir negatīva pie pH=7,36 negatīva $\Delta G_{\text{transfer}} = -33 \text{ kJ/mol}$, bet minimizējas līdz

$$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -18,8 \text{ kJ/mol} \text{ sasniedzot līdzsvara maisījumu:}$$

$$K_{\text{a}} K_{\text{bb}} = K_{\text{abb}} = \frac{[\text{Glycerat3P}^{3-}] \cdot [\text{ATP}^{4-}]}{[\text{Glycerat13P}^{4-}] \cdot [\text{ADP}^{3-}]} = 433562158,5 * 0,000004535142 = 1966,266;$$

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min}

sasniegšana līdzsvara maisījumā. $\text{Glyc31P}^{4-} + \text{ADP}^{3-}$ reaktanti $\text{Glyc3P}^{3-} + \text{ATP}^{4-}$ (C+D) produkti.



TERMODINAMIKA VINGRINĀJUMS V h **PyruvateEnolP³⁻** hidrolīze par **H₃CC=OCOO⁻+HPO₄²⁻**

$$\Delta G_{\text{Lehninger}} = -61,9 \text{ kJ/mol, PyruvEnolP}^{3-} + \text{H}_2\text{O} \Rightarrow \text{H}_3\text{CC=OCOO}^- + \text{HPO}_4^{2-}; \text{pH}=7,36;$$

$$I=0,25 \text{ M, BioTherm06, pH}=7,36, \Delta G_{\text{H}} = \Delta G^\circ_{\text{H}_3\text{CC=OCOO}^-} + \Delta G^\circ_{\text{HPO}_4^{2-}} - \Delta G^\circ_{\text{PyruvEnolP}^{3-}} - \Delta G^\circ_{\text{H}_2\text{O}} = -60,484 \text{ kJ/mol};$$

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

PyruvEnolP³⁻	-1400	-1100	-1189,73
H₃CC=OCOO⁻	-597,4	-850	-350,78
H₃CC=OCOO⁻	-603,7	-433,54	-474,44
H₃CC=OCOO⁻	-597,04	-846,66	-344,62
H₃O⁺	-285,81	-3,854	-213,275
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549
H₂PO₄⁻	-1296,3	90,4	-1130,2
H₂PO₄⁻	-1302,6	92,5	-1137,3
HPO₄²⁻	-1292,14	-33,47	-1089,28
HPO₄²⁻	-1298,89	-810,792	-1057,143

$$\text{CRC10} = -474,44 - 1057,143 - (-1189,73 - 151,549) = -190,3 \text{ kJ/mol}$$

$$1. \Delta H_{\text{H}} = \Delta H^\circ_{\text{pyruvat}} + \Delta H^\circ_{\text{HPO}_4^{2-}} - \Delta H^\circ_{\text{PyruvEnolP}^{3-}} - \Delta H^\circ_{\text{H}_2\text{O}} = -209 \text{ kJ/mol};$$

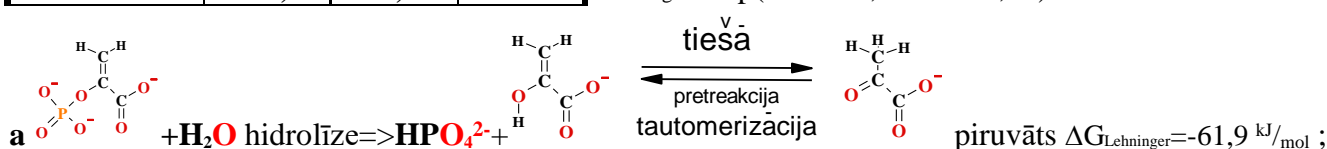
$$= -597,04 - 1298,89 - (-1400 - 286,65) = -209 \text{ kJ/mol}; \text{exothermic}$$

$$\Delta S_{\text{H}} = \Delta S^\circ_{\text{pyruvat}} + \Delta S^\circ_{\text{HPO}_4^{2-}} - \Delta S^\circ_{\text{PyruvEnolP}^{3-}} - \Delta S^\circ_{\text{H}_2\text{O}} = -104,3 \text{ J/K/mol};$$

$$= -846,66 - 810,792 - (-1100 - 453,188) = -104,3 \text{ kJ/mol}; \text{exothermic}$$

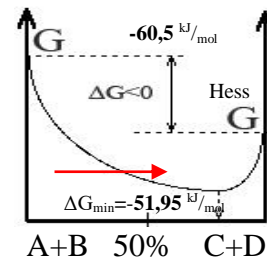
$$\Delta G_{\text{Hess}} = \Delta H_{\text{H}} - T * \Delta S_{\text{H}} = -209 - 298,15 * -0,104264 = -177,9 \text{ kJ/mol};$$

$$K_{\text{Lehninger}} = \exp(61900/8,3144/298,15) = 69902464988 = 10^{10,84}$$



$$K_a = 69902464988 = \frac{[\text{CH}_3\text{C=OCOO}^-] \cdot [\text{HPO}_4^{2-}]}{[\text{H}_2\text{O}] \cdot [\text{PyruvEnolP}^{3-}]} = 10^{10,844}; \text{pH}=7,36.$$

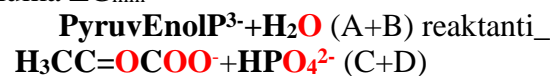
Eksotermiska un eksoerģiska **PyruvEnolP³⁻** hidrolīzes Hesa brīvā enerģijas izmaiņa negatīva pie pH=7,36 $\Delta G_{\text{hidrolīze}} = -190,3 \text{ kJ/mol}$, bet minimizējas $\Delta G_{\text{min}} = \Delta G_a = -61,9 \text{ kJ/mol}$ sasniedzot



$$\text{līdzsvara maisījumu } K_a = 69902464988 = \frac{[\text{CH}_3\text{C=OCOO}^-] \cdot [\text{HPO}_4^{2-}]}{[\text{H}_2\text{O}] \cdot [\text{PyruvEnolP}^{3-}]} = 10^{10,844}.$$

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars. produkti.



$$\text{PyruvEnolP}^{3-} + \text{ADP}^{3-} + \text{H}_3\text{O}^+ \Rightarrow \text{H}_3\text{CC=OCOO}^- + \text{ATP}^4 + \text{H}_2\text{O}; \Delta G_{\text{ab}} = \Delta G_a + \Delta G_{\text{bb}} = -61,9 + 30,5 = -31,4 \text{ kJ/mol};$$

$$\Delta G_{\text{H}} = \Delta G^\circ_{\text{ATP}^4} + \Delta G^\circ_{\text{H}_2\text{O}} + \Delta G^\circ_{\text{H}_3\text{CC=OCOO}^-} - \Delta G^\circ_{\text{PyruvEnolP}^{3-}} - \Delta G^\circ_{\text{ADP}^{3-}} - \Delta G^\circ_{\text{H}_3\text{O}^+} = -90,724 \text{ kJ/mol};$$

$$= -2267,64 - 151,549 - 474,44 - (-1189,73 - 1399,9 - 213,275) = -90,724 \text{ kJ/mol};$$

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T * \Delta S_{\text{Hess}} = -187,58 - 298,15 * -0,3434 = -85,195 \text{ kJ/mol};$$

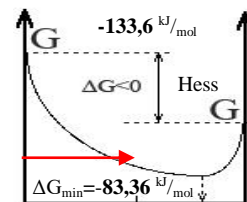
$$K_{\text{abb}} = \exp(31400/8,3144/298,15) = 317017,6$$

$$K_{\text{abb}} = K_a K_b = 69902464988 * 0,000004535142 = 317017,6 =$$

$$\frac{[\text{H}_2\text{O}] \cdot [\text{ATP}^4] \cdot [\text{CH}_3\text{C=OCOO}^-]}{[\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+] \cdot [\text{PyruvEnolP}^{3-}]}$$

Eksotermiska un eksoerģiska **PyruvEnolP³⁻** hidrolīzes reakcijas Hesa brīvā enerģijas izmaiņa negatīva pie pH=7,36 $\Delta G_{\text{hidrolīze}} = -190,3 \text{ kJ/mol}$ un $-90,724 \text{ kJ/mol}$, bet minimizējas $\Delta G_{\text{min}} = \Delta G_{\text{abb}} = -61,9 \text{ kJ/mol}$ un $-31,4 \text{ kJ/mol}$ sasniedzot līdzsvara maisījumu:

$$69902464988 = \frac{[\text{CH}_3\text{C=OCOO}^-] \cdot [\text{HPO}_4^{2-}]}{[\text{H}_2\text{O}] \cdot [\text{PyruvEnolP}^{3-}]} = K_a; K_{\text{abb}} = \frac{[\text{H}_2\text{O}] \cdot [\text{ATP}^4] \cdot [\text{CH}_3\text{C=OCOO}^-]}{[\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+] \cdot [\text{PyruvEnolP}^{3-}]} = 317017,6.$$



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

sasniegšana maisījumā. **PyruvEnolP³⁻+ADP³⁻+H₃O⁺ reaktanti**

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars. produkti **H₃CC=OCOO⁻+ATP⁴⁻+H₂O**



$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{ATP3}} + \Delta G^\circ_{\text{H2O}} - \Delta G^\circ_{\text{H2PO4}} - \Delta G^\circ_{\text{ADP2}} = -2267,64 - 151,549 - (-1399,9 - 1057,143) = 37,85 \text{ kJ/mol};$$

$$K_{\text{bl}} = [\text{H}_2\text{O}] K_{\text{Lehninger}} = 0,000004535142 * 55,34573393 = 0,000251001 = 10^{-3,6004} = \frac{[\text{H}_2\text{O}] \cdot [\text{ATP}^{4-}]}{[\text{H}_2\text{PO}_4^-] \cdot [\text{ADP}^{3-}]}$$

$$\Delta G_{\text{bbLehninger}} = -R \cdot T \cdot \ln(K_{\text{blLehninger}}) = -8,3144 * 298,15 * \ln(0,000251001) / 1000 = 20,551 \text{ kJ/mol};$$



$$K_{\text{bb}} = K_{\text{Lehninger}} = \exp(-30500 / 8,3144 / 298,15) = 0,000004535142 = \frac{[\text{H}_2\text{O}]^2 \cdot [\text{ATP}^{4-}]}{[\text{HPO}_4^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]}$$

$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{ATP4}} + 2\Delta G^\circ_{\text{H2O}} - \Delta G^\circ_{\text{HPO42}} - \Delta G^\circ_{\text{ADP3}} - \Delta G^\circ_{\text{H3O}} = 99,58 \text{ kJ/mol};$$

$$= -2267,64 - 2 * 151,549 - (-1057,143 - 1399,9 - 213,275) = 99,58 \text{ kJ/mol}; \text{Biothermodynamic 2006}; [\text{H}_2\text{O}] / [\text{H}_3\text{O}^+] \text{ CRC 2010}$$

Endotermiska un endoergiska ADP^{3-} fosforilēšanas reakcijas Hesa brīvās enerģijas

izmaiņa pozitīva $\Delta G_{\text{fosforilēšana}} = 99,58 \text{ kJ/mol}$, bet minimizējas līdz vērtībai

$$\Delta G_{\text{bb}} = 30,5 \text{ kJ/mol} \text{ sasniedzot līdzsvara maisījumu :}$$

$$0,000004535142 = K_{\text{bb}} = \frac{[\text{H}_2\text{O}]^2 \cdot [\text{ATP}^{4-}]}{[\text{HPO}_4^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]}. \text{ Lešatelje princips ir}$$

Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana; reaktanti_ maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

$$\Delta G_{\text{H}} = \Delta G^\circ_{\text{ATP4}} + \Delta G^\circ_{\text{H2O}} + \Delta G^\circ_{\text{H3CC=OCCO}} - \Delta G^\circ_{\text{PyruvEnolP3}} - \Delta G^\circ_{\text{ADP3}} - \Delta G^\circ_{\text{H3O}} = -90,724 \text{ kJ/mol}; \text{ADP}^{3-} + \text{HPO}_4^{2-} + \text{H}_3\text{O}^+ \rightarrow$$

$$= -2267,64 - 151,549 - 474,44 - (-1189,73 - 1399,9 - 213,275) = -90,724 \text{ kJ/mol}; \text{produkti } \text{ATP}^{4-} + 2\text{H}_2\text{O};$$

$$\text{PyruvEnolP}^{3-} + \text{ADP}^{3-} + \text{H}_3\text{O}^+ \Rightarrow \text{H}_3\text{CC=OCCO}^- + \text{ATP}^{4-} + \text{H}_2\text{O}; \Delta G_{\text{ab}} = \Delta G_{\text{a}} + \Delta G_{\text{bb}} = -61,9 + 30,5 = -31,4 \text{ kJ/mol};$$

$$K_{\text{abb}} = \exp(31400 / 8,3144 / 298,15) = 317017,6$$

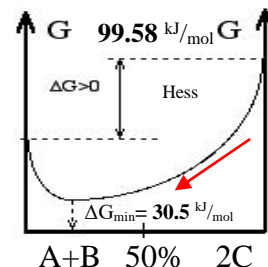
$$K_{\text{abb}} = K_{\text{a}} K_{\text{b}} = 69902464988 * 0,000004535142 = 317017,6 = \frac{[\text{H}_2\text{O}] \cdot [\text{ATP}^{4-}] \cdot [\text{CH}_3\text{C=OCCO}^-]}{[\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+] \cdot [\text{PyruvEnolP}^{3-}]}$$

Eksotermiska un eksoergiska PyruvEnolP^{3-} hidrolīzes reakcijas Hesa brīvās enerģijas

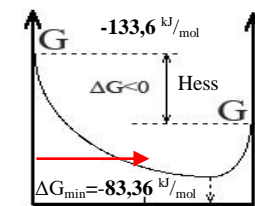
izmaiņa negatīva $\Delta G_{\text{hidrolīze}} = -90,7 \text{ kJ/mol}$, bet minimizējas sasniedzot līdzsvara maisījumu

līdz vērtībai $\Delta G_{\text{abb}} = -31,4 \text{ kJ/mol}$, $K_{\text{eq}} = \frac{[\text{H}_2\text{O}] \cdot [\text{ATP}^{4-}] \cdot [\text{CH}_3\text{C=OCCO}^-]}{[\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+] \cdot [\text{PyruvEnolP}^{3-}]}$ 317017,6. Lešatelje

pcprincips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana.

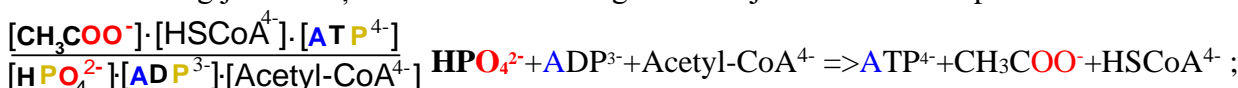


A+B 50% 2C
reaktanti $\text{ADP}^{3-} + \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$
produkti $\text{ATP}^{4-} + 2\text{H}_2\text{O}$;



A+B+C 50% D+E+F
reaktanti $\text{PyruvEnolP}^{3-} + \text{ADP}^{3-} + \text{H}_3\text{O}^+$
produkti $\text{H}_3\text{CC=OCCO}^- + \text{ATP}^{4-} + \text{H}_2\text{O}$

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



$$\Delta G_{\text{H}} = \Delta G^\circ_{\text{ATP4}} + \Delta G^\circ_{\text{CH3COO}} + \Delta G^\circ_{\text{CoA2}} - \Delta G^\circ_{\text{HPO42}} - \Delta G^\circ_{\text{ADP3}} - \Delta G^\circ_{\text{Acetyl-CoA2}} = -6,025 \text{ kJ/mol};$$

$$= -2267,64 - 241,663 - 5,6616 - (-1057,143 - 1399,9 - 51,8968) = -6,025 \text{ kJ/mol};$$

$$K_{\text{abKopēja}} = K_{\text{eqb}} K_{\text{eqa}} = 318243,5442 * 4,519 * 10^{-6} = 1,438142576$$

$$\Delta G_{\text{ab}} = -8,3144 * 298,15 * \ln(1,438142576) = -0,9007 \text{ kJ/mol}. \text{ Eksotermiskas un eksoergiskas}$$

PyruvEnolP^{3-} hidrolīzes reakcijas Hesa brīvās enerģijas izmaiņa negatīva pie $\text{pH} = 7,36$

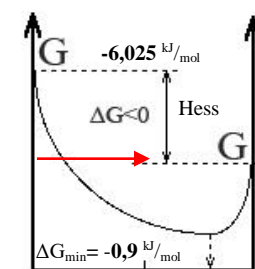
$\Delta G_{\text{hidrolīze}} = -6 \text{ kJ/mol}$, bet minimizējas līdz $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -0,9 \text{ kJ/mol}$ līdzsvara maisījumā

$$K_{\text{ab}} = \frac{[\text{CH}_3\text{COO}^-] \cdot [\text{HSCoA}^4] \cdot [\text{ATP}^{4-}]}{[\text{HPO}_4^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{Acetyl-CoA}^4]} = 1,4381; \text{ Lešatelje princips ir Prigožina}$$

atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana maisījumā. Acetyl- $\text{CoA}^4 + \text{HPO}_4^{2-} + \text{ADP}^{3-}$

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars. Produkti $\text{ATP}^{4-} + \text{CH}_3\text{COO}^- + \text{HSCoA}^4$

$$\Delta G_{\text{kopēja}} = \Delta G_{\text{a}} + \Delta G_{\text{b}} = \Delta G_{\text{ab}} = 30,5087 - 31,409 = -0,9003 \text{ kJ/mol};$$



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

TERMODINAMIKA VINGRINĀJUMS V h AcylCoA⁴ hidrolīze par skābi+ HSCoA⁴



ΔG_{Hess}=ΔG°_{CH₃COOH}+ΔG°_{CoA2}-ΔG°_{Acetyl-CoA2}-ΔG_{H2O}=-531,743-5,6616-(-51,8968-151,549)=-333,96 kJ/mol;

ΔG_{aL}=-R•T•ln(K_{aL})=-8,3144*298,15*ln(5727,95006026944)/1000=-21,45 kJ/mol.;

I=0,25 M, BioTherm06, CRC10; ΔG_{Lehninger}=-31,4 kJ/mol; pH=7,36, Acetyl-CoA³+2H₂O=>CH₃COO⁻+HSCoA³+H₃O⁺

AcetylCoA ⁴	-	-	-51,8968
AcetylCoA ⁴	-	-	-58,06
HSCoA ⁴	-	-	-7,26
HSCoA ³	BioTherm06		-5,6616
H ₃ CCOO ⁻	-486,836	-813,043	-241,663
C ₁₆ H ₃₂ O _{2s}	-891.5	452.4	-
C ₁₆ H ₃₂ O _{2liqui}	-838.1	-	-
Palmitate-	-	-	-1003,54
Palmitate-	-	-	-1067,238
H ₃ CCOO ⁻	-486,84	82,23	-247,83
H ₃ CCOO ⁻	-485,64	87,58	-369,37
PalmtylCoA ⁴	PalmitateCoA	-	-784,9391
H ₃ CCOOH	-484,09	159,83	-531,743
C ₂ H ₄ OOCCCH ₃	-485,3	-1644,15	4,9176
C ₂ H ₄ OOCCCH ₃	-	-	-11.52
CH ₃ CH ₂ OH	-	-	62.96
CH ₃ CH ₂ OH	-277.6	160.7	-174.8
CH ₃ CH ₂ OH	-290,77	-1227,76	75,2864
H ₃ O ⁺	-285,81	-3,854	-213,275
H ₂ O	-285,85	69,9565	-237,191
H ₂ O	-286,65	-453,188	-151,549

ΔG_{Hess}=ΔG°_{CH₃COO}+ΔG°_{CoA2}+ΔG°_{H3O+}-ΔG°_{Acetyl-CoA2}-2*ΔG_{H2O}=-105,6 kJ/mol
 =-241,663-5,6616-213,275-(-51,8968+2*-151,549)=-105,6 kJ/mol;
 K_a=K_{Lehninger}=exp(31400/8,3144/298,15)=317017,64

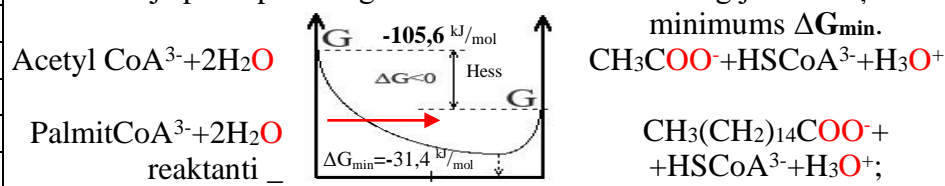
$$\frac{[\text{CH}_3\text{COOH}] \cdot [\text{HSCoA}^{2-}]}{[\text{H}_2\text{O}] \cdot [\text{Acetyl-CoA}^{2-}]}$$

$$K_a = K_{Lehninger} = 317017,64 = \frac{[\text{CH}_3\text{COO}^-] \cdot [\text{HSCoA}^{3-}] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2 \cdot [\text{Acetyl-CoA}^{3-}]}$$

=15,125*-51,8968=-784,9391

Eksoergiska AcylCoA³ hidrolīzes Hesa brīvās enerģijas izmaiņa pie pH=7,36 negatīva ΔG_{Hess}=-105,6 kJ/mol, bet minimizējas līdz ΔG_{min}=ΔG_a=-31,4 kJ/mol sasniedzot līdzsvara maisījumu.

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas



Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars. A+2B 50% C+D+E produkti.

Hidrolīzes līdzsvars: PalmitateCoA²+H₂O=>CH₃(CH₂)₁₄COOH+HSCoA²; ΔG_{aLr}=-22.35 kJ/mol; pie p H<5

ΔG_{aL}=-R•T•ln(K_{aL})=-8,3144*298,15*ln(8235,15078047156)=-22,35 kJ/mol; [CH₃(CH₂)₁₄COOH][HSCoA²]

K_{aL}=K_{Lehninger}/[H₂O]=455782,655095979/55,346=8235,15078047156c6= [Palmitate-CoA²][H₂O]

ΔG_{Hess}=ΔG°_{HSCoA2}+ΔG°_{Palmitate}-(ΔG_{PalmitateCoA2}+ΔG_{H2O})=-194,7954 kJ/mol;

1/455782,655095979=1/K_a; K_a=K_{Lehninger}=455782,655095979= [CH₃(CH₂)₁₄COO⁻][HSCoA³⁻].[H₃O⁺]
 PalmitCoA³+2H₂O=>CH₃(CH₂)₁₄COO⁻+HSCoA³+H₃O⁺; ΔG_{Lehninger}=-32.3 kJ/mol; [H₂O]².[Palmitate-CoA³⁻]

ΔG_{Hess}=ΔG°_{HSCoA2}+ΔG°_{Palmitate}-(ΔG_{PalmitateCoA2}+ΔG_{H2O})=-5,6616-1067,238-(-784,9391-151,549)=-136,4 kJ/mol;

ΔG_{Hess}=ΔG°_{HSCoA3}+ΔG°_{Palmitate}+ΔG°_{H3O+}-(ΔG_{PalmitateCoA3}+2ΔG_{H2O})=-5,6616-1067,238-213,275-(-784,9391+2*-151,549)=-198,14 kJ/mol;

K_a=K_{Lehninger}=exp(32300/8,3144/298,15)=455782,655095979; Eksoergiska PalmitCoA³ hidrolīzes Hesa brīvās enerģijas izmaiņa pie pH=7,36 negatīva ΔG_{Hess}=-198 kJ/mol, bet minimizējas līdz ΔG_{min}=ΔG_a=-32,3 kJ/mol; K_a=K_{Lehninger}=455782,655095979 sasniedzot līdzsvara maisījumu: Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



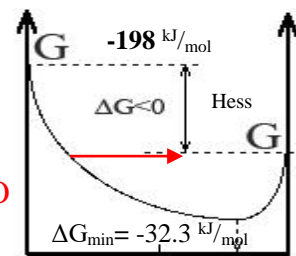
K_a=exp(19200/8,3144/298,15)=2310,5736; K_b=EXP(-ΔG_a/R/T)= 97462087,2480605;



ΔG_{abc}=-45,6-19,2+31,4=-33,4 kJ/mol, K_{abc}=2310,5736*97462087,2480605*0,0000031544=710349,826891739;

ΔG_{ppbcHess}=ΔG_{ppHess}+ΔG_{bHess}+ΔG_{cHess}=-85.6-111,45+105,6=-91.45 kJ/mol.

ΔG_{abc}=-R•T•ln(K)=-8,3144*298,15*ln(710349,826891739)=-33,4 kJ/mol;



A+2B 50% C+D+E

TERMODINAMIKA VINGRINĀJUMS V h PalmylCoA⁴⁻ hidrolīze par skābi HSCoA⁴⁻

Hidrolīzes līdzsvars: PalmitateCoA²⁻+H₂O=>CH₃(CH₂)₁₄COOH+HSCoA²⁻; ΔG_{aL}=-22.35 kJ/mol; at p H<5

$$\Delta G_{aL} = -R \cdot T \cdot \ln(K_{aL}) = -8,3144 \cdot 298,15 \cdot \ln(8235,15078047156) = -22,35 \text{ kJ/mol};$$

$$K_{aL} = K_{Lehninger} / [H_2O] = 455782,655095979 / 55,346 = 8235,15078047156 = \frac{[CH_3(CH_2)_{14}COOH][HSCoA^{4-}]}{[Palmitate-CoA^{4-}][H_2O]}$$

$$\Delta G_{Hess} = \Delta G^{\circ}_{HSCoA2} + \Delta G^{\circ}_{Palmitate} - (\Delta G_{PalmitateCoA4} + \Delta G_{H2O}) = -136,4 \text{ kJ/mol};$$

$$= -5,6616 - 1067,238 - (-784,9391 - 151,549) = -136,4 \text{ kJ/mol}; = -5,6616 - 1067,238 - 213,275 - (-784,9391 + 2 \cdot (-151,549 - 237,191)/2) = -112,5 \text{ kJ/mol};$$

Hidrolīzes līdzsvars: PalmitCoA³⁻+2H₂O=>CH₃(CH₂)₁₄COO⁻+HSCoA³⁻+H₃O⁺; ΔG_{Lehninger}=-32.3 kJ/mol; pH=7,36

HSCoA ⁴⁻	-	-	-7,26
HSCoA ³⁻	-	-	-5,6616
PalmitateCoA	-999,745	Palmitate-	-1003,54
PalmitateCoA	-784,9391	Palmitate-	-1067,238
C ₁₆ H ₃₂ O _{2s}	-891.5	452.4	-1026,383
C ₁₆ H ₃₂ O _{2li}	-838.1	-	-
H ₃ O ⁺	-285,81	-3,854	-213,275
H ₂ O	-285,85	69,9565	-237,191
H ₂ O	-286,65	-453,188	-151,549
HP ₂ O ₇ ³⁻	-2291,04	-1181,25	-1938,85
HP ₂ O ₇ ³⁻	-2247,8	46	-1940,66
H ₂ P ₂ O ₇ ²⁻	-	-	-1952,27

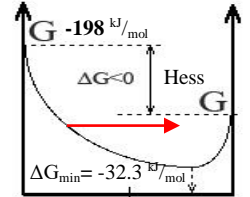
$$\Delta G_{Hess} = \Delta G^{\circ}_{HSCoA3} + \Delta G^{\circ}_{Palmitate} + \Delta G^{\circ}_{H3O+} - (\Delta G_{PalmitateCoA4} + 2\Delta G_{H2O}) = -112,5 \text{ kJ/mol}$$

$$K_a = K_{Lehninger} = \exp(32300/8,3144/298,15) = 455782,655095979$$

$$K_a = K_{Lehninger} = 455782,655 = \frac{[CH_3(CH_2)_{14}COO^-][HSCoA^{3-}][H_3O^+]}{[H_2O]^2 \cdot [Palmitate-CoA^{3-}]}$$
 pie pH=7,36

Endoergiska PalmitCoA⁴⁻ hidrolīzes Hesa brīvās enerģijas izmaiņa

negatīva ΔG_{aHess}=-198 kJ/mol pie pH=7,36, bet minimizējas ΔG_{min}=ΔG_a=-32,3 kJ/mol sasniedzot līdzsvara maisījumu: 455782,655=K_a. Lešatēle princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimums ΔG_{min}. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



$$\Delta G_{Hess} = \Delta G^{\circ}_{H2P2O73} - \Delta G^{\circ}_{AMP2} - \Delta G^{\circ}_{ATP4} - \Delta G^{\circ}_{H2O} = -1938,85 - 530,066 - (-2267,64 - 151,549) = -49,727 \text{ kJ/mol};$$

$$\Delta G_{mppL} = -R \cdot T \cdot \ln(K_{mppL}) = -8,3144 \cdot 298,15 \cdot \ln(1760959,91125033)/1000 = -35,65 \text{ kJ/mol};$$

$$K_{mppL} = K_{Lehninger} / [H_2O] = 97462087,2480605 / 55,346 = 1760959,91125033 = \frac{[H_2P_2O_7^{2-}][AMP]}{[H_2O] \cdot [ATP^{3-}]}$$

$$K_{Lehninger} = 97462087,2480605 = K_{ab} = 1/1,02604/10^{(-8)} = 97462087,2480605;$$

$$K_{ab} = K_{Lehninger} = \exp(-\Delta G_{Lehninger}/R/T) = \exp(45600/8,3144/298,15) = 97462087,2480605 = \frac{[HP_2O_7^{3-}][AMP^3-][H_3O^+]}{[H_2O]^2 \cdot [ATP^4-]}$$

Eksotermiska un eksoergiska pārnese Hesa brīvā enerģijas izmaiņa negatīva pH=7,36

ΔG_{transfer}=-111,45 kJ/mol, bet minimizējas sasniedzot līdzsvaru 97462087=K_{mpp} to ΔG_{min}=ΔG_{eq}=-45,6 kJ/mol:

ab ATP⁴⁻+2H₂O=>AMP²⁻+HP₂O₇³⁻+H₃O⁺. ΔG_{Lehninger}=-45,6 kJ/mol; pH=7.36;

$$\Delta G_{Hess} = \Delta G^{\circ}_{HP2O73} + \Delta G^{\circ}_{AMP2} + \Delta G^{\circ}_{H3O+} - \Delta G^{\circ}_{ATP4} - 2\Delta G^{\circ}_{H2O} = -111,45 \text{ kJ/mol};$$

$$= -213,275 - 1938,85 - 530,066 - (-2267,64 + 2 \cdot (-151,549)) = -111,45 \text{ kJ/mol}$$

abc CH₃(CH₂)₁₄COO⁻+HSCoA³⁻+ATP⁴⁻ =>HP₂O₇³⁻+AMP²⁻+PalmitateCoA³⁻;

$$pH=7,36; \Delta G_{abc} = -45,6 - 19,2 + 32,3 = -32,5 \text{ kJ/mol},$$

$$K_{abc} = 2310,5736 \cdot 97462087,2480605 \cdot 1/455782,655095979 = 494080,5;$$

$$K_{abc} = \exp(-\Delta G_{Lehninger}/R/T) = \exp(32500/8,3144/298,15) = 494079,2;$$

$$K_{abc} = 494079,2 = \frac{[HP_2O_7^{3-}][AMP^3-][Palmitate-CoA^3-]}{[CH_3(CH_2)_{14}COO^-][HSCoA^3-][ATP^4-]}$$

bba) HPO₄²⁻+ADP³⁻+Palmitate-CoA³⁻ =>CH₃(CH₂)₁₄COO⁻+HSCoA³⁻+ATP⁴⁻;

$$\Delta G_{bbaLehninger} = \Delta G_{bb} + \Delta G_a = 30,5 - 32,3 = -1,8 \text{ kJ/mol}; \text{reaktanti } -CH_3(CH_2)_{14}COO^- + HSCoA^{4-} + ATP^{4-}$$

$$= -1938,85 - 530,066 - 1067,238 - (-2267,64 - 5,6616 - 1067,238) = -195,6 \text{ kJ/mol}; \text{produkti } -ADP^{3-} + HPO_4^{2-} + Palmitate-CoA^4$$

$$\Delta G_{Hess} = \Delta G^{\circ}_{ATP4} + \Delta G^{\circ}_{HSCoA3} + \Delta G^{\circ}_{Palmitat} - \Delta G^{\circ}_{HP2O73} - \Delta G^{\circ}_{AMP2} - \Delta G^{\circ}_{PalmitateCoA3} = -195,6 \text{ kJ/mol};$$

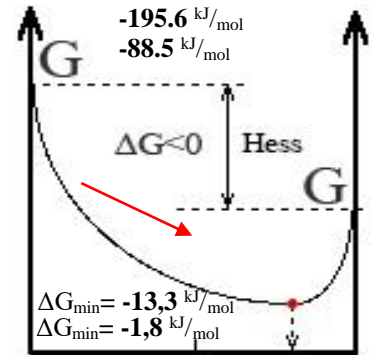
$$\Delta G_{Hess} = \Delta G^{\circ}_{ATP4} + \Delta G^{\circ}_{HSCoA3} + \Delta G^{\circ}_{Palmitat} - \Delta G^{\circ}_{HP042} - \Delta G^{\circ}_{ADP3} - \Delta G^{\circ}_{PalmitateCoA3} = -88,5 \text{ kJ/mol};$$

$$= -2267,64 - 5,6616 - 1067,238 - (-1067,238 - 1399,9 - 784,9391) = -88,5 \text{ kJ/mol}; \text{Biothermodynamic 2006; CRC 2010}$$

$$K_{bbaLehninger} = \exp(-\Delta G_{bbaLehninger}/R/T) = \exp(1800/8,3144/298,15) = 2,067 = \frac{[CH_3(CH_2)_{14}COO^-][HSCoA^3-][ATP^4-]}{[HPO_4^{2-}][ADP^3-][Palmitate-CoA^3-]}$$

ΔG_{bbaL}=-R·T·ln(K_{abbaL})=-8,3144·298,15·ln(2,0671)=-1,8 kJ/mol; Pārnese Hesa brīvās enerģijas izmaiņa pie pH=7,36 negatīva ΔG_{Hess}=-88,5 kJ/mol, bet minimizējas līdz ΔG_{ab}=-1,8 kJ/mol sasniedzot līdzsvara maisījumu:

2,067=K_{ab}. Lešatēle princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



cL $\text{CH}_3(\text{CH}_2)_{14}\text{COOH} + \text{HSCoA}^{2-} \Rightarrow \text{PalmitateCoA}^{2-} + \text{H}_2\text{O}$; $\Delta G_{\text{aL}} = 22,35 \text{ kJ/mol}$; at p H < 5

$$\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{HSCoA}^{2-}} + \Delta G^{\circ}_{\text{Palmitate}} - (\Delta G^{\circ}_{\text{PalmitateCoA}^{2-}} + \Delta G^{\circ}_{\text{H}_2\text{O}}) = -784,9391 - 151,549 - (-5,6616 - 1067,238) = 136,4 \text{ kJ/mol};$$

$$K_{\text{aLehninger}} = K_{\text{Lehninger}} = 455782,7 * [\text{H}_2\text{O}] = 2,194 * 10^{(-6)} * 55,34573393 = 0,000121429$$

$$\Delta G_{\text{eqLehn}} = -R \cdot T \cdot \ln(K_{\text{eqLehninger}}) = -8,3144 * 298,15 * \ln(0,000121429) = 22,35 \text{ kJ/mol};$$

c $\text{CH}_3(\text{CH}_2)_{14}\text{COO}^- + \text{HSCoA}^{3-} + \text{H}_3\text{O}^+ \Rightarrow \text{PalmitateCoA}^{3-} + 2 \text{H}_2\text{O}$; pH = 7,36; $\Delta G_{\text{Lehn}} = 32,3 \text{ kJ/mol}$;

$$\Delta G_{\text{aHess}} = \Delta G_{\text{Lehn}} + 2\Delta G_{\text{H}_2\text{O}} - \Delta G_{\text{H}_3\text{O}^+} = 784,9391 + 2 * -151,549 - (-5,6616 - 1067,238 - 213,275) = 198,14 \text{ kJ/mol};$$

$$K_{\text{c}} = K_{\text{Lehninger}} = \text{EXP}(-\Delta G_{\text{H}} / R/T) = \text{EXP}(-32300 / 8,3144 / 298,15) = 2,194 * 10^{-6} = \frac{[\text{H}_2\text{O}]^2 \cdot [\text{Palmitate-CoA}^{3-}]}{[\text{CH}_3(\text{CH}_2)_{14}\text{COO}^-] \cdot [\text{HSCoA}^{3-}] \cdot [\text{H}_3\text{O}^+]}$$

$$\Delta G_{\text{c}} = -RT \ln(K_{\text{c}}) = -8,3144 * 298,15 * \ln(2,194 * 10^{(-6)}) / 1000 = 32,3 \text{ kJ/mol};$$

aLehninger $\text{H}_2\text{P}_2\text{O}_7^{2-} + \text{H}_2\text{O} \Rightarrow \text{H}_2\text{PO}_4^- + \text{H}_2\text{PO}_4^-$; pH < 7,199; $\Delta G_{\text{cLehninger}} = -29,15 \text{ kJ/mol}$;

$$\Delta G_{\text{Hess}} = 2\Delta G^{\circ}_{\text{H}_2\text{PO}_4^-} - \Delta G^{\circ}_{\text{H}_2\text{P}_2\text{O}_7^{2-}} - \Delta G^{\circ}_{\text{H}_2\text{O}} = 2 * -1137,3 - (-1952,27 - 151,549) = -170,8 \text{ kJ/mol};$$

$$\Delta G_{\text{cLehninger}} = -R \cdot T \cdot \ln(K_{\text{cLehninger}}) = -8,3144 * 298,15 * \ln(127880,391691282) / 1000 = -29,15 \text{ kJ/mol};$$

$$K_{\text{cLehninger}} = K_{\text{Lehninger}} * [\text{H}_2\text{O}] = 2310,5736 * 55,34573393 = 127880,391691282 = \frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{H}_2\text{PO}_4^-]}{[\text{H}_2\text{O}] \cdot [\text{H}_2\text{P}_2\text{O}_7^{2-}]}$$

a $\text{HP}_2\text{O}_7^{3-} + 2\text{H}_2\text{O} \Rightarrow \text{HPO}_4^{2-} + \text{HPO}_4^{2-} + \text{H}_3\text{O}^+ + \Delta G + \text{Q}$; pH = 7,36; $\Delta G_{\text{Lehninger}} = -19,2 \text{ kJ/mol}$;

$$\Delta G_{\text{Hess}} = 2\Delta G^{\circ}_{\text{HPO}_4^{2-}} + \Delta G^{\circ}_{\text{H}_3\text{O}^+} - \Delta G^{\circ}_{\text{HP}_2\text{O}_7^{3-}} - 2\Delta G^{\circ}_{\text{H}_2\text{O}} = 2 * -1057,143 - 213,275 - (-1938,85 + 2 * (-151,549)) = -85,6 \text{ kJ/mol}$$

$$\Delta G_{\text{a}} = -R \cdot T \cdot \ln(K_{\text{a}}) = -8,3144 * 298,15 * \ln(3,2927 * 10^{(-8)}) / 1000 = 42,71 \text{ kJ/mol},$$

$$K_{\text{c}} = K_{\text{Lehninger}} = \text{exp}(-\Delta G_{\text{Lehninger}} / R/T) = \text{exp}(19200 / 8,3144 / 298,15) = 2310,5736 = \frac{[\text{HPO}_4^{2-}]^2 \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2 \cdot [\text{HP}_2\text{O}_7^{3-}]}$$

$$\Delta G_{\text{Habb}} = \Delta G^{\circ}_{\text{Glycerol}} + \Delta G^{\circ}_{\text{ATP4}} + \Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{ADP3}} - \Delta G^{\circ}_{\text{Glyol3P}} - \Delta G^{\circ}_{\text{H}_3\text{O}^+} = 101,724 \text{ kJ/mol};$$

$$= -154,912 - 2267,64 - 151,549 - (-1399,9 - 1062,65 - 213,275) = 101,724 \text{ kJ/mol};$$

$$= -171,35 - 2267,64 + (-237,191 - 151,549) / 2 - (-1399,9 - 1062,65 - 213,275) = 42,465 \text{ kJ/mol};$$

$\Delta G_{\text{Lehninger}} = -9,2 \text{ kJ/mol}$; Glycerol-3-phosphate²⁻ + H₂O + ΔG + Q ⇒ Glycerol + HP₂O₇³⁻; pH = 7.36;

bb $\text{ADP}^{3-} + \text{HP}_2\text{O}_7^{3-} + \text{H}_3\text{O}^+ \Rightarrow \text{ATP}^{4-} + 2 \text{H}_2\text{O}$; $\Delta G_{\text{bb}} = 30,5 \text{ kJ/mol}$;

Glycerol1P²⁻ + ADP³⁻ + H₃O⁺ ⇒ Glycerol + ATP⁴⁻ + H₂O; $\Delta G_{\text{abb}} = 21,3 \text{ kJ/mol}$; $\Delta G_{\text{abb}} = \Delta G_{\text{a}} + \Delta G_{\text{bb}} = -9,2 + 30,5 = 21,3 \text{ kJ/mol}$;

Glyc1P⁺ + ADP²⁻ ⇒ Glycerol + ATP³⁻; $\Delta G_{\text{Lehninger}} = 11,35 \text{ kJ/mol}$; $K_{\text{aL}} = 0,010267$

$$K_{\text{abbL}} = K_{\text{aL}} * [\text{H}_2\text{O}] = 0,000185506741578019 * 55,346 = 0,010267056119377$$

$$\Delta G_{\text{HabbL}} = \Delta G^{\circ}_{\text{Glyc}} + \Delta G^{\circ}_{\text{ATP4}} - \Delta G^{\circ}_{\text{ADP3}} - \Delta G^{\circ}_{\text{Glyol3P}} = -154,912 - 2267,64 - (-1399,9 - 1062,65) = 39,998 \text{ kJ/mol}$$

$$\Delta G_{\text{abbLehninger}} = -R \cdot T \cdot \ln(K_{\text{abbLehninger}}) = -8,3144 * 298,15 * \ln(0,010267056119377) / 1000 = 11,35 \text{ kJ/mol};$$

Fruc6P²⁻ + H₂O ⇒ Fruc + HP₂O₇³⁻ + ΔG + Q; $\Delta G_{\text{Lehninger}} = -15,9 \text{ kJ/mol}$

$$\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{Fruc}} + \Delta G^{\circ}_{\text{HP}_2\text{O}_7^{3-}} - \Delta G^{\circ}_{\text{Fruc6P}} - \Delta G^{\circ}_{\text{H}_2\text{O}} = -70,951 \text{ kJ/mol}$$

$$= -426,32 - 1089,28 - (-1293,1 - 151,549) = -70,951 \text{ kJ/mol exoergic}$$

$$\Delta H_{\text{Hess}} = \Delta H^{\circ}_{\text{Fruc}} + \Delta H^{\circ}_{\text{HP}_2\text{O}_7^{3-}} - \Delta H^{\circ}_{\text{Fruc6P}} - \Delta H^{\circ}_{\text{H}_2\text{O}} = -8,51 \text{ kJ/mol}$$

$$= -1264,32 - 1298,89 - (-2268,05 - 286,65) = -14,154 \text{ kJ/mol exoergic}$$

$$\Delta S_{\text{disperse}} = -\Delta H_{\text{Hess}} / T = 8,51 / 298,15 = 28,54 \text{ J/(mol K)};$$

$$\Delta S_{\text{Hess}} = \Delta S^{\circ}_{\text{Fruc}} + \Delta S^{\circ}_{\text{HP}_2\text{O}_7^{3-}} - \Delta S^{\circ}_{\text{Fruc6P}} - \Delta S^{\circ}_{\text{H}_2\text{O}} = 19,066 \text{ kJ/mol}$$

$$= -2893,39 - 810,792 - (-3270,06 - 453,188) = -14,154 \text{ kJ/mol exoergic}$$

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T * \Delta S_{\text{Hess}} = -8,51 - 298,15 * 0,019066 = -14,2 \text{ kJ/mol exoergic}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{Hess}} + \Delta S_{\text{disperse}} = 19,066 + 28,54 = 47,606 \text{ J/mol/K}$$

$$T * \Delta S_{\text{total}} = 0,047606 * 298,15 = 14,194 \text{ kJ/mol T} \Delta S_{\text{dispersed}}$$

Fruc6P²⁻ + ADP³⁻ + H₃O⁺ ⇒ Fruc + ATP⁴⁻ + H₂O; $\Delta G_{\text{Lehninger}} = 14,6 \text{ kJ/mol}$; pH = 7.36

$$\Delta G_{\text{Habb}} = \Delta G^{\circ}_{\text{Fruc}} + \Delta G^{\circ}_{\text{ATP4}} + \Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{ADP3}} - \Delta G^{\circ}_{\text{Fruc6P}} - \Delta G^{\circ}_{\text{H}_3\text{O}^+} = 85,426 \text{ kJ/mol};$$

$$= -401,66 - 2267,64 - 151,549 - (-1399,9 - 1293,1 - 213,275) = 85,426 \text{ kJ/mol};$$

Fruc6P⁺ + ADP²⁻ ⇒ Fruc + ATP³⁻; $\Delta G_{\text{Lehninger}} = 4,65 \text{ kJ/mol}$; $K_{\text{Lehninger}} = 0,153199602471084$

$$\Delta G_{\text{Habb}} = \Delta G^{\circ}_{\text{Fruc}} + \Delta G^{\circ}_{\text{ATP4}} - \Delta G^{\circ}_{\text{ADP3}} - \Delta G^{\circ}_{\text{Fruc6P}} = 23,7 \text{ kJ/mol};$$

$$= -401,66 - 2267,64 - (-1399,9 - 1293,1) = 23,7 \text{ kJ/mol};$$

$$K_{\text{abbL}} = K_{\text{abbL}} * [\text{H}_2\text{O}] = 0,00276803386823048 * 55,346 = 0,153199602471084$$

$$\Delta G_{\text{abbLehninger}} = -R \cdot T \cdot \ln(K_{\text{abbLehninger}}) = -8,3144 * 298,15 * \ln(0,153199602471084) / 1000 = 4,65 \text{ kJ/mol};$$

TERMODINAMIKA VINGRINĀJUMS V h Glycerol-3-fosfāta²⁻ un Fruktoze-6-fosfāta²⁻ hidrolīze

Aprēķināt ΔH_H ΔS_H ΔG_H standarta apstākļos 298.15 K vai ir **eksotermiska**, **atermiska**, **endotermiska**?

Fosfāta hidrolīzi **Glycerol3P²⁻** ar ūdeni! Miniet vai reakcija būs **eksoergiska** vai **endoergiska**!

$\Delta G_{Leninger} = -9,2 \text{ kJ/mol}$; Glycerol-3-phosphate²⁻+H₂O+ΔG+Q=>Glycerol+HPO₄²⁻; pH=7.36;

Viela $\Delta H_H^{\circ} \text{ kJ/mol}$ $\Delta S_H^{\circ} \text{ J/mol/K}$ $\Delta G_H^{\circ} \text{ kJ/mol}$; Glycerol-3-phosphate+H₂O+ΔG+Q=>Glycerol+ H₂PO₄⁻; pH<7.199;

H ₃ O ⁺	-285,81	-3,854	-213,275	Miščenko ; $\Delta G_H = \Delta G^{\circ}_{\text{Glycerol}} + \Delta G^{\circ}_{\text{HPO42-}} - \Delta G^{\circ}_{\text{Glyol3P}} - \Delta G^{\circ}_{\text{H2O}} = -14.294 \text{ kJ/mol}$
H ₂ O	-285,85	69,9565	-237,191	= -171,35-1057,143-(-1062,65-151,549)=-14.294 kJ/mol exoergic
H ₂ O	-286,65	-453,188	-151,549	B06; K_a=K_{Lehninger}=exp(9200/8,3144/298,15)=40,9055659488465
H ₂ PO ₄ ⁻	-1296,3	90,4	-1130,2	$\Delta G_H = \Delta G^{\circ}_{\text{Glycerol}} + \Delta G^{\circ}_{\text{H2PO4-}} - \Delta G^{\circ}_{\text{Glyol3P}} - \Delta G^{\circ}_{\text{H2O}} = -70.913 \text{ kJ/mol}$; exoergic
H ₂ PO ₄ ⁻	-1302,6	92,5	-1137,3	= -154,912-1130,2-(-1062,65-151,549)=-70.913 kJ/mol
HPO ₄ ²⁻	-1292,14	-33,47	-1089,28	Glycerol1P ²⁻ +ADP ³⁻ +H ₃ O ⁺ =>Glycerol+ATP ⁴⁻ +H ₂ O; $\Delta G_{abb}=21.3 \text{ kJ/mol}$;
HPO ₄ ²⁻	-1298,89	-810,792	-1057,143	$\Delta G_{abb} = \Delta G_a + \Delta G_{bb} = -9,2 + 30,5 = 21.3 \text{ kJ/mol}$;
ADP ³⁻	-2627,4	-4010	-1424,7	$K_{abb} = K_a K_{bb} = 40,9055659488465 * 4,535 * 10^{(-6)} = 0,000185506741578019$
ATP ⁴⁻	-3617,15	-4520	-2292,5	$\Delta G_{Habb} = \Delta G^{\circ}_{\text{Glyc}} + \Delta G^{\circ}_{\text{ATP4}} + \Delta G^{\circ}_{\text{H2O}} - \Delta G^{\circ}_{\text{ADP3}} - \Delta G^{\circ}_{\text{Glyol3P}} - \Delta G^{\circ}_{\text{H3O}} = 101.724 \text{ kJ/mol}$
ADP ³⁻	-2627,4	-4117,11	-1399,9	= -154,912-2267,64-151,549-(-1399,9-1062,65-213,275)=101.724 kJ/mol;
ATP ⁴⁻	-3617,1	-4526,1	-2267,64	= -171,35-2267,64+(-237,191-151,549)/2-(-1399,9-1062,65-213,275)=42.465 kJ/mol
Glyat3P ³⁻	-	-	-1347,73	Glyc1P ⁺ +ADP ²⁻ =>Glycerol+ATP ³⁻ ; $\Delta G_{Leninger} = 11.35 \text{ kJ/mol}$; $K_{aL} = 0.010267$
Glyt31P ⁴⁻	-1725,76	-2290,6	-2207,30	$K_{abbL} = K_{abL} * [H_2O] = 0,000185506741578019 * 55,346 = 0,010267056119377$
Glyat2P ³⁻	-	-	-1341,79	$\Delta G_{HabbL} = \Delta G^{\circ}_{\text{Glyc}} + \Delta G^{\circ}_{\text{ATP4}} - \Delta G^{\circ}_{\text{ADP3}} - \Delta G^{\circ}_{\text{Glyol3P}} = -154,912-2267,64-(-1399,9-1062,65) = 40 \text{ kJ/mol}$
Glyat2P ³⁻	-	-	-1333,2	BioThe06;
Glycerol	-	-	-171,35	Fruc6P ²⁻ +H ₂ O=>Fruc+HPO ₄ ²⁻ +ΔG+Q; $\Delta G_{Leninger} = -15,9 \text{ kJ/mol}$;
Glycerol	-679,85	-1760,65	-154,912	$\Delta G_{Hess} = \Delta G^{\circ}_{\text{Fruc}} + \Delta G^{\circ}_{\text{HPO42-}} - \Delta G^{\circ}_{\text{Fruc6P}} - \Delta G^{\circ}_{\text{H2O}} = -70.951 \text{ kJ/mol}$; exoergic
Glycerate ⁻	-	-	-452,31	= -426,32-1089,28-(-1293,1-151,549) = -70.951 kJ/mol exoergic
Glyol3P ²⁻	-	-	-1077,13	$K_a = K_{Lehninger} = \exp(15900/8,3144/298,15) = 610,3521266$
Glyol3P ²⁻	-1725,81	-2224,26	-1062,65	
Fruc16P ⁴⁻	-	-	-2206,78	$ADP^{2-} + H_2PO_4^- \Rightarrow ATP^{3-} + H_2O$; $\Delta G_{bLehninger} = 20,55 \text{ kJ/mol}$; pH<7,199
Fruc16P ⁴⁻	-3340,81	-3872,58	-2186,2	$K_{bL} = [H_2O] K_{Lehninger} = 0,000004535142 * 55,34573393 = 0,000251001$
Fruc6P ²⁻	-	-	-1315,74	$\Delta G_{bL} = -R \cdot T \cdot \ln(K_{bL}) = -8,3144 * 298,15 * \ln(0,000251001) / 1000 = 20.55 \text{ kJ/mol}$
Fruc6P ²⁻	-2268,05	-3270,06	-1293,1	
Fruc	-	-	-426,32	$bb ADP^{3-} + HPO_4^{2-} + H_3O^+ \Rightarrow ATP^4 + 2 H_2O$; pH=7.36; $\Delta G_{bb} = 30,5 \text{ kJ/mol}$;
Fruc	-1264,32	-2893,39	-401,66	$K_{bb} = K_{Leninger} = \exp(-\Delta G_{Lehning}/R/T) = \exp(-30500/8,3144/298,15) = 4,535 * 10^{-6}$;
Glc6P ²⁻	-2260	-3291,56	-1318,92	$\Delta G_{bbHess} = \Delta G^{\circ}_{\text{ATP4}} + 2\Delta G^{\circ}_{\text{H2O}} - \Delta G^{\circ}_{\text{HPO42-}} - \Delta G^{\circ}_{\text{ADP3}} - \Delta G^{\circ}_{\text{H3O}} = 99.58 \text{ kJ/mol}$
Glc6P ²⁻	-2279,314	-3297,196	-1296,262	= -2267,64-2*151,549-(-1057,143-1399,9-213,275)=99.58 kJ/mol;

$Fruc6P^{2-} + ADP^{3-} + H_3O^+ \Rightarrow Fruc + ATP^4 + H_2O$; $\Delta G_{Leninger} = 14,6 \text{ kJ/mol}$; $\Delta G_{abb} = \Delta G_a + \Delta G_{bb} = -15,9 + 30,5 = 14.6 \text{ kJ/mol}$;

$\Delta G_{Habb} = \Delta G^{\circ}_{\text{Fruc}} + \Delta G^{\circ}_{\text{ATP4}} + \Delta G^{\circ}_{\text{H2O}} - \Delta G^{\circ}_{\text{ADP3}} - \Delta G^{\circ}_{\text{Fruc6P}} - \Delta G^{\circ}_{\text{H3O}} = -401,66 - 2267,64 - 151,549 - (-1399,9 - 1293,1 - 213,275) = -85.426 \text{ kJ/mol}$;

$K_{abb} = \exp(-14600/8,3144/298,15) = 0,00276803386823048$;

$Fruc6P^{2-} \Rightarrow Glc6P^{2-}$; $\Delta G_{Leninger} = -1,7 \text{ kJ/mol}$; $\Delta G_H = \Delta G^{\circ}_{\text{Glc6P}} + \Delta G^{\circ}_{\text{Fruc6P}} = -1296,262 + 1293,1 = -3,162 \text{ kJ/mol}$;

$K_{Leninger} = \exp(-\Delta G_{Lehninger}/R/T) = \exp(1700/8,3144/298,15) = \exp(0,29783) = 1,98531$;

$\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = -8,3144 \cdot 298,15 \cdot \ln(1,98531) = -1,7 \text{ kJ/mol}$ eksotermiska un eksoergiska

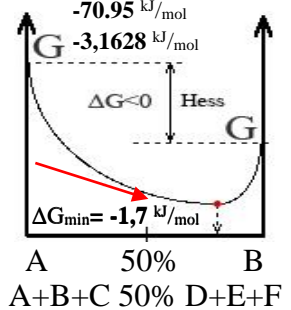
pārnesē uz Glc, Fruc6P, ATP⁴⁻ $\Delta G_{hidrolīze} = -3,173$, $-70,95$ un $-99,58 \text{ kJ/mol}$ Hesa brīvās

enerģijas izmaiņa negatīva, bet minimizējas $\Delta G_{min} = \Delta G_{eq} = -1,7$, $-15,9$ un $-30,5 \text{ kJ/mol}$

līdzsvara maisījumu $K_{Leninger} = 1,985 = \frac{[Glc6P^{2-}]}{[Fruc6P^{2-}]}$; $K_a = 610,35$; $K_{bLeninger} = 220500$;

$\Delta G_{min} = -30.5 \text{ kJ/mol}$ $\Delta G_{min} = -15.9 \text{ kJ/mol}$

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana maisījumā. Reaktanti A fruktoze-6-fosfāts produkti glikoze-6-fosfāts B Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



TERMODINAMIKA VINGRINĀJUMS V e (H₃CCO)₂O hidrolīze par acetātu CH₃COO⁻ pie pH<4,76, pH=7,36.
 CH₃COOOCCH₃+H₂O=2CH₃COOH; CH₃COOOCCH₃+3H₂O=2CH₃COO⁻+2H₃O⁺; ΔG_{Lehninger}=-91,1 kJ/mol ;

Viela	ΔH ^o _H /kJ/mol	ΔS ^o _H /J/mol/K	ΔG ^o _H /kJ/mol
H ₃ O ⁺	-285,81	-3,854	-213,275
H ₂ O	-285,85	69,9565	-237,191
H ₂ O	-286,65	-453,188	-151,549
(H ₃ CCO) ₂ O	-624,4	658,853	-820,81
(H ₃ CCO) ₂ O	-624,4	658,853	-820,81
H ₃ CCOO ⁻	-	-	-247,83
H ₃ CCOO ⁻	-486,836	-822,3	-241,663
H ₃ C-COOH	-484,09	159,83	-531,743

$$=2 \cdot -531,743 - (820 - 151,549) = -91,13 \text{ kJ/mol}$$

$$\text{CRC10; } \Delta G_H = 2\Delta G^\circ_{\text{CH}_3\text{COOH}} - \Delta G^\circ_{(\text{H}_3\text{CCO})_2\text{O}} - \Delta G^\circ_{\text{H}_2\text{O}} = -97,385 \text{ kJ/mol;}$$

$$\text{CRC10; } 2\Delta G^\circ_{\text{CH}_3\text{COOH}} + 91,1 - \Delta G^\circ_{\text{H}_2\text{O}} = \Delta G^\circ_{(\text{H}_3\text{CCO})_2\text{O}} = -728,91 \text{ kJ/mol;}$$

$$\text{B06; } \Delta H_{\text{Hess}} = 2 \cdot -531,743 - (-728,91 - 237,191) = -97,385 \text{ kJ/mol;}$$

$$\text{CRC10; } \Delta H_{\text{Hess}} = 2\Delta H^\circ_{\text{CH}_3\text{COOH}} - \Delta H^\circ_{(\text{H}_3\text{CCO})_2\text{O}} - \Delta H^\circ_{\text{H}_2\text{O}} = -57,93 \text{ kJ/mol;}$$

$$\Delta S_H = 2\Delta S^\circ_{\text{CH}_3\text{COOH}} - \Delta S^\circ_{(\text{H}_3\text{CCO})_2\text{O}} - \Delta S^\circ_{\text{H}_2\text{O}} = 113,995 \text{ J/mol/K;}$$

$$\text{CRC10; } = 2 \cdot 159,83 - (658,853 - 453,188) = 113,995 \text{ J/mol/K;}$$

$$\text{B06; } \Delta S_{\text{dispeHse}} = -\Delta H_{\text{Hess}}/T = 57130/298,15 = 191,615 \text{ J/mol/K;}$$

$$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -57,93 - 298,15 \cdot 0,113995 = -91,92 \text{ kJ/mol exoergic}$$

$$\Delta S_{\text{total}} = \Delta S_H + \Delta S_{\text{dispeHsed}} = 191,615 + 113,995 = 305,61 \text{ J/mol/K; } T \cdot \Delta S_{\text{total}} = 0,30561 \cdot 298,15 = 91,12 \text{ kJ/mol } T \Delta S_{\text{total}} \text{ dispersed}$$

$$K_{\text{eq}} = K_{\text{Lehninger}} = \exp(-\Delta G_{\text{Lehninger}}/R/T) = \exp(91100/8,3144/298,15) = \exp(36,75) = 9,12 \cdot 10^{15} = 10^{15,96};$$

Eksotermiskas un eksoerģiskas (H₃CCO)₂O hidrolīzes Hesa brīvās enerģijas izmaiņa negatīva pie pH<4,76 CH₃COOH ΔG_{hidrolīze}= -97,4 kJ/mol, bet minimizējas

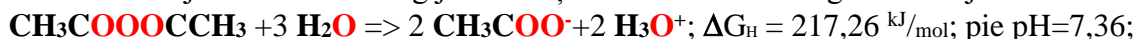
ΔG_{min}=ΔG_{eq}= -91,1 kJ/mol sasniedzot līdzsvara maisījumu

$$9,12 \cdot 10^{15} = 10^{15,96} = K_{\text{eq}} = \frac{[\text{CH}_3\text{COOH}]^2}{[\text{CH}_3\text{COOOCCH}_3] \cdot [\text{H}_2\text{O}]}$$

reaktanti A+B (H₃CCO)₂O+ H₂O

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min}

sasniegšana līdzsvara maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



$$\Delta G_{\text{Hess}} = 2\Delta G^\circ_{\text{CH}_3\text{COO}^-} + 2\Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{(\text{H}_3\text{CCO})_2\text{O}} - 3\Delta G^\circ_{\text{H}_2\text{O}} = 2 \cdot -241,663 + 2 \cdot -213,275 - (-728,91 + 3 \cdot -151,549) = 273,7 \text{ kJ/mol;}$$

$$= 2 \cdot -241,663 + 2 \cdot -213,275 - (-728,91 + 3 \cdot -151,549) = 273,7 \text{ kJ/mol endoergic}$$

$$\Delta H_H = 2\Delta H^\circ_{\text{CH}_3\text{COO}^-} + 2\Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{(\text{H}_3\text{CCO})_2\text{O}} - 3\Delta H^\circ_{\text{H}_2\text{O}} = -60,942 \text{ kJ/mol; } \Delta S_{\text{dispeHse}} = -\Delta H_H/T = 60,942/298,15 = 204,4 \text{ J/mol/K;}$$

$$= 2 \cdot -486,836 + 2 \cdot -285,81 - (-624,4 + 3 \cdot -286,65) = -60,942 \text{ kJ/mol;}$$

$$\Delta S_H = 2\Delta S^\circ_{\text{CH}_3\text{COO}^-} + 2\Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{(\text{H}_3\text{CCO})_2\text{O}} - 3\Delta S^\circ_{\text{H}_2\text{O}} = \Delta S_{\text{total}} = \Delta S_H + \Delta S_{\text{dispeHsed}} = -951,597 + 204,4 = -747,197 \text{ J/mol/K;}$$

$$= 2 \cdot -822,3 + 2 \cdot -3,854 - (658,853 + 3 \cdot -453,188) = -951,597 \text{ J/mol/K;}$$

$$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -60,942 - 298,15 \cdot -0,9516 = 222,777 \text{ kJ/mol; } T \Delta S_{\text{total}} = -0,747197 \cdot 298,15 = -222,777 \text{ kJ/mol } T \Delta S_{\text{total}} \text{ dispersed}$$

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(0,000102504)/1000 = 22,77 \text{ kJ/mol,}$$

$$K_{\text{eq}} = K_{\text{Lehninger}} [\text{H}_3\text{O}^+]^2 / [\text{H}_2\text{O}]^2 = 9,12 \cdot 10^{15} \cdot 10^{(-7,36 \cdot 2)} / 55,34573393^2 = 0,0056732 =$$

Endotermiska un endoerģiska anhidrīda hidrolīzes Hesa brīvās enerģijas izmaiņa

ΔG_{hidrolīze} pozitīva 223 kJ/mol, bet minimizējas līdz ΔG_{min}=ΔG_{eq}=12,82 kJ/mol sasniedzot

$$\text{līdzsvara maisījumu } K_{\text{eq}} = \frac{[\text{CH}_3\text{COO}^-]^2 \cdot [\text{H}_3\text{O}^+]^2}{[\text{CH}_3\text{COOOCCH}_3] \cdot [\text{H}_2\text{O}]^3} = 0,000102504. \text{ Lešatelje princips ir}$$

Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

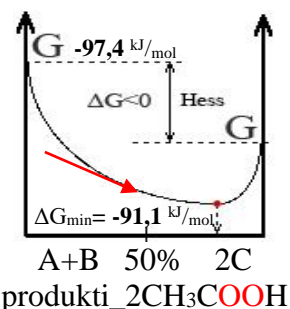
Reaktanti (H₃CCO)₂O+3 H₂O produkti 2 CH₃COO⁻+2 H₃O⁺.

$$\text{H}_2\text{P}_2\text{O}_7^{2-} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HP}_2\text{O}_7^{3-}; \Delta G_{\text{Hess}} = \Delta G^\circ_{\text{H}_3\text{O}^+} + \Delta G^\circ_{\text{HP}_2\text{O}_7^{3-}} - \Delta G^\circ_{\text{H}_2\text{P}_2\text{O}_7^{2-}} - \Delta G^\circ_{\text{H}_2\text{O}} = 25,73 \text{ kJ/mol;}$$

$$= -213,275 - 1938,85 - (-1940,66 - 237,191) = 25,73 \text{ kJ/mol;}$$

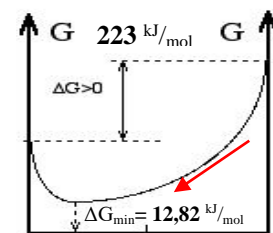
$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(10^{-8,463}) = 48,31 \text{ kJ/mol,}$$

$$K_{\text{eq}} = K_{\text{H}_2\text{P}_2\text{O}_7} / [\text{H}_2\text{O}] = 10^{-6,72} / 55,3 = 3,4436 \cdot 10^{-9} = 10^{-8,463} = \frac{[\text{H}_3\text{O}^+] \cdot [\text{HP}_2\text{O}_7^{3-}]}{[\text{H}_2\text{P}_2\text{O}_7^{2-}]} ;$$



reaktanti A+B 50% 2C produkti 2CH₃COOH

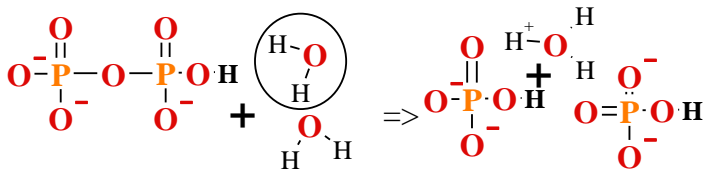
$$\frac{[\text{CH}_3\text{COO}^-]^2 \cdot [\text{H}_3\text{O}^+]^2}{[\text{CH}_3\text{COOOCCH}_3] \cdot [\text{H}_2\text{O}]^3}$$



A+3B 50% 2C+2D

TERMODINAMIKA VINGRINĀJUMS V e Pirofosfāta hidrolīze par $\text{HPO}_4^{2-} + \text{HPO}_4^{2-}$

Aprēķināt ΔH_H ΔS_H ΔG_H standarta apstākļos 298,15 K vai ir **eksotermiska**, **atermiska**, **endotermiska**? Fosfāts hidrolīzē no pirofosfāta ar ūdeni! Reakcija būs **eksoerģiska** vai **endoerģiska**!



Pirofosfāts	pKa	ΔH°	C
$\text{H}_4\text{P}_2\text{O}_7 = \text{H}^+ + \text{H}_3\text{P}_2\text{O}_7^-$	0,83	-9,2	-90
$\text{H}_3\text{P}_2\text{O}_7^- = \text{H}^+ + \text{H}_2\text{P}_2\text{O}_7^{2-}$	2,26	-5,0	-130
$\text{H}_2\text{P}_2\text{O}_7^{2-} = \text{H}^+ + \text{HP}_2\text{O}_7^{3-}$	6,72	0,5	-136
$\text{HP}_2\text{O}_7^{3-} = \text{H}^+ + \text{P}_2\text{O}_7^{4-}$	9,46	1,4	-141

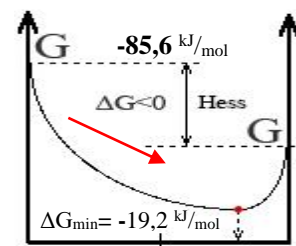
1. $\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{produkti}} - \Delta H^\circ_{\text{reaktanti}}$; $\text{HP}_2\text{O}_7^{3-} + 2\text{H}_2\text{O} \Rightarrow \text{HPO}_4^{2-} + \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$; $\Delta G_{\text{Lehningerpp}} = -19,2 \text{ kJ/mol}$; $\text{pH} = 7,36$
 Viela $\Delta H^\circ_{\text{Hess}} \text{ kJ/mol}$ $\Delta S^\circ_{\text{Hess}} \text{ J/mol/K}$ $\Delta G^\circ_{\text{Hess}} \text{ kJ/mol}$; $\text{HP}_2\text{O}_7^{3-} + \text{ADP}^{3-} \Rightarrow \text{HPO}_4^{2-} + \text{ATP}^{4-}$; $\Delta G_{\text{abbpp}} = 11,3 \text{ kJ/mol}$; $\text{pH} = 7,36$

H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
H_2PO_4^-	-1296,3	90,4	-1130,2
H_2PO_4^-	-1302,6	92,5	-1137,3
HPO_4^{2-}	-1292,14	-33,47	-1089,28
HPO_4^{2-}	-1298,89	-810,792	-1057,143
$\text{H}_2\text{P}_2\text{O}_7^{2-}$	-	-	-1952,27
$\text{HP}_2\text{O}_7^{3-}$	-	-	-1940,66
$\text{HP}_2\text{O}_7^{3-}$	-2291,04	-1181,25	-1938,85
adenosine	-626,66	-3316,57	362,172
adenosine	-	-	335,46

Miščenko; $\Delta G_{\text{abbpp}} = \Delta G_{\text{app}} + \Delta G_{\text{bb}} = -19,2 + 30,5 = 11,3 \text{ kJ/mol}$;
 $\Delta G_H = \Delta G^\circ_{\text{H}_3\text{O}^+} + 2\Delta G^\circ_{\text{HPO}_4^{2-}} - \Delta G^\circ_{\text{H}_2\text{P}_2\text{O}_7^{2-}} - 2\Delta G^\circ_{\text{H}_2\text{O}} = -85,6 \text{ kJ/mol}$;
 $= -213,275 + 2 \cdot (-1057,143) - (-1938,85) + 2 \cdot (-151,549) = -85,6 \text{ kJ/mol}$;

Endotermiska un endoerģiska HPO_4^{2-} pārnese no $\text{HP}_2\text{O}_7^{3-}$ Hesa brīvās enerģijas izmaiņa negatīva pie $\text{pH} = 7,36$ $\Delta G_{\text{Hess}} = -85,6$, bet minimizējas $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -19,2 \text{ kJ/mol}$ sasniegto līdzsvaru

$$K_{\text{app}} = K_{\text{Lehningerpp}} = 2310,57 = \frac{[\text{HPO}_4^{2-}]^2 \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2 \cdot [\text{HP}_2\text{O}_7^{3-}]}$$

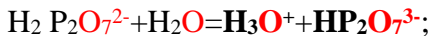


A+2B 50% 2C+D
 reaktanti $\text{HP}_2\text{O}_7^{3-} + 2\text{H}_2\text{O}$
 produkti $2\text{HPO}_4^{2-} + \text{H}_3\text{O}^+$

Līdzsvara sasniegšana ir Prigožina atraktors brīvās enerģijas izmaiņas minimums ΔG_{min} .

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

$$K_{\text{app}} = K_{\text{Lehningerpp}} = \exp(-\Delta G_{\text{Lehninger}}/R/T) = \exp(19200/8,3144/298,15) = 2310,57 = \frac{[\text{HPO}_4^{2-}]^2 \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2 \cdot [\text{HP}_2\text{O}_7^{3-}]}$$



$$K_{\text{eq}} = K_{\text{H}_2\text{P}_2\text{O}_7^{2-}} / [\text{H}_2\text{O}] = 10^{-6,72} / 55,3457 = 3,4436 \cdot 10^{-9} = 10^{-8,463} = \frac{[\text{H}_3\text{O}^+] \cdot [\text{HP}_2\text{O}_7^{3-}]}{[\text{H}_2\text{O}] \cdot [\text{H}_2\text{P}_2\text{O}_7^{2-}]}$$



$$K_{\text{pp}} = K_{\text{Lehningerpp}} / [\text{H}_2\text{O}] = 2310,57 / 55,34573393 = 41,748 = \frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{H}_2\text{PO}_4^-]}{[\text{H}_2\text{O}] \cdot [\text{H}_2\text{P}_2\text{O}_7^{2-}]}$$

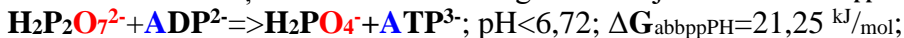
$$\Delta G_{\text{pp}} = -R \cdot T \cdot \ln(K_{\text{pp}}) = -8,3144 \cdot 298,15 \cdot \ln(41,74799819) = -9,251 \text{ kJ/mol};$$

$$\Delta G_{\text{Hess}} = 2\Delta G^\circ_{\text{H}_2\text{PO}_4^-} - \Delta G^\circ_{\text{H}_2\text{P}_2\text{O}_7^{2-}} - \Delta G^\circ_{\text{H}_2\text{O}} = -70,94 \text{ kJ/mol}; = 2 \cdot (-1130,2) - (-1952,27) - (-237,191) = -70,94 \text{ kJ/mol};$$

Eksotermiskas un eksoerģiskas $\text{H}_2\text{P}_2\text{O}_7^{2-}$ hidrolītiska Hesa brīvās enerģijas izmaiņa uz $\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-}$ negatīva $\Delta G_{\text{Hess}} = -70,94 \text{ kJ/mol}$, bet minimizējas sasniegto līdzsvara $\Delta G_{\text{min}} = \Delta G_{\text{pp}} = -9,251 \text{ kJ/mol}$ maisījumu bez $\text{pH} < 7,199$

$$41,748 = K_{\text{pp}} = \frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{H}_2\text{PO}_4^-]}{[\text{H}_2\text{O}] \cdot [\text{H}_2\text{P}_2\text{O}_7^{2-}]} \text{ Lešatelje princips ir Prigožina atraktora brīvās}$$

enerģijas izmaiņas minimuma ΔG_{min} sasniegšana maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars. $K_{\text{pp}} = 41,748$;



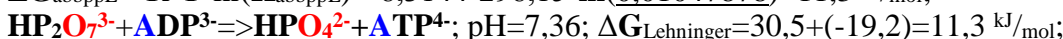
$$K_{\text{abbppPH}} = K_{\text{abbpp}} / [\text{H}_2\text{O}] = 0,01047878 / 55,3457 = 0,0001893$$

$$\Delta G_{\text{abbppPH}} = -R \cdot T \cdot \ln(K_{\text{abbppPH}}) = -8,3144 \cdot 298,15 \cdot \ln(0,0001893) / 1000 = 21,25 \text{ kJ/mol};$$

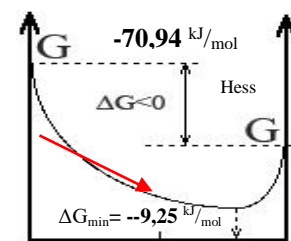
$$K_{\text{abbppL}} = \exp(-\Delta G_{\text{Lehninger}}/R/T) = \exp(-11300/8,3144/298,15) = 0,01047878$$

$$K_{\text{abl}} = K_{\text{aL}} \cdot K_{\text{bL}} = 41,748 \cdot 0,000250942 = 0,010476327;$$

$$\Delta G_{\text{abbppL}} = -R \cdot T \cdot \ln(K_{\text{abbppL}}) = -8,3144 \cdot 298,15 \cdot \ln(0,01047878) = 11,3 \text{ kJ/mol};$$



$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{HPO}_4^{2-}} + \Delta G^\circ_{\text{ATP}^{4-}} - \Delta G^\circ_{\text{HP}_2\text{O}_7^{3-}} - \Delta G^\circ_{\text{ADP}^{3-}} = -1057,143 - 2267,64 - (-1938,85 - 1399,9) = 13,967 \text{ kJ/mol};$$



A+B 50% 2C
 Reaktanti $\text{HP}_2\text{O}_7^{3-} + \text{H}_2\text{O}$
 produkti $\text{H}_2\text{PO}_4^- + \text{H}_2\text{PO}_4^-$

H₃O⁺	-285,81	-3,854	-213,275
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549
H₂PO₄⁻	-1296,3	90,4	-1130,2
H₂PO₄⁻	-1302,6	92,5	-1137,3
HPO₄²⁻	-1292,14	-33,47	-1089,28
HPO₄²⁻	-1298,89	-810,792	-1057,143

$$\Delta H_{\text{Hess}} = \Delta H^{\circ}_{\text{Gln}} + \Delta H^{\circ}_{\text{H}_2\text{O}} - \Delta H^{\circ}_{\text{Glu}} - \Delta H^{\circ}_{\text{NH}_4^+} = 19,5 \text{ kJ/mol}$$

$$= -809,12 - 286,65 - (-982,77 - 132,5) = 19,5 \text{ kJ/mol endothermic}$$

$$\Delta S_{\text{Hess}} = \Delta S^{\circ}_{\text{Gln}} + \Delta S^{\circ}_{\text{H}_3\text{O}^+} - \Delta S^{\circ}_{\text{Glu}} - \Delta S^{\circ}_{\text{NH}_4^+} = -842,478 \text{ J/mol/K}$$

$$= -2379,04 - 453,188 - (-2103,15 + 113,4) = -842,478 \text{ J/mol/K}$$

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = 19,5 - 298,15 \cdot (-0,842478) = 270,7 \text{ kJ/mol; endoergic}$$

$$\text{a) } \text{Glu}^- + \text{NH}_4^+ \Rightarrow \text{Gln} + \text{H}_2\text{O}; \Delta G_{\text{aLehninger}} = 14,2 \text{ kJ/mol; pH} = 7,36;$$

$$\Delta K_{\text{aLehninger}} = \exp(-\Delta G_{\text{aLehninger}}/R/T) = \exp(14200/8,3144/298,15) = 307,43$$

$$\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{Gln}} + \Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{Glu}} - \Delta G^{\circ}_{\text{NH}_4^+} = -99,8112 - 151,549 - (-355,712 - 79,3) = 183,7 \text{ kJ/mol;}$$

$$K_{\text{aLehninger}} = \exp(-\Delta G_{\text{aLehninger}}/R/T) = \exp(-14200/8,3144/298,15) = 0,003252737 =$$

Endoergiska Glu aminēšanas par Gln Hesa brīvās enerģijas izmaiņa ΔG_{Hess} pozitīva

$$\text{Gln} + \text{H}_2\text{O} \Rightarrow \text{Glu} + \text{NH}_4^+; \Delta G_{\text{aLehninger}} = -14,2 \text{ kJ/mol; } K_{\text{aLehninger}} = 307,43 =$$

183,65 kJ/mol, bet minimizējas līdz $\Delta G_{\text{min}} = \Delta G_{\text{aLehninger}} = 14,2 \text{ kJ/mol}$ sasniedzot līdzsvara

maisījumu: $K_{\text{aLehninger}} = 0,003252737 = [\text{Glu}^-] \cdot [\text{NH}_4^+] / [\text{Gln}] \cdot [\text{H}_2\text{O}]$. Eksoergiskas Glu aminēšana Gln ar **ATP⁴⁻** Hesa

AMP²⁻	-	-	-554,83
ADP³⁻	-2627,4	-4010	-1424,7
ATP⁴⁻	-3617,15	-4520	-2292,5
AMP²⁻	-1638,34	-3717,19	-530,066
ADP³⁻	-2627,4	-4117,11	-1399,9
ATP⁴⁻	-3617,1	-4526,1	-2267,64
NH₄⁺(aq)	-132,5	113,4	-79,3
Glu ²⁻	-	-	-372,16
Glu ⁻	-982,77	-2103,15	-355,712
Gln ⁻	-	-	-120,36
Gln	-809,12	-2379,04	-99,8112

brīvās enerģijas izmaiņa $\Delta G_{\text{Hess}} = -40,2 \text{ kJ/mol}$ negatīva pie pH < 7,199, bet minimizējas sasniedzot līdzsvara

maisījumu: $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -6,35 \text{ kJ/mol}$

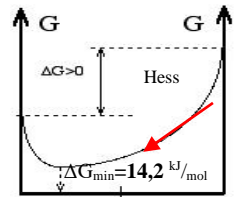
$$\frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{ADP}^{2-}] \cdot [\text{Gln}]}{[\text{Glu}^-] \cdot [\text{NH}_4^+] \cdot [\text{ATP}^{3-}]} = 12,959 = K_{\text{abLehninger}}$$

$$\text{a) } \text{ATP}^{3-} + \text{H}_2\text{O} \Rightarrow \text{ADP}^{2-} + \text{H}_2\text{PO}_4^-; \Delta G_{\text{bl}} = -20,55 \text{ kJ/mol;}$$

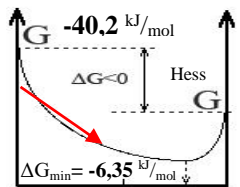
$$K_{\text{bLehninger}} = \exp(20550/8,3144/298,15) = 3984.$$

$$\Delta G_{\text{aLehninger}} = -RT \ln(K_{\text{aLehninger}}) = -8,3144 \cdot 298,15 \cdot \ln(3984) = -20,55 \text{ kJ/mol;}$$

$$K_{\text{a}} = K_{\text{Lehninger}} = \exp(-\Delta G_{\text{Lehninger}}/R/T) = \exp(30500/8,3144/298,15) = 220500$$



A+B 50% C+D



$$\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{H}_2\text{PO}_4^-} + \Delta G^{\circ}_{\text{Gln}} + \Delta G^{\circ}_{\text{ADP}^{2-}} - \Delta G^{\circ}_{\text{NH}_4^+} - \Delta G^{\circ}_{\text{Glu}} - \Delta G^{\circ}_{\text{ATP}^{3-}} = 20,292 \text{ kJ/mol;}$$

$$= -1137,3 - 120,36 - 1424,7 - (-79,3 - 355,712 - 2267,64) = 20,292 \text{ kJ/mol;}$$

$$K_{\text{aLehninger}} = K_{\text{Lehninger}} / [\text{H}_2\text{O}] = 220500 / 55,34573393 = 3984 =$$

$$\text{pH} < 7,199; \text{Glu}^- + \text{NH}_4^+ + \text{ATP}^{3-} \Rightarrow \text{Gln} + \text{ADP}^{2-} + \text{H}_2\text{PO}_4^-; \Delta G_{\text{abl}} = 14,2 - 20,55 = -6,35 \text{ kJ/mol}$$

$$\text{pH} < 7,199; K_{\text{abLehninger}} = K_{\text{aLehninger}} \cdot K_{\text{bLehninger}} = 3984 \cdot 0,003252737 = 12,959 =$$

$$\Delta G_{\text{abl}} = -R \cdot T \cdot \ln(K_{\text{abl}}) = -8,3144 \cdot 298,15 \cdot \ln(12,958904208) = -6,35 \text{ kJ/mol; pH} < 7,199$$

$$\Delta H_{\text{Hess}} = \Delta H^{\circ}_{\text{H}_2\text{PO}_4^-} + \Delta H^{\circ}_{\text{Gln}} + \Delta H^{\circ}_{\text{ADP}^{3-}} - \Delta H^{\circ}_{\text{NH}_4^+} - \Delta H^{\circ}_{\text{Glu}} - \Delta H^{\circ}_{\text{ATP}^{4-}} = -6,75 \text{ kJ/mol;}$$

$$= -1302,6 - 809,12 - 2627,4 - (-132,5 - 982,77 - 3617,1) = -6,75 \text{ kJ/mol exo}$$

$$\Delta S_{\text{Hess}} = -\Delta S^{\circ}_{\text{H}_2\text{PO}_4^-} + \Delta S^{\circ}_{\text{Gln}} + \Delta S^{\circ}_{\text{ADP}^{3-}} - \Delta S^{\circ}_{\text{NH}_4^+} - \Delta S^{\circ}_{\text{Glu}} - \Delta S^{\circ}_{\text{ATP}^{4-}} = 112,2 \text{ J/mol/K;}$$

$$= 92,5 - 2379,04 - 4117,11 - (-113,4 - 2103,15 - 4526,1) = 112,2 \text{ J/mol exo}$$

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = -6,75 - 298,15 \cdot 0,1122 = -40,2 \text{ kJ/mol endoergic;}$$

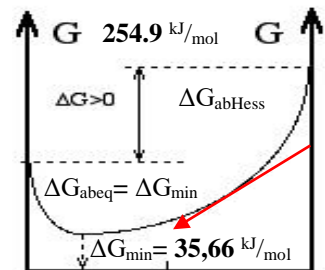
$$\text{Glu}^- + \text{NH}_4^+ + \text{ATP}^{4-} + \text{H}_2\text{O} \Rightarrow \text{Gln} + \text{ADP}^{3-} + \text{HPO}_4^{2-} + \text{H}_3\text{O}^+; \Delta G_{\text{ab}} = 14,2 - 30,5 = -16,3 \text{ kJ/mol;}$$

$$\Delta H_{\text{Hess}} = -809,12 - 2627,4 - 1298,89 - 285,81 - (-982,77 - 132,5 - 3617,1 - 285,85) = -3 \text{ kJ/mol;}$$

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = -3 - 298,15 \cdot (-0,8649) = 254,9 \text{ kJ/mol;}$$

$$\frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{ADP}^{2-}]}{[\text{H}_2\text{O}] \cdot [\text{ATP}^{3-}]}$$

$$\frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{ADP}^{2-}] \cdot [\text{Gln}]}{[\text{Glu}^-] \cdot [\text{NH}_4^+] \cdot [\text{ATP}^{3-}]}$$



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

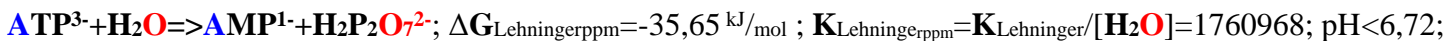
$$K_{\text{abLehninger}} = K_{\text{aLehninger}} \cdot K_{\text{bLehninger}} = 220500 \cdot 0,003252737 = 717,23 = \frac{[\text{HPO}_4^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{Gln}] \cdot [\text{H}_3\text{O}^+]}{[\text{Glu}^-] \cdot [\text{NH}_4^+] \cdot [\text{ATP}^{4-}] \cdot [\text{H}_2\text{O}]}$$

$$\Delta S_{\text{Hess}} = -2379,04 - 4117,11 - 810,792 - 3,854 - (-2103,15 + 113,4 - 4526,1 + 69,9565) = -864,9 \text{ J/mol/K;}$$

$$\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{Gln}} + \Delta G^{\circ}_{\text{ADP}^{3-}} + \Delta G^{\circ}_{\text{HPO}_4^{2-}} + \Delta H^{\circ}_{\text{H}_3\text{O}^+} - \Delta G^{\circ}_{\text{Glu}} - \Delta G^{\circ}_{\text{NH}_4^+} - \Delta G^{\circ}_{\text{ATP}^{4-}} - \Delta G^{\circ}_{\text{H}_2\text{O}} = 84,0718 \text{ kJ/mol;}$$

$$\Delta G_{\text{H}} = -99,8112 - 1057,143 - 1399,9 - 213,275 - (-355,712 - 79,3 - 2267,64 - 151,549) = 84,072 \text{ kJ/mol;}$$

$$\Delta G^{\circ}_{\text{abHess}} = (\Delta G^{\circ}_{\text{Hess}}) 84,07 \text{ (} \Delta H^{\circ}_{\text{Hess}}, \Delta S^{\circ}_{\text{Hess}} \text{) } 254,9 \text{ kJ/mol; } \Delta G_{\text{ab}} = 66,16 - 30,5 = 35,66 \text{ kJ/mol;}$$

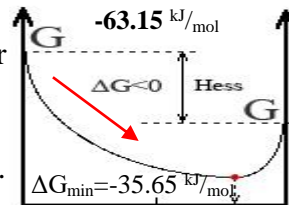


$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{H}_2\text{P}_2\text{O}_7} - \Delta G^\circ_{\text{AMP}^{2-}} - \Delta G^\circ_{\text{ATP}^{4-}} - \Delta G^\circ_{\text{H}_2\text{O}} = -1938,85 - 530,066 - (-2267,64 - 151,549) = -49,727 \text{ kJ/mol};$$

$$\Delta G_{\text{Lehningerppm}} = -R \cdot T \cdot \ln(K_{\text{Lehningerppm}}) = -8,3144 \cdot 298,15 \cdot \ln(1760968,37691823) / 1000 = -35,65 \text{ kJ/mol};$$

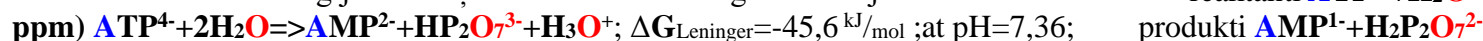
Eksotermiskas un eksoerģiskas ATP^{4-} hidrolīzes Hesa brīvās enerģijas izmaiņa negatīva par $\text{H}_2\text{P}_2\text{O}_7^{2-}$ $\Delta G_{\text{Hess}} = -63,15 \text{ kJ/mol}$, bet minimizējas $\Delta G_{\text{min}} = \Delta G_{\text{ppm}} = -35,65 \text{ kJ/mol}$ maisījumā

$$K_{\text{Lehningerppm}} = K_{\text{Lehn}} / [\text{H}_2\text{O}] = 97462087,25 / 55,34573 = 1760959,91125033 = \frac{[\text{H}_2\text{P}_2\text{O}_7^{2-}] \cdot [\text{AMP}^{1-}]}{[\text{H}_2\text{O}] \cdot [\text{ATP}^{3-}]}$$



Līdzsvara sasniegšana ir Prigožina atraktors brīvās enerģijas izmaiņas minimums ΔG_{min} .

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{H}_3\text{O}} + \Delta G^\circ_{\text{HP}_2\text{O}_7} + \Delta G^\circ_{\text{AMP}^{2-}} - \Delta G^\circ_{\text{ATP}^{4-}} - 2\Delta G^\circ_{\text{H}_2\text{O}} = -213,275 - 1938,85 - 530,066 - (-2267,64 + 2 \cdot -151,549) = -111,45 \text{ kJ/mol};$$

$$K_{\text{Lehningerppm}} = \exp(-\Delta G_{\text{Lehninger}} / R/T) = \exp(45600 / (8,3144 / 298,15)) = 97461823,49; \Delta S_{\text{dispersed}} = -\Delta H_H / T = 24,79 / 298,15 = 83,15 \text{ J/(mol K)};$$

$$\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{H}_3\text{O}} + \Delta H^\circ_{\text{HP}_2\text{O}_7} + \Delta H^\circ_{\text{AMP}^{2-}} - \Delta H^\circ_{\text{ATP}^{4-}} - 2\Delta H^\circ_{\text{H}_2\text{O}} = -285,81 - 2291,04 - 1638,34 - (-3617,1 + 2 \cdot -286,65) = -24,79 \text{ kJ/mol};$$

$$\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{H}_3\text{O}} + \Delta S^\circ_{\text{HP}_2\text{O}_7} + \Delta S^\circ_{\text{AMP}^{2-}} - \Delta S^\circ_{\text{ATP}^{4-}} - 2\Delta S^\circ_{\text{H}_2\text{O}} = -3,854 - 1181,25 - 3717,19 - (-4526,1 + 2 \cdot -453,188) = 530,182 \text{ J/(mol K)};$$

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = -24,79 - 298,15 \cdot 0,530182 = -182,9 \text{ kJ/mol}$$
 eksoerģiska;

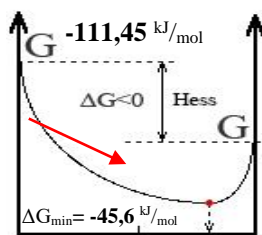
$$\Delta S_{\text{total}} = \Delta S_H + \Delta S_{\text{dispersed}} = 530,182 + 83,15 = 613,332 \text{ J/mol/K}; T \cdot \Delta S_{\text{total}} = 0,613332 \cdot 298,15 = 182,86 \text{ kJ/mol}$$
 TΔSn izkliede.

Līdzsvara sasniegšana brīvās enerģijas izmaiņas minimums vielu maisījuma attiecība Prigožina atraktora konstantes izteiksmē ir labvēlīga lielāka par vienu:

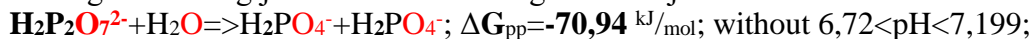
$$1 < K_{\text{Lehningerppm}} = \exp(-\Delta G_{\text{Lehninger}} / R/T) = \exp(45600 / (8,3144 / 298,15)) = 97462087,2480605 = \frac{[\text{HP}_2\text{O}_7^{3-}] \cdot [\text{AMP}^{2-}] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2 \cdot [\text{ATP}^{4-}]}$$

Eksotermiska un eksoerģiska pirofosfāta hidrolīzes Hesa brīvās enerģijas izmaiņa ΔG_{Hess} negatīva $-111,45 \text{ kJ/mol}$, bet minimizējas līdz $\Delta G_{\text{min}} = \Delta G_{\text{Lehningerppm}} = -45,6 \text{ kJ/mol}$ sasniedzot

$$\text{līdzsvara maisījumu } K_{\text{Lehningerppm}} = \frac{[\text{HP}_2\text{O}_7^{3-}] \cdot [\text{AMP}^{2-}] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2 \cdot [\text{ATP}^{4-}]} = 97462087,2480605.$$



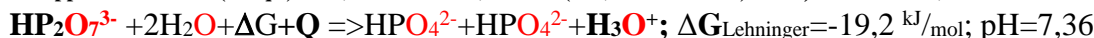
Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana. Enerģijas minimuma sasniegšanā iestājas līdzsvars.



$$\Delta G_{\text{Hess}} = 2\Delta G^\circ_{\text{H}_2\text{PO}_4} - \Delta G^\circ_{\text{H}_2\text{P}_2\text{O}_7} - \Delta G^\circ_{\text{H}_2\text{O}} = 2 \cdot -1130,2 - (-1952,27 - 237,191) = -70,94 \text{ kJ/mol};$$

$$K_{\text{pp}} = K_{\text{Lehningerpp}} / [\text{H}_2\text{O}] = 2310,57 / 55,34573393 = 41,748 = \frac{[\text{H}_2\text{PO}_4^-]^2}{[\text{H}_2\text{O}] \cdot [\text{H}_2\text{P}_2\text{O}_7^{2-}]};$$

$$\Delta G_{\text{ppL}} = -R \cdot T \cdot \ln(K_{\text{eqL}}) = -8,3144 \cdot 298,15 \cdot \ln(41,74799819) = -9,251 \text{ kJ/mol};$$



$$K_{\text{app}} = K_{\text{Lehningerpp}} = \exp(-\Delta G_{\text{Lehninger}} / R/T) = \exp(19200 / (8,3144 / 298,15)) = 2310,57 = \frac{[\text{HPO}_4^{2-}]^2 \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2 \cdot [\text{HP}_2\text{O}_7^{3-}]}$$

$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{H}_3\text{O}} + 2\Delta G^\circ_{\text{HPO}_4} - \Delta G^\circ_{\text{HP}_2\text{O}_7} - 2\Delta G^\circ_{\text{H}_2\text{O}} = -85,6 \text{ kJ/mol};$$

$$= -213,275 + 2 \cdot -1057,143 - (-1938,85 + 2 \cdot -151,549) = -85,6 \text{ kJ/mol}$$

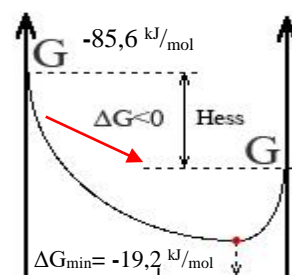
Eksoerģiska pirofosfāta $\text{HP}_2\text{O}_7^{3-}$ hidrolīzes Hesa brīvās enerģijas izmaiņa pie

$$\text{pH} = 7,36 \Delta G_{\text{Hess}} \text{ negatīva } -85,6 \text{ kJ/mol}, \text{ bet minimizējas } \Delta G_{\text{min}} = \Delta G_{\text{eq}} = -19,2 \text{ kJ/mol}$$

$$\text{sasniedzot līdzsvara maisījumu } K_a = \frac{[\text{HPO}_4^{2-}]^2 \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2 \cdot [\text{HP}_2\text{O}_7^{3-}]} = 2310,57. \text{ Lešatelje princips ir}$$

Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana maisījumā.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars



A+2B 50% C+2D
reaktanti $\text{HP}_2\text{O}_7^{3-} + 2\text{H}_2\text{O}$
produkti $2 \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$

pp) $\text{HP}_2\text{O}_7^{3-} + 2\text{H}_2\text{O} \Rightarrow \text{HPO}_4^{2-} + \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$; $\Delta G_{\text{ppLehninger}} = -19.2 \text{ kJ/mol}$; $\Delta G_{\text{ppHess}} = -85.6 \text{ kJ/mol}$;

b) $\text{ATP}^4 + 2\text{H}_2\text{O} \Rightarrow \text{AMP}^{2-} + \text{HP}_2\text{O}_7^{3-} + \text{H}_3\text{O}^+$; $\Delta G_{\text{bLehninger}} = -45.6 \text{ kJ/mol}$; $\Delta G_{\text{bHess}} = -111.45 \text{ kJ/mol}$;

ppb) $\text{ATP}^4 + 4\text{H}_2\text{O} \Rightarrow \text{AMP}^{2-} + \text{HPO}_4^{2-} + \text{HPO}_4^{2-} + 2\text{H}_3\text{O}^+$; $\Delta G_{\text{ppbL}} = -64.6 \text{ kJ/mol}$; $\Delta G_{\text{ppbHess}} = -197.05 \text{ kJ/mol}$;

$\Delta G_{\text{ppbH}} = \Delta G_{\text{ppH}} + \Delta G_{\text{bH}} = -85.6 - 111.45 = -197.05 \text{ kJ/mol}$;

$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{AMP}^{2-}} + 2\Delta G^\circ_{\text{H}_3\text{O}^+} + 2\Delta G^\circ_{\text{HPO}_4^{2-}} - \Delta G^\circ_{\text{ATP}^4} - 4\Delta G^\circ_{\text{H}_2\text{O}} = -197 \text{ kJ/mol}$;

$= -530,066 - 2 \cdot 213,275 + 2 \cdot (-1057,143) - (-2267,64 + 4 \cdot (-151,549)) = -197.066 \text{ kJ/mol}$

Eksotermiskas un eksoerģiskas $\text{ATP}^4 + 4\text{H}_2\text{O}$ hidrolīzes Hesa brīvās enerģijas izmaiņa

negatīva $\Delta G_{\text{ppb}} = -197 \text{ kJ/mol}$, bet $\Delta G_{\text{min}} = \Delta G_{\text{ppbL}} = -64.6 \text{ kJ/mol}$; minimizējas

sasniedzot līdzsvaru: $K_{\text{ppbLehninger}} = 207737828686$. produkti $\text{AMP}^{2-} +$

$K_{\text{ppb}} = K_{\text{Lehningerppb}} = \exp(-\Delta G_{\text{Lehningerppb}}/R/T) = \exp(64600/8,3144/298,15) = 207737828686 =$

bb) $\text{ADP}^{3-} + \text{HPO}_4^{2-} + \text{H}_3\text{O}^+ \Rightarrow \text{ATP}^4 + 2\text{H}_2\text{O}$; $\Delta G_{\text{bbLehninger}} = 30,5 \text{ kJ/mol}$;

$K_{\text{bbLehninger}} = \exp(-\Delta G_{\text{bbLehninger}}/R/T) = \exp(-30500/8,3144/298,15) = 0.000004535142 =$

$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{ATP}^4} - 2\Delta G^\circ_{\text{H}_2\text{O}} - \Delta G^\circ_{\text{ADP}^{3-}} - \Delta G^\circ_{\text{HPO}_4^{2-}} - \Delta G^\circ_{\text{H}_3\text{O}^+} = 99,58 \text{ kJ/mol}$;

$= -1399,9 - 1057,143 - 213,275 - (-2267,64 + 2 \cdot (-151,549)) = 99,58 \text{ kJ/mol}$;

Eksotermiskas un eksoerģiskas ADP^{3-} fosforilēšanas Hesa brīvās enerģijas izmaiņa

pozitīva pie pH 7,36 $\Delta G_{\text{pšrnese}} = 99,58 \text{ kJ/mol}$, bet minimizējas $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = 30,5 \text{ kJ/mol}$

sasniedzot līdzsvara maisījumu: $K_{\text{bbLehninger}} = 0.000004535142$: Līdzsvara sasniegšana ir

Prigožina atraktors brīvās enerģijas izmaiņas minimums ΔG_{min} .

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

reaktanti_

$\text{HP}_2\text{O}_7^{3-} + \text{ADP}^{3-} \Rightarrow \text{HPO}_4^{2-} + \text{ATP}^4$; $\Delta G_{\text{abpp}} = \Delta G_{\text{app}} + \Delta G_{\text{bb}} = -19,2 + 30,5 = 11,3 \text{ kJ/mol}$; pH=7,36

$\Delta G_{\text{H}} = \Delta G^\circ_{\text{HPO}_4^{2-}} + \Delta G^\circ_{\text{ATP}^4} - \Delta G^\circ_{\text{HP}_2\text{O}_7^{3-}} - \Delta G^\circ_{\text{ADP}^{3-}} = -1057,143 - 2267,64 - (-1938,85 - 1399,9) = 13,967 \text{ kJ/mol}$;

$K_{\text{abpp}} = K_{\text{app}} K_{\text{bbLehninger}} = 2310,57 \cdot 0,000004535142 = 0,010478763$

$\Delta G_{\text{abpp}} = -R \cdot T \cdot \ln(K_{\text{abpp}}) = -8,3144 \cdot 298,15 \cdot \ln(0,010478763) / 1000 = 11,3 \text{ kJ/mol}$;

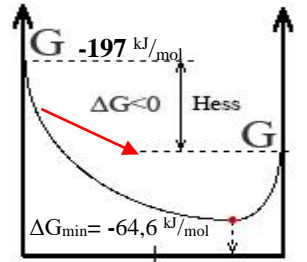
Endotermiskas un endoerģiskas fosfāta pārneses Hesa brīvās enerģijas izmaiņa pozitīva

$\Delta G_{\text{transfer}} = 13,967 \text{ kJ/mol}$, bet minimizējas līdz $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = 11,3 \text{ kJ/mol}$ sasniegšanā līdzsvara

maisījumu: $K_{\text{abpp}} = 0,010478763 = \frac{[\text{HPO}_4^{2-}] \cdot [\text{ATP}^4]}{[\text{HP}_2\text{O}_7^{3-}] \cdot [\text{ADP}^{3-}]}$. Lešatelje princips ir Prigožina

atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā. reaktanti $\text{HP}_2\text{O}_7^{3-} + \text{ADP}^{3-}$

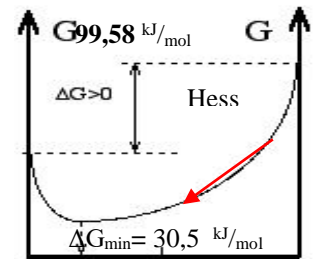
Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



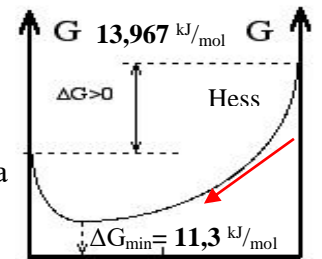
A+2B 50% 2C+D
reaktanti $\text{ATP}^4 + 4\text{H}_2\text{O}$
 $\text{HPO}_4^{2-} + \text{HPO}_4^{2-} + 2\text{H}_3\text{O}^+$

$$\frac{[\text{HPO}_4^{2-}]^2 \cdot [\text{H}_3\text{O}^+]^2 \cdot [\text{AMP}^{2-}]}{[\text{H}_2\text{O}]^4 \cdot [\text{ATP}^4]}$$

$$\frac{[\text{H}_2\text{O}]^2 \cdot [\text{ATP}^4]}{[\text{HPO}_4^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]}$$



A+B+C 50% D+2E
 $\text{ADP}^{3-} + \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$
products $\text{ATP}^4 + 2\text{H}_2\text{O}$



A+B 50% C+D

produkti $\text{HPO}_4^{2-} + \text{ATP}^4$



$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{ATP}^{3-}} + \Delta G^\circ_{\text{H}_2\text{O}} - \Delta G^\circ_{\text{H}_2\text{PO}_4^-} - \Delta G^\circ_{\text{ADP}^{2-}} = -2267,64 - 151,549 - (-1399,9 - 1057,143) = 37,85 \text{ kJ/mol}$;

$= K_{\text{bbLehninger}} = \exp(-\Delta G_{\text{Lehninger}}/R/T) = \exp(-30500/8,3144/298,15) = 0,00004535142$

$\frac{[\text{H}_2\text{O}] \cdot [\text{ATP}^{3-}]}{[\text{H}_2\text{PO}_4^-] [\text{ADP}^{2-}]} = K_{\text{bbL}} = K_{\text{bbLehninger}} [\text{H}_2\text{O}] = 0,00004535142 * 55,3457339 = 0,000251001$.

$\Delta G_{\text{bL}} = -R \cdot T \cdot \ln(K_{\text{bL}}) = -8,3144 * 298,15 * \ln(0,000250993)/1000 = 20,5512 \text{ kJ/mol}$;

Endotermiska un endoergiska ADP^{2-} fosforilēšanas Hesa brīvās enerģijas izmaiņa

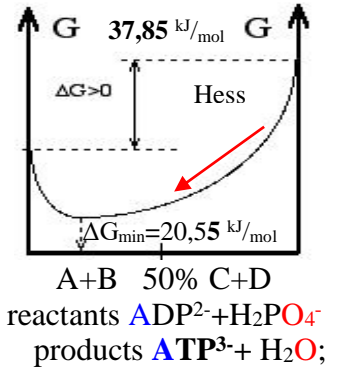
negatīva bez pH=? $\Delta G_{\text{transfer}} = 37,85 \text{ kJ/mol}$,

bet minimizējas līdz $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = 20,55 \text{ kJ/mol}$ sasniedzot līdzsvara maisījumu:

$K_{\text{bL}} = K_{\text{bbLehninger}} [\text{H}_2\text{O}] = 0,000250993 = \frac{[\text{H}_2\text{O}] \cdot [\text{ATP}^{3-}]}{[\text{H}_2\text{PO}_4^-] [\text{ADP}^{2-}]}$

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{ATP}^{3-}} - 2\Delta G^\circ_{\text{H}_2\text{O}} - \Delta G^\circ_{\text{ADP}^{2-}} - \Delta G^\circ_{\text{HPO}_4^{2-}} - \Delta G^\circ_{\text{H}_3\text{O}^+} = -1399,9 - 1057,143 - 2(13,275) - (-2267,64 + 2 * -151,549) = 99,58 \text{ kJ/mol}$;

$\frac{[\text{H}_2\text{O}]^2 \cdot [\text{ATP}^{4-}]}{[\text{HPO}_4^{2-}] [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]} = K_{\text{bbLehninger}} = \exp(-\Delta G_{\text{Lehninger}}/R/T) = \exp(-30500/8,3144/298,15) = 0,00004535142$

Endotermiska un endoergiska ADP^{3-} fosforilēšanas Hesa brīvās enerģijas izmaiņa

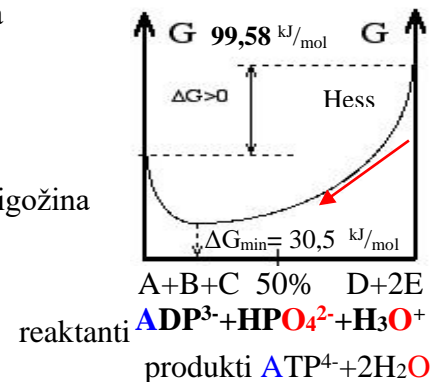
pozitīva pie pH vērtības 7,36 $\Delta G_{\text{transfer}} = 99,58 \text{ kJ/mol}$, bet minimizējas līdz

$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = 30,5 \text{ kJ/mol}$ sasniedzot līdzsvara maisījumu:

$K_{\text{bbLehninger}} = 0,00004535142 = \frac{[\text{H}_2\text{O}]^2 \cdot [\text{ATP}^{4-}]}{[\text{HPO}_4^{2-}] [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]}$:Lešatelje princips ir Prigožina

atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



b0) $\text{ATP}^{3-} + \text{H}_2\text{O} \Rightarrow \text{ADP}^{2-} + \text{H}_2\text{PO}_4^-$; $\Delta G_{b0\text{Lehninger}} = -20,55 \text{ kJ/mol}$; $K_{b0\text{Lehninger}} = K_{b\text{Lehninger}}/[\text{H}_2\text{O}] = 3984,1$; bez pH=?.

$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{ADP}^{3-}} + \Delta G^\circ_{\text{HPO}_4^{2-}} - \Delta G^\circ_{\text{ATP}^{4-}} - \Delta G^\circ_{\text{H}_2\text{O}} = -1399,9 - 1057,143 - (-2267,64 - 151,549) = -37,854 \text{ kJ/mol};$$

$$K_{b0\text{Lehninger}} = K_{b\text{Lehninger}}/[\text{H}_2\text{O}] = 220500,2/55,3457 = 3984,1 = \frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{ADP}^{3-}]}{[\text{H}_2\text{O}] \cdot [\text{ATP}^{4-}]}$$

$$\Delta G_{b0\text{Lehninger}} = -R \cdot T \cdot \ln(K_{b0\text{Lehninger}}) = -8,3144 \cdot 310,15 \cdot \ln(3984,052962)/1000 = -21,38 \text{ kJ/mol};$$

b) $\text{ATP}^{4-} + 2\text{H}_2\text{O} \Rightarrow \text{ADP}^{3-} + \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$; $\Delta G_{b\text{Lehninger}} = -30,5 \text{ kJ/mol}$; $K_{b\text{Lehninger}} = K_{\text{Lehninger}}[\text{H}_2\text{O}]/[\text{H}_3\text{O}^+] = 220500,2$;

$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{ADP}^{3-}} + \Delta G^\circ_{\text{HPO}_4^{2-}} + \Delta G^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{\text{ATP}^{4-}} - 2\Delta G^\circ_{\text{H}_2\text{O}} = -1399,9 - 1057,143 - 213,275 - (-2267,64 + 2 \cdot -151,549) = -99,58 \text{ kJ/mol};$$

T=298,15 K (25° C);

$$K_{b\text{Lehninger}} = \exp(-\Delta G_{b\text{Lehninger}}/R/T) = \exp(30500/8,3144/298,15) = 220500,2 = \frac{[\text{HPO}_4^{2-}][\text{ADP}^{3-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2[\text{ATP}^{4-}]}$$

T=310,15 K (37° C); $K_{\text{Lehninger}} = \exp(-\Delta G_{\text{Lehninger}}/R/T) = \exp(30500/8,3144/310,15) = 136983,2474$;

Eksotermiska un eksoergiska ATP^{2-} hidrolīzes Hesa brīvās enerģijas izmaiņa

$\Delta G_{\text{Hess}} = \Delta G_{\text{Hess}} = -37,85 \text{ kJ/mol}$ $\Delta G_{\text{Hess}} = -99,58 \text{ kJ/mol}$ negatīva bez pH = 7,36, bet minimizējas

$\Delta G_{\text{min}} = \Delta G_{\text{eq}} - 21,38 \text{ kJ/mol}$ un $-30,5 \text{ kJ/mol}$ sasniedzot līdzsvara maisījumu

$$K_{b0\text{Lehninger}} = K_{b\text{Lehninger}}/[\text{H}_2\text{O}] = 3984,1 = \frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{ADP}^{3-}]}{[\text{H}_2\text{O}] \cdot [\text{ATP}^{4-}]}$$

$$\text{un } K_{b\text{Lehninger}} = 220500,2 = \frac{[\text{HPO}_4^{2-}][\text{ADP}^{3-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2 \cdot [\text{ATP}^{4-}]}$$

Lešateljē princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{creatine}} + \Delta G^\circ_{\text{HPO}_4^{2-}} - \Delta G^\circ_{\text{Pcreatine}} - \Delta G^\circ_{\text{H}_2\text{O}} = 107,69 - 1089,28 - (-689,08 - 237,191) = -55,3 \text{ kJ/mol};$$

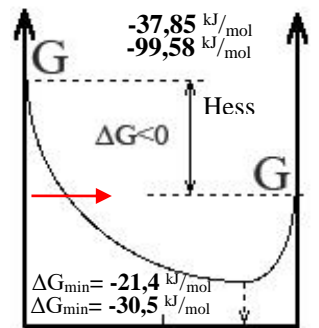
$$\Delta G_{\text{Hess}} = 107,69 - 1089,28 - (-689,08 - 237,191) = -55,3 \text{ kJ/mol};$$

$$\Delta G_{\text{Hess}} = 126,1868 - 1089,28 - (-736,4 - 237,191) = 10,5 \text{ kJ/mol};$$

$$\Delta G_{\text{CRC Hess}} = \Delta G^\circ_{\text{creatine}} + \Delta G^\circ_{\text{ATP}^{3-}} - \Delta G^\circ_{\text{Pcreatine}} - \Delta G^\circ_{\text{ADP}^{2-}} = -71,03 \text{ kJ/mol}; \text{ exoergic CRC2010}$$

$$= 107,69 - 2292,5 - (-689,08 - 1424,7) = -71,03 \text{ kJ/mol CRC 2010}$$

$$\Delta G_{\text{CRC}} = -R \cdot T \cdot \ln(K_{\text{CRC}}) = -8,3144 \cdot 310,15 \cdot \ln(173)/1000 = -13,3 \text{ kJ/mol};$$



A+2B 50% C+D+E
 reaktanti $\text{ATP}^{4-} + 2\text{H}_2\text{O}$
 produkti $\text{ADP}^{3-} + \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$

bd) $\text{ADP}^{2-} + \text{H}_2\text{O} \Rightarrow \text{AMP}^- + \text{H}_2\text{PO}_4^-$; $\Delta G_{\text{bd}} = -22.85 \text{ kJ/mol}$; without pH=?

$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{H}_2\text{PO}_4^-} + \Delta G^\circ_{\text{AMP}^-} - \Delta G^\circ_{\text{ADP}^{2-}} - \Delta G^\circ_{\text{H}_2\text{O}} = -530,066 - 1130,2 - (-1399,9 - 151,549) = -108,8 \text{ kJ/mol};$$

$$\Delta G_{\text{bd}} = -R \cdot T \cdot \ln(K_{\text{bd}}) = -8,3144 \cdot 298,15 \cdot \ln(10075,75322)/1000 = -22,85 \text{ kJ/mol};$$

$$K_{\text{bd}} = \frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{AMP}^-]}{[\text{H}_2\text{O}] \cdot [\text{ADP}^{2-}]}$$

$$\Delta G_{\text{bd}} = -R \cdot T \cdot \ln(K_{\text{bd}}) = -8,3144 \cdot 298,15 \cdot \ln(10075,75322)/1000 = -22,85 \text{ kJ/mol};$$

$$K_{\text{bdLeninger}} = \exp(-\Delta G_{\text{Lehninger}}/R/T) = \exp(32800/8,3144/298,15) = 557649,957 = \frac{[\text{H}_2\text{O}]^2 \cdot [\text{ADP}^{3-}]}{[\text{H}_3\text{O}^+] \cdot [\text{AMP}^{2-}]}$$

bd) $\text{ADP}^{3-} + 2\text{H}_2\text{O} \Rightarrow \text{AMP}^{2-} + \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$; pH=7,36; $\Delta G_{\text{Lehninger}} = -32.8 \text{ kJ/mol}$;

$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{H}_3\text{O}^+} + \Delta G^\circ_{\text{HPO}_4^{2-}} + \Delta G^\circ_{\text{AMP}^{2-}} - \Delta G^\circ_{\text{ADP}^{3-}} - 2\Delta G^\circ_{\text{H}_2\text{O}} = -213,275 - 1057,143 - 530,066 - (-1399,9 + 2 \cdot (-151,549)) = -97,49 \text{ kJ/mol};$$

H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
H_2PO_4^-	-1296,3	90,4	-1130,2
H_2PO_4^-	-1302,6	92,5	-1137,3
HPO_4^{2-}	-1292,14	-33,47	-1089,28
HPO_4^{2-}	-1298,89	-810,792	-1057,143
ADP^{3-}	-2627,4	-4010	-1424,7
AMP^{2-}	-	-	-554,83
ADP^{3-}	-2627,4	-4117,11	-1399,9
AMP^{2-}	-1638,34	-3717,19	-530,066
Adenosin	-	-	335,46
Adenosine	-626,66	-3316,57	362,172

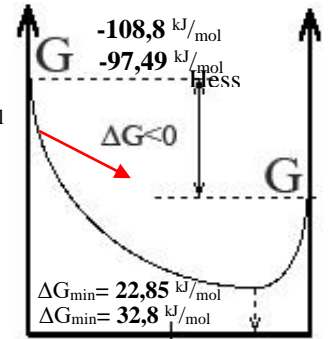
Eksotermiskas, eksoergiskas ADP^{2-} un ADP^{3-} hidrolīzes bez pH=? un pie pH=7,36 Hesa brīvās enerģijas izmaiņa negatīva $\Delta G_{\text{hidrolīze}} = -108,8 \text{ kJ/mol}$ un $-97,49 \text{ kJ/mol}$, bet minimizējas

$\Delta G_{\text{min}} = \Delta G_{\text{bd}} = -22,8 \text{ kJ/mol}$ un $-32,8 \text{ kJ/mol}$ sasniegto

līdzsvara maisījumu $K_{\text{bd}} = 10075,75322$ un

$$K_{\text{bdLeninger}} = 557649,957.$$

reaktanti $\text{ADP}^{2-} + \text{H}_2\text{O}$ A+B 50% C+D
 produkti $\text{H}_2\text{PO}_4^- + \text{AMP}^{2-}$
 reaktanti $\text{ADP}^{3-} + 2\text{H}_2\text{O}$ A+2B 50% C+D+E
 produkti $\text{AMP}^{2-} + \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$



Līdzsvara sasniegšana ir Prigožina atraktors brīvās enerģijas izmaiņas minimums ΔG_{min} .

Brīvās enerģijas minimuma sasniegšanā iestājas līdzsvars.

Am) $\text{AMP}^{2-} + \text{H}_2\text{O} \Rightarrow \text{Adenosine} + \text{HPO}_4^{2-}$; $\Delta G_{\text{Lehninger}} = -14.2 \text{ kJ/mol}$; $K_{\text{Am}} = \exp(14200/8,3144/298,15) = 307,43344$;

$$K_{\text{Am}} = \frac{[\text{HPO}_4^{2-}] \cdot [\text{Adenosin}]}{[\text{H}_2\text{O}] \cdot [\text{AMP}^{2-}]} = K_{\text{Leninger}} = \exp(14200/8,3144/298,15) = 307,43344 \text{ at pH}=7,36.$$

$$\Delta G_{\text{HessAm}} = \Delta G^\circ_{\text{adenosin}} + \Delta G^\circ_{\text{HPO}_4^{2-}} - \Delta G^\circ_{\text{AMP}^{2-}} - \Delta G^\circ_{\text{H}_2\text{O}} = 362,172 - 1089,28 - (-530,066 - 151,549) = -45,5 \text{ kJ/mol};$$

AmL) $\text{AMP}^- + \text{H}_2\text{O} \Rightarrow \text{Adenosine} + \text{H}_2\text{PO}_4^-$; at les pH<7.199 $\Delta G_{\text{AmL}} = -14,2 \text{ kJ/mol}$.

$$K_{\text{AmL}} = \frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{Adenosin}]}{[\text{H}_2\text{O}] \cdot [\text{AMP}^-]} = K_{\text{Leninger}} = \exp(14200/8,3144/298,15) = 307,43344$$

$$\Delta G_{\text{HessAmL}} = \Delta G^\circ_{\text{adenosin}} + \Delta G^\circ_{\text{H}_2\text{PO}_4^-} - \Delta G^\circ_{\text{AMP}^-} - \Delta G^\circ_{\text{H}_2\text{O}} = 362,172 - 1137,3 - (-530,066 - 151,549) = -93,5 \text{ kJ/mol}; \text{ pH}<7.199;$$

$$\Delta G_{\text{HessAm}} = \Delta H_{\text{HessAm}} - T \cdot \Delta S_{\text{HessAm}} = -4,27 - 298,15 \cdot 0,946308 = -286,4 \text{ kJ/mol} \text{ exoergic};$$

Eksotermiska un eksoergiskas Hesa brīvās enerģijas izmaiņa negatīva AMP^- pie mazākiem

pH<7,199 un pie pH=7,36 AMP^{2-} hidrolīze $\Delta G_{\text{hidrolīze}} = -286,4 \text{ kJ/mol}$ un $-93,5 \text{ kJ/mol}$, bet

minimizējas līdz $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -14,2 \text{ kJ/mol}$ sasniegto līdzsvara maisījumu

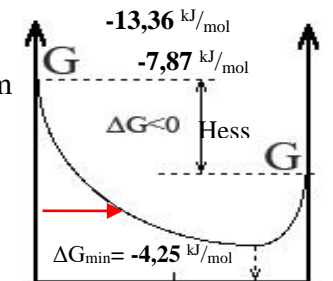
$$K_{\text{AmL}} = 307,4 = \frac{[\text{HPO}_4^{2-}] \cdot [\text{Adenosin}]}{[\text{H}_2\text{O}] \cdot [\text{AMP}^{2-}]}$$

: Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

$$\Delta H_{\text{HessAm}} = \Delta H^\circ_{\text{adenosin}} + \Delta H^\circ_{\text{HPO}_4^{2-}} - \Delta H^\circ_{\text{AMP}^-} - \Delta H^\circ_{\text{H}_2\text{O}} = -626,66 - 1302,6 - (-1638,34 - 286,65) = -4,27 \text{ kJ/mol};$$

$$\Delta S_{\text{HessAm}} = \Delta S^\circ_{\text{adenosin}} + \Delta S^\circ_{\text{HPO}_4^{2-}} - \Delta S^\circ_{\text{AMP}^-} - \Delta S^\circ_{\text{H}_2\text{O}} = -3316,57 + 92,5 - (-3717,19 - 453,188) = 946,308 \text{ kJ/K/mol};$$



A+B 50% C+D
 reaktanti $\text{AMP}^{2-} + \text{H}_2\text{O}$
 produkti $\text{Adenosine} + \text{HPO}_4^{2-}$.

$\text{H}_2\text{P}_2\text{O}_7^{2-} + \text{ADP}^{2-} \Rightarrow \text{H}_2\text{PO}_4^- + \text{ATP}^{3-}$; $\text{pH} < 6,72$; $K_{\text{abbppPH}} = K_{\text{abbpp}} / [\text{H}_2\text{O}] = 0,01047878 / 55,3457 = 0,0001893$

$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{H}_2\text{PO}_4} + \Delta G^\circ_{\text{ATP}^3} - \Delta G^\circ_{\text{H}_2\text{P}_2\text{O}_7} - \Delta G^\circ_{\text{ADP}^2} = -1057,143 - 2267,64 - (-1952,27 - 1399,9) = 27,39 \text{ kJ/mol}$;

$\Delta G_{\text{abbppPH}} = -R \cdot T \cdot \ln(K_{\text{abbppPH}}) = -8,3144 \cdot 298,15 \cdot \ln(0,0001893) / 1000 = 21,25 \text{ kJ/mol}$

pp) $\text{HP}_2\text{O}_7^{3-} + \text{ADP}^{3-} \Rightarrow \text{HPO}_4^{2-} + \text{ATP}^{4-}$; $\Delta G_{\text{abbppL}} = 30,5 + (-19,2) = 11,3 \text{ kJ/mol}$; $\text{pH} = 7,36$; $\Delta G_{\text{Hess}} = 13,967 \text{ kJ/mol}$;

$\Delta G_{\text{H}} = \Delta G^\circ_{\text{HPO}_4} + \Delta G^\circ_{\text{ATP}^4} - \Delta G^\circ_{\text{HP}_2\text{O}_7} - \Delta G^\circ_{\text{ADP}^3} = -1057,143 - 2267,64 - (-1938,85 - 1399,9) = 13,967 \text{ kJ/mol}$;

$\Delta H_{\text{H}} = \Delta H^\circ_{\text{HPO}_4} + \Delta H^\circ_{\text{ATP}^4} - \Delta H^\circ_{\text{HP}_2\text{O}_7} - \Delta H^\circ_{\text{ADP}^3} = -1298,89 - 3617,1 - (-2291,04 - 2627,4) = 2,45 \text{ kJ/mol}$;

2. $\Delta S_{\text{dispehse}} = -\Delta H_{\text{H}} / T = -2,45 / 298,15 = -8,22 \text{ J/(mol K)}$; $\Delta S_{\text{total}} = \Delta S_{\text{H}} + \Delta S_{\text{dispehse}} = -38,532 - 8,2173 = -46,75 \text{ J/mol K}$

$\Delta S_{\text{H}} = \Delta S^\circ_{\text{HPO}_4} + \Delta S^\circ_{\text{ATP}^4} - \Delta S^\circ_{\text{HP}_2\text{O}_7} - \Delta S^\circ_{\text{ADP}^3} = -810,792 - 4526,1 - (-1181,25 - 4117,11) = -38,53 \text{ J/(mol K)}$;

$\Delta G_{\text{H}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = 2,45 - 298,15 \cdot (-0,038532) = 13,94 \text{ kJ/mol}$ endoergic; $T \cdot \Delta S_{\text{total}} = -0,0467493 \cdot 298,15 = -13,94 \text{ kJ/mol}$;

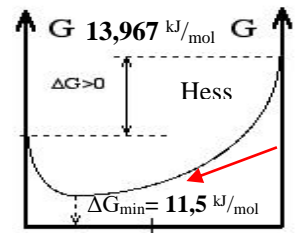
$K_{\text{abbpp}} = \exp(-\Delta G_{\text{Lehninger}} / R/T) = \exp(-11300 / 8,3144 / 298,15) = 0,01047878$;

$\Delta G_{\text{abbppL}} = -R \cdot T \cdot \ln(K_{\text{abbppL}}) = -8,3144 \cdot 298,15 \cdot \ln(0,01047878) = 11,3 \text{ kJ/mol}$. Endotermiskas

un endoerģiskas $\text{H}_2\text{P}_2\text{O}_7^{2-}$ hidrolīzes pārnēsē uz ADP^{3-} Hesa brīvās enerģijas izmaiņa

pozitīva pie $\text{pH} = 7,36$ $\text{HP}_2\text{O}_7^{3-}$ $\Delta G_{\text{Hess}} = 13,967 \text{ kJ/mol}$, bet minimizējas sasniedzot

līdzsvara $\Delta G_{\text{min}} = 11,3 \text{ kJ/mol}$ maisījumu: $0,01047878 = K_{\text{abbpp}} = \frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{ATP}^4]}{[\text{H}_2\text{P}_2\text{O}_7^{2-}] \cdot [\text{ADP}^3]}$.



A+B 50% C+D
reaktanti $\text{HP}_2\text{O}_7^{3-} + \text{ADP}^{3-}$

produkti $\text{HPO}_4^{2-} + \text{ATP}^{4-}$

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

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

H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
H_2PO_4^-	-1296,3	90,4	-1130,2
H_2PO_4^-	-1302,6	92,5	-1137,3
HPO_4^{2-}	-1292,14	-33,47	-1089,28
HPO_4^{2-}	-1298,89	-810,792	-1057,143
ADP^{3-}	-2627,4	-4010	-1424,7
ATP^{4-}	-3617,15	-4520	-2292,5
ADP^{3-}	-2627,4	-4117,11	-1399,9
ATP^{4-}	-3617,1	-4526,1	-2267,64
Pcreatine ²⁻	-736,4	CRC	-689,08
Pcreatine ²⁻	Lehninger	$\Delta G^\circ_{\text{Hess}}$	-701,4
creatine ⁻	-537,48	189,5	126,1868
creatine ⁻	-	CRC 2010	107,69

$\Delta G_{\text{CARLSON1963}} = -41 \pm 2 \text{ kJ/mol}$; $K_a = 617083,9$; $\Delta G_a = -33,05 \text{ kJ/mol}$;

$\text{Pcreatine}^{2-} + \text{H}_2\text{O} = \text{creatine} + \text{HPO}_4^{2-}$;

$\Delta G_{\text{Lehninger}} = -43 \text{ kJ/mol}$;

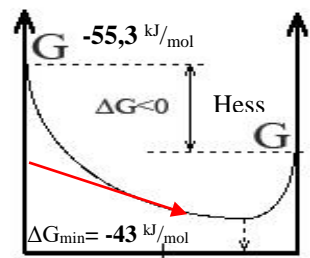
$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{creatine}} + \Delta G^\circ_{\text{HPO}_4} - \Delta G^\circ_{\text{Pcreatine}} - \Delta G^\circ_{\text{H}_2\text{O}} = -55,32 \text{ kJ/mol}$;

$= 107,69 - 1089,28 - (-689,08 - 237,191) = -55,3 \text{ kJ/mol}$;

$K_{\text{Ellington}} = 3,64 \cdot 10^7 = 36400000$; $t = 35^\circ \text{ C}$; 308 K

$\Delta G_{\text{Lehninger}} = 43 + 126,1868 - 1057,143 + 151,549 = \Delta G^\circ_{\text{Pcreatine}} = -736,4 \text{ kJ/mol}$

Eksotermiskas un eksoerģiskas Pcreatine²⁻ hidrolīzes Hesa brīvās enerģijas izmaiņa ir negatīva pie $\text{pH} = 7,36$ $\Delta G_{\text{hidrolīze}} = -55,3 \text{ kJ/mol}$, bet minimizējas $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -43 \text{ kJ/mol}$ sasniedzot līdzsvara maisījumu



A+B 50% C+D

$K_{\text{Leninge}} = 34145290,295 = \frac{[\text{creatine}] \cdot [\text{HPO}_4^{2-}]}{[\text{Pcreatine}^{2-}] \cdot [\text{H}_2\text{O}]}$

$\text{CARLSON } \Delta G_{\text{Pcreatine}} = 41 + 107,69 - 1089,28 + 237,191 = \Delta G^\circ_{\text{Pcreatine}} = -703,4 \text{ kJ/mol}$

$\text{Lehninger } \Delta G_{\text{Pcreatine}} = 43 + 107,69 - 1089,28 + 237,191 = \Delta G^\circ_{\text{Pcreatine}} = -701,4 \text{ kJ/mol}$;

$K_{\text{CARLSON}} = \exp(-\Delta G_{\text{Carlson}} / R/T) = \exp(41000 / 8,3144 / 298,15) = 15238538,963622$

$K_{\text{Leninge}} = \exp(-\Delta G_{\text{Lehninger}} / R/T) = \exp(43000 / 8,3144 / 298,15) = 34145290,2951607$;

$\Delta G_{\text{Ellington}} = -R \cdot T \cdot \ln(K_{\text{Ellington}}) = -8,3144 \cdot 308 \cdot \ln(3,46 \cdot 10^7) / 1000 = -44,45 \text{ kJ/mol}$;

$K_{\text{CRC}} = 1 / (5,78 \cdot 10^{-3}) = 173$ (310,15 K); $\text{pMg} = 2,47$; $\text{pH} = < 7,199$;

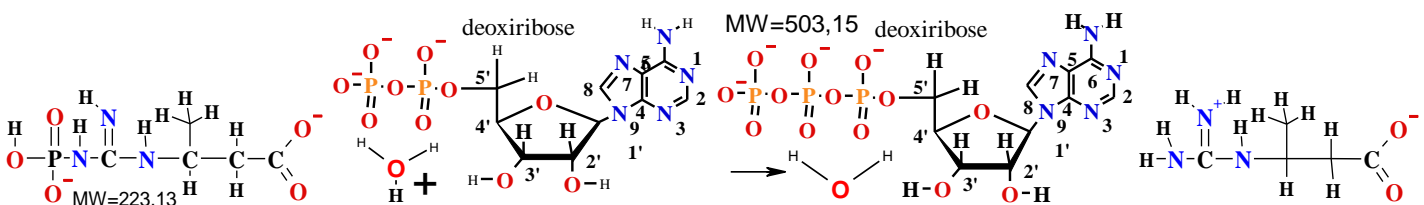
$[\text{Pcreatine}^-] \cdot [\text{ADP}^{2-}]$

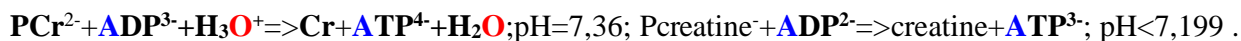
$\text{Pcreatine}^{2-} + \text{ADP}^{3-} + \text{H}_3\text{O}^+ \Rightarrow \text{creatine} + \text{ATP}^{4-} + \text{H}_2\text{O}$;

$\Delta G_{\text{abbLehninger}} = -R \cdot T \cdot \ln(K_a K_{\text{bb}}) = -8,3144 \cdot 298,15 \cdot \ln(154,854) / 1000 = -12,5 \text{ kJ/mol}$;

$K_{\text{abbLehninger}} = K_a K_{\text{bb}} = 34145290,295 \cdot 0,000004535142 = 154,854$;

$[\text{Pcreatine}^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]$





$$\frac{[\text{creatine}][\text{ATP}^{4-}][\text{H}_2\text{O}]}{[\text{Pcreatine}^{2-}][\text{ADP}^{3-}][\text{H}_3\text{O}^+]} = \mathbf{K_{abbLehninger}} = \mathbf{K_a K_{bb}} = 34145290,295 * 0,000004535142 = 154,854; \text{pie } \text{pH}=7,36.$$

$$\Delta G_{\text{abbHess}} = \Delta G^\circ_{\text{cheatine}} + \Delta G^\circ_{\text{ATP}^{4-}} + \Delta G^\circ_{\text{H}_2\text{O}} - \Delta G^\circ_{\text{Pcheatine}} - \Delta G^\circ_{\text{ADP}^{3-}} - \Delta G^\circ_{\text{H}_3\text{O}^+} = -94,946 \text{ kJ/mol}; \text{eksoergiskas CRC2010} = 107,69 - 2292,5 - 237,191 - (-689,08 - 1424,7 - 213,275) = -94,946 \text{ kJ/mol}$$

$$\Delta G_{\text{CRC Hess}} = \Delta G^\circ_{\text{cheatine}} + \Delta G^\circ_{\text{ATP}^{3-}} - \Delta G^\circ_{\text{Pcheatine}} - \Delta G^\circ_{\text{ADP}^{2-}} = -71,03 \text{ kJ/mol}; \text{CRC2010};$$

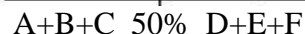
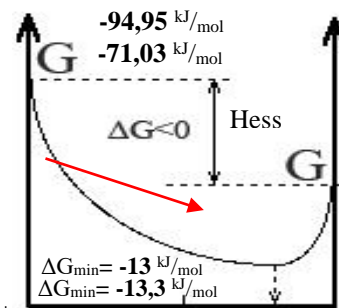
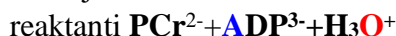
$$\Delta G_{\text{CRC}} = -R \cdot T \cdot \ln(\mathbf{K_{CRC}}) = -8,3144 * 310,15 * \ln(173)/1000 = -13,3 \text{ kJ/mol}; \text{CRC2010};$$

Eksotermiskas, eksoergiskas Pcreatin²⁻ un ATP⁴⁻ kināzes Hesa brīvās enerģijas izmaiņa pie pH=7,36 un pH<7,199 negatīva $\Delta G_{\text{hidrolīze}} = -94,946 \text{ kJ/mol}$, bet minimizējas līdz

$$\Delta G_{\text{min}} = \Delta G_{\text{abbLehninger}} = -12,5 \text{ kJ/mol un } \Delta G_{\text{CRC}} = -13,3 \text{ kJ/mol sasniedzot līdzsvara maisījumu}$$

$\mathbf{K_{abbLehninger}} = \mathbf{K_a K_{bb}} = 154,854$, $\mathbf{K_{CRC}} = 173$ (310,15 K). Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



$$\Delta G_{\text{abbLehninger}} = -R \cdot T \cdot \ln(\mathbf{K_{abb}}) = -8,3144 * 310,15 * \ln(154,854)/1000 = -13 \text{ kJ/mol}; \text{ produkti (creatine) Cr} + \text{ATP}^{4-} + \text{H}_2\text{O}$$

Ellingtona konstante 1989. gadā pie temperatūras $t=35^\circ \text{C}$; 308 K ir $\mathbf{K_{Ellington}} = 3,46 * 10^7$;

$$\mathbf{K_{Ellington}} = \exp(-\Delta G_{\text{Ellington}}/R/T) = \exp(44454,478/3144/308) = 3,46 * 10^7; \text{ J.exp.Biol.143,177-194,1989};$$

Kreatīna fosfo kināzes $\mathbf{K'_{cpk}} = 100$ to 160 (Lawson & Veech 1979), $[\text{Pcreatine}^{3-}]/[\text{ATP}^{4-}] = 3$ līdz 4 un

$$[\text{Pcreatine}^{3-}]/[\text{creatine}] = 2,5, [\text{ATP}^{4-}]/[\text{ADP}^{3-}] = 10^2 \text{ to } 10^3. \text{ Šķīdība } 25,51 \text{ mg/mL}; 3,52 \text{ g/L};$$

Homeostāzes brīvās enerģijas izmaiņa $\Delta G_{\text{Homeostāzes}} = \Delta G_{\text{eq}} + R \cdot T \cdot \ln \mathbf{K_{Homeostāzes}}$ ir mazāka par līdzsvara minimumu.

Hesa brīvās enerģijas izmaiņas tīriem produktiem mīnus tīras izejvielas $\Delta G_{\text{Hess}} = -94,95 \text{ kJ/mol}$ minimizējas sasniedzot vielu maisījumu līdzsvarā $\Delta G_{\text{eq}} = -13 \text{ kJ/mol}$: (310,15 K)

Homeostāzes izmaiņa $\Delta G_{\text{Homeostāzes}} < \Delta G_{\text{eq}} = -13 \text{ kJ/mol}$ pirmajos un otrajos apstākļos:

$$1. \Delta G_{\text{Homeostāzes}} = -6,832 \text{ kJ/mol pie } [\text{creatine}] = 28 \text{ nM}, [\text{Pcreatine}^{2-}] = 28 \text{ mM}, [\text{ATP}^{4-}] = 8,05 \text{ mM}, [\text{ADP}^{3-}] = 0,93 \text{ mM un } [\text{H}_2\text{O}] = 55,1398 \text{ M}, [\text{H}_3\text{O}^+] = 10^{-7,36} \text{ M};$$

$$\text{Ja } [\text{creatine}]/[\text{Pcreatine}^{2-}] = 28 * 10^{-9} / 28 / 10^{-3} = 10^{-6}; \text{ tad } \Delta G_{\text{Homeostāzes}} = -6,832 \text{ kJ/mol, ja } [\text{creatine}] = 28 * 10^{-9} \text{ M}$$

26. [lapas pusē](#):

$$\mathbf{K_{Homeostāzes}} = \frac{[\text{creatine}][\text{ATP}^{4-}][\text{H}_2\text{O}]}{[\text{Pcreatine}^{2-}][\text{ADP}^{3-}][\text{H}_3\text{O}^+]} = \frac{28 \cdot 10^{-9} \cdot 8,05 \cdot 10^{-5} \cdot 55,1398}{28 \cdot 10^{-3} \cdot 9,3 \cdot 10^{-3} \cdot 10^{-7,36}} = 10,9339760517278; \ln(10,934) = 2,3919.$$

$$\Delta G_{\text{Homeostāzes}} = \Delta G_{\text{eq}} + R \cdot T \cdot \ln \mathbf{K_{Homeostāzes}} \text{ ir } = (-13000 + 8,3144 * 310,15 * \ln(28 * 10^{-9} * 8,05 * 10^{-5} * 55,1398 / (28 / 10^{-3} * 9,3 / 10^{-3} * 10^{-7,36}))) / 1000 = -6,832 \text{ kJ/mol, } = -13000 + 8,3144 * 310,15 * 2,3919 = (-13000 + 6168) / 1000 = -6,832 \text{ kJ/mol,}$$

$$2. \Delta G_{\text{Homeostāzes}} = -0,3942 \text{ kJ/mol pie } [\text{creatine}] = 280 \text{ nM}, [\text{Pcreatine}^{2-}] = 28 \text{ mM}, [\text{ATP}^{4-}] = 8,05 \text{ mM}, [\text{ADP}^{3-}] = 0,93 \text{ mM un } [\text{H}_2\text{O}] = 55,1398 \text{ M}, [\text{H}_3\text{O}^+] = 10^{-7,36} \text{ M};$$

$$\text{Ja } [\text{creatine}]/[\text{Pcreatine}^{2-}] = 28 * 10^{-8} / 28 / 10^{-3} = 0,001; \text{ tad } \Delta G_{\text{Homeostāzes}} = -22,67 \text{ kJ/mol, ja } [\text{creatine}] = 28 * 10^{-6} \text{ M}$$

$$\mathbf{K_{Homeostāzes}} = \frac{[\text{creatine}][\text{ATP}^{4-}][\text{H}_2\text{O}]}{[\text{Pcreatine}^{2-}][\text{ADP}^{3-}][\text{H}_3\text{O}^+]} = \frac{28 \cdot 10^{-8} \cdot 8,05 \cdot 10^{-5} \cdot 55,1398}{28 \cdot 10^{-3} \cdot 9,3 \cdot 10^{-3} \cdot 10^{-7,36}} = 109,339760517278; \ln(109,34) = 4,6945.$$

$$\Delta G_{\text{Homeostāzes}} = \Delta G_{\text{eq}} + R \cdot T \cdot \ln \mathbf{K_{Homeostāzes}} \text{ ir } = (-13000 + 8,3144 * 310,15 * \ln(28 * 10^{-8} * 8,05 * 10^{-5} * 55,1398 / (28 / 10^{-3} * 9,3 / 10^{-3} * 10^{-7,36}))) / 1000 = -0,8943 \text{ kJ/mol, } = -13000 + 8,3144 * 310,15 * 4,6945 = (-13000 + 12105,76) / 1000 = -0,8943 \text{ kJ/mol,}$$



$$\frac{[\text{H}_2\text{O}][\text{ATP}^{4-}]}{[\text{H}_2\text{PO}_4^-][\text{ADP}^{3-}]} = \mathbf{K_{bbL}} = \mathbf{K_{bbLehninger}}[\text{H}_2\text{O}] = 0,000004535142 * 55,3457339 = 0,000251001.$$

$$\Delta G_{\text{bHL}} = -R \cdot T \cdot \ln(\mathbf{K_{bL}}) = -8,3144 * 298,15 * \ln(0,000251001) = 20,5512 \text{ kJ/mol};$$

$$\frac{[\text{H}_2\text{O}]^2 \cdot [\text{ATP}^{4-}]}{[\text{HPO}_4^{2-}][\text{ADP}^{3-}][\text{H}_3\text{O}^+]} = \mathbf{K_{bb}} = \mathbf{K_{bbLehninger}} = \exp(-\Delta G_{\text{Lehninger}}/R/T) = \exp(-30500/8,3144/298,15) = 0,000004535142; \Delta G_{\text{bLehninger}} = 30,5 \text{ kJ/mol};$$

TERMODINAMIKA V i **Glc 6-P²**-hidrolīze par **Glc+HPO₄²⁻** un **Glc 6-P²**-par **Glc 1-P²**- izomerizācija

Aprēķināt ΔH_H ΔS_H ΔG_H standarta apstākļos 298.15 K vai ir **eksotermiska** , **atermiska**, **endotermiska**, **eksoerģiska** **endoerģiska**!/? aa2 $\Delta G_{Lehninger} = -13,8$ kJ/mol; **Glc6P²⁻+H₂O=>Glc+HPO₄²⁻**; pH=7,36; $\Delta G_{aa2Hess} = -18.39$ kJ/mol ;

Viela	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
H₃O⁺	-285,81	-3,854	-213,275
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549
Glc	CRC10	I=0,25 M	-419,74
Glc	-1263,78	269,45	-919,96
Glc	-1267,13	-2901,49	-402,05
H₂PO₄⁻	-1302,6	92,5	-1137,3
HPO₄²⁻	-1292,14	-33,47	-1089,28
HPO₄²⁻	-1298,89	-810,792	-1057,143
Glc6P²⁻	-2260	-3291,56	-1318,92
Glc6P²⁻	-2279,314	-3297,196	-1296,26
Glc1P²⁻	-2260	-3291,56	-1311,89
Glc1P²⁻	-	-	-1289,22
ADP³⁻	-2627,4	-4010	-1424,7
ATP⁴⁻	-3617,15	-4520	-2292,5
ADP³⁻	-2627,4	-4117,11	-1399,9
ATP⁴⁻	-3617,1	-4526,1	-2267,64

$\Delta G_{aa2Hess} = \Delta G^\circ_{Glc} - \Delta G^\circ_{HPO42} - \Delta G^\circ_{Glc6P} - \Delta G^\circ_{H2O} = -18.39$ kJ/mol **eksoerģiskas**
 $= -419,74 - 1089,28 - (-1296,262 + ((-151,549 - 237,191)/2)) = -18.39$ kJ/mol;
 $K_{a2Lehninger} = \text{EXP}(13800/8,3144/298,15) = \text{EXP}(5,566899) = 261,62$;
 $K_{a2Lehninger} = [\text{Glc}] \cdot [\text{HPO}_4^{2-}] / [\text{Glc6P}^{2-}] \cdot [\text{H}_2\text{O}] = 261,62$;
 $\Delta G_{a22Lehninger} = +13,8$ kJ/mol; **Glc+HPO₄²⁻=>Glc6P²⁻+H₂O**; pH=7,36;
 $\Delta G_{Hess} = \Delta G^\circ_{H2O} + \Delta G^\circ_{Glc6P} - \Delta G^\circ_{Glc} - \Delta G^\circ_{HPO42} = +38,55$ kJ/mol **endoerģiska**
 $= -151,549 - 1318,92 - (-419,74 - 1089,28) = +38,55$ kJ/mol
 $K_{bLehninger310} = \text{exp}(-\Delta G_{bLehninger}/R/T) = \text{exp}(30500/8,3144/310,15) = 136983,25$
 $K_{aaLehninger} = \text{EXP}(-13800/8,3144/310,15) = 0,0047409841$
 $K_{aaLehninger} = \text{EXP}(-13800/8,3144/298,15) = 0,003822314$
 $K_{a22Lehninger} = [\text{Glc6P}^{2-}] \cdot [\text{H}_2\text{O}] / [\text{Glc}] \cdot [\text{HPO}_4^{2-}] = 0,003822314$;
 $\Delta G_{a22Lehninger} = 13,8$ kJ/mol; $\Delta G_{bLehninger} = -30,5$ kJ/mol; $\Delta G_{a22b} = 13,8 - 30,5$ kJ/mol
Glc+ATP⁴⁻+H₂O =>Glc6P²⁻+ADP³⁻+H₃O⁺; $\Delta G_{a22b} = -16,7$ kJ/mol
 $\Delta G_{a22b} = \Delta G_{a22} + \Delta G_{bLehninger} = 13,8 + -30,5 = -16,7$ kJ/mol ;
 $\Delta G_H = \Delta G^\circ_{ADP3} + \Delta G^\circ_{Glc6P} + \Delta G^\circ_{H3O} - \Delta G^\circ_{Glc} - \Delta G^\circ_{ATP4} - \Delta G^\circ_{H2O} = -25,2$ kJ/mol
 $= -1399,9 - 1318,92 - 213,275 - (-402,05 - 2267,64 - 237,191) = -25,2$ kJ/mol
 $K_{a22b} = \text{EXP}(16700/8,3144/298,15) = 842,82$; $\frac{[\text{Glc6P}^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]}{[\text{Glc}] \cdot [\text{H}_2\text{O}] \cdot [\text{ATP}^{4-}]}$
 $K_{aaLb310} = \text{EXP}(16700/8,3144/310,15) = 649,44$

310,15 K; $K_{a22b310} = K_{a22} \cdot K_{bLehninger} = 0,004741 \cdot 136983,25 = 649,438$; $K_{a22Lehninger310} = 0,004741$;

$\Delta G_{a22b310} = -8,3144 \cdot 310,15 \cdot \ln(649,438) = -16,7$ kJ/mol;

310,15 K; $K_{a22b310} = K_{a22} \cdot K_{bLehninger} = 0,004741 \cdot 136983,25 = 649,438 = \frac{[\text{Glc6P}^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]}{[\text{Glc}] \cdot [\text{H}_2\text{O}] \cdot [\text{ATP}^{4-}]}$

Endotermiska, endoerģiska **Glc** fosforilēšanas **Glc6P²⁻** Hesa brīvās enerģijas izmaiņa ir pozitīva

$\Delta G_{fosforilēšana} = +38,55$ bet ar **ATP⁴⁻** negatīvs **-25,2** kJ/mol, bet minimizējas sasniedzot līdzsvara

maisījumu $\Delta G_{min} = \Delta G_{eq} = +13,8$ kJ/mol bet ar **ATP⁴⁻** **-16,7** kJ/mol

$$\frac{[\text{Glc6P}^{2-}] \cdot [\text{H}_2\text{O}]}{[\text{Glc}] \cdot [\text{HPO}_4^{2-}]} = K_a = 0,0382 \text{ un } K_{a22b} = 842,82 = \frac{[\text{Glc6P}^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]}{[\text{Glc}] \cdot [\text{H}_2\text{O}] \cdot [\text{ATP}^{4-}]}$$

Līdzsvara sasniegšana ir Prigožina atraktors brīvās enerģijas izmaiņas minimums ΔG_{min} .

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

Glc+ATP⁴⁻+H₂O=>Glc1P²⁻+ADP³⁻+H₃O⁺; $\Delta G_{Lehninger} = -9,6$ kJ/mol;

$\Delta G_H = \Delta G^\circ_{Glc1P} + \Delta G^\circ_{ADP3} + \Delta G^\circ_{H3O} - \Delta G^\circ_{Glc} - \Delta G^\circ_{ATP4} - \Delta G^\circ_{H2O} = -43,35$ kJ/mol; $\Delta G_{ab} = \Delta G_a + \Delta G_b = 20,9 - 30,5 = -9,6$ kJ/mol ;

$= -1289,221 - 1399,9 - 237,191 - (-402,05 - 2267,64 - 213,275) = -43,35$ kJ/mol; $K_{Lehninger} = \text{EXP}(9600/8,3144/298,15) = 48,07$;

Glc+HPO₄²⁻=>Glc1P²⁻+H₂O; $\Delta G_{Lehninger} = 20,9$ kJ/mol; $\Delta G_{Hess} = \Delta G^\circ_{Glc1P} + \Delta G^\circ_{H2O} - \Delta G^\circ_{Glc} - \Delta G^\circ_{HPO42} = 68,25$ kJ/mol;

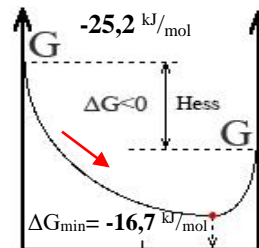
$= -1289,221 - 151,549 - (-419,74 - 1089,28) = 68,25$ kJ/mol; I=0,25 M;

Glc1P²⁻=>Glc6P²⁻; $\Delta G_{Lehninger} = -7,02$ kJ/mol; $K_{eq} = [\text{Glc6P}^{2-}] / [\text{Glc1P}^{2-}] = 17$; $\Delta G_{eq} = -8,3144 \cdot 298,15 \cdot \ln(17) = -7,02$ kJ/mol;

$\Delta G_H = \Delta G^\circ_{Glc6P} + \Delta G^\circ_{Glc1P} = -1296,262 - (-1289,221) = -7,04$ kJ/mol; $= -1318,92 - (-1311,89) = -7,03$ kJ/mol;

$\Delta G_b = -R \cdot T \cdot \ln(K_b) = -8,3144 \cdot 298,15 \cdot \ln(1,9667 \cdot 10^{-6}) / 1000 = 31,4095$ kJ/mol ;

Glc 1-P²⁻=>Glc6-P²⁻; $\Delta G_{totalHess} = \Delta G^\circ_{G1P} + \Delta G^\circ_{G6P} = -20,9 + 13,8 = -7,1$ kJ/mol **eksoerģiska**.....kJ/mol



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

Glc+ATP⁴⁻+H₂O

Glc6P²⁻+ADP³⁻+H₃O⁺

TERMODINAMIKA V i **Glc 1-P²**-hidrolīze **Glc + HPO₄²⁻** un **Glc 1-P²**-defosforilēšana
Aprēķināt ΔH_H ΔS_H ΔG_H standarta apstākļos 298,15 K. Reakcija ir **eksotermiskas**, **atermiska**,

endotermiska? Ir **eksoerģiskas** vai **endoerģiska!**

a22 $\Delta G_{Lehninger} = +20,9$ kJ/mol; **Glc+HPO₄²⁻+ΔG+Q=> Glc1P²⁻+H₂O**; pH=7,36; $\Delta G_{Hess} = 68,25$ kJ/mol;

a2 $\Delta G_{Lehninger} = -20,9$ kJ/mol; **Glc1P²⁻+H₂O =>Glc+HPO₄²⁻+ΔG+Q**; pH=7,36; $\Delta G_H = -68,25$ kJ/mol ;

Substance	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
H₃O⁺	-285,81	-3,854	-213,275
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549
Glc	CRC10	I=0,25 M	-419,74
Glc	-1263,78	269,45	-919,96
Glc	-1267,13	-2901,49	-402,05
H₂PO₄⁻	-1302,6	92,5	-1137,3
HPO₄²⁻	-1292,14	-33,47	-1089,28
HPO₄²⁻	-1298,89	-810,792	-1057,143
Glc6P²⁻	-2260	-3291,56	-1318,92
Glc6P²⁻	-2279,314	-3297,196	-1296,262
Glc1P²⁻	-2260	-3291,56	-1311,89
Glc1P²⁻	-	-	-1289,221
ADP³⁻	-2627,4	-4010	-1424,7
ATP⁴⁻	-3617,15	-4520	-2292,5
ADP³⁻	-2627,4	-4117,11	-1399,9
ATP⁴⁻	-3617,1	-4526,1	-2267,64

$\Delta G_{Hess} = \Delta G^\circ_{H_2O} + \Delta G^\circ_{Glc1P} - \Delta G^\circ_{Glc} - \Delta G^\circ_{HPO42} = 36,113$ kJ/mol **endoerģiska**
 $= -151,549 - 1289,221 - (-419,74 - 1057,143) = 36,113$ kJ/mol

$K_{a22Lehninger} = \text{EXP}(-20900/8,3144/298,15) = 0,000217997$;

$\Delta G_H = \Delta G^\circ_{Glc} + \Delta G^\circ_{HPO42} - \Delta G^\circ_{H_2O} - \Delta G^\circ_{Glc1P} = -36,113$ kJ/mol **exoerģic**
 $= -419,74 - 1057,143 - (-151,549 - 1289,221) = -36,113$ kJ/mol

$K_{a2Lehninger} = \text{EXP}(20900/8,3144/298,15) = 4587,215687$;

Glc+ATP⁴⁻+H₂O=>Glc1P²⁻+ADP³⁻+H₃O⁺; pH=7,36; I=0,2 M.

$K_{a22b} = K_{a22}K_b = 0,000217997 * 220500,2 = 48,07$;

$\Delta G_{a22b} = -R \cdot T \cdot \ln(K_{a22b}) = -8,3144 * 298,15 * \ln(48,0684) = -9,6$ kJ/mol;

Glc1P²⁻+ADP³⁻+H₃O⁺=> Glc+ATP⁴⁻+H₂O; pH=7,36; I=0,2 M.

$K_{a2b} = K_{a2}K_b = 4587,215687 * 4,54 * 10^{(-6)} = 0,02083$

$\Delta G_{a2b} = -R \cdot T \cdot \ln(K_{a2b}) = -8,3144 * 298,15 * \ln(0,02083) = 9,6$ kJ/mol

$$K_{a2b} = K_{a2}K_b = 0,02083 = \frac{[\text{Glc}] \cdot [\text{H}_2\text{O}] \cdot [\text{ATP}^{4-}]}{[\text{Glc1P}^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]}$$

Lehningera līdzsvars ; **ATP³⁻+H₂O<=>ADP²⁻+H₂PO₄⁻**; $K_{Lehninger} = 0,0001739$; without pH=7,36;

$\Delta G_{Lehninger} = -R \cdot T \cdot \ln(K_{Lehninger}) = -8,3144 * 298,15 * \ln(0,0001739) = 21,46$ kJ/mol ;

$$K_{Lehninger} = K_bLehninger * \frac{[\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]} = 220500,2 * 10^{(-7,36)}/55,3457 = 0,0001739 = \frac{[\text{H}_2\text{PO}_4^-] \cdot [\text{ADP}^{3-}]}{[\text{H}_2\text{O}] \cdot [\text{ATP}^{4-}]}$$

$\Delta G_H = \Delta G^\circ_{ADP3} + \Delta G^\circ_{H_2PO4} - \Delta G^\circ_{ATP4} - \Delta G^\circ_{H_2O} = -1399,9 - 1057,143 - (-2267,64 - 237,191) = 47,79$ kJ/mol;

b) **ATP⁴⁻+2H₂O=>ADP³⁻+HPO₄²⁻+H₃O⁺**; $\Delta G_{bLehninger} = -30,5$ kJ/mol;

$$K_{bLehninger} = \exp(-\Delta G_{bLehninger}/R/T) = \exp(30500/8,3144/298,15) = \exp(12,304) = 220500,2 = \frac{[\text{HPO}_4^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2 [\text{ATP}^{4-}]}$$

$\Delta G_H = \Delta G^\circ_{ADP3} + \Delta G^\circ_{HPO42} + \Delta G^\circ_{H_3O} - \Delta G^\circ_{ATP4} - 2\Delta G^\circ_{H_2O} =$

$= -1399,9 - 1057,143 - 213,275 - (-2267,64 + 2 * -151,549) = -99,58$ kJ/mol;

sum **Glc1P²⁻+ADP³⁻+H₃O⁺=> Glc+ATP⁴⁻+H₂O**; $\Delta G_{a2b} = \Delta G_{a2} + \Delta G_b = -20,9 + 30,5 = 9,6$ kJ/mol ;

sum **Glc+ATP⁴⁻+H₂O=>Glc1P²⁻+ADP³⁻+H₃O⁺+ΔG+Q**; $\Delta G_{a22b} = \Delta G_{a22} + \Delta G_b = 20,9 + -30,5 = -9,6$ kJ/mol ;

$\Delta G_{Hess} = \Delta G^\circ_{ADP3} + \Delta G^\circ_{Glc1P} + \Delta G^\circ_{H_3O} - \Delta G^\circ_{Glc} - \Delta G^\circ_{ATP4} - \Delta G^\circ_{H_2O} = -38,607$ kJ/mol;

$= -1399,9 - 1289,221 - 213,275 - (-419,74 - 2292,5 - 151,549) = -38,607$ kJ/mol;

$\Delta G_{a22b} = -R \cdot T \cdot \ln(K_{a22b}) = -8,3144 * 298,15 * \ln(3,79204 * 10^{-8}) = 42,36$ kJ/mol.

Eksotermiska, eksoerģiska **Glc1P²⁻** defosforilēšanas fosforilēšanas Hesa brīvās enerģijas

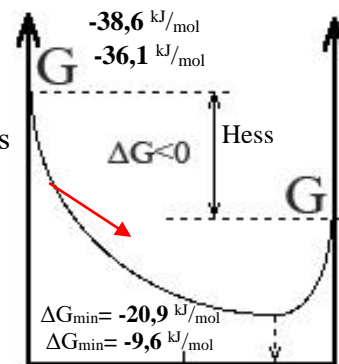
izmaiņa ir negatīva $\Delta G_{defosforilešana} = -36,113$ un $-38,607$ kJ/mol,, bet minimizējas

līdzsvara $\Delta G_{min} = \Delta G_{a2Lehninger} = -20,9$ kJ/mol un $\Delta G_{a22b} = -9,6$ kJ/mol maisījumā

$$K_{a2Lehninger} = 4587 = \frac{[\text{Glc}] \cdot [\text{HPO}_4^{2-}]}{[\text{Glc1P}^{2-}] \cdot [\text{H}_2\text{O}]} \text{ and } K_{a22b} = \frac{[\text{Glc1P}^{2-}] \cdot [\text{ADP}^{3-}] \cdot [\text{H}_3\text{O}^+]}{[\text{Glc}] \cdot [\text{H}_2\text{O}] \cdot [\text{ATP}^{4-}]} = 48,07$$

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min}

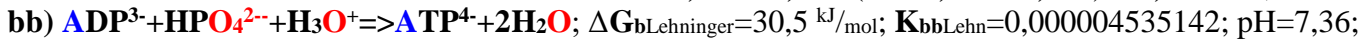
sasniegšana. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



A+B+C 50% D+E+F
 reaktanti **Glc1P²⁻+ H₂O**
 produkti **Glc+ HPO₄²⁻**



$\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{ATP}^{3-}} + \Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{H}_2\text{PO}_4^{-}} - \Delta G^{\circ}_{\text{ADP}^{2-}} = -2267,64 - 151,549 - (-1399,9 - 1057,143) = 37,85 \text{ kJ/mol}$;



$$\frac{[\text{H}_2\text{O}] \cdot [\text{ATP}^{3-}]}{[\text{H}_2\text{PO}_4^{-}]_{\text{aqua}} \cdot [\text{ADP}^{2-}]} = K_{\text{bHL}} = K_{\text{bbLehninger}} [\text{H}_2\text{O}] = 0,000004535142 * 55,3457339 = 0,000250993$$

$$\Delta G_{\text{bL}} = -R \cdot T \cdot \ln(K_{\text{bL}}) = -8,3144 * 298,15 * \ln(0,000250993) / 1000 = 20,5512 \text{ kJ/mol}$$
;

$$\frac{[\text{H}_2\text{O}]^2 \cdot [\text{ATP}^{4-}]}{[\text{HPO}_4^{2-}] [\text{ADP}^{3-}] [\text{H}_3\text{O}^+]} = K_{\text{bbLehninger}} = \exp(-\Delta G_{\text{Lehninger}} / R/T) = \exp(-30500 / 8,3144 / 298,15) = 0,000004535142$$

$$K_{\text{bbLehnH}} = 1 / 220500,2 = 0,000004535142$$
;

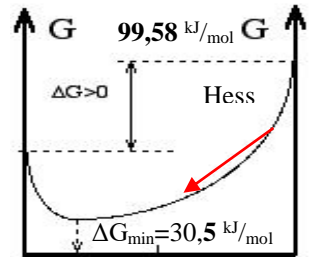
$\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{ATP}^{3-}} - 2\Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{ADP}^{2-}} - \Delta G^{\circ}_{\text{HPO}_4^{2-}} - \Delta G^{\circ}_{\text{H}_3\text{O}^+} = -1399,9 - 1057,143 - 213,275 - (-2267,64 + 2 * -151,549) = 99,58 \text{ kJ/mol}$;

Endotermiska un endoerģiska **ADP³⁻** fosforilēšanas Hesa brīvās enerģijas izmaiņa negatīva pie pH 7,36 $\Delta G_{\text{hidrolize}} = 99,58 \text{ kJ/mol}$, bet minimizējas $\Delta G_{\text{min}} = \Delta G_{\text{b}} = 30,5 \text{ kJ/mol}$ sasniežot

līdzsvara maisījumu: $0,000004535142 = K_{\text{bbLehninger}} = \frac{[\text{H}_2\text{O}]^2 \cdot [\text{ATP}^{4-}]}{[\text{HPO}_4^{2-}] [\text{ADP}^{3-}] [\text{H}_3\text{O}^+]}$. Lešatelje

princips ir Prigožina atraktors brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana

līdzsvara maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



reaktanti **HPO₄²⁻ + H₃O⁺ + ADP³⁻**
 produkti **2H₂O + ATP⁴⁻**

$K_{\text{aaLehninger}} = \text{EXP}(-13800 / 8,3144 / 298,15) = 0,003822314$;

$K_{\text{aaLehninger}} = \text{EXP}(-13800 / 8,3144 / 310,15) = 0,0047409841$; **T=310,15 K**

$\Delta G_{\text{aaHess}} = \Delta G^{\circ}_{\text{Glc6P}} + \Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{Glc}} - \Delta G^{\circ}_{\text{HPO}_4^{2-}} = -1296,262 + ((-151,549 - 237,191) / 2) - (-419,74 - 1089,28) = 18,39 \text{ kJ/mol}$

$\Delta G_{\text{aaHess}} = \Delta G^{\circ}_{\text{Glc6P}} + \Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{Glc}} - \Delta G^{\circ}_{\text{HPO}_4^{2-}} = -1296,262 - 151,549 - (-419,74 - 1089,28) = 61,209 \text{ kJ/mol}$

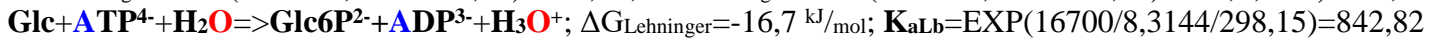
$\Delta G_{\text{aaHess}} = \Delta G^{\circ}_{\text{Glc6P}} + \Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{Glc}} - \Delta G^{\circ}_{\text{HPO}_4^{2-}} = -1318,92 - 237,191 - (-419,74 - 1089,28) = -47,09 \text{ kJ/mol}$

$\Delta G_{\text{aaHess}} = \Delta G^{\circ}_{\text{Glc6P}} + \Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{Glc}} - \Delta G^{\circ}_{\text{HPO}_4^{2-}} = -1296,262 - 151,549 - (-402,05 - 1057,143) = 11,38 \text{ kJ/mol}$



$\Delta G_{\text{aa2Hess}} = \Delta G^{\circ}_{\text{Glc}} - \Delta G^{\circ}_{\text{HPO}_4^{2-}} - \Delta G^{\circ}_{\text{Glc6P}} - \Delta G^{\circ}_{\text{H}_2\text{O}} = -419,74 - 1089,28 - (-1296,262 + ((-151,549 - 237,191) / 2)) = -18,39 \text{ kJ/mol}$;

$K_{\text{aa2Lehninger}} = \text{EXP}(13800 / 8,3144 / 298,15) = 261,62$; $K_{\text{aa2Lehninger}} = \text{EXP}(13800 / 8,3144 / 310,15) = 210,9$; **310,15 K**;



$K_{\text{aLb}} = \text{EXP}(16700 / 8,3144 / 310,15) = 649,44$; $\Delta G_{\text{aLb}} = -R \cdot T \cdot \ln(K_{\text{aLb}}) = -8,3144 * 298,15 * \ln(842,82) = -16,7 \text{ kJ/mol}$;

$\Delta G_{\text{abHess}} = \Delta G^{\circ}_{\text{Glc6P}} + \Delta G^{\circ}_{\text{ADP}^{3-}} + \Delta G^{\circ}_{\text{H}_3\text{O}^+} - \Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{ATP}^{4-}} - \Delta G^{\circ}_{\text{Glc}} = -25,2 \text{ kJ/mol}$

$= -1399,9 - 1318,92 - 213,275 - (-402,05 - 2267,64 - 237,191) = -25,2 \text{ kJ/mol}$;

$K_{\text{aLb}} = \text{EXP}(16700 / 8,3144 / 298,15) = 842,82 = \frac{[\text{Glc6P}^{2-}] [\text{ADP}^{3-}] [\text{H}_3\text{O}^+]}{[\text{Glc}] [\text{H}_2\text{O}] [\text{ATP}^{4-}]}$

$K_{\text{a2b}} = K_{\text{aa2}} K_{\text{b}} = 0,003822314 * 220500,2 = 842,82$; $\Delta G_{\text{Lehninger}} = 16,7 \text{ kJ/mol}$;



Eksotermiskas un eksoerģiskas fosforilēšanas Hesa brīvās enerģijas izmaiņa

$\Delta G_{\text{phosphonilation}} = 25,2 \text{ kJ/mol}$ negatīva, bet minimizējas sasniežot līdzsvaru

$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = 16,7 \text{ kJ/mol}$; 298,15 K;

$$K_{\text{aLb}}_{298} = 261,62 * 0,000004535142 = 0,00118648385004 = \frac{[\text{H}_2\text{O}] [\text{ATP}^{4-}] [\text{Glc}]}{[\text{Glc6P}^{2-}] [\text{ADP}^{3-}] [\text{H}_3\text{O}^+]}$$

$\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{Glc}} + \Delta G^{\circ}_{\text{ATP}^{4-}} + \Delta G^{\circ}_{\text{H}_2\text{O}} - \Delta G^{\circ}_{\text{ADP}^{3-}} - \Delta G^{\circ}_{\text{Glc6P}} - \Delta G^{\circ}_{\text{H}_3\text{O}^+} = -25,2 \text{ kJ/mol}$

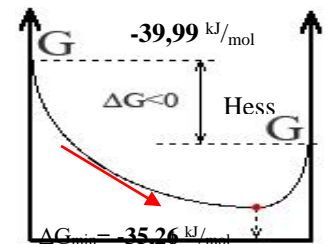
$= -402,05 - 2267,64 - 237,191 - (-1399,9 - 1318,92 - 213,275) = 25,2 \text{ kJ/mol}$;

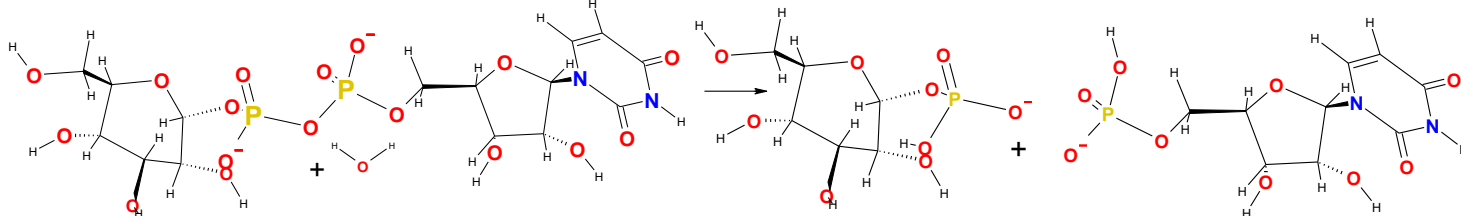
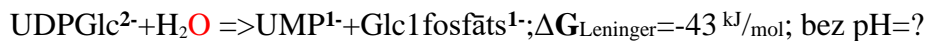
$\Delta G_{\text{aaLbb}} = -RT \ln(K_{\text{aaLbb}}) = -8,3144 * 298,15 * \ln(0,00118648385) = 16,7 \text{ kJ/mol}$; Reaktanti **Glc6P²⁻ + ADP³⁻ + H₃O⁺**

$K_{\text{aLb}}_{310} = 210,9 * 0,0000073001623 = 0,00153960422907$; produkti **Glc + ATP⁴⁻ + H₂O**;

Lešatelje princips ir Prigožina atraktors brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

$\Delta G_{\text{aaLbb310}} = -RT \ln(K_{\text{aaLbb310}}) = -8,3144 * 310,15 * \ln(0,00153960422907) / 1000 = 16,7 \text{ kJ/mol}$





$$K_{\text{Lehninger}} = \text{EXP}(-\Delta G_{\text{H}}/R/T) = \text{EXP}(43000/8,3144/298,15) = \text{EXP}(17,346) = 34145290 = 10^{-pK_{\text{eq}}} = 10^{7,75333}$$

$$K_{\text{Lehninger}} = \text{EXP}(-\Delta G_{\text{L}}/R/T) = \text{EXP}(43000/8,3144/298,15) = \text{EXP}(17,346) = \frac{[\text{Glc1P}^{1-}][\text{UMP}^{1-}]}{[\text{UDP}^{2-}\text{Glc}][\text{H}_2\text{O}]} = 34145290$$

$$|\Delta G_{\text{aLehninger}} = -43| \text{ kJ/mol} < |\Delta G_{\text{Hess}} = \Delta G_{\text{UMP1}} + \Delta G_{\text{Glc1phosphate1}} - \Delta G_{\text{UDPGlc2}} - \Delta G_{\text{H}_2\text{O}} = -128,642 \text{ kJ/mol}|;$$

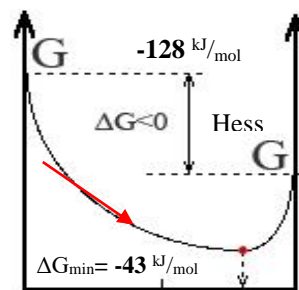
$$\Delta G_{\text{H}} = \Delta G_{\text{Lehninger}} - \Delta G_{\text{H}_2\text{O}} (\text{BioThermodybamic 2006}) + \Delta G_{\text{H}_2\text{O}} (\text{CRC 2010}) = -43 + 151,549 - 237,191 = -128 \text{ kJ/mol};$$

Eksotermiska un eksoerģiska UDPGlc²⁻ hidrolīzes Hesa brīvās enerģijas izmaiņa negatīva bez pH=? $\Delta G_{\text{hidrolīze}} = -128,642 \text{ kJ/mol}$, bet minimizējas sasniedzot līdzsvara maisījumu:

$$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -43 \text{ kJ/mol}$$

$$K_{\text{Lehninger}} = \text{EXP}(-\Delta G_{\text{Lehni}}/R/T) = \text{EXP}(43000/8,3144/298,15) = 34145290 = \frac{[\text{Glc1P}^{1-}][\text{UMP}^{1-}]}{[\text{UDP}^{2-}\text{Glc}][\text{H}_2\text{O}]}$$

Lešatēļe princips ir Prigožina atraktors brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā.



Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars. Reaktanti

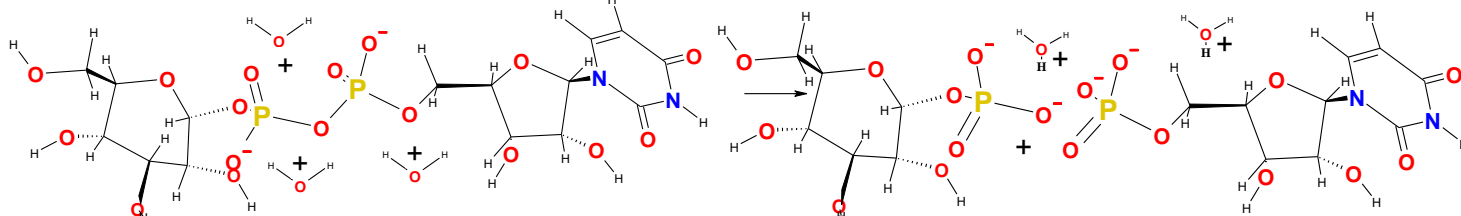
produkti UMP¹⁻ + Glc1 fosfāts¹⁻;



$$\Delta G_{\text{H}} = \Delta G_{\text{UMP2}} + \Delta G_{\text{Glc1phosphate2}} + 2\Delta G_{\text{H}_3\text{O}} - \Delta G_{\text{UDPGlc2}} - 3\Delta G_{\text{H}_2\text{O}} = -14,9 \text{ kJ/mol}; \text{ pH}=7,36$$

$$\Delta G_{\text{H}} = \Delta G_{\text{Lehninger}} + 2\Delta G_{\text{H}_3\text{O}} - 3\Delta G_{\text{H}_2\text{O}} = -43 - 2 \cdot 213,275 - (3 \cdot -151,549) = -14,9 \text{ kJ/mol}; \text{ pH}=7,36;$$

Alberty, Robert A., Biochemical Thermodynamics: Applications of Mathematica, © 2006, Massachusetts Techn Inst.



$$K_{\text{a}} = K_{\text{Lehninger}} \cdot [\text{H}_2\text{O}]^2 = 34145290 \cdot 55,3457339^2 = 104592153973,017 = 10^{11,019};$$

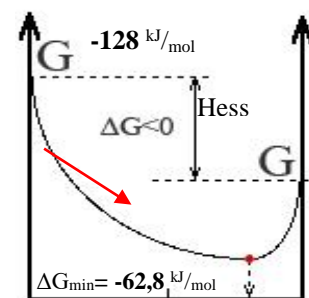
$$\Delta G_{\text{a}} = -R \cdot T \cdot \ln(K_{\text{a}}) = -8,3144 \cdot 298,15 \cdot \ln(104592153973,017)/1000 = -62,8 \text{ kJ/mol};$$

Eksotermiska un eksoerģiska UDPGlc²⁻ hidrolīzes Hesa brīvās enerģijas izmaiņa negatīva pie pH=7,36 $\Delta G_{\text{hidrolīze}} = -128 \text{ kJ/mol}$, bet minimizējas sasniedzot

līdzsvara maisījumu: $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -62,8 \text{ kJ/mol}$

$$10^{-12,416} = K_{\text{a}} = \frac{[\text{Glc1P}^{2-}][\text{UMP}^{2-}][\text{H}_3\text{O}^+]^2}{[\text{UDP}^{2-}\text{Glc}][\text{H}_2\text{O}]^3}. \text{ Lešatēļe princips ir}$$

Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā.



Reaktanti

UDPGlc²⁻ + 3H₂O

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

produkti UMP²⁻ + Glc1 fosfāts²⁻ + 2H₃O⁺;

V.j sukcināta $\text{S}^2\text{CoA}^4 - \text{O}_2 \text{H}_2\text{O}_2$ fumarāta reakcija peroksisomas dehidrogenāzē

Sukcināta $\text{S}^2\text{CoA}^4 - \text{O}_2 \text{H}_2\text{O}_2$ fumarāts dehidrogenēšanas reakcija! Ir eksoerģiska vai endoerģiska! CRC 2010 I=0,25 M; $C_{\text{osm}}=0,305 \text{ M}$; **Biochemistry Thermodynamic data, 2006**; Izejvielas => produkti
 Massachusetts Techn.Institute; pH=7,36; **Succinat** $\text{S}^2\text{CoA}^4 + \text{O}_{2\text{aqua}} + \text{H}_3\text{O}^+ \Rightarrow \text{fumarate}^{2-} + \text{HSCoA}^3 + \text{H}_2\text{O}_{2\text{aqua}} + \text{H}_2\text{O}$;

$^\circ$ Viela	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol
H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
$\text{H}_2\text{O}_{2\text{aqua}}$	-191,99	-481,688	-48,39
$\text{H}_2\text{O}_{2\text{aqua}}$	-191,17	143,9	143,9
$\text{O}_{2\text{aqua}}$	-11,70	-94,2	16,4
$\text{O}_{2\text{aqua}}$	-11,715	110,876	16,4
Succinat $^{2-}$	-908,69	-1295,576	-522,414
Succinat S^2CoA^4	-	-	-339,2476
HSCoA^{3-}	-	-	-7,26
HSCoA^3	-	-	-5,7716
Fumarate $^{2-}$	-776,56	-862,288	-519,4688
UbiQuinRed	Ubiquinol6	-	3849,6004
UbiQuinOx	-	-	3853,8792

$$1. \Delta H_{\text{Hess}} = \sum \Delta H^\circ_{\text{produkti}} - \sum \Delta H^\circ_{\text{izejvielas}}; 2. \Delta S_{\text{Hess}} = \sum \Delta S^\circ_{\text{produkti}} - \sum \Delta S^\circ_{\text{izejvielas}}$$

$$3. \Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}}$$

$$\Delta G_{\text{H}} = \Delta G^\circ_{\text{fumarat}} + \Delta G^\circ_{\text{HSCoA}} + \Delta G^\circ_{\text{H}_2\text{O}_2} + \Delta G^\circ_{\text{H}_2\text{O}} - \Delta G^\circ_{\text{O}_2} - \Delta G^\circ_{\text{SuccinatS}^2\text{CoA}} - \Delta G^\circ_{\text{H}_3\text{O}^+} = -189,06 \text{ kJ/mol};$$

$$= -519,4688 - 5,7716 - 48,39 - 151,549 - (16,4 - 339,2476 - 213,275) = -189,06 \text{ kJ/mol exoergic}$$

$$\text{Succinat}^{2-} + \text{O}_{2\text{aqua}} \Rightarrow \text{fumarate}^{2-} + \text{H}_2\text{O}_{2\text{aqua}} + \Delta G$$

$$\Delta G_{\text{H}} = \Delta G^\circ_{\text{fumarat}^{2-}} + \Delta G^\circ_{\text{H}_2\text{O}_2} - \Delta G^\circ_{\text{O}_2} - \Delta G^\circ_{\text{Succinat}^{2-}} = -61,845 \text{ kJ/mol};$$

$$= -519,4688 - 48,39 - (16,4 - 522,414) = -61,845 \text{ kJ/mol exoergic}$$

$$\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{fumarat}^{2-}} + \Delta H^\circ_{\text{H}_2\text{O}_2} - \Delta H^\circ_{\text{O}_2} - \Delta H^\circ_{\text{Succinat}^{2-}} = -48,16 \text{ kJ/mol};$$

$$= -776,56 - 191,99 - (-11,70 - 908,69) = -48,16 \text{ kJ/mol exothermic}$$

$$\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{fumarat}^{2-}} + \Delta S^\circ_{\text{H}_2\text{O}_2} - \Delta S^\circ_{\text{O}_2} - \Delta S^\circ_{\text{Succinat}^{2-}} = 45,8 \text{ J/mol/K};$$

$$= -862,288 - 481,688 - (-94,2 - 1295,576) = 45,8 \text{ J/mol/K exothermic}$$

$$\Delta G_{\text{Hess}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -48,16 - 298,15 \cdot 0,0458 = -61,82 \text{ kJ/mol}$$

Patvalīga $\Delta G_{\text{Hess}} = -61,82 \text{ kJ/mol}$; pie pH=7,36 Eksoerģiska

$\text{Ox} \text{O}_{2\text{aqua}} + 2\text{H}_3\text{O}^+ + 2\text{e}^- = \text{H}_2\text{O}_{2\text{aqua}} + 2\text{H}_2\text{O}$; $E^\circ_{\text{OxO}_2} = 0,4495 \text{ V}$ Thermodynamic University Alberta

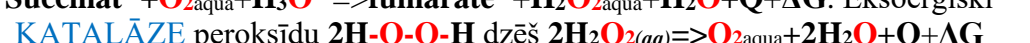
Red Succinate $^{2-} + 2\text{H}_2\text{O} = \text{Fumarate}^{2-} + 2\text{H}_3\text{O}^+ + 2\text{e}^-$; $E^\circ_{\text{RedSuccinate}} = 0,2512 \text{ V}$; Thermodynamic Lehninger 2000 ;

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

peroxide, hydroxonium and anion of peroxide: $G_{\text{H}_2\text{O}_2} = 274,5 \text{ kJ/mol}$; $G_{\text{H}_3\text{O}^+} + G_{\text{H}_2\text{O}} = 22,44 + 328 = 350,4 \text{ kJ/mol}$;

$$K_{\text{eq}} = \exp(-\Delta G_{\text{eq}}/R/T) = \exp(382565,95/8,3144/298,15) = 5057721 ;$$

Eksoerģiska dehidrogenēšanas reakcija labvēlīga izejvielām pārvērsties produktos :



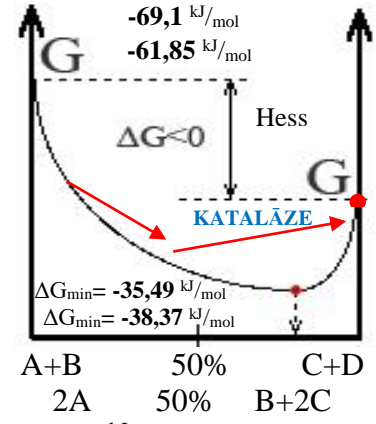
KATALĀZE peroksīdu $2\text{H}-\text{O}-\text{O}-\text{H}$ dzēš $2\text{H}_2\text{O}_{2(\text{aq})} \Rightarrow \text{O}_{2\text{aqua}} + 2\text{H}_2\text{O} + \text{Q} + \Delta G$

dismutējot par $\text{O}_{2\text{aqua}}$ un $2\text{H}_2\text{O}$. Kompleksajās reakcijās secīgi veicina neaizstājamo

nepiesātināto $\text{H} > \text{C} = \text{C} < \text{H}$ divkāršo saišu iznākumu • 100% , jo dzēš $[\text{H}_2\text{O}_2] = 0$

$$\text{molekulas } K_{\text{eq}} = 5057721 = \frac{[\text{Fumarate}^{2-}] \cdot [\text{H}_2\text{O}_2] \cdot \text{KATALĀZE}}{[\text{Succinate}^{2-}] \cdot [\text{O}_2]} = 5057721.$$

$$K_{\text{eq}} = 90471011,97 = \frac{[\text{UbiQuinOx}] \cdot [\text{H}_2\text{O}_2] \cdot \text{KATALĀZE}}{[\text{UbiQuinRed}] \cdot [\text{O}_2]} \dots$$



Formation $\text{H}_2\text{gas} + \text{O}_2\text{gas} \Rightarrow \text{H}_2\text{O}_2$; $\Delta G^\circ_{\text{UnivAlberta}} = -134,03 \text{ kJ/mol}$; $\Delta G^\circ_{\text{Alberty}} = -48,39 \text{ kJ/mol}$;

$$\Delta G_{\text{Alberty}} = G_{\text{H}_2\text{O}_2} - (G_{\text{O}_2\text{gas}} + G_{\text{H}_2\text{gas}}) = 274,5 - (85,64 + 303) = -114,14 \text{ kJ/mol} (-134,03 \text{ kJ/mol}); (-48,39 \text{ kJ/mol})$$

UbiQuinRed + $\text{O}_{2\text{aqua}} \Rightarrow \text{UbiQuinOx} + 2 \text{H}_2\text{O}_{2\text{aqua}} + \Delta G + \text{Q}$; Ubihinola dehidrogenēšana ar skābekli

$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{UbiQuinOx}} + \Delta G^\circ_{\text{H}_2\text{O}_2} - \Delta G^\circ_{\text{O}_2} - \Delta G^\circ_{\text{UbiQuinRed}} = -3853,8792 + 2 \cdot -48,39 - (16,4 - 3849,6004) = -69,07 \text{ kJ/mol}$$

$$\Delta G^\circ_{\text{Ox}} = 3668,94 \text{ kJ/mol}; \Delta G^\circ_{\text{Red}} = 3660,55 \text{ kJ/mol}; \text{CRC 2010} = 3668,94 + 2 \cdot -48,39 - (16,4 + 3660,55) = -104,79 \text{ kJ/mol};$$

$\text{Ox} \text{O}_{2\text{aqua}} + 2\text{H}_3\text{O}^+ + 2\text{e}^- = \text{H}_2\text{O}_{2\text{aqua}} + 2\text{H}_2\text{O}$; $E^\circ_{\text{OxO}_2} = 0,4495 \text{ V}$ Thermodynamic University Alberta

Red Ubiquinol + $2\text{H}_2\text{O} = \text{Ubiquinone} + 2\text{H}_3\text{O}^+ + 2\text{e}^-$; $E^\circ_{\text{RedH}_2\text{O}} = 0,2656 \text{ V}$ Thermodynamic Lehninger 2000 ;

$$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = (E^\circ_{\text{Red}} - E^\circ_{\text{Ox}}) \cdot F \cdot n = (0,2656 - 0,4495) \cdot 96485 \cdot 2 = (-0,1839) \cdot 96485 \cdot 2 = -35,49 \text{ kJ/mol}; \text{Lehninger 2000}$$

$$K_{\text{eq}} = \text{EXP}(-\Delta G_{\text{eq}}/R/T) = \text{EXP}(35490/8,3144/298,15) = 1650539;$$

Red: Ubiquinol6 + $2\text{H}_2\text{O} = \text{Ubiquinone6} + 2\text{H}_3\text{O}^+ + 2\text{e}^-$; $E^\circ_{\text{Red}} = E^\circ_{\text{H}_2\text{O}} = -0,845 \text{ V}$; $E^\circ = -1,05 \text{ V}$ CRC 2010 ;

$$E^\circ_{\text{H}_2\text{O}} = -1,05 + 0,10166 + 0,0591/2 \cdot \log([\text{H}_2\text{O}]^2) = (-1,05 + 0,0591/2 \cdot \log(55,34573393^2)) = -0,947 + 0,10166 = -0,845 \text{ V}$$

$$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = (E^\circ_{\text{Red}} - E^\circ_{\text{Ox}}) \cdot F \cdot n = (-0,8453 - 0,89916) \cdot 96485 \cdot 2 = (-1,7445) \cdot 96485 \cdot 2 = -336,6 \text{ kJ/mol};$$

TERMODINAMIKA vingrinājums V k AcetylCoA³⁻ hidrolīze

Aprēķināt ΔH_H , ΔS_H , ΔG_H standarta apstākļos 298,15 K. Reakcija ir **eksotermiska**, **atermiska**, **endotermiska**? AcetylCoA³⁻ un **ADP³⁻** deacilēšana, fosforilēšana! **Eksotermiska** vai **endoerģiska** hidrolīzes reakcijas!

a) $\Delta G_{Lehninger} = -31,4 \text{ kJ/mol}$; AcetylCoA³⁻ + 2 H₂O + $\Delta G + Q \Rightarrow$ CH₃COO⁻ + CoA³⁻ + H₃O⁺; pH=7,36;

$K_{Lehninger} = \exp(31400/8,3144/298,15) = 317017,64 = K_a$;

$\Delta G_H = \Delta G^\circ_{CH_3COO} + \Delta G^\circ_{CoA2} + \Delta G^\circ_{H_3O} - \Delta G^\circ_{Acetyl-CoA2} - 2 * \Delta G_{H_2O} = -240,963 - 5,7716 - 213,275 - (-51,8968 + 2 * -151,549) = -105,015 \text{ kJ/mol}$;

Viela	$\Delta H^\circ_H \text{ kJ/mol}$	$\Delta S^\circ_H \text{ J/mol/K}$	$\Delta G^\circ_H \text{ kJ/mol}$
H ₃ O ⁺	-285,81	-3,854	-213,275
H ₂ O	-285,85	69,9565	-237,191
H ₂ O	-286,65	-453,188	-151,549
H ₂ PO ₄ ⁻	-1296,3	90,4	-1130,2
H ₂ PO ₄ ⁻	-1302,6	92,5	-1137,3
HPO ₄ ²⁻	-1292,14	-33,47	-1089,28
HPO ₄ ²⁻	-1298,89	-810,792	-1057,143
ADP ³⁻	-2627,4	-4010	-1424,7
ATP ⁴⁻	-3617,15	-4520	-2292,5
ADP ³⁻	-2627,4	-4117,11	-1399,9
ATP ⁴⁻	-3617,1	-4526,1	-2267,64
AMP ²⁻	-	-	-554,83
AMP ²⁻	-1638,34	-3717,19	-530,066
AcetylCoA ³⁻	-	-	-58,06
AcetylCoA ⁴⁻	-	-	-51,8968
CoA ³⁻	-	-	-7,26
CoA ³⁻	-	-	-5,7716
H ₃ CCOOH	-484,3	159,8	-389,9
H ₃ CCOO ⁻	-486,84	82,23	-247,83
H ₃ CCOO ⁻	-486	85,3	-240,963

$$K_a = K_{Lehninger} = \frac{[CH_3COO^-] \cdot [HSCoA^4] \cdot [H_3O^+]}{[H_2O]^2 \cdot [Acetyl-CoA^4]} = 317017,64$$

ADP²⁻ + H₂PO₄⁻ => ATP³⁻ + H₂O; $\Delta G_{Lehninger} = 20,55 \text{ kJ/mol}$; pH=?

$$\Delta G_{Hess} = \Delta G^\circ_{ATP3} + \Delta G^\circ_{H_2O} - \Delta G^\circ_{H_2PO_4} - \Delta G^\circ_{ADP2} = 37,85 \text{ kJ/mol};$$

$$= -2267,64 - 151,549 - (-1399,9 - 1057,143) = 37,85 \text{ kJ/mol}$$

$$K_{eq} = K_{Lehninger} * [H_2O] = 0,000004535142 * 55,3 = 0,000250993;$$

$$\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = -8,3144 \cdot 298,15 \cdot \ln(0,000250993) = 20,55 \text{ kJ/mol};$$

$$K_{bHL} = K_{bbLehninger} [H_2O] = 0,000250993 = \frac{[H_2O] \cdot [ATP^{3-}]}{[H_2PO_4^-] [ADP^{2-}]}$$

bb ADP³⁻ + HPO₄²⁻ + H₃O⁺ => ATP⁴⁻ + 2H₂O;

$\Delta G_{bbLehninger} = 30,5 \text{ kJ/mol}$; $K_{bbLehn} = 0,000004535142$; pH=7,36

$$K_{Lehninger} = \exp(-30,5/8,3144/298,15) = 0,000004535142;$$

$$\Delta G_H = \Delta G^\circ_{ATP4} + 2\Delta G^\circ_{H_2O} - \Delta G^\circ_{HPO_4} - \Delta G^\circ_{ADP3} - \Delta G^\circ_{H_3O} = 46,015 \text{ kJ/mol};$$

$$= -2267,64 - 2 * 151,549 - (-1057,143 - 1399,9 - 213,275) = 46,015 \text{ kJ/mol};$$

$$K_{bbLehninger} = \exp(-\Delta G_{Lehninger}/R/T) = \exp(-30500/8,3144/298,15) = 0,000004535142 = \frac{[H_2O]^2 \cdot [ATP^{4-}]}{[HPO_4^{2-}] [ADP^{3-}] \cdot [H_3O^+]}$$
 ;

AcetylCoA⁴⁻ + ADP³⁻ + HPO₄²⁻ => CH₃COO⁻ + CoA⁴⁻ + ATP⁴⁻;

$\Delta G_H = \Delta G^\circ_{CH_3COO} + \Delta G^\circ_{CoA2} + \Delta G^\circ_{ATP4} - \Delta G^\circ_{Acetyl-CoA2} - \Delta G^\circ_{ADP3} - \Delta G^\circ_{HPO_4} = -5,4348 \text{ kJ/mol}$;

$$= -2267,64 - 240,963 - 5,7716 - (-1057,143 - 1399,9 - 51,8968) = -5,4348 \text{ kJ/mol};$$

$$K_{abb} = K_a K_{bbLehninger} = 317017,64 * 0,000004535142 = 1,43772001390488 = \frac{[CH_3COO^-] \cdot [HSCoA^4] \cdot [ATP^{4-}]}{[HPO_4^{2-}] [ADP^{3-}] [Acetyl-CoA^4]}$$

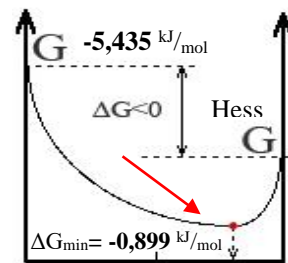
$\Delta G_{abb} = \Delta G_a + \Delta G_{bb} = -31,409 + 30,51 = -0,899 \text{ kJ/mol}$;

$$\Delta G_{abb} = -R \cdot T \cdot \ln(K_{abb}) = -8,3144 * 298,15 * \ln(1,4375) = -0,899 \text{ kJ/mol};$$

Eksotermiska un endoerģiska AcetylCoA³⁻ un **ADP³⁻** deacilēšanas, fosforilēšanas Hesa brīvās enerģijas izmaiņa pie pH 7,36 negatīva $\Delta G_{esterifikācija} = -5,435 \text{ kJ/mol}$, bet minimizējas $\Delta G_{min} = \Delta G_{abb} = -0,899 \text{ kJ/mol}$ sasniedzot līdzsvara maisījumu:

$$K_{abb} = K_a K_{bbLehninger} = 317017,64 * 0,000004535142 = 1,43772;$$

Lešatļe princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



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

Reaktanti **HPO₄²⁻ + H₃O⁺ + ADP³⁻**;
 produkti **2H₂O + ATP⁴⁻**

TERMODINAMIKA vingrinājums V I **Glyc31P=Glyc3P** hidrolīze

Aprēķināt ΔH_H ΔS_H ΔG_H standarta apstākļos 298,15 K. Reakcija ir **eksotermiska**, **atermiska**, **endotermiska**?

Glicerāta defosforilēšana **Glyc31P=Glyc3P** ūdenī! **Eksoerģiskas** vai **endoerģiska** hidrolīze? **Reaktanti => produkti**

Lehninger 2000 $\Delta G_{aL} = -39,351$ kJ/mol; **cGlycerat31P⁴⁻ + H₂O => Glycerat3P³⁻ + H₂PO₄⁻**; pH<7,199

Lehninger 2000 $\Delta G_{aLehninger} = -49,3$ kJ/mol; **Glycerat31P⁴⁻ + 2H₂O => Glycerat3P³⁻ + HPO₄²⁻ + H₃O⁺ + ΔG + Q**; pH=7,36

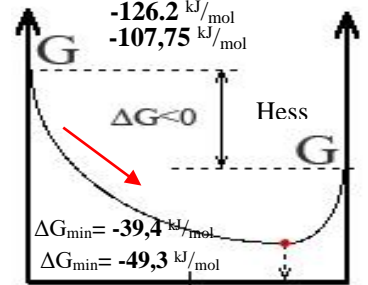
Viela	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
H₃O⁺	-285,81	-3,854	-213,275
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549
H₂PO₄⁻	-1296,3	90,4	-1130,2
H₂PO₄⁻	-1302,6	92,5	-1137,3
HPO₄²⁻	-1292,14	-33,47	-1089,28
HPO₄²⁻	-1298,89	-810,792	-1057,143
Glycerate ⁻	-	-	-452,31
Glycerat2P ³⁻	-	-	-1341,79
Glycerat2P ³⁻	-	-	-1333,2
Glycerat3P ³⁻	-1725,81	-2224,26	-1347,73
Glycerat31P ⁴⁻	-1725,76	-2290,6	-2207,30

$K_{aL} = K_{aLehninger} / [H_2O] = 433562158,5 / 55,3457339 = 7833705,111$
 $\Delta G_{aL} = -R \cdot T \cdot \ln(K_{aL}) = -8,3144 \cdot 298,15 \cdot \ln(7833705,111) = -39,351$ kJ/mol

$\Delta G_{Hess} = \Delta G^{\circ}_{Glyc3P} + \Delta G^{\circ}_{H2PO4} - \Delta G^{\circ}_{Glyc31P} - \Delta G^{\circ}_{H2O} = -126,2$ kJ/mol;
 $= -1347,73 - 1137,3 - (-2207,3) + (-151,549) = -126,2$ kJ/mol

$K_{aLehninger} = \exp(49300 / 8,3144 / 298,15) = 433562158,5$

Eksoerģiskas Glycerat31P⁴⁻ hidrolīzes Hesa brīvās enerģijas izmaiņa $\Delta G_{esterification} = -126,2$ kJ/mol negatīva un **-107,75** kJ/mol, bet minimizējas $\Delta G_{aL} = -39,4$ kJ/mol un $\Delta G_{aLehninger} = -49,3$ kJ/mol sasniedzot ΔG_{min} līdzsvara maisījuma minimumu pie pH=7,36:



$$\frac{[HPO_4^{2-}] \cdot [H_3O^+] \cdot [Glycerat3P^{3-}]}{[H_2O]^2 \cdot [Glycerat31P^{4-}]} = 433562158,5 = K_{aLehninger}; K_{aL} = K_{aLehninger} / [H_2O] = 7833705; A + 2B \quad 50\% \quad C + D + E$$

$\Delta G_{Hess} = \Delta G^{\circ}_{H3O+} + \Delta G^{\circ}_{Glyc3P} + \Delta G^{\circ}_{HP042-} - \Delta G^{\circ}_{Glyc31P} - 2\Delta G^{\circ}_{H2O} = -107,75$ kJ/mol; Reaktanti **Glycerat31P⁴⁻ + 2H₂O**
 $= -213,275 - 1347,73 - 1057,143 - (-2207,30 + 2 \cdot -151,549) = -107,75$ kJ/mol. produkti **Glycerat3P³⁻ + HPO₄²⁻ + H₃O⁺**

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

pH<7,199; **PyruvEnolP³⁻ + H₂O + H₃O⁺ => H₃CC=OCOO⁻ + H₂PO₄⁻**;

$\Delta G_H = \Delta G^{\circ}_{H3CC=OCOO} + \Delta G^{\circ}_{H2PO4} - \Delta G^{\circ}_{PyruvEnolP3} - \Delta G^{\circ}_{H2O} - \Delta G^{\circ}_{H3O} = -474,44 - 1137,3 - (-1189,73 - 155,66 - 213,275) = -53,075$ kJ/mol.

a PyruvEnolP³⁻ + H₂O => H₃CC=OCOO⁻ + HPO₄²⁻ + ΔG + Q; pH=7,36 $\Delta G_{Lehninger} = -61,9$ kJ/mol; Lehninger 2000;

$\Delta G_H = \Delta G^{\circ}_{H3CC=OCOO} + \Delta G^{\circ}_{HP042-} - \Delta G^{\circ}_{PyruvEnolP3} - \Delta G^{\circ}_{H2O} = -344,62 - 1057,14 - (-1189,73 - 151,549) = -60,481$ kJ/mol.

$K_{Lehninger} = \exp(-\Delta G_{Lehninger} / R / T) = \exp(61900 / 8,3144 / 298,15) = 69902464988$

$K_{aL} = K_{Lehninger} / [H_2O] = 69902464988 / 55,3457339 = 1263014510$

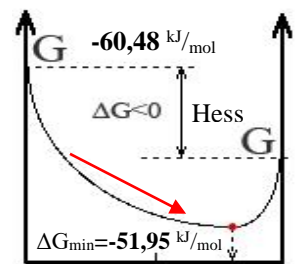
$\Delta G_a = -R \cdot T \cdot \ln(K_a) = -8,3144 \cdot 298,15 \cdot \ln(1263014510) / 1000 = -51,95$ kJ/mol;

Eksoerģiska **PyruvEnolP³⁻** hidrolīzes Hesa brīvās enerģijas izmaiņa ΔG_{Hess} negatīva **-60,48** kJ/mol, bet minimizējas $\Delta G_{min} = \Delta G_{eq} = -51,95$ kJ/mol līdzsvara

maisījumā: $\frac{[CH_3C=OCOO^-] \cdot [HPO_4^{2-}]}{[H_2O] \cdot [PyruvEnolP^{3-}]} = 1263014510 = K_a$; Lešatelje princips ir

Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



A + B 50% C + D

Reaktanti **PyruvEnolP³⁻ + H₂O**
 produkti **H₃CC=OCOO⁻ + HPO₄²⁻**

TERMODINAMIKA V m **Glc 6-P²**-hidrolīze par **Glc+HPO₄²⁻** un **Glc 6-P²**-par **Glc 1-P²**- izomerizācija.

Aprēķināt ΔH_H ΔS_H ΔG_H standarta apstākļos 298,15 K. Reakcija ir **eksotermiska**, **atermiska**, **endotermiska**? **Glc 6-P²**, **Glc 1-P²**-defosforilēšana par Glikozi! **Eksoerģiskas** vai **endoerģiska** hidrolīze? **Reaktanti** => **produkti**

Lehninger 2000 $\Delta G_{Lehninger} = -13,8 \text{ kJ/mol}$; **Glc6P²⁻+H₂O => Glc+HPO₄²⁻+Q+ΔG**; pH=7,36; $\Delta G_H = -11,38 \text{ kJ/mol}$

$\Delta G_{Lehninger} = -20,9 \text{ kJ/mol}$; **Glc1P²⁻+H₂O => Glc+HPO₄²⁻+ΔG+Q**; pH=7,36; $\Delta G_H = -18,42 \text{ kJ/mol}$ **BioThermodyn 2006**

Viela	$\Delta H_H^{\circ} \text{ kJ/mol}$	$\Delta S_H^{\circ} \text{ J/mol/K}$	$\Delta G_H^{\circ} \text{ kJ/mol}$
H ₂ O	-285,85	69,9565	-237,191
H ₂ O	-286,65	-453,188	-151,549
Glc	-1263,78	269,45	-919,96
Glc	-1267,13	-2901,49	-402,05
H ₂ PO ₄ ⁻	-1302,6	92,5	-1137,3
HPO ₄ ²⁻	-1292,14	-33,47	-1089,28
HPO ₄ ²⁻	-1298,89	-810,792	-1057,143
Glc6P ²⁻	-2260	3291,56	-1318,92
Glc6P ²⁻	-2279,314	-3297,196	-1296,262
Glc1P ²⁻	-2260	-3291,56	-1311,89
Glc1P ²⁻	-	-	-1289,221

1. $\Delta H_{Hess} = \sum \Delta H^{\circ}_{\text{produkti}} - \sum \Delta H^{\circ}_{\text{izejvielas}}$; 2. $\Delta S_{Hess} = \sum \Delta S^{\circ}_{\text{produkti}} - \sum \Delta S^{\circ}_{\text{izejvielas}}$; 3. $\Delta G_{Hess} = \Delta H_{Hess} - T \cdot \Delta S_{Hess}$

$\Delta G_H = \Delta G^{\circ}_{\text{Glc}} + \Delta G^{\circ}_{\text{HPO42}} - \Delta G^{\circ}_{\text{H2O}} - \Delta G^{\circ}_{\text{Glc6P}} = -11,382 \text{ kJ/mol}$ **eksoerģiska**
 $= -402,05 - 1057,143 - (-151,549 - 1296,262) = -11,382 \dots \text{ kJ/mol}$

$\Delta G_H = \Delta G^{\circ}_{\text{Glc}} + \Delta G^{\circ}_{\text{HPO42}} - \Delta G^{\circ}_{\text{H2O}} - \Delta G^{\circ}_{\text{Glc1P}} = -18,423 \text{ kJ/mol}$ **eksoerģiska**
 $= -402,05 - 1057,143 - (-151,549 - 1289,221) = -18,423 \dots \text{ kJ/mol}$

1. $\Delta H_H = \Delta H^{\circ}_{\text{Glc}} + \Delta H^{\circ}_{\text{HPO42}} - \Delta H^{\circ}_{\text{H2O}} - \Delta H^{\circ}_{\text{Glc6P}} = -0,056 \text{ kJ/mol}$ **atermiska**
 $= -1267,13 - 1298,89 - (-286,65 - 2279,314) = -0,056 \dots \text{ kJ/mol}$

2. $\Delta S_{izkļiedāta} = \Delta H_H / T = 56 / 298,15 = 0,188 \dots \text{ J/(mol K)}$

2. $\Delta S_H = \Delta S^{\circ}_{\text{Glc}} + \Delta S^{\circ}_{\text{HPO42}} - \Delta S^{\circ}_{\text{H2O}} - \Delta S^{\circ}_{\text{Glc6P}} = 38,102 \text{ J/mol/K}$
 $= -2901,49 - 810,792 - (-453,188 - 3297,196) = 38,102 \dots \text{ J/mol/K}$

$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -0,056 - 298,15 \cdot 0,038102 = -11,42 \text{ kJ/mol}$

3. $\Delta S_{kopēja} = \Delta S_H + \Delta S_{izkļiedāta} = 0,188 + 38,102 = 38,29 \text{ J/(mol K)}$; $T \cdot \Delta S_{kopēja} = 38,29 \cdot 298,15 = 11,42 \text{ kJ/mol}$ **patvaļīga**

$\Delta H_{H1} = \Delta H^{\circ}_{\text{Glc}} + \Delta H^{\circ}_{\text{HPO42}} - \Delta H^{\circ}_{\text{H2O}} - \Delta H^{\circ}_{\text{Glc1P}} = -16,02 \text{ kJ/mol}$; $\Delta S_{H1} = \Delta S^{\circ}_{\text{Glc}} + \Delta S^{\circ}_{\text{HPO42}} - \Delta S^{\circ}_{\text{H2O}} - \Delta S^{\circ}_{\text{Glc1P}} = 32,466 \text{ J/mol/K}$;
 $\Delta G_{H1} = \Delta H_{H1} - T \cdot \Delta S_{H1} = -16,02 - 298,15 \cdot 0,032466 = -25,6997 \text{ kJ/mol}$; $\Delta G_{H66} = \Delta H_{H66} - T \cdot \Delta S_{H66} = 0,056 - 298,15 \cdot -0,038102 = 11,42 \text{ kJ/mol}$

$\frac{[\text{Glc}] \cdot [\text{HPO}_4^{2-}]}{[\text{Glc6P}^{2-}] \cdot [\text{H}_2\text{O}]}$ $\Delta G_{Lehninger} = -13,8$; $K_{Lehninger6} = \text{EXP}(-\Delta G_H / R / T) = \text{EXP}(13800 / 8,3144 / 298,15) = 261,62$; 210,93
 $= K_{eq6} = 4,727$; 3,811; 298,15 K, 310,15; $K_{eq6} = K_{Lehninger6} / [\text{H}_2\text{O}] = 261,62 / 55,3457339 = 4,727$
 $\Delta G_{eq1} = -R \cdot T \cdot \ln(K_{eq1}) = -8,3144 \cdot 298,15 \cdot \ln(4,727) / 1000 = -3,851 \text{ kJ/mol}$; $-3,45 \text{ kJ/mol}$
 $K_{Lehninger} = \text{EXP}(-\Delta G_H / R / T) = \text{EXP}(20900 / 8,3144 / 298,15) = 4587,22$; 3310,4
 $= K_{eq1} = 82,883$; 0, 59,813; 298,15, 310,15; $K_{eq1} = K_{Lehninger1} / [\text{H}_2\text{O}] = 4587,22 / 55,3457339 = 82,883$
 $\Delta G_{eq1} = -R \cdot T \cdot \ln(K_{eq1}) = -8,3144 \cdot 298,15 \cdot \ln(82,883) / 1000 = -10,95 \text{ kJ/mol}$; $-10,55 \text{ kJ/mol}$;

$\Delta G_{Lehninger66} = 13,8$; $K_{Lehninger66} = \text{EXP}(-\Delta G_{L66} / R / T) = \text{EXP}(-13800 / 8,3144 / 298,15) = 0,003822314$; 0,004740984
 $K_{eq66} = K_{Lehninger66} \cdot [\text{H}_2\text{O}] = 0,003822314 \cdot 55,3457339 = 0,21154877$; 0,262393; 298,15 K, 310,15 K.
 $\Delta G_{eq66} = -R \cdot T \cdot \ln(K_{eq66}) = -8,3144 \cdot 298,15 \cdot \ln(0,21154877) / 1000 = 3,85 \text{ kJ/mol}$; $3,45 \text{ kJ/mol}$

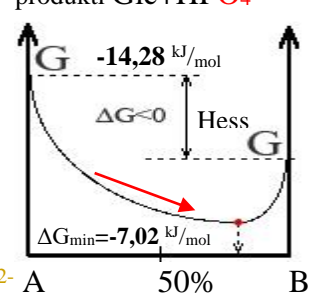
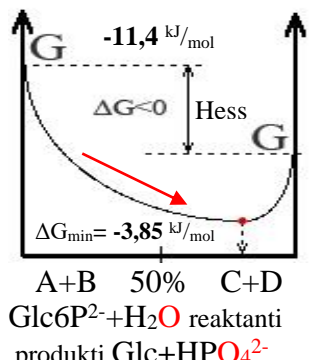
Endotermiska un eksoerģiska defosforilēšanas reakcijas brīvās enerģijas izmaiņa
 $\Delta G_{\text{fosforilēšana}}$ negatīva $-11,42 \text{ kJ/mol}$, bet minimizējas līdz $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -3,851 \text{ kJ/mol}$
 sasniedzot līdzsvaru $K_{eq} = 4,727$. Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars. **Glc1P²⁻ <=> Glc6P²⁻** konstante $K_{\text{Glc1PGlc6P}} = 17$;

$\Delta G_H = \Delta G^{\circ}_{\text{Glc6P}} - \Delta G^{\circ}_{\text{Glc1P}} = -1296,262 - (-1289,221) = -7,042 \text{ kJ/mol}$ **eksoerģiska**.....kJ/mol
 $\Delta G_{\text{kopēja}} = \Delta G^{\circ}_{\text{H66}} + \Delta G^{\circ}_{\text{H1}} = 11,42 - 25,7 = -14,28 \text{ kJ/mol}$ **exoerģic**.....kJ/mol

$K_{eq} = [\text{Glc 6-fosfāts}] / [\text{Glc 1-fosfāts}] = 17 \text{ mM} / 1 \text{ mM}$
 $\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = -8,3144 \cdot 298,15 \cdot \ln(17) = -7,02 \text{ kJ/mol}$. Endotermiska un eksoerģiska izomerizācijas reakcijas brīvās enerģijas izmaiņa $\Delta G_{\text{isomerisation}}$ negatīva

$-14,28 \text{ kJ/mol}$, bet minimizējas līdz $\Delta G_{eq} = -7,02 \text{ kJ/mol}$ sasniedzot līdzsvaru ΔG_{min} . Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars. $K_{\text{aGlc1PGlc6P}} = 17$;



TERMODINAMIKA VINGRINĀJUMS VI Enzīma CA protolīzes līdzsvars $\text{H}_2\text{O}^{\text{CA}}/\text{CO}_2/\text{H}_3\text{O}^++\text{HCO}_3^-$
 Enzīma karboanhidrāzes (CA) hidrolīze-protolīze $\text{H}_2\text{O}^{\text{CA}}/\text{CO}_2/\text{H}_3\text{O}^++\text{HCO}_3^-$ virza CO_2aq ar $2\text{H}_2\text{O}$!. Būs
eksoerģiska vai endoerģiska! $\text{CO}_2\uparrow_{\text{gas}}$ nereaģē ar H_2O tikai šķīst ūdenī. $\text{CO}_2\uparrow_{\text{gas}} + \Delta\text{G} \rightleftharpoons \text{CO}_2\text{aq} + \text{Q}$;

Viela	$\Delta\text{H}^\circ_{\text{H}}$ kJ/mol	$\Delta\text{S}^\circ_{\text{H}}$ J/mol/K	$\Delta\text{G}^\circ_{\text{H}}$ kJ/mol
H_3O^+	-285.81	-3.854	-213,274599
OH^-	-230,015	-10,9	-157,2
HCO_3^-	-689.93	98.324	-586,93988
HCO_3^-	-692,4948	-494,768	-544,9688
H_2O	-285.85	69.9565	-237,191
H_2O	-286,65	-453,188	-151,549
CO_2aq	-413.7976	117.5704	-385,98
$\text{CO}_2\uparrow_{\text{gas}}$	-393,509	213,74	-394,359

$$\Delta\text{H}_{\text{H}} = \Delta\text{H}^\circ_{\text{CO}_2\text{aq}} - \Delta\text{H}^\circ_{\text{CO}_2\text{gas}} = -413.7976 + 393.509 = -20,3 \text{ kJ/mol}$$

$$\Delta\text{S}_{\text{Hess}} = \Delta\text{S}^\circ_{\text{CO}_2\text{aq}} - \Delta\text{S}^\circ_{\text{CO}_2\text{gas}} = 117,57 - 213,74 = -96,17 \text{ J/mol/K};$$

$$= 117,57 + 69,9565 - (213,74 + 69,9565) = -96,17 \dots \text{ J/mol/K}$$

$$\Delta\text{G}_{\text{H}} = \Delta\text{H}_{\text{H}} - T \cdot \Delta\text{S}_{\text{H}} = -20,3 + 298,15 \cdot 0,09617 = 8,385 \text{ kJ/mol};$$

$$\Delta\text{G}_{\text{šk}} = \Delta\text{G}^\circ_{\text{CO}_2\text{aq}} - \Delta\text{G}^\circ_{\text{CO}_2\text{gas}} = -385,98 + 394,359 = 8,379 \text{ kJ/mol}$$

$$K_{\text{šk}} = \text{EXP}(-\Delta\text{G}_{\text{eq}}/R/T) = \text{EXP}(-8379/8,3144/298,15) = 0,034045$$

$$K_{\text{šk}} = 0,0341 = \frac{X_{\text{CO}_2\text{aq}}}{[\text{CO}_2\text{gas}]} = \frac{[\text{CO}_2\text{aq}]}{[\text{CO}_2\text{gas}] \cdot [\text{H}_2\text{O}]} \quad 100\% \text{ mol daļa ir}$$

$$[\text{CO}_2\text{gas}] = 1; [\text{CO}_2\text{aq}] = K_{\text{šk}} [\text{H}_2\text{O}] = 0,034 \cdot 55,346 = 1,878 \text{ M}$$

Gaisa 0,04% $[\text{CO}_2\text{gas}] = 0,0004$; $[\text{CO}_2\text{aq}] = K_{\text{šk}} \cdot [\text{CO}_2\uparrow_{\text{gas}}] \cdot [\text{H}_2\text{O}] = 0,034045 \cdot 0,0004 \cdot 55,3457339 = 0,000754 \text{ M}$;

Hidrolīzes reakcija $\text{CO}_2\text{aq} + 2\text{H}_2\text{O} + \Delta\text{G} + \text{Q} \xrightarrow{\text{CA}} \text{H}_3\text{O}^+ + \text{HCO}_3^-$ un skābes neutralizācijas līdzsvars

- $\Delta\text{H}_{\text{H}} = \Delta\text{H}^\circ_{\text{H}_3\text{O}^+} + \Delta\text{H}^\circ_{\text{HCO}_3^-} - 2\Delta\text{H}^\circ_{\text{H}_2\text{O}} - \Delta\text{H}^\circ_{\text{CO}_2} = -285.81 - 689.93 - (2 \cdot -285.85 - 413.7976) = 9.7576 \dots \text{ kJ/mol};$
 $\Delta\text{S}_{\text{izkļiedēta}} = -\Delta\text{H}_{\text{H}}/T = -9.7576 / 298.15 = -32.727 \dots \text{ J/mol/K};$ **endotermiska**.....
- $\Delta\text{S}_{\text{H}} = \Delta\text{S}^\circ_{\text{H}_3\text{O}^+} + \Delta\text{S}^\circ_{\text{HCO}_3^-} - 2\Delta\text{S}^\circ_{\text{H}_2\text{O}} - \Delta\text{S}^\circ_{\text{CO}_2} = -3.854 + 98.324 - (2 \cdot 69.9565 + 117.5704) = -163.0134 \text{ J/mol/K};$
 $\Delta\text{S}_{\text{kopēja}} = \Delta\text{S}_{\text{H}} + \Delta\text{S}_{\text{izkļiedēta}} = -32.727 - 163.0134 = -195.169 \dots \text{ J/mol/K};$
- $\Delta\text{G}_{\text{H}} = \Delta\text{H}_{\text{H}} - T \cdot \Delta\text{S}_{\text{H}} = 9.7576 + 298.15 \cdot 0.1630134 = 58.19 \dots \text{ kJ/mol};$
 $T \cdot \Delta\text{S}_{\text{kopēja}} = -195.7404 \cdot 298,15 \text{ K} = -58,19 \dots \text{ kJ/mol};$ saistīta $T\Delta\text{S}_{\text{H}} \leftarrow$ **uzkrāj brīvo enerģiju endoerģiska** ;
- $\Delta\text{G}_{\text{Hess}} = \Delta\text{G}^\circ_{\text{H}_3\text{O}^+} + \Delta\text{G}^\circ_{\text{HCO}_3^-} - 2\Delta\text{G}^\circ_{\text{H}_2\text{O}} - \Delta\text{G}^\circ_{\text{CO}_2} = -213,2746 - 544,9688 - (2 \cdot -237,191 - 385,98) = 102 \text{ kJ/mol};$
 $\Delta\text{G}_{\text{Absolute}} = \text{G}_{\text{H}_3\text{O}^+} + \text{G}_{\text{HCO}_3^-} - (2\text{G}_{\text{H}_2\text{O}} + \text{G}_{\text{CO}_2\text{aq}}) = 22,44 + 46,08 - (2 \cdot 0 + 8,379) = 60,14 \text{ kJ/mol};$

Termodinamiski nelabvēlīgs $\frac{[\text{HCO}_3^-]_{\text{aq}} \cdot [\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aq}} \cdot [\text{H}_2\text{O}]^2} = K_{\text{eqCA}} = K_{\text{HCO}_3} / [\text{H}_2\text{O}]^2 = 10^{-(7,0512)} / 55,3457339^2 = 2,906 \cdot 10^{-11}$

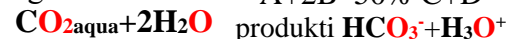
$$\Delta\text{G}_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(2,906 \cdot 10^{-(11)}) = 60 \text{ kJ/mol},$$

Endoerģiskas CO_2gas šķīdības un CO_2aq protolīzes $\Delta\text{G}_{\text{hidratācijas}} = 10,77 \text{ kJ/mol}$ Hesa brīvās enerģijas izmaiņa pozitīva un $\Delta\text{G}_{\text{protolīzes}} = 102 \text{ kJ/mol}$, bet minimizējas sasniedzot maisījumu šķīdībai $\Delta\text{G}_{\text{eq}} = 60 \text{ kJ/mol}$ un protolīzei $\Delta\text{G}_{\text{min}} = \Delta\text{G}_{\text{eq}} = 60 \text{ kJ/mol}$:

$$K_a = K_{\text{CA}} = K_{\text{eqCA}} \cdot [\text{H}_2\text{O}]^2 = \frac{[\text{HCO}_3^-]_{\text{aq}} \cdot [\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aq}}} = 10^{-7,0512}$$

$\text{pK}_a = \text{pK}_{\text{CA}} = 7,0512$ kļūst draudzīga fizioloģiskai $\text{pH} = 7,36$ vērtībai. Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma $\Delta\text{G}_{\text{min}}$ sasniegšana.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



$$\text{G}_{\text{H}_3\text{O}^+} + \text{G}_{\text{HCO}_3^-} = \text{G}_{\text{H}_3\text{O}^+} + \text{G}_{\text{HCO}_3^-} = 22.44 + 46.08 = \Delta\text{G}_{\text{spCO}_2\text{aq}} + \Delta\text{G}_{\text{eqCO}_2\text{aq}} = 8.379 + 60.14 = 68.52 \text{ kJ/mol} \quad [1,8,14]$$

Okeānā ar hidroksīda anjonu neatgriezeniski $\text{CO}_2\text{aq} + \text{OH}^- \Rightarrow \text{HCO}_3^- + \Delta\text{G}(-39,67 \text{ kJ/mol}) + \Delta\text{H}(-48,68 \text{ kJ/mol})$.

$$\Delta\text{H}_{\text{Hess}} = \Delta\text{H}^\circ_{\text{HCO}_3^-} - \Delta\text{H}^\circ_{\text{CO}_2} - \Delta\text{H}^\circ_{\text{OH}^-} = -692,4948 - (-413,7976 - 230,015) = -48,68 \text{ kJ/mol}; \text{ eksotermiska} \dots \dots \dots$$

$$\Delta\text{S}_{\text{izkļiede}} = -\Delta\text{H}_{\text{Hess}}/T = 48682,2/298,15 = 163,3 \text{ J/mol/K} \quad \Delta\text{S}_{\text{kopēja}} = \Delta\text{S}_{\text{Hess}} + \Delta\text{S}_{\text{izkļiede}} = 163,3 - 601,44 = -438,14 \text{ J/mol/K};$$

$$2. \Delta\text{S}_{\text{Hess}} = \Delta\text{S}^\circ_{\text{HCO}_3^-} - \Delta\text{S}^\circ_{\text{CO}_2} - \Delta\text{S}^\circ_{\text{OH}^-} = -494,768 - (117,5704 - 10,9) = -601,44 \text{ J/mol/K};$$

$$3. \Delta\text{G}_{\text{Hess}} = \Delta\text{H}_{\text{Hess}} - T \cdot \Delta\text{S}_{\text{Hess}} = -48,6822 - 298,15 \cdot -0,6014384 = 130,6 \text{ kJ/mol}; \text{ endoerģiska} \dots \dots \dots$$

$T \cdot \Delta\text{S}_{\text{kopēja}} = -0,43814 \cdot 298,15 \text{ K} = -130,6 \text{ kJ/mol}$; saistītā **akumulētā enerģija produktos**

$$3. \Delta\text{G}_{\text{Hess}} = \Delta\text{G}^\circ_{\text{HCO}_3^-} - \Delta\text{G}^\circ_{\text{CO}_2} - \Delta\text{G}^\circ_{\text{OH}^-} = -544,9688 - (-385,98 - 157,2) = -1,7888 \text{ kJ/mol}; \text{ pH} = 7,36; \text{ pOH} = 6,64$$

$\Delta\text{G}_{\text{eqOH}} = -R \cdot T \cdot \ln(K_{\text{eqOH}}) = -8,3144 \cdot 298,15 \cdot \ln(9180981,6)/1000 = -39,7 \text{ kJ/mol}$; Reakcija pie $\text{pOH} = 6,64$ ir lēna.

$$\frac{[\text{HCO}_3^-]}{[\text{CO}_2]_{\text{aq}} \cdot [\text{OH}^-]} = K_{\text{eqOH}} = K_{\text{eqCA}} / K_{\text{H}_2\text{O}} = 2,906 \cdot 10^{-11} / 3,26 / 10^{-18} = 9180981,6; \text{ Atgriezeniski CA klātienē};$$

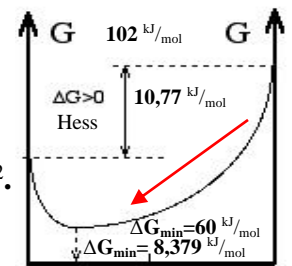
$$\Delta\text{G}_{\text{OH}} = -R \cdot T \cdot \ln(K_{\text{eqOH}} [\text{OH}^-]) = -8,3144 \cdot 298,15 \cdot \ln(2,1032413768) / 1000 = -1,84 \text{ kJ/mol}$$

$$[\text{HCO}_3^-] = K_{\text{eq}} [\text{OH}^-] \cdot [\text{CO}_2\text{aq}] = 2,103 \cdot 0,00075125 = 0,00158 \text{ M};$$

$$\text{Sum is } [\text{CO}_2\text{aq}] + [\text{HCO}_3^-] = 0,00075125 + 0,00158 = 0,0023 \text{ M};$$

$([\text{CO}_2\text{aq}] + [\text{HCO}_3^-]) / [\text{CO}_2\text{aq_no_GAISA}] = 0,0023 / 0,000754 = 30,5$ reizes lielāka ar CA karbo anhidrāzi.

CA izzušana uz planēts Zeme ūdens akvasfērā bikarbonātu ogleklis CO_2 samazinās 30,5 reizes.



TERMODINAMIKA VINGRINĀJUMS VII $\text{H}_2\text{O}+\text{CO}_2$ lietojot jonu kanālus $\text{H}_3\text{O}^++\text{HCO}_3^-$ virza uz CO_2gas
 Gaisa 0,04% mol daļa $[\text{CO}_2\uparrow_{\text{air}}]=0,0004$ kā 400 ppm miljonās daļas atmosfērā izšķīst ūdenī: (skat. 4. lpp.)

$$[\text{CO}_2\text{aqua}]=K_{\text{eq}}*[\text{CO}_2\uparrow_{\text{air}}]=1,878*0,0004=0,0007512 \text{ M. Plaušās reakciju}$$

$\text{H}^++\text{HCO}_3^-$ izelpojot CO_2gas ar ūdeni H_2O eksotermiski, atermiski vai endotermiski? Būs eksoerģiska vai endoerģiska! \leftarrow asimilējas fotosintēzes vajadzībām augu atvārsnītēs $\rightarrow \text{H}_3\text{O}^++\text{HCO}_3^- \Rightarrow \text{CO}_2\text{aqua}+2\text{H}_2\text{O}+Q+\Delta G$

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_3O^+	-285.81	-3.854	-213,274599
OH^-	-230,015	-10,9	-157,2
HCO_3^-	-689.93	98.324	-586,93988
HCO_3^-	-692,4948	-494,768	-544,9688
H_2O	-285.85	69.9565	-237,191
H_2O	-286,65	-453,188	-151,549
CO_2aqua	-413.7976	117.5704	-385,98
$\text{CO}_2\uparrow_{\text{gas}}$	-393,509	213,74	-394,359

$$\Delta G_{\text{Hess}}=2\Delta G^\circ_{\text{H}_2\text{O}}+\Delta G^\circ_{\text{CO}_2}-\Delta G^\circ_{\text{H}_3\text{O}^+}-\Delta G^\circ_{\text{HCO}_3^-}=-102 \text{ kJ/mol}$$

$$=2*(-237,191-385,98)-(-213,2746-544,9688)=-102 \text{ kJ/mol}$$

$$\Delta H_{\text{H}}=2\Delta H^\circ_{\text{H}_2\text{O}}+\Delta H^\circ_{\text{CO}_2}-\Delta H^\circ_{\text{H}_3\text{O}^+}-\Delta H^\circ_{\text{HCO}_3^-}=-7,1928 \text{ kJ/mol}$$

$$=2*(-285,85-413,7976)-(-285,81-692,4948)=-7,1928 \text{ kJ/mol}$$

$$\Delta S_{\text{izkļiedēta}}=-\Delta H_{\text{Hess}}/T=7,1928/298,15=24,125 \text{ J/mol/K;}$$

$$\Delta S_{\text{skopēja}}=\Delta S_{\text{H}}+\Delta S_{\text{izkļiedēta}}=756,1054+24,125=780,23 \text{ J/mol/K;}$$

$$\Delta G_{\text{H}}=\Delta H_{\text{H}}-T*\Delta S_{\text{H}}=-7,1928-298,15*0,7561054=-232,6 \text{ kJ/mol}$$

$$\Delta S_{\text{Hess}}=2\Delta S^\circ_{\text{H}_2\text{O}}+\Delta S^\circ_{\text{CO}_2}-\Delta S^\circ_{\text{H}_3\text{O}^+}-\Delta S^\circ_{\text{HCO}_3^-}=756,1054 \text{ J/mol/K}$$

$$=2*69,9565+117,5704-(-3,854-494,768)=756,1054 \text{ J/mol/K}$$

$T*\Delta S_{\text{skopēja}}=0,78023*298,15 \text{ K}=232,63 \text{ kJ/mol}$; saistīta izkļiedēta enerģija eksoerģiska nepatvaļīga

CAII; RBCs, kidney, osteoclasts, eye, GI tract, lung, brain, and testis; Cytosol; Glaucoma, epilepsy, edema, altitude sickness;
 $k_{\text{cat}}=1,4 \times 10^6(\text{s}^{-1})$; $k_1\text{CO}_2\text{aqua}=1,5 \times 10^8(\text{M}^{-1} \text{s}^{-1})$; [Biomed Res Int.](#) 2015;2015:453543. Review Article 3KS3,
 $v_1=k_1\text{CO}_2\text{aqua}[\text{CO}_2\text{aqua}]=1,5*10^8*0,0007512=112680 \text{ s}^{-1}$; as $v_1=k_{\text{cat}}/K_{\text{M}}*[E_i][S_i]$; $[E_i]=1 \text{ M}$; $S_i=[\text{CO}_2\text{aqua}]$;

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

$$k_2=k_1\text{CO}_2\text{aqua}/K_{\text{eqCA}}=1,5*10^8/2,9016/10^{(-11)}=5,17*10^{18} \text{ s}^{-1}=10^{18,7} \text{ M}^{-2}\text{s}^{-1};$$

Neutralizācijas ātruma konstante $k_2=10^{18,7} \text{ M}^{-2}\text{s}^{-1}$; $\text{H}_3\text{O}^++\text{HCO}_3^- \Rightarrow \text{CO}_2\text{aqua}+2\text{H}_2\text{O}$;

$$K_a=K_{\text{eqCA}}*[\text{H}_2\text{O}]^2=2,902*10^{(-11)}*(55,3457339)^2=8,892*10^{(-8)}=10^{(-7,0512)}; K_{\text{eqCA}}=\frac{[\text{HCO}_3^-] \cdot [\text{H}_3\text{O}^+]}{[\text{CO}_2]_{\text{aqua}}[\text{H}_2\text{O}]^2}$$

Neutralizācijas ātrums $\text{H}_3\text{O}^++\text{HCO}_3^- \Rightarrow \text{CO}_2\text{aqua}+2\text{H}_2\text{O}$ according bicarbonate concentration in okeāns

$\text{pOH}_{\text{okeāns}}=5,9$; $\text{pH}_{\text{okeāns}}=8,1$; $[\text{HCO}_3^-]=0,003 \text{ M}$; Haack Weltmeer Atlas 1969:

$$v_2=k_2*[\text{H}_3\text{O}^+][\text{HCO}_3^-]=10^{18,7}*10^{(-8,1)}*0,003=119432151 \text{ s}^{-1};$$

Ekstra Mitochondrijas telpā $\text{pH}=5$ $v_2=k_2*[\text{H}_3\text{O}^+][\text{HCO}_3^-]=10^{18,7}*10^{(-5)}*0,0154=771828339786 \text{ s}^{-1}$;

Neutralizācijas ātruma konstante ir lielāka par lēno hidroksīda anjona reakciju $k_1\text{OH}^-=1,5*10^2 \text{ M}^{-2}\text{s}^{-1}$;

$\text{HCO}_3^- \Rightarrow \text{CO}_2\text{aqua}+\text{OH}^-+\Delta G+Q$ sadalīšanās reakcija: $k_{\text{HCO}_3^-}=1,5*10^2/8914110=0,00001683 \text{ M}^{-1}\text{s}^{-1}$;

$$K_{\text{eqOH}^-}=k_1\text{OH}^-/k_{\text{HCO}_3^-}=[\text{HCO}_3^-]/[\text{CO}_2\text{aqua}][\text{OH}^-]=1,5*10^2 \text{ M}^{-2}\text{s}^{-1}/k_{\text{HCO}_3^-}=8914110.$$

$$v_{\text{HCO}_3^-}=k_{\text{HCO}_3^-}[\text{HCO}_3^-]=0,00001683*0,0154=0,000000259182 \text{ s}^{-1};$$

$\text{CO}_2\text{aqua}+\text{OH}^- \Rightarrow \text{HCO}_3^-$: $v_{1\text{OH}^-}=k_1\text{OH}^-*[\text{CO}_2\text{aqua}][\text{OH}^-]=1,5*10^2*0,0076*10^{(-6,63)}=0,000000267; \text{s}^{-1}$;

Ātrums hidroksīdam $k_1\text{OH}^-/k_1\text{CO}_2\text{aqua}=1,5*10^2/1,5/10^8=10^{-6}$ miljons reižu lēnāks par CA.

$$\text{Labvēlīgs OH}^- \text{ bet lēnāks bez CA } K_{\text{eqOH}^-}=K_{\text{eqCA}}/K_{\text{H}_2\text{O}}=2,993*10^{(-11)}/3,26/10^{(-18)}=9180981,6=\frac{[\text{HCO}_3^-]}{[\text{CO}_2]_{\text{aqua}}[\text{OH}^-]}$$

$\Delta G_{\text{eqOH}^-}=-R*T*\ln(K_{\text{eqOH}^-})=-8,3144*298,15*\ln(9180981,6)/1000=-39,7 \text{ kJ/mol}$; Favored equilibrium.

$\Delta G_{\text{Hess}}=\Delta G^\circ_{\text{HCO}_3^-}-\Delta G^\circ_{\text{OH}^-}-\Delta G^\circ_{\text{CO}_2}=-586,93988-(-157,2-385,98)=-43,76 \text{ kJ/mol}$;

$K_{\text{eqOH}^-}=K_{\text{eqCA}}/K_{\text{H}_2\text{O}}=2,993*10^{(-11)}/3,26/10^{(-18)}=9180981,6$; $K_{\text{eqHCO}_3^-}=1/K_{\text{eqOH}^-}=1/9180981,6=0,0000001089$;

Neutralizācija ir reizes 34463449218 ātrāka par karbo anhidrāzi CA ātrumu $k_1\text{CO}_2\text{aqua}=1,5*10^8 \text{ M}^{-1} \text{s}^{-1}$;

$1/K_{\text{eqCA}}=k_2/k_1\text{CO}_2\text{aqua}=10^{18,7}/1,5/10^8=34463449218$; $K_{\text{eqCA}}=k_1\text{CO}_2\text{aqua}/k_2=1,5*10^8/10^{18,7}=2,993*10^{(-11)}$;

Eksotermiska un eksoerģiska neutralizācija $\text{H}_3\text{O}^++\text{HCO}_3^- \rightleftharpoons \text{CO}_2\text{aqua}+2\text{H}_2\text{O}$ Hesa brīvā enerģija negatīva

-102 kJ/mol , $-43,76 \text{ kJ/mol}$ $\text{CO}_2\text{aqua}+\text{OH}^- \Rightarrow \text{HCO}_3^-$, bet minimizējas $\Delta G_{\text{min}}=\Delta G_{\text{eq}}=-60 \text{ kJ/mol}$,

$-39,67 \text{ kJ/mol}$, sasniedzot līdzsvara $K_{\text{eqHCO}_3^-}=1/K_{\text{eqOH}^-}=1/9180981,6=0,0000001089$

maisījumu $K_{\text{eqOH}^-}=K_{\text{eqCA}}/K_{\text{H}_2\text{O}}=9180981,6$.

Lešateljē princips ir Prigožina atraktors brīvās enerģijas izmaiņas minimuma

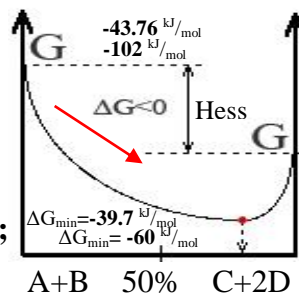
sasniegšana ΔG_{min} maisījumā. Beīvās enerģijas minimumā iestājas līdzsvars.

$$\Delta G_{1/\text{eqOH}^-}=-R*T*\ln(1/K_{\text{eqOH}^-})=-8,3144*298,15*\ln(34463449218)/1000=-60 \text{ kJ/mol};$$

$\text{CO}_2\text{aqua}+\text{OH}^-$; $\text{H}_3\text{O}^++\text{HCO}_3^-$ reaktanti produkti $\text{CO}_2\text{aqua}+2\text{H}_2\text{O}$;

$$\text{Protolysis of water } \text{pH}=\text{pOH}=7 \text{ } G_{\text{H}_3\text{O}^+}+G_{\text{OH}^-}=G_{\text{H}_3\text{O}^+}+G_{\text{OH}^-}=22,44+77,36=99,8 \text{ kJ/mol}$$

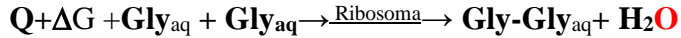
$$\text{CA } G_{\text{H}_3\text{O}^+}+G_{\text{HCO}_3^-}=G_{\text{H}_3\text{O}^+}+G_{\text{HCO}_3^-}=22,44+46,08=\Delta G_{\text{spCO}_2\text{aqua}}+\Delta G_{\text{eqCO}_2\text{aqua}}=8,379+60,14=68,52 \text{ kJ/mol} \cdot [1,8,14]$$



TERMODINAMIKA VINGRINĀJUMS VIII Glicīns+glicīns→ glicilglicīns dipeptīda sintēze

Aprēķināt ΔH_H ΔS_H ΔG_H standarta apstākļos (298.15 K). Reakcija ir **eksotermiska**, **atermiska**, **endotermiska**? Peptīdu sintēzē polikondensācijas Enzīms ribosoma vada reakciju ar aminoskābi glicīnu Gly (G)! Vai būs **eksoerģiska** vai **endoerģiska**!

Glicīns+glicīns→ glicilglicīns dipeptīda sintēze;



1. $\Delta H_H = \Delta H^\circ_{\text{Gly-Gly}} + \Delta H^\circ_{\text{H}_2\text{O}} - 2 \Delta H^\circ_{\text{Gly}} = -747,7 - 285,83 - (2 \cdot -514,36) = -1033,53 + 1028,72 = -4,81 \text{ kJ/mol}$ **eksotermiskas.**

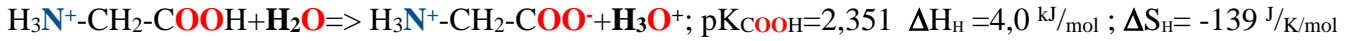
2. $\Delta S_{\text{izkliede}} = - \Delta H_H / T = - (-4,81) / 298,15 = 16,13 \text{ J/mol/K}$;

$\Delta S_H = \Delta S^\circ_{\text{Gly-Gly}} + \Delta S^\circ_{\text{H}_2\text{O}} - 2 \Delta S^\circ_{\text{Gly}} = 111 + 69,9565 - (2 \cdot 158,45) = 180,957 - 316,9 = -135,9435 \text{ J/mol/K}$;

3. $\Delta S_{\text{kopējā}} = \Delta S_H + \Delta S_{\text{izkliede}} = -135,9435 + 16,13 = -119,81 \text{ J/mol/K}$;

$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -4,81 - 298,15 \cdot (-0,1359435) = -4,81 + 41,128 = 35,72 \text{ kJ/mol}$; **endoerģiska** nepatvaļīga
 $T \cdot \Delta S_{\text{kopējā}} = -119,81 \text{ J/K/mol} \cdot 298,15 \text{ K} = -35,72 \text{ kJ/mol}$; saistīta akumulēta enerģija peptīda produktā.

Glicīna karbonskābes COOH protolīzes konstante: $K_{\text{eq}} = K_{\text{COOH}} / [\text{H}_2\text{O}] = 1/12416,5 = 10^{(-4,094)} =$



$\Delta H_H = \Delta H^\circ_{\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-} + \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{H}_3\text{N}^+\text{CH}_2\text{COOH}} - \Delta H^\circ_{\text{H}_2\text{O}} = 4 \text{ kJ/mol}$; $K_a = K_{\text{COOH}} = 1/224,39 = 10^{(-2,351)} =$

$\Delta H^\circ_{\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-} = 4 + \Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{H}_3\text{O}^+} + \Delta H^\circ_{\text{H}_3\text{N}^+\text{CH}_2\text{COOH}} = 4 - 286,65 + 285,81 - 525,06 = -521,9 \text{ kJ/mol}$;

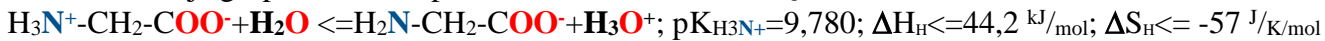
$\Delta S^\circ_{\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-} = -139 + \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{H}_3\text{O}^+} + \Delta S^\circ_{\text{H}_3\text{N}^+\text{CH}_2\text{COOH}} = -139 - 453,188 + 3,854 - 1204,952 = -1793,3 \text{ J/K/mol}$;

$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = 4 - 298,15 \cdot (-0,139) = 45,44 \text{ kJ/mol}$; **endoerģiskas** ;

$$K_{\text{COOH}} = 10^{-2,351} = \frac{[\text{H}^+] \cdot [\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]_{\text{Gly}}}{[\text{H}_3\text{N}^+\text{CH}_2\text{COOH}]} ; K_{\text{eq}} = K_{\text{COOH}} / [\text{H}_2\text{O}] = 10^{-2,351} / 55,33 = 10^{-4,094} = \frac{[\text{H}_3\text{O}^+] \cdot [\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]_{\text{Gly}}}{[\text{H}_2\text{O}] \cdot [\text{H}_3\text{N}^+\text{CH}_2\text{COOH}]}$$

$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(10^{(-4,094)}) = 23,37 \text{ kJ/mol}$,

Glicīna amonija grupas H_3N^+ - deprotonēšanas konstante: $K_{\text{eq}} = K_{\text{H}_3\text{N}^+} / [\text{H}_2\text{O}] = 1/108902871 = 10^{(-9,78)} =$



$\Delta H_H = \Delta H^\circ_{\text{H}_2\text{NCH}_2\text{COO}^-} + \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-} - \Delta H^\circ_{\text{H}_2\text{O}} = 44,2 \text{ kJ/mol}$; $K_a = K_{\text{H}_3\text{N}^+} = 1/6025595861 = 10^{(-9,78)} =$

$\Delta H^\circ_{\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-} = -44,2 + \Delta H^\circ_{\text{H}_2\text{NCH}_2\text{COO}^-} + \Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{H}_3\text{O}^+} = -44,2 - 525,06 - 286,65 + 285,81 = -570,1 \text{ kJ/mol}$;

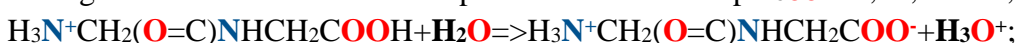
$\Delta S^\circ_{\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-} = -57 + \Delta S^\circ_{\text{H}_2\text{NCH}_2\text{COO}^-} + \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{H}_3\text{O}^+} = -57 - 1204,952 - 453,188 + 3,854 = -1597,3 \text{ J/K/mol}$;

$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = 44,2 - 298,15 \cdot (-0,057) = 27,2 \text{ kJ/mol}$; **endoerģiska**

$$K_{\text{COOH}} = 10^{-9,78} = \frac{[\text{H}^+] \cdot [\text{H}_2\text{NCH}_2\text{COO}^-]}{[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]_{\text{Gly}}} ; K_{\text{eq}} = K_{\text{H}_3\text{N}^+} / [\text{H}_2\text{O}] = 10^{(-9,78)} / 55,33 = 10^{-11,523} = \frac{[\text{H}_3\text{O}^+] \cdot [\text{H}_2\text{NCH}_2\text{COO}^-]}{[\text{H}_2\text{O}] \cdot [\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]_{\text{Gly}}}$$

$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(10^{(-11,523)}) = -65,773 + 23,37 = -42,403 \text{ kJ/mol}$;

Glicilglicīna karbonskābes COOH protolīzes konstante: $pK_{\text{COOH}} = 3,14$; $\Delta H_H = 0,11 \text{ kJ/mol}$; $\Delta S_H = -128 \text{ J/K/mol}$



$\Delta H_H = \Delta H^\circ_{\text{H}_3\text{N}^+\text{glyglyCOO}^-} + \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{H}_3\text{N}^+\text{glyglyCOOH}} - \Delta H^\circ_{\text{H}_2\text{O}} = 0,11 \text{ kJ/mol}$;

$\Delta H^\circ_{\text{H}_3\text{N}^+\text{glyglyCOO}^-} = 0,11 + \Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{H}_3\text{O}^+} + \Delta H^\circ_{\text{H}_3\text{N}^+\text{glyglyCOOH}} = 0,11 - 286,65 + 285,81 - 737,55 = -738,3 \text{ kJ/mol}$;

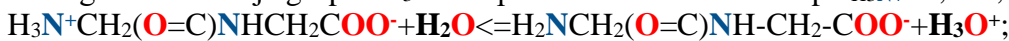
$\Delta S^\circ_{\text{H}_3\text{N}^+\text{glyglyCOO}^-} = -128 + \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{H}_3\text{O}^+} + \Delta S^\circ_{\text{H}_3\text{N}^+\text{glyglyCOOH}} = -128 - 453,188 + 3,854 - 1877,952 = -2455,3 \text{ J/K/mol}$;

$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = 0,11 - 298,15 \cdot (-0,128) = 38,27 \text{ kJ/mol}$; **eksoerģiskas** $K_a = K_{\text{COOH}} = 1/1380,4 = 10^{(-3,14)}$;

$$K_{\text{COOH}} = 10^{-3,14} = \frac{[\text{H}^+] \cdot [\text{H}_3\text{N}^+\text{glyglyCOO}^-]_{\text{Gly}}}{[\text{H}_3\text{N}^+\text{glyglyCOOH}]} ; K_{\text{eq}} = K_{\text{COOH}} / [\text{H}_2\text{O}] = 10^{-3,14} / 55,33 = 10^{-4,883} = \frac{[\text{H}_3\text{O}^+] \cdot [\text{H}_3\text{N}^+\text{glyglyCOO}^-]_{\text{Gly}}}{[\text{H}_2\text{O}] \cdot [\text{H}_3\text{N}^+\text{glyglyCOOH}]}$$

$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(10^{(-4,883)}) = 27,872 \text{ kJ/mol}$,

Glicilglicīna amonija grupas H_3N^+ - deprotonēšanas konstante: $pK_{\text{H}_3\text{N}^+} = 8,265$; $\Delta H_H = 43,4 \text{ kJ/mol}$; $\Delta S_H = -16 \text{ J/K/mol}$;



$\Delta H_H = \Delta H^\circ_{\text{H}_2\text{NglyglyCOO}^-} + \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{H}_3\text{N}^+\text{glyglyCOO}^-} - \Delta H^\circ_{\text{H}_2\text{O}} = 43,4 \text{ kJ/mol}$;

$\Delta H^\circ_{\text{H}_3\text{N}^+\text{glyglyCOO}^-} = -(43,4 - \Delta H^\circ_{\text{H}_2\text{NglyglyCOO}^-} + \Delta H^\circ_{\text{H}_2\text{O}} - \Delta H^\circ_{\text{H}_3\text{O}^+}) = -(43,4 + 737,55 - 286,65 + 285,81) = -780,11 \text{ kJ/mol}$;

$\Delta S^\circ_{\text{H}_3\text{N}^+\text{glyglyCOO}^-} = (-16 - \Delta S^\circ_{\text{H}_2\text{NglyglyCOO}^-} + \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{H}_3\text{O}^+}) = (-16 + 1877,952 - 453,188 + 3,854) = -1412,6 \text{ J/K/mol}$;

$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = 43,4 - 298,15 \cdot (-0,016) = 48,17 \text{ kJ/mol}$; **endoerģic**

$K_{\text{eq}} = K_{\text{H}_3\text{N}^+} / [\text{H}_2\text{O}] = 1/10232929923 = 10^{(-10,01)}$; $K_a = K_{\text{H}_3\text{N}^+} = 1/184077200 = 10^{(-8,265)} =$

$$K_{\text{COOH}} = 10^{-8,265} = \frac{[\text{H}^+] \cdot [\text{H}_2\text{N Glygly COO}^-]}{[\text{H}_3\text{N}^+\text{glyglyCOO}^-]_{\text{Gly}}} ; K_{\text{eq}} = K_{\text{COOH}} / [\text{H}_2\text{O}] = 10^{-8,265} / 55,33 = 10^{-10,01} = \frac{[\text{H}_3\text{O}^+] \cdot [\text{H}_2\text{N Glygly COO}^-]}{[\text{H}_2\text{O}] \cdot [\text{H}_3\text{N}^+\text{glyglyCOO}^-]_{\text{Gly}}}$$

$$\Delta G_{eq} = -R \cdot T \cdot \ln(K_{eq}) = -8,3144 \cdot 298,15 \cdot \ln(10^{-10,01}) = -57,137 + 27,873 = -29,262 \text{ kJ/mol},$$

Viela	$\Delta H^{\circ}_H \text{ kJ/mol}$	$\Delta S^{\circ}_H \text{ J/mol/K}$	$\Delta G^{\circ}_H \text{ kJ/mol}$	I=0,1 M	I=0,2 M	Protolīze palielina $\Delta G^{\circ}_{Hees} \text{ kJ/mol}$
Gly_{aqua}	-554,56	76,45	-180,13	-177,07	-176,08	= -176,08 - 42,403 = -218,48
GlyGly_{aq}	-790,99	-1	-200,55	-195,65	-194,07	= -194,07 - 29,262 = -223,332
Gly_{aqua}	-525,06	-1204,952	-165,8056	; I=1 M	-	= -165,8056 - 42,403 = -208,209
GlyGly_{aq}	-737,55	-1877,952	-177,6324	; I=1 M	-	= -177,6324 - 29,262 = -206,8944
H ₃ NCH ₂ COO-	-521,9	-1793,3	23,37	pK _a < 2,351	-	23,37
H ₃ NCH ₂ COO-	-570,1	-1597,3	-65,773	pK _a > 9,78	-	-65,773
Protolīze Summa	-546	-1695,3	-42,403	pH 7,36	-	-42,403
H ₃ NglyglyCOO-	-738,3	-2455,3	27,873	pK _a < 3,14	-	27,873
H ₃ NglyglyCOO-	-780,11	-1412,6	-57,137	pK _a > 8,265	-	-57,137
Protolīze Summa	-759,205	-1933,95	-29,262	pH 7,36	-	-29,262
H₃O⁺	-285,81	-3,854	-213,275	-	-	-
H₂O	-285,85	69,9565	-237,191	-	-	-
H₂O	-286,65	-453,188	-151,549	-	-	Peptīda sintēze:

$$\Delta H_H = \Delta H^{\circ}_{GlyGly} + \Delta H^{\circ}_{H_2O} - 2\Delta H^{\circ}_{Gly} = -737,55 - 286,65 - (2 \cdot -525,06) = 25,92 \text{ kJ/mol} = -759,205 - 286,65 - (2 \cdot -546) = 46,145 \text{ kJ/mol};$$

$$\Delta S_H = \Delta S^{\circ}_{GlyGly} + \Delta S^{\circ}_{H_2O} - 2\Delta S^{\circ}_{Gly} = -1877,952 - 453,188 - (2 \cdot -1204,952) = 78,764 \text{ J/mol/K}; = -1933,95 - 453,188 - (2 \cdot -1695,3) = 1003,5 \text{ J/mol/K};$$

$$\Delta S_{izkliede} = -\Delta H_H / T = -25,92 / 298,15 = -86,94 \text{ J/(mol K)}; \Delta S_{kopējā} = \Delta S_H + \Delta S_{izkliede} = -86,94 + 78,764 = -8,176 \text{ J/(mol K)};$$

$$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = 25,92 - 298,15 \cdot 0,078764 = 2,4365 \text{ kJ/mol}; \text{ endoergiska}; = 46,145 - 298,15 \cdot 0,10035 = 16,226 \text{ kJ/mol};$$

$$K_{Lehninger} = \exp(-9200 / 8,3144 / 298,15) = 1/40,9 = 0,02445 \text{ ab) Gly}_{aq} + \text{Gly}_{aq} \Rightarrow \text{Gly-Gly}_{aq} + \text{H}_2\text{O}; \Delta G_{abLehninger} = 9,2 \text{ kJ/mol};$$

$$\text{Chem. Phys. CRC, 2010, 1148; BioThermodynamic, Alberty, 2006.}$$

$$\text{Gly}_{aq} + \text{Gly}_{aq} \Rightarrow \text{GlyGly}_{aqua} + \text{H}_2\text{O}; \Delta G_H = \Delta G^{\circ}_{GlyGly} + \Delta G^{\circ}_{H_2O} - 2\Delta G^{\circ}_{Gly} =$$

$$= 16,2; \text{ Lehninger} = 9,2; 8,16; 6,94; 6,54; 2,43 \text{ kJ/mol}; \text{ protolīze}$$

$$\Delta G_{Hess} = \Delta H_H - T \cdot \Delta S_H = 46,145 - 298,15 \cdot 0,10035 = 16,2265 \text{ kJ/mol}; I=0 \text{ M}$$

$$\Delta G_{Heq} = -200,55 - 151,549 - (2 \cdot -180,13) = 8,161 \text{ kJ/mol endoergic}; I=0 \text{ M}$$

$$\Delta G_{Heq} = -195,65 - 151,549 - (2 \cdot -177,07) = 6,941 \text{ kJ/mol endoergic}; I=0,1 \text{ M}$$

$$\Delta G_{0,2M} = -194,07 - 151,549 - (2 \cdot -176,08) = 6,541 \text{ kJ/mol endoergic}; I=0,2 \text{ M}$$

$$\Delta G_{Heq} = -177,6324 - 151,549 - (2 \cdot -165,8056) = 2,4298 \text{ kJ/mol}; I=1 \text{ M};$$

$$\text{Sintēze: } \Delta G_{0,2M} = \Delta G^{\circ}_{GlyGly} + \Delta G^{\circ}_{H_2O} - 2\Delta G^{\circ}_{Gly} = 6,541 \text{ kJ/mol}; I=0,2 \text{ M}; K_{0,2M} = \exp(-6541 / 8,3144 / 298,15) = 0,07146;$$

$$\text{Hidrolīze: GlyGly}_{aqua} + \text{H}_2\text{O} \Rightarrow \text{Gly}_{aqua} + \text{Gly}_{aqua}; \Delta G_{Leninger} = -9,2 \text{ kJ/mol}; I=0 \text{ M}$$

$$\frac{[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]_{\text{Gly}}^2}{[\text{H}_2\text{O}] \cdot [\text{H}_3\text{N}^+\text{GlyGlyCOO}^-]_{\text{Gly}}} = K_{Leninger} = \exp(-\Delta G_{Leninger} / R/T) = \exp(-9200 / 8,3144 / 298,15) = 0,02445 \text{ sintēze.}$$

$$\frac{[\text{H}_2\text{O}] \cdot [\text{H}_3\text{N}^+\text{GlyGlyCOO}^-]_{\text{Gly}}}{[\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-]_{\text{Gly}}^2} = K_{Leninger} = \exp(-\Delta G_{Leninger} / R/T) = \exp(9200 / 8,3144 / 298,15) = 40,91 \text{ hidrolīze.}$$

$$K_{0,2M} = \exp(-\Delta G_{0,2M} / R/T) = \exp(6541 / 8,3144 / 298,15) = 13,994; \text{pH} = 7,36; \Delta G_{0,2M} = -8,3144 \cdot 298,15 \cdot \ln(14) = -6,54 \text{ kJ/mol}$$

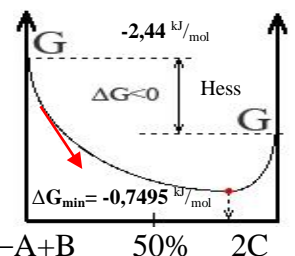
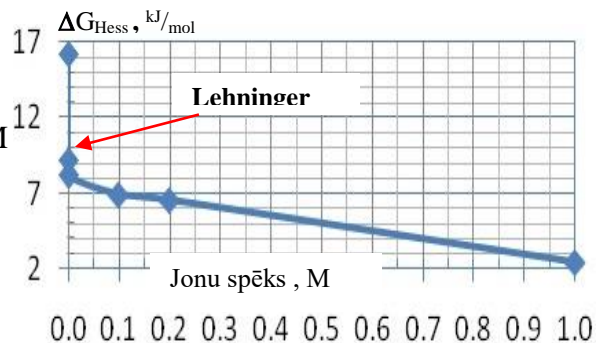
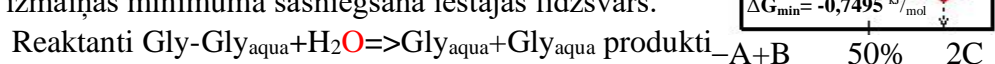
Endotermiskas un endoergiskas hidrolīzes Hesa brīvās enerģijas izmaiņa negatīva

$$\Delta G_{hidrolīze} = -16,23 \text{ kJ/mol}, \text{ bet minimizējas sasniedzot līdzsvara maisījumu ar jonu spēku}$$

$$I=0,2 \text{ M} \quad \Delta G_{min} = \Delta G_{0,2M} = -6,54 \text{ kJ/mol}; K_{0,2M} = 13,994.$$

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min}

sasniegšana. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.



$$\Delta G_{bLehninger} = -R \cdot T \cdot \ln(K_{bLehninger}) = -8,3144 \cdot 298,15 \cdot \ln(220500,2) / 1000 = -30,5 \text{ kJ/mol};$$

$$K_{eq} = K_{bLehninger} = \exp(-\Delta G_{bLehninger} / R/T) = \exp(30500 / 8,3144 / 298,15) = \exp(12,304) = 220500,2 = \frac{[H_2PO_4^-] \cdot [ADP^{3-}] \cdot [H_3O^+]}{[H_2O]^2 \cdot [ATP^{4-}]}$$

$$\Delta G_{Lehninger} = -R \cdot T \cdot \ln(K_{Lehninger}) = -8,3144 \cdot 298,15 \cdot \ln(0,0001739) / 1000 = -21,46 \text{ kJ/mol}.$$

pH < 7,199. $ATP^{3-} + H_2O \Rightarrow ADP^{2-} + H_2PO_4^-$; $K_{Lehninger} = K_{bLehninger} \cdot [H_3O^+] / [H_2O] = 0,0001739 = \frac{[H_2PO_4^-] \cdot [ADP^{2-}]}{[H_2O] \cdot [ATP^{3-}]}$;

$$\Delta G_{Hess} = \Delta G^\circ_{ADP3} + \Delta G^\circ_{HPO42} - \Delta G^\circ_{ATP4} - \Delta G^\circ_{H2O} = -1399,9 - 1057,143 - (-2267,64 - 237,191) = 47,79 \text{ kJ/mol};$$

b) $ATP^{4-} + 2H_2O \Rightarrow ADP^{3-} + HPO_4^{2-} + H_3O^+$; $\Delta G_{bLehninger} = -30,5 \text{ kJ/mol}$; $K_{bLehninger} = K_{Lehninger} [H_2O] / [H_3O^+] = 220500,2$;

$$\Delta G_H = \Delta G^\circ_{ADP3} + \Delta G^\circ_{HPO42} + \Delta G^\circ_{H3O} - \Delta G^\circ_{ATP4} - 2\Delta G^\circ_{H2O} = -1399,9 - 1057,143 - 213,275 - (-2267,64 + 2 \cdot -151,549) = -99,58 \text{ kJ/mol};$$

a) $Gly_{aq} + Gly_{aq} \Rightarrow Gly-Gly_{aq} + H_2O$; $\Delta G_{0,2M} = 6,54 \text{ kJ/mol}$; $K_{0,2M} = \exp(-6541 / 8,3144 / 298,15) = 0,07146$.

$$K_{0,2M \text{ hydrolyse}} = 1 / K_{0,2M} = 1 / 0,07146 = 13,994;$$

ab) $Gly_{aq} + Gly_{aq} + ATP^{4-} + H_2O \Rightarrow GlyGly_{aq} + ADP^{3-} + HPO_4^{2-} + H_3O^+$; $\Delta G_{ab} = \Delta G_{0,2M} + \Delta G_{bLehninger} = 6,54 - 30,5 = -23,96 \text{ kJ/mol}$;

$$\Delta G_H = \Delta G^\circ_{Gly-Gly} + \Delta G^\circ_{ADP3} + \Delta G^\circ_{HPO42} + \Delta G^\circ_{H3O} - 2\Delta G^\circ_{Gly} - \Delta G^\circ_{ATP4} - \Delta G^\circ_{H2O} =$$

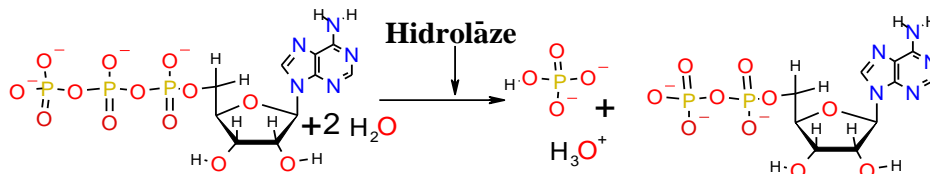
$$= -177,632 - 1399,9 - 1057,143 - 213,275 - (2 \cdot -165,806 - 2267,64 - 151,549) = -97,15 \text{ kJ/mol};$$

Viela $\Delta H^\circ_{Hess} \text{ kJ/mol}$ $\Delta S^\circ_{H} \text{ J/mol/K}$ $\Delta G^\circ_{Hess} \text{ kJ/mol}$; $= -177,632 - 1399,9 - 1057,143 - 213,275 - (2 \cdot -165,806 - 2267,64 - 151,549) = -97,15 \text{ kJ/mol}$;

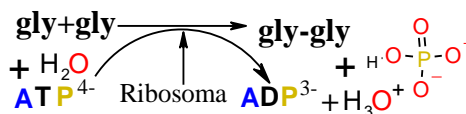
Viela	$\Delta H^\circ_{Hess} \text{ kJ/mol}$	$\Delta S^\circ_{H} \text{ J/mol/K}$	$\Delta G^\circ_{Hess} \text{ kJ/mol}$
H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
$H_2PO_4^-$	-1296,3	90,4	-1130,2
$H_2PO_4^-$	-1302,6	92,5	-1137,3
HPO_4^{2-}	-1292,14	-33,47	-1089,28
HPO_4^{2-}	-1298,89	-810,792	-1057,143
ADP^{3-}	-2627,4	-4010	-1424,7
ATP^{4-}	-3617,15	-4520	-2292,5
ADP^{3-}	-2627,4	-4117,11	-1399,9
ATP^{4-}	-3617,1	-4526,1	-2267,64
Gly_{aqua}	-554,56	76,45	-176,08
$GlyGly_{aq}$	-790,99	-1	-194,07
Gly_{aqua}	-525,06	-1204,95	-165,806
$GlyGly_{aq}$	-737,55	-1877,95	-177,632

b) $ATP^{4-} + 2H_2O \Rightarrow ADP^{3-} + HPO_4^{2-} + H_3O^+$; $\Delta G_{bLehninger} = -30,5 \text{ kJ/mol}$;

$$K_{bLehninger} = 220500,2; \text{ pH} = 7,36;$$



a) $Gly_{aq} + Gly_{aq} \Rightarrow Gly-Gly_{aq} + H_2O$; $\Delta G_{0,2M} = 6,54 \text{ kJ/mol}$;



ab) $Gly_{aq} + Gly_{aq} + ATP^{4-} + H_2O \Rightarrow GlyGly_{aq} + ADP^{3-} + HPO_4^{2-} + H_3O^+$;

$$\Delta G_{ab} = \Delta G_{0,2M} + \Delta G_{bLehninger} = 6,54 - 30,5 = -23,96 \text{ kJ/mol};$$

Peptīda saitēs sintēze ribosomās.

$$K_{eq} = K_{0,2M} K_b = 0,07146 \cdot 220500,2 = [GlyGly] \cdot [ADP^{3-}] \cdot [HPO_4^{2-}] \cdot [H_3O^+] / [Gly]^2 \cdot [ATP^{4-}] \cdot [H_2O] = 15756,9.$$

$$K_{eq \text{ a0,2Mb}} = K_{0,2M} K_b = \frac{[H_3N^+ GlyGly COO^-] Gly \cdot [HPO_4^{2-}] \cdot [ADP^{3-}] \cdot [H_3O^+]}{[H_3N^+ CH_2COO^-] Gly^2 \cdot [H_2O] \cdot [ATP^{4-}]} = 15756,944.$$

$$\Delta G_{eqLehninger} = -R \cdot T \cdot \ln(K_{eqLehninger}) = -8,3144 \cdot 298,15 \cdot \ln(15756,944) / 1000 = -23,959 \text{ kJ/mol}.$$

$$K_{eqLehninger} = K_{Lehninger} [H_2O] / [H_3O^+] = 0,000012428 \cdot 55,3457 / 10^{(-7,36)} = 15756,944.$$

Lēnindžera eksoerģiska ATP^{4-} hidrolīzes $GlyGly$ sintēzes ribosomā Hesa brīvās

enerģijas izmaiņa pie pH=7,36 ir negatīva $\Delta G_{hidrolīze} = -99,58 \text{ kJ/mol}$, $-97,15 \text{ kJ/mol}$, bet

minimizējas $\Delta G_{min} = \Delta G_{eq} = -30,5 \text{ kJ/mol}$ un $-23,96 \text{ kJ/mol}$ sasniedzot līdzsvara maisījumu

$$K_{bLehninger} = 220500,2 \text{ and } K_{eq \text{ a0,2Mb}} = 15757. \text{ Lešatelje princips ir Prigožina atraktora}$$

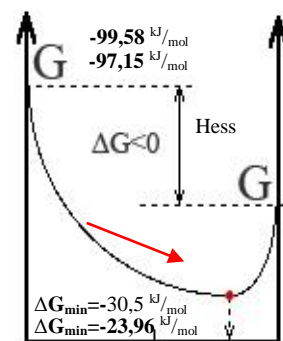
brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

reaktanti $A + 2B + C$ 50% $D + E + F + G$

$ATP^{4-} + Gly_{aq} + Gly_{aq} + H_2O$

produkti $GlyGly_{aq} + ADP^{3-} + HPO_4^{2-} + H_3O^+$;



TERMODINAMIKA VINGRINĀJUMS VIII a Maltozes hidrolīze par **Glc+Glc**

Aprēķināt ΔH_H ΔS_H ΔG_H standarta apstākļos 298,15 K. Reakcija **eksotermiska**, **atermiska**, **endotermiska**?

Laktozes-hidrolīze par Glikozi un Galaktozi! Ir **eksoerģiska** vai **endoerģiska**!

Lehninger 2000 $\Delta G_{Lehninger} = -15,9$ kJ/mol; Laktoze + **H₂O** \rightleftharpoons Glc + Gal; pH=7,36; $\Delta G_{Hess} = -20,3$ kJ/mol ;

Maltozes-hidrolīze par Glikozi! Ir **eksoerģiska** vai **endoerģiska**!

Lehninger 2000 $\Delta G_{Lehninger} = -15,5$ kJ/mol; Maltoze + **H₂O** \rightleftharpoons Glc + Glc; pH=7,36; $\Delta G_{Hess} = -19,92$ kJ/mol ;

BioThermodyn 2006 pH=7,36; reaktanti => produkti pH=7,36 ; I=0,25 M

Viela	ΔH_H° kJ/mol	ΔS_H° J/mol/K	ΔG_H° kJ/mol
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549
Gal	-1260,14	-2901,428	-395,08
Glc	-1263,78	269,45	-919,96
Glc	-1267,13	-2901,49	-402,05
Maltoze	-2247,12	-5415,032	-632,6312
Laktoze	-2242,14	-5423,03	-625,27

Biochemistry Thermodynamic 2006 Massachusetts Techn.Inst.

$\Delta G_H = \Delta G^\circ_{Glc} + \Delta G^\circ_{Gal} - \Delta G^\circ_{Laktoze} - \Delta G^\circ_{H_2O} = -402,052 - 395,08 - (-625,27 - 151,549) = -20,3$ kJ/mol **eksoerģiskas**;

$\Delta G_H = 2\Delta G^\circ_{Glc} - \Delta G^\circ_{Maltoze} - \Delta G^\circ_{H_2O} = 2 * -402,05 - (-632,6312 - 151,549) = -19,92$ kJ/mol **eksoerģiskas**;

1. $\Delta H_H = 2\Delta H^\circ_{Glc} - \Delta H^\circ_{Maltoze} - \Delta H^\circ_{H_2O} = 2 * -1267,13 - (-2247,12 - 151,549) = -135,591$ kJ/mol **eksotermiska** ;

2. $\Delta S_{izklyede} = \Delta H_H / T = -135,591 / 298,15 = -454,774442$ J/(mol K) ;

2. $\Delta S_H = 2\Delta S^\circ_{Glc} - \Delta S^\circ_{Maltoze} - \Delta S^\circ_{H_2O} = 2 * -2901,49 - (-5415,032 - 453,188) = 65,24$ J/mol/K;

3. $\Delta S_{kopēja} = \Delta S_H + \Delta S_{izklyede} = 65,24 + (-454,774442) = -389,534442$ J/(mol K) ;

$\Delta G_H = \Delta H_H - T * \Delta S_H = -135,591 - 298,15 * 0,06524 = -155,0423$ kJ/mol **eksoerģiskas** ;

3. $T * \Delta S_{kopēja} = 298,15 * (-389,534442) = -116,13$ kJ/mol $T \Delta S_{kopēja}$ bound energy izklyede spontaneous.

$K_{Lehninger} = \exp(-\Delta G_{Lehninger} / R / T) = \exp(15500 / 8,3144 / 298,15) = 519,4 = 10^{2,7155}$

$$K_{eq} = K_{Lehninger} = 519,4 = \frac{[Glc] \cdot [Glc]}{[Maltoze] \cdot [H_2O]}$$

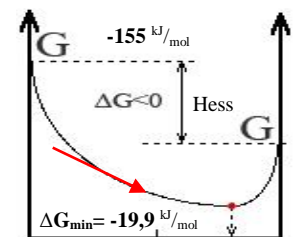
Prigožina atraktors minimums $\Delta G_{min} = \Delta G_{eq} = -19,9$ kJ/mol ; $\Delta G_{Lehninger} = -15,5$ kJ/mol ; $\Delta G_{Hess} = -155$ kJ/mol ;

Endotermiska un eksoerģiska hidrolīzes Hesa brīvās enerģijas izmaiņa negatīva

$\Delta G_{hidrolīze} = -155$ kJ/mol , bet Prigožina labvēlīgā atraktora līdzsvara konstantes

brīvās enerģijas izmaiņas minimums $\rightarrow \Delta G_{min} = \Delta G_{eq} = -19,9$ kJ/mol ;

$$\text{sasniedzot līdzsvara maisījumu } K_{eq} = \frac{[Glc] \cdot [Glc]}{[Maltoze] \cdot [H_2O]} = 519,4 ;$$



Maltoze + **H₂O** A+B 50% C+D
Reaktanti un produkti
Glc + Glc .

Lešateljē princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min}

sasniegšana. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

TERMODINAMIKA VINGRINĀJUMS VIII b Laktozes hidrolīze par **Glc+Gal**

Aprēķināt ΔH_H ΔS_H ΔG_H standarta apstākļos 298,15 K. Reakcija **eksotermiska**, **atermiska**, **endotermiska**?

Laktozes hidrolīze par Glikozi un Galaktozi! Ir **eksoerģiska** vai **endoerģiska**!

Lehninger 2000 $\Delta G_{Lehninger} = -15,9 \text{ kJ/mol}$; Laktoze + **H₂O** \rightleftharpoons Glc + Gal; pH=7,36; $\Delta G_H = -20,3 \text{ kJ/mol}$; I=0,25 M

BioThermodyn 2006 pH=7,36 reaktanti \rightleftharpoons produkti ;

Viela	$\Delta H^\circ_H \text{ kJ/mol}$	$\Delta S^\circ_H \text{ J/mol/K}$	$\Delta G^\circ_H \text{ kJ/mol}$	
H₂O	-285,85	69,9565	-237,191	
H₂O	-286,65	-453,188	-151,549	BioThermodyn 2006
Glc	-1263,78	269,45	-919,96	CRC 2010
Glc	-1267,13	-2901,49	-402,05	BioThermodyn 2006
Gal	-1260,14	-2901,43	-395,08	BioThermodyn 2006
Laktoze	-2242,14	-5423,03	-625,27	

$\Delta G_{Hess} = \Delta G^\circ_{Glc} + \Delta G^\circ_{Gal} - \Delta G^\circ_{Laktoze} - \Delta G^\circ_{H_2O} = -402,05 - 395,08 - (-625,27 - 151,549) = -20,311 \text{ kJ/mol}$ **eksoerģiska**

1. $\Delta H_H = 2\Delta H^\circ_{Glc} - \Delta H^\circ_{Maltose} - \Delta H^\circ_{H_2O} = 2 \cdot (-1267,13) - (-2247,12) - 151,549 = -135,591 \text{ kJ/mol}$ **exothermic** ;

2. $\Delta S_{disperse} = \Delta H_H / T = -135,591 / 298,15 = 454,774442 \text{ J/(mol K)}$;

2. $\Delta S_H = 2\Delta S^\circ_{Glc} - \Delta S^\circ_{Maltose} - \Delta S^\circ_{H_2O} = 2 \cdot (-2901,49) - (-5415,032) - 453,188 = 65,24 \text{ J/mol/K}$;

3. $\Delta S_{total} = \Delta S_H + \Delta S_{disperse} = 454,774442 + 65,24 = 520,014442 \text{ J/(mol K)}$;

$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -135,591 - 298,15 \cdot 0,06524 = -155,0423 \text{ kJ/mol}$ **exoergic** ;

3. $T \cdot \Delta S_{total} = 520,014442 \cdot 298,15 = 155,0423 \text{ kJ/mol}$ $T\Delta S_{total}$ bound energy dispersed spontaneous.

$K_{Lehninger} = \exp(-\Delta G_{Lehninger} / R / T) = \exp(20300 / 8,3144 / 298,15) = 3601$

$$K_{eq} = K_{Lehninger} = 3601 = \frac{[Glc] \cdot [Gal]}{[Laktoze] \cdot [H_2O]}$$

Prigožina atraktors minimums $\Delta G_{min} = \Delta G_{eq} = -5,951 \text{ kJ/mol}$; $\Delta G_{Lehninger} = -15,9 \text{ kJ/mol}$; $\Delta G_{Hess} = -20,311 \text{ kJ/mol}$;

Prigožina atraktors labvēlīga līdzsvara konstante Hesa likumā $K = 10^{3,558} = 3617$.

Endotermiska un eksoerģiska hidrolīzes Hesa brīvās enerģijas izmaiņa negatīva

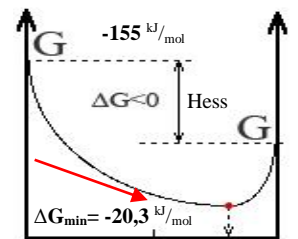
$\Delta G_{hidrolīze} \approx -155 \text{ kJ/mol}$, bet Prigožina atraktora veicināta līdzsvara brīvās

enerģijas izmaiņa minimizējas $\longrightarrow \Delta G_{min} = \Delta G_{eq} = -20,3 \text{ kJ/mol}$

sasniedzot atraktoru maisījumā $K_{eq} = \frac{[Glc] \cdot [Gal]}{[Laktoze] \cdot [H_2O]} = 3601$. Lešateljē princips

ir Prigožina atraktors brīvās enerģijas izmaiņas minimums ΔG_{min} sasniedzot maisījumu.

Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars. Laktoze + H₂O A+B 50% C+D
Glc + Gal_reaktanti & produkti.



TERMODINAMIKA VINGRINĀJUMS IX bikarbonāta neutralizēšanās CO₂ iztvaikošanas reakcijā

Koncentrācijas gradientu virzienā [H₃O]_{palabi}/[H₃O]_{pa_kheisi}, paralēli cauri protonu H⁺,
[HCO₃]_{palabi}/[HCO₃]_{pa_kheisi} bikarbonāta HCO₃⁻ kanāliem plaušās izelpojot CO₂, H₂O.

Viela	ΔH ^o _H kJ/mol	ΔS ^o _H J/mol/K	ΔG ^o _H kJ/mol
H ₃ O ⁺	-285,81	-3,854	-213,275
HCO ₃ ⁻	-689,93	98,324	-586,94
HCO ₃ ⁻	-692,4948	-494,768	-544,9688
H ₂ O	-285,85	69,9565	-237,191
H ₂ O	-286,65	-453,188	-151,549
H ₂ O↑ _{gas}	-241,8352	188,7402	-228,6
CO ₂ ↑ _{gas}	-393,509	213,74	-394,359
CO _{2aq}	-413,798	117,5704	-385,98

H₃O⁺+HCO₃⁻+Q=kanāli H⁺; HCO₃⁻=>H₂O+H₂O_{gas}+CO₂↑_{gas}+ΔG
 ΔH_H=ΔH^o_{H₂O}+ΔH^o_{H₂O_{gas}}+ΔH^o_{CO₂gas}-ΔH^o_{H₃O}-ΔH^o_{HCO₃}=54,546 kJ/mol;
 =-285,85-241,8352-393,509-(-285,81-689,93)=54,546 kJ/mol
 ΔG_H=ΔG^o_{H₂O}+ΔG^o_{H₂O_{gas}}+ΔG^o_{CO₂gas}-ΔG^o_{H₃O}-ΔG^o_{HCO₃}=-59,935 kJ/mol
 =-237,191-228,6-394,359-(-213,275-586,94)=-59,935 kJ/mol **eksoerģisks**
 ΔS_{izkļiedēta}=-ΔH_H/T=-54,546/298,15= -182,948 J/mol/K;
 ΔS_{kopēja}= ΔS_H+ ΔS_{izkļiedēta}= -182,948+377,966 =195,016 J/mol/K;
 ΔG_H=ΔH_H-T*ΔS_H=54,546-298,15*0,377966= -58,144 kJ/mol;
 ΔS_H=ΔS^o_{H₂O}+ΔS^o_{H₂O↑_{gas}}+ΔS^o_{CO₂↑_{gas}}-ΔS^o_{H₃O}-ΔS^o_{HCO₃}=377,966 J/mol/K; **eksoerģiska**
 =69,956+188,74+213,74-(-3,854+98,324)= 353,652-94,47= +377,966 J/mol/K;
 T*ΔS_{kopēja}=195,016 J/mol/K*298,15 K=**58,144** kJ/mol
 saistīta TΔSn← zaudēta brīvā enerģija ΔG_{pretreakc.} Hess **produktos. patvaļīga** ΔG^o_{Hess} =-58,14 kJ/mol;
 H⁺ kanāli: ΔG_H=RTln([H₃O⁺]_{right}/[H₃O⁺]_{left}); HCO₃⁻ kanāli: ΔG_{HCO₃}=RTln([HCO₃⁻]_{right}/[HCO₃⁻]_{left})
 ΔS_H=-Rln(10^{^(-5,5)}/0,02754)=75,42909 J/mol/K; ΔS_{HCO₃}=-Rln(0,0154/0,0338919)=6,55847 J/mol/K;
 ΔG_H=RTln([H₃O]_{palabi}/[H₃O]_{pa_kheisi})=-22,48918 kJ/mol; ΔG_{HCO₃}=RTln([HCO₃]_{palabi}/[HCO₃]_{pa_kreisi})=-1,9554kJ/mol;
 ΔS_H=377,966+75,42909+6,55847 = 459,954 J/mol/K;
 ΔS_{Hkopēja}= ΔS_H+ ΔS_{izkļiedēta}= -182,95+459,954=277,004 J/mol/K;
 ΔG_{HH}= ΔH_H - T*ΔS_{HH} = +54,546-298,15*0,459954 = -82,589 kJ/mol; **eksoerģiska**.....
 T*ΔS_{Hkopēja}=277,004 J/mol/K*298,15 K=**82,589** kJ/mol.....
 saistīta TΔSn← zaudēta brīvā enerģija ΔG_{pretreakc.} Q= -54,546 kJ/mol.....**patvaļīga** ΔG^o_{Hess} =-82,589 kJ/mol...

TERMODINAMIKA VINGRINĀJUMS X. HCO₃⁻+H₃O⁺ produkti šķietama ogļskābe H₂O+H₂CO₃

Aprēķināt ΔH_H ΔS_H ΔG_H standarta apstākļos 298.15 K. Reakcija ir **eksotermiska**, **atermiska**, **endotermiska**?
 Bikarbonāta un protona pārnese cauri membrānas kanāliem **plaušās** uz epitēlija šūnu virsmas H₂O+H₂CO₃.
 Vai būs **eksoerģiska** vai **endoerģiska**!

Viela	ΔH ^o _H kJ/mol	ΔS ^o _H J/mol/K	ΔG ^o _H kJ/mol
H ₃ O ⁺	-285,81	-3,854	-213,275
HCO ₃ ⁻	-689,93	98,324	-586,94
HCO ₃ ⁻	-692,4948	-494,768	-544,9688
H ₂ CO ₃	-699,65	187,00	-755,47
H ₂ O	-285,85	69,9565	-237,191
H ₂ O	-286,65	-453,188	-151,549
H ₂ O↑ _{gas}	-241,8352	188,7402	-228,6
CO ₂ ↑ _{gas}	-393,509	213,74	-394,359
CO _{2aq}	-413,798	117,5704	-385,98

H₃O⁺ + HCO₃⁻ Membrānu> H₂O + H₂CO₃ +ΔG+Q.
 ΔH_{Hess}=ΣΔH^o_{produkti}-ΣΔH^o_{izejvielas}; ΔS_{Hess}=ΣΔS^o_{produkti}-ΣΔS^o_{izejvielas}
 ΔG_{Hess}= ΔH_{Hess}-T*ΔS_{Hess}
 ΔH_{Hess}=ΔH^o_{H₂O}+ΔH^o_{H₂CO₃}-ΔH^o_{H₃O}-ΔH^o_{HCO₃}=-7,9952 kJ/mol
 =-285,85-699,65-(-285,81-689,93)= -9,76 kJ/mol **eksotermiska**
 =-286,65-699,65-(-285,81-692,4948)= -7,9952 kJ/mol
 ΔG_{Hess}=ΔG^o_{H₂O}+ΔG^o_{H₂CO₃}-ΔG^o_{H₃O}-ΔG^o_{HCO₃}=-148,8 kJ/mol
 =-237,191-755,47-(-213,275-586,94)=-192,4 kJ/mol **eksoerģisks**
 =-151,549-755,47-(-213,275-544,9688)=-148,8 kJ/mol **eksoerģisks**
 ΔS_{Hess}=ΔS^o_{H₂O}+ΔS^o_{H₂CO₃}-ΔS^o_{H₃O}-ΔS^o_{HCO₃}=232,4 J/mol/K;
 =69,956+187-(-3,854+98,324)=162,486 J/mol/K;
 ΔS_{kopēja}=ΔS_H+ΔS_{izkļiedēta}=**26,816**+**232,4**=**259,216** J/mol/K; =-453,188+187-(-3,854-494,768)=**232,4** J/mol/K;
 ΔG_{Hess}=ΔH_{Hess}-T*ΔS_{Hess}=-7,9952-298,15*0,2324=-77,3 kJ/mol ; **eksoerģiska**.
 T*ΔS_{kopēja}=**0,259216** J/mol/K*298,15 K=**77,3** kJ/mol ; ΔS_{izkļiedēta}=-ΔH_H/T=**7,9952**/298,15=**26,82** J/mol/K;
 saistīta TΔSn← zaudēta brīvā enerģija izkļiedēta produktos un apkārtējā vidē.

TERMODINAMIKA VINGRINĀJUMS XIII, XIV. $O_2\uparrow$ gāze asimilācija reakcijā cauri akvaporīniem veido $O_{2\text{aqua-Asins}}$

No GAISA ūdenī $O_2\uparrow_{\text{gais}}$ asimilācija reakcijā cauri membrānu akvaporīniem veido $[O_{2\text{aqua-arteriālu}}]=6\cdot 10^{-5}$ M

koncentrāciju. **endoergic** $\Delta G + O_2\uparrow_{\text{gas}} + H_2O \xrightarrow{\text{Aqaporin}} O_{2\text{aqua-asins}} + Q$; $O_{2\text{aqua}} + Q \rightarrow O_{2\text{gas}} + H_2O + \Delta G$

Viela	ΔH_H° kJ/mol	ΔS_H° J/mol/K	ΔG_H° kJ/mol
$O_{2\text{aqua}}$	-11.70	-94,2	16,40
$O_{2\text{aqua}}$	-11.715	110,876	16,4
$O_2\uparrow_{\text{gas}}$	0	205,152	0
H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549

$$\Delta G_{\text{Hess}} = \Delta G^\circ_{O_{2\text{aqua}}} - \Delta G^\circ_{O_{2\text{gas}}} - \Delta G^\circ_{H_2O} = 16.4 - (0 - 151,549) = 168 \text{ kJ/mol};$$

$$\text{Alberty } [8]; \Delta G_{\text{HAlberty}} = G_{O_{2\text{aqua}}} - G_{O_{2\text{gas}}} - G_{H_2O} = 330 - 303 - 0 = 27 \text{ kJ/mol};$$

$$\Delta H_H = \Delta H^\circ_{O_{2\text{aqua}}} - \Delta H^\circ_{O_{2\text{gas}}} - \Delta H^\circ_{H_2O} = -11.7 - 0 + 286,65 = 274,95 \text{ kJ/mol};$$

$$\Delta S_{\text{dispersed}} = -\Delta H_{\text{Hess}}/T = -274,95/298.15 = -922,2 \text{ J/mol/K};$$

$$\Delta S_{\text{Hess}} = \Delta S^\circ_{O_{2\text{aq}}} - \Delta S^\circ_{O_{2\text{gas}}} - \Delta S^\circ_{H_2O} = -164,2 \text{ J/mol/K}$$

$$= 110,876 - 205,152 - 69,9565 = -164,2 \text{ J/mol/K}$$

$$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = 274,95 - 298,15 \cdot (-0,1642) = 323,9 \text{ kJ/mol endoergic};$$

$$\Delta S_{\text{kopēja}} = \Delta S_H + \Delta S_{\text{izkliede}} = -164,2 - 922,2 = -1086,4 \text{ J/mol/K};$$

$$T \cdot \Delta S_{\text{kopēja}} = -1,0864 \text{ kJ/K/mol} \cdot 298,15 \text{ K} = -323,9 \text{ kJ/mol}; \text{ saistīta } T \Delta S_n \leftarrow \text{uzkrātā enerģija. ne-patvaļīga};$$

[ELSEVIER](#) Rotating Electrode Method un Oxygen reduction Electrocatalysts, 2014, p.1-31,

1. WeiXingMinYinbQingLvYangHubChangpengLiubJiuJunZhangc. Tīrā latm mol daļā ir $X_{O_{2\text{gas}}}=1$.

$$\text{Šķīdība } K_{\text{šk}} = \frac{[O_{2\text{aqua}}]}{[O_{2\text{gas}}] \cdot [H_2O]} = K_{O_2}/[H_2O] = 1.22 \cdot 10^{-3}/55.3 = 2.205 \cdot 10^{-5} \text{ un attiecība } \frac{X_{O_{2\text{aqua}}}}{X_{O_{2\text{gas}}}} = K_{O_2} = 1.22 \cdot 10^{-3} \text{ M/l}$$

[ELSEVIER](#) sadalījums gāzes un šķīdībai ūdenī no gaisa 20.95% $[O_{2\text{Air}}]=0.2095$

ir koncentrācija $[O_{2\text{aqua}}]=1.22 \cdot 10^{-3} \cdot 0.2095 = 2.556 \cdot 10^{-4}$ M; $[O_{2\text{aqua}}]/0.2095 = 1.22 \cdot 10^{-3}$ M; Šķīdības brīvās enerģijas

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

Hesa endotermiskā un endoergiskā skābekļa šķīdības brīvās enerģijas izmaiņa pozitīva $\Delta G_{\text{solubility}} = 323,9 \text{ kJ/mol}$,

bet minimizējas līdzsvarā $K_{\text{šk}} = \frac{[O_{2\text{aqua}}]}{[O_{2\text{gas}}] \cdot [H_2O]} = 2.205 \cdot 10^{-5} = 10^{-4.66}$ brīvās enerģijas

izmaiņa $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = 26.58 \text{ kJ/mol}$. Lešatrljē princips ir Prigožina atraktors brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvarā.

$$\text{Iztvaikojot } K_{\text{eq}} = \frac{[O_{2\text{gas}}] \cdot [H_2O]}{[O_{2\text{aqua}}]} = [H_2O]/K_{O_2} = 55,3457339/1,22/10^{(-3)} = 45365,4;$$

Hesa eksotermiska un eksoergiska skābekļa $O_{2\text{gas}}$ iztvaikošanas brīvās enerģijas izmaiņa ir negatīva $\Delta G_{\text{Hess}} = -323,9 \text{ kJ/mol}$, bet minimizējas iztvaikošanas līdzsvara stāvoklī:

$$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(45365,35566) = -26,58 \text{ kJ/mol}$$

sasniedzot līdzsvara stāvokli $K_{\text{eq}} = 45365,4$ - Prigožina atraktoru ne līdzsvara stāvokļiem.

Brīvās enerģijas izmaiņas minimuma sasniegšan.a iestājas līdzsvars. Šķīdība no gaisa ir

$[O_{2\text{aqua}}]=9.77 \cdot 10^{-5}$ M ja osmolārā, jonu spēka $C_{\text{osm}}=0.305$ M, $I=0.25$ M, skābekļa gaisa

20.95% koncentrācija fizioloģiskos apstākļos, bet nulles osmolārās un jonu spēka

koncentrācijās $C_{\text{osm}}=0$ un $I=0$ M ir tīrā destilētā ūdenī $[O_{2\text{aqua}}]=2.556 \cdot 10^{-4}$ M.

Fizioloģiskā $K_{O_2\text{Asins}} = [O_{2\text{aqua}}]/[O_{2\text{gas}}] = 9.768 \cdot 10^{-5}/0.2095 = 4.663 \cdot 10^{-4} = 10^{-3.3314} = 10^{\text{pK}}$ ir

līdzsvara konstante. Arteriālā $[O_{2\text{aqua}}] = 6 \cdot 10^{-5}$ M and venous $[O_{2\text{aqua}}]=0.486 \cdot 10^{-5}$ M

koncentrācijas ir izooksijas norma cilvēka asiņu $[O_{2\text{aqua}}]$ [koncentrācijām](#).

Iztvaikošana $\Delta H_H = \Delta H^\circ_{O_{2\text{gas}}} + \Delta H^\circ_{H_2O} - \Delta H^\circ_{O_{2\text{aqua}}} = -286,65 + 0 - 11,7 = -274,95 \text{ kJ/mol}$ ir

eksotermiska un eksoergiska $\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -274,95 - 298,15 \cdot (-0,1642) = -323,9 \text{ kJ/mol}$.

[Alberty](#) [8] brīvā enerģija ūdenraža gāzei $G_{H_2\text{gas}} = 85.64 \text{ kJ/mol}$ ļauj [aprēķināt](#) skābekļa brīvo enerģiju gāzei un ūdenī $G_{O_{2\text{gas}}} = 303.1 \text{ kJ/mol}$ un $G_{O_{2\text{aqua}}} = 329.68 \text{ kJ/mol}$,

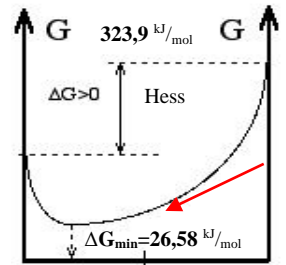
Fotosintēze atjauno globālo atmosfēras atraktoru $[O_{2\text{gas_AIR}}]=0,2095$ skābekļa moldaļu.

Līdzsvara koncentrāciju ūdenī $[O_{2\text{aqua}}] = [O_{2\text{gas_AIR}}] \cdot [H_2O]/K_{\text{šk}} = 0,2095 \cdot 55,3/45365 = 0,0002556$ M uztur atmosfēras

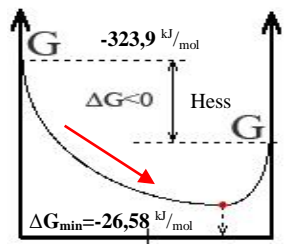
skābekļa $[O_{2\text{gas_AIR}}]=0,2095$ moldaļa. Fotosintēze aktivē koncentrāciju $[O_{2\text{aqua_photosynthesis}}] > [O_{2\text{aqua}}] = 0,0002556$ M

ūdenī virs līdzsvara: un skābeklis iztvaiko. Fotosintēze apstājas sasniedzot līdzsvara koncentrāciju

$[O_{2\text{aqua}}] = 0,0002556$ M. Prigožina atraktors brīvās enerģijas izmaiņas minimums globālā fotosintēzes procesā uztur skābekļa moldaļu atmosfērā $[O_{2\text{gas_AIR}}]=0,2095$.



A+B 50% C+D
izejvielas $O_2\uparrow_{\text{gas}} + H_2O$
produkts $O_{2\text{aqua}}$.



A+B 50% C+D
izejviela $O_{2\text{aqua}}$
produkti $O_2\uparrow_{\text{gas}} + H_2O$

Alberty un CRC termodinamikas dati. [8,1] Exel $2\text{H}_2\text{O}_2 \Rightarrow \text{O}_2\text{aq} + 2\text{H}_2\text{O} + \text{Q} + \Delta G$;

Substance	$\Delta H^\circ_{\text{H}} \text{ kJ/mol}$	$\Delta S^\circ_{\text{H}} \text{ J/mol/K}$	$\Delta G^\circ_{\text{H}} \text{ kJ/mol}$
C _{gr}	0	5.74	0
G _{C_{CO2gr}}	G _{gr}	-	91.26
CO↑ _{gas}	-110.525	197.674	-137.2
CO ₂ ↑ _{gas}	-393.5	2.9	-394.36
CO _{2aq}	-413.8	117.5704	-385.98
HCO ₃ ⁻	-692.495	-494.768	-544.9688
H _{2aq}	-5.02	-363.92	103.24
H _{2gas}	-0.82	-283.82	85.64
H _{2gas}	0	130.68	0
H _{atomic}	218,0	114,7	203,3
OH ⁻	-230,00	-10,539	-157,2
O ₂ ↑ _{gas}	0	205,152	0
O _{2aq}	-11,715	110,876	16,4
O _{2aq}	-11,7	-94,2	16,4
H _{2O} _{2aq}	-191,99	-481,688	-48,39
H _{2O} _{2(aq)}	-191,17	143,9	-134,03
H _{2O}	-285,85	69,9565	-237,191
H _{2O}	-286,65	-453,188	-151,549
H _{2O} ↑ _{gas}	-241,8352	188,74024	-228,6
CH _{4aq}	-90,69	-763,476	136,95
CH _{4gas}	-76,46	-648,44	120,56
CH _{4gas}	-74,6	186,3	-50,5

$\Delta G_{\text{EqStandart}} = (E^\circ_{\text{Red}} - E^\circ_{\text{Ox}}) * F * n = (0.89916 - 2.08366) * 96485 * 2 = -228.6 \text{ kJ/mol}$
 $\Delta G_{\text{EqStandart}} = G_{\text{O2aq}} + 2 * G_{\text{H2O BioChemistry}} - 2 * G_{\text{H2O2}} = -228,6 \text{ kJ/mol}$;
 carbon (graphite) $G_{\text{gr}} = 91.26 \text{ kJ/mol}$;
 $= 329,68 + 2 * 85.65 - (2 * G_{\text{H2O2}}) = -228,6 \text{ kJ/mol}$; Alberty
 $G_{\text{H2O2}} = (G_{\text{O2aq}} + 2G_{\text{H2O BioChemistry}} - \Delta G_{\text{EqStandart}}) / 2 = 364,79 \text{ kJ/mol}$;
 $\Delta G^\circ_{\text{H2O2}} = 729,58 / 2 = (329,68 + 2 * 85.65 + 228,6) / 2 = 364,79 \text{ kJ/mol}$;
 $G_{\text{CgrCH4gas}} = G_{\text{CO2gr}} - G_{\text{Hess CO2gas}} - G_{\text{O2gas}} = 394.36 - 303.1 = 91.26 \text{ kJ/mol}$;
 $G^\circ_{\text{H2aq}} = 103.24 \text{ kJ/mol}$; Alberty R.A. Biochem. Thermodynamic's, 2006.
 $G^\circ_{\text{H2gas}} = 85.64 \text{ kJ/mol}$; Alberty R.A. Biochem. Thermodynamic's, 2006
 $G_{\text{O2gas}} = 303,1 \text{ kJ/mol}$; $\text{H}_2\text{gas} + 1/2 \text{O}_2\text{gas} \Rightarrow \text{H}_2\text{O}$; $G^\circ_{\text{H2O}} = -237,19 \text{ kJ/mol}$;
 $2\text{H}_2\text{gas} + \text{O}_2\text{aq} \Rightarrow 2\text{H}_2\text{O} \Leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$;
 $\Delta G_{\text{EqH2gas+O2gas}} = (2G_{\text{H2O}} - 2G^\circ_{\text{H2gas}} - G_{\text{O2gas}}) / 2 = -474,38 / 2 = -237,19 \text{ kJ/mol}$;
 $\Delta G^\circ_{\text{H2O Hesa}} = 2 * 0 - 2 * 85,64 - 303,1 = -474,38 / 2 = -237,19 \text{ kJ/mol}$;
 $G_{\text{O2gas}} = (-\Delta G^\circ_{\text{H2O Hesa}} - G^\circ_{\text{H2gas}}) * 2 = (237,19 - 85,64) * 2 = 303,1 \text{ kJ/mol}$;
 Oxygen aqua $G_{\text{O2aq}} = G_{\text{O2gas}} + G_{\text{O2sp}} = 303,1 + 26,58 = 329,68 \text{ kJ/mol}$;
 $G_{\text{O2sp}} = -R * T * \ln(K_{\text{sp}}) = 26,58 \text{ kJ/mol}$; $K_{\text{sp}} = 2,205 * 10^{-5}$; 3rd page; [14]
 $\Delta G_{\text{HessH2O}} = G^\circ_{\text{H2O}} - (-\text{Hess}G^\circ_{\text{H2}} - \text{Hess}G^\circ_{\text{O2gas}} / 2) = -237,19 - (0 + 0) = -237,19 \text{ kJ/mol}$
 Bioķīmijas nulls atskaites skala $G_{\text{CO2gasO2}} = G_{\text{H2O}} = 0 \text{ kJ/mol}$;
 $2G_{\text{OH}} - G_{\text{H2aq}} - G_{\text{O2aq}} = 2G_{\text{OH}} - 103,24 - 329,68 =$
 $\text{H}_{2\text{aq}} + \text{O}_{2\text{aq}} + 2e^- \Leftrightarrow 2\text{OH}^-$; $E^\circ_{\text{H2aqO2aq}} = 2\text{OH}^- = ??? \text{ Volts}$
BioTherm2006 Alberty R.A. $G_{\text{H2O BioChemistry}} = 85,65 \text{ kJ/mol}$
BioTherm2006 Alberty R.A. Biochem. Thermodynamic's 463, 2006
 $\text{Hess}G_{\text{O2gas}} = 0$; $\text{Hess}G^\circ_{\text{H2}} = 0$; $\text{Hess}G^\circ_{\text{gr}} = 0$; $\text{Hess}G^\circ_{\text{N2gas}} = 0$; $\text{Hess}G^\circ_{\text{Srombic}} = 0$;

Red $\text{H}_2\text{O}_2 + 2\text{H}_2\text{O} - 2e^- = \text{O}_2\text{aq} + 2\text{H}_3\text{O}^+$; absolūtā $E^\circ_{\text{H2O2aqRed}} = 0,4495 \text{ V}$ Alberta University classic $E^\circ_{\text{H2O2}} = 0,7975 \text{ V}$;
 $E_{\text{Red}} = E^\circ_{\text{H2O2}} + 0,0591 / 2 * \lg([O_{2aq}] * [H_3O^+]^2 / [H_2O_2] / [H_2O]^2) = 0,4495 + 0,0591 / 2 * \lg(6 * 10^{-5} * 10^{(-7,36 * 2)} / 1 / 55,3^2) = 0,23643 \text{ V}$
 Oks $\text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2e^- = 4\text{H}_2\text{O}$; $E^\circ_{\text{H2O2aqOx}} = 1,6855 \text{ V}$ [18]; $[H_2O_2] = 1 \text{ M}$; $[O_{2aq}] = 6 * 10^{-5} \text{ M}$, $[H_3O^+] = 10^{-7,36} \text{ M}$, $[H_2O] = 55,3 \text{ M}$
 $E_{\text{Ox}} = E^\circ_{\text{H2O2Ox}} + 0,0591 / 2 * \lg([H_2O_2] * [H_3O^+]^2 / [H_2O]^4) = 2,08366 + 0,0591 / 2 * \lg(10^{(-7,36 * 2)} * 1 / 55,3^4) = 1,443 \text{ V}$;

$$\Delta G_{\text{EqStandart}} = (E_{\text{Red}} - E_{\text{Ox}}) * F * n = (0,4495 - 1,6855) * 96485 * 2 = (-1,236) * 96485 * 2 = -238,51 \text{ kJ/mol}$$

$$\Delta G_{\text{Alberty}} = -238,51 \text{ kJ/mol}$$
; $G_{\text{StandartaH2O2}} = G_{\text{O2aq}} + 2 * G_{\text{H2O}} + \Delta G_{\text{Alberty}} = (330 + 2 * 0 + 238,51) / 2 = 568,5 / 2 = 284,25 \text{ kJ/mol}$;

$$\Delta G_{\text{EqBioChem}} = (E_{\text{Red}} - E_{\text{Ox}}) * F * n = (-0,2132 - 1,0455) * 96485 * 2 = (-1,2066) * 96485 * 2 = -242,9 \dots \text{ kJ/mol}$$
 ;

$$2 * G_{\text{H2O2}} = G_{\text{O2Biochem_arteriaj}} + 2 * G_{\text{H2OBioChemistry}} + \Delta G_{\text{Alberty}} = 330 + 2 * 0 + 238,51 = 2 * 284,5 = 568,5 \text{ kJ/mol}$$
;

Šķīdība $\text{H}_2\text{gas} + \text{H}_2\text{O Aquaporin} \Rightarrow \text{H}_{2\text{aq}}$ akumulē $\Delta G_{\text{H2skAlberty}} = G_{\text{H2aq}} - G_{\text{H2gas}} - G_{\text{H2O}} = 103,24 - 85,64 - 85,6 = -68,05 \text{ kJ/mol}$ Alberty;

$$[\text{H}_{2\text{aq}}] / [\text{H}_{2\text{gas}}] / [\text{H}_2\text{O}] = K_{\text{sk}} = \text{EXP}(-\Delta G_{\text{H2spAlberty}} / R / T) = \text{EXP}(68050 / 8,3144 / 298,15) = 10^{11,9}$$
. [8] Alberty

Šķīdība $[\text{H}_{2\text{aq}}] = K_{\text{sk}} * [\text{H}_2\text{O}] = 10^{11,9} * 55,3 = 10^{13,6} \text{ M}$, ja $\text{H}_{2\text{gas}}$ moldaļa ir viens $[\text{H}_{2\text{gas}}] = 1$ tīrai gāzei.

Hidroksionija protona reducēšana satverot elektronu no kristāla režģa (Pt)+e⁻. Hesa brīvās enerģijas izmaiņa

$$\text{H}_3\text{O}^+ + (\text{Pt}) + e^- \Leftrightarrow (\text{Pt})\text{H} + \text{H}_2\text{O}$$
 ir $\Delta G_{\text{Hess(Pt)H}} = G_{\text{H3O}^+} + G_{(\text{Pt})} + G_{e^-} - (G_{\text{H2O}} + G_{\text{H(Pt)}}) = 22,44 + 38,375 + 0 - (0 + 51,05) = 9,765 \text{ kJ/mol}$.

$\Delta G_{\text{eq(Pt)H}} = E^\circ_{\text{H}} * F * 1 = 0,10166 * 96485 / 1000 = 9,81 \text{ kJ/mol}$ dod brīvās enerģijas izmaiņas minimumu metaliskam ūdeņradim (Pt)H

oksidējot nulles skalā $G_{(\text{Pt})} + G_{e^-} = G_{\text{H2O}} = G_{\text{CO2gas}} = 0 \text{ kJ/mol}$ indiferentam (Pt), +e⁻, ūdenim un CO_{2gas}.

Ūdeņraža elektroda termodinamiskais standarta potenciāls $E^\circ_{\text{H}} = 0,10166 \text{ V}$ ir virs klasiskās nulles $E^\circ_{\text{H klasika}} = 0 \text{ V}$.

Red: $\text{H}_{2\text{aq}} + 2(\text{Pt}) \Leftrightarrow 2(\text{Pt})\text{H} + \text{H}_2\text{O}$; $\Delta G_{\text{Hess sk(Pt)H}} = 2G_{\text{H(Pt)}} + G_{\text{H2O}} - (G_{\text{H2aq}} + 2G_{(\text{Pt})}) = 2 * 51,05 + 0 - (103,24 + 2 * 38,375) = -77,89 \text{ kJ/mol}$.

$$E^\circ_{\text{H3O}^+} = -77,89 * 1000 / 96485 / 2 = -0,4036 \text{ V}$$
; $\text{H}_{2\text{aq}} + 2(\text{Pt}) \Leftrightarrow 2(\text{Pt})\text{H} + \text{H}_2\text{O}$; $2\text{H}_3\text{O}^+ + 2e^- \Leftrightarrow \text{H}_{2\text{aq}} + 2\text{H}_2\text{O}$;

$$K_{\text{sk(Pt)H}} = [\text{H}_2\text{O}] * [(\text{Pt})\text{H}]^2 / [\text{H}_{2\text{aq}}] / [(\text{Pt})]^2 = \text{EXP}(-\Delta G_{(\text{Pt)H}} / R / T) = \text{EXP}(77890 / 8,3144 / 298,15) = 10^{13,65}$$
. [8]

Ox: $2\text{H}_3\text{O}^+ + 2e^- \Leftrightarrow \text{H}_{2\text{aq}} + 2\text{H}_2\text{O}$; $\Delta G_{\text{Hess H3O}^+} = 2G_{\text{H3O}^+} + 2G_{e^-} - (G_{\text{H2aq}} + 2G_{\text{H2O}}) = -58,36 \text{ kJ/mol}$; $E^\circ_{\text{H3O}^+} = -58,36 * 1000 / 96485 / 2 = -0,302$

$\text{V} \Delta E^\circ_{\text{eqH3O}^+} = 0,10166 - (-0,302) = 0,40366 \text{ V}$; $\Delta G_{\text{eqH3O}^+} = \Delta E^\circ_{\text{H3O}^+} * F * 2 = 0,40366 * 96485 * 2 = 77,89 \text{ kJ/mol}$; Metāls ūdeņradis nešķīst.

$$2(\text{Pt})\text{H} + \text{H}_2\text{O} \Leftrightarrow \text{H}_{2\text{aq}} + 2(\text{Pt}); K_{\text{sk(Pt)H}} = [\text{H}_{2\text{aq}}] / [(\text{Pt})]^2 [\text{H}_2\text{O}] * [(\text{Pt})\text{H}]^2 = \text{EXP}(-\Delta G_{(\text{Pt)H}} / R / T) = \text{EXP}(-77890 / 8,3144 / 298,15) = 10^{(-13,65)}$$
;

Metāliska ūdeņraža moldaļa ir viens $[(\text{Pt})\text{H}] = 1$ un $[(\text{Pt})\text{H}]^2 = 1$. Metālisks ūdeņradis (Pt)H veido šķīdības koncentrāciju:

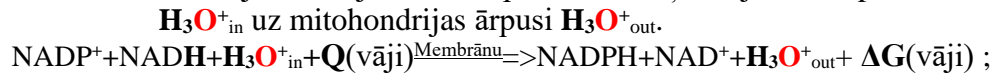
$[\text{H}_{2\text{aq}}] = K_{\text{sk}} * [\text{H}_2\text{O}] = 10^{11,9} * 55,3 = 10^{13,6} \text{ M}$ un gāzes $[\text{H}_{2\text{aq}}] = K_{\text{sk}} * [\text{H}_2\text{O}] = 10^{11,9} * 55,3 = 10^{13,6} \text{ M}$ ūdeņraža šķīdības

koncentrāciju, ja $\text{H}_{2\text{gas}}$ moldaļa ir viens $[\text{H}_{2\text{gas}}] = 1$ tīrai gāzei. Ja 0,000771899 M destilētā ūdenī tad minimālā mol daļa gāzei ir

$$[\text{H}_{2\text{gas}}] = 0,000771899 \text{ M} / 10^{13,6} \text{ M} = 10^{(-16,7)}$$
.

TERMODINAMIKA VINGRINĀJUMS XV Vitamīns B₃ H₃O⁺_{in} pārnese H₃O⁺_{out} cauri membrānai

Reakcija Vitamīnam B₃ reducētā forma NADH un oksidējas veidojot NADP⁺ pārnesot ūdeņraža jonus kā protonus cauri membrānai no iekšpusēs



Viela	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol
H ₃ O ⁺ _{in_out}	-285,81	-3,854	-213,275
NADH _(aq)	-1036,66	-140,5	-
NADH _(aq)	-41,41	-4081,784	1175,5732
NAD ⁺ _(aq)	-1007,48	-183	-
NAD ⁺ _(aq)	-10,3	-3766,008	1112,534
NADPH	-1036,66	763,005	-
NADPH	-1040,78	-4465,708	290,6776
NADP ⁺	-1007,48	577,897	-
NADP ⁺	-1014,07	-4166,096	228,052

Protonu trans lokācijas ENZĪMS trans hidrogenāze (EC1.6.1.1) baktērijās un dzīvnieku mitohondrijās kas sakabināts ar reducējošo ekvivalentu pārnesi starp NAD(H) un NADP(H) protonu trans lokācijā cauri membrānai

$$\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{NADPH}} + \Delta H^\circ_{\text{NAD}} - \Delta H^\circ_{\text{NADP}} - \Delta H^\circ_{\text{NADH}} = 4,4 \text{ kJ/mol};$$

$$= -1036,66 - 1007,48 - (-1007,48 - 1036,66) = 0,0 \text{ kJ/mol atermiska}$$

$$= -1040,78 - 10,3 - (-1014,07 - 41,41) = 4,4 \text{ kJ/mol}$$

$$\Delta S_{\text{izkļiedēta}} = -\Delta H_{\text{Hess}}/T = -4,4/298,15 = -14,76 \text{ J/mol/K};$$

.....Membrānas kanālu šķērsošana ir atermisks-neitrāls process $\Delta H_{\text{H}} = 0,0 \text{ kJ/mol}$ bez berzes.

.....Nav siltuma izkļiedes membrānas kanālā

$$\Delta S_{\text{H}} = \Delta S^\circ_{\text{NADPH}} + \Delta S^\circ_{\text{NAD}} - \Delta S^\circ_{\text{NADP}} - \Delta S^\circ_{\text{NADH}} = -4465,708 - 3766,008 - (-4166,096 - 4081,784) = 16,164 \text{ J/mol/K};$$

$$\Delta S_{\text{skopēja}} = \Delta S_{\text{H}} + \Delta S_{\text{izkļiedēta}} = 16,164 - 14,76 = 1,404 \text{ J/mol/K};$$

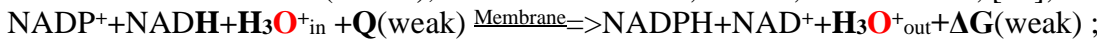
$$\Delta G_{\text{H}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = 4,4 - 298,15 \cdot 0,016164 = -0,4193 \text{ kJ/mol}; \text{ vāji eksoergiska.}$$

$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{NADPH}} + \Delta G^\circ_{\text{NAD}} - \Delta G^\circ_{\text{NADP}} - \Delta G^\circ_{\text{NADH}} = 290,6776 + 1112,534 - (228,052 + 1175,5732) = -0,4136 \text{ kJ/mol};$$

$$T \cdot \Delta S_{\text{skopēja}} = 0,001404 \text{ J/K/mol} \cdot 298,15 \text{ K} = 0,419 \text{ kJ/mol}; \text{ saistīta zaudēta enerģija protona gradientā } \text{H}^+ \text{ vāja patvaļīga eksoergiska}$$

$$\text{Ox } \text{NADP}^+ + \text{H}^+(\text{H}^+ + 2\text{e}^-) = \text{NADPH}; \text{ absolute } \text{E}^\circ_{\text{NADP}} = -0,4135 \text{ V};$$

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



$$\Delta \text{E}^\circ = \text{E}^\circ_{\text{NADH}} - \text{E}^\circ_{\text{NADP}} = -0,4095 - (-0,4135) = 0,004 \text{ V}, \text{ n is 2};$$

$$\Delta G_{\text{eq}} = \Delta \text{E}^\circ \cdot \text{F} \cdot \text{n} = 0,004 \text{ V} \cdot 2 \text{ mol} \cdot 96485 \text{ C/mol} = (-0,4095 - (-0,4135)) \cdot 2 \cdot 96485 = -\text{R} \cdot \text{T} \cdot \ln(\text{K}_{\text{eq}}) = 0,77188 \text{ kJ/mol}$$

$$\text{EXP}(-\Delta G_{\text{eqAerobi}}/\text{R}/\text{T}) = \text{EXP}(-771,88/8,3144/298,15) = 0,7324 = \text{K}_{\text{eqAerobi}};$$

$$\text{K}_{\text{eqAerobi}} = \frac{[\text{NAD}^+][\text{NADPH}][\text{H}_3\text{O}^+]}{[\text{NADH}][\text{NADP}^+][\text{H}_3\text{O}^+]} = e^{-\frac{\Delta G_{\text{eqAerobi}}}{\text{R} \cdot \text{T}}} = e^{-\frac{771,88}{8,314 \cdot 298,15}} = 0,7324;$$

Mitohondrijas kanālos H⁺ :

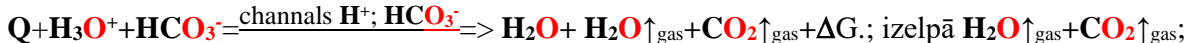
$$\Delta G_{\text{H}} = \text{RT} \ln([\text{H}_3\text{O}^+]_{\text{right}}/[\text{H}_3\text{O}^+]_{\text{left}}) \text{ ģenerētais gradients kvazi līdzsvars } \text{K}_{\text{eq}} = 10^{(-5,5)}/10^{(-7,36)} = 72,44 ;$$

$$\Delta S_{\text{eq}} = -8,3144 \cdot \ln(10^{(-5,5)}/10^{(-7,36)}) = -35,609 \text{ J/mol/K};$$

$$\Delta G_{\text{eq}} = 8,3144 \cdot 298,15 \cdot \ln(10^{(-5,5)}/10^{(-7,36)}) = 10,617 \text{ kJ/mol};$$

$$\Delta S_{\text{Hess_sum}} = 16,164 - 35,609 = 459,954 \text{ J/mol/K};$$

$$\Delta G_{\text{eq}} = -\text{R} \cdot \text{T} \cdot \ln(\text{K}_{\text{eq}}) = -8,3144 \cdot 298,15 \cdot \ln(72,4436) = -10,617 \text{ kJ/mol};$$



$$\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{H}_2\text{O}_{\text{gas}}} + \Delta S^\circ_{\text{CO}_2_{\text{gas}}} - \Delta S^\circ_{\text{H}_3\text{O}} - \Delta S^\circ_{\text{HCO}_3} = 69,956 + 188,74 + 213,74 - (-3,854 + 98,324) = 377,966 \text{ J/mol/K};$$

$$\text{Kanālos } \text{HCO}_3^-: \Delta G_{\text{HCO}_3} = \text{RT} \ln([\text{HCO}_3^-]_{\text{right}}/[\text{HCO}_3^-]_{\text{left}})$$

$$\Delta S_{\text{HCO}_3} = -\text{R} \ln(0,0154/0,0338919) = 6,55847 \text{ J/mol/K}$$

$$\Delta G_{\text{HCO}_3} = \text{RT} \ln(0,0154/0,0338919) = -1,9554 \text{ kJ/mol};$$

$$\Delta S_{\text{Hess_sum}} = 377,966 + 75,42909 + 6,55847 = 459,954 \text{ J/mol/K};$$

$$\Delta S_{\text{Hess_sum}} = 377,966 + 35,609 + 6,55847 = 420,1 \text{ J/mol/K};$$

$$= 0,0591/2 \cdot \log([\text{H}_2\text{O}]) = 0,0591/2 \cdot \log(55,34573393) = 0,051508 \text{ V}$$

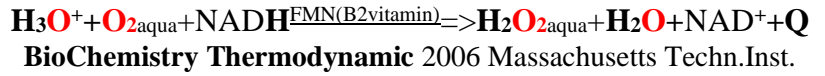
$$= 0,0591/2 \cdot \log([\text{H}_2\text{O}]^2) = 0,0591/2 \cdot \log(55,34573393^2) = 0,1030 \text{ V}$$

TERMODINAMIKA VINGRINĀJUMS XVI. $\text{NADH} + \text{H}_3\text{O}^+ + \text{O}_{2\text{aqua}} \xleftarrow{\text{FMN(B2vitamin)}} \text{NAD}^+ + \text{H}_2\text{O} + \text{H}_2\text{O}_{2\text{aqua}} + \Delta G + Q$

Vitamīna B3 reducētā forma NADH vai NADPH flavīna B2 vitamīna FMN enzīms pielietojiet skābekli $\text{O}_{2\text{aqua}}$ kā elektronu akceptoru oksidē NADH producējot ūdeņraža peroksīdu.

CRC Handbook of Chemistry and Physics 90. redakcija CD-ROM versija 2010; Izejvielas => produkti

Viela	$\Delta H_{\text{H}}^{\circ} \text{ kJ/mol}$	$\Delta S_{\text{H}}^{\circ} \text{ J/mol/K}$	$\Delta G_{\text{H}}^{\circ} \text{ kJ/mol}$
$\text{O}_{2\text{aqua}}$	-11.70	-94,2	16,40
$\text{O}_{2\text{aqua}}$	-11.715	110,876	16,4
$\text{NADH}_{(\text{aq})}$	-1036,66	-140,5	-
$\text{NADH}_{(\text{aq})}$	-1041,41	-4081,784	1175,5732
H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
$\text{NAD}^+_{(\text{aq})}$	-1007,48	-183	-
$\text{NAD}^+_{(\text{aq})}$	-1010,3	-3766,008	1112,534
H_2O_2	-237,129	69,91	-237,129
$\text{H}_2\text{O}_{2\text{aqua}}$	-191,17	143,9	-134,03
$\text{H}_2\text{O}_{2\text{aqua}}$	-191,99	-481,688	-48,39



$\Delta H_{\text{H}} = \Delta H^{\circ}_{\text{H}_2\text{O}_2} + \Delta H^{\circ}_{\text{H}_2\text{O}} + \Delta H^{\circ}_{\text{NAD}} - \Delta H^{\circ}_{\text{H}_3\text{O}} - \Delta H^{\circ}_{\text{O}_2} - \Delta H^{\circ}_{\text{NADH}} = -150 \text{ kJ/mol}$
 $\Delta H_{\text{H}} = -191,99 - 286,65 - 1010,3 - (-285,81 - 11,70 - 1041,41) = -150 \text{ kJ/mol}$
 $= -191,17 - 285,85 - 1007,48 - (-285,81 - 11,715 - 1036,66) = 150,315 \text{ kJ/mol}$
 $\Delta S_{\text{H}} = \Delta S^{\circ}_{\text{H}_2\text{O}_2} + \Delta S^{\circ}_{\text{H}_2\text{O}} + \Delta S^{\circ}_{\text{NAD}} - \Delta S^{\circ}_{\text{H}_3\text{O}} - \Delta S^{\circ}_{\text{O}_2} - \Delta S^{\circ}_{\text{NADH}} = -521,05 \text{ J/mol/K}$
 $= -481,688 - 453,188 - 3766,008 - (-3,854 - 94,2 - 4081,784) = -521,05 \text{ J/mol/K}$
 $= 143,9 + 69,9565 - 183 - (-3,854 + 110,876 - 140,5) = 64,3345 \text{ J/mol/K}$
 $\Delta G_{\text{H}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -150,02 - 298,15 \cdot (-0,52105) = 5,33 \text{ kJ/mol}$; **endoergic**
 $\Delta G_{\text{H}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -150,315 - 298,15 \cdot 0,064335 = -169,5 \text{ kJ/mol}$; **exoergic**
 $\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{H}_2\text{O}_2} + \Delta G^{\circ}_{\text{H}_2\text{O}} + \Delta G^{\circ}_{\text{NAD}} - \Delta G^{\circ}_{\text{H}_3\text{O}} - \Delta G^{\circ}_{\text{O}_2} - \Delta G^{\circ}_{\text{NADH}} =$

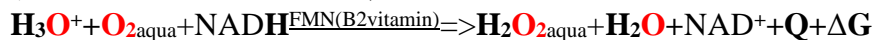
$\Delta G_{\text{Hess}} = -134,03 + (-237,191 - 151,549)/2 + 1112,534 - (-213,275 + 16,4 + 1175,5732) = -194,56 \text{ kJ/mol}$;

$\Delta S_{\text{izhkliedēta}} = -\Delta H_{\text{Hess}}/T = 150/298,15 = 503,1 \text{ J/mol/K}$; $\Delta S_{\text{izhkliedēta}} = -\Delta H_{\text{Hess}}/T = 150,315/298,15 = 504,1 \text{ J/mol/K}$;

$\Delta S_{\text{kopēja}} = \Delta S_{\text{Hess}} + \Delta S_{\text{izhkliedēta}} = -521,1 + 503,1 = -18 \text{ J/mol/K}$; $\Delta S_{\text{kopēja}} = \Delta S_{\text{Hess}} + \Delta S_{\text{izhkliedēta}} = 64,3345 + 504,1 = 568,44 \text{ J/mol/K}$;

$T \cdot \Delta S_{\text{kopēja}} = 0,5684345 \text{ J/K/mol} \cdot 298,15 \text{ K} = +169,5 \text{ kJ/mol}$; bound $T \Delta S_{\text{n}} \leftarrow \text{izhkliedēta-lost energy}$ and is **spontaneous**
 $\text{Ox } \text{O}_{2\text{aqua}} + \text{H}_3\text{O}^+ + \text{H}^+ (\text{H}^+ + 2\text{e}^-) = \text{H}_2\text{O}_{2\text{aqua}} + \text{H}_2\text{O}$; $\text{E}^{\circ}_{\text{H}_2\text{O}_2} = 0.4495 \text{ V}$ Alberta University NADH and NADPH oxidase.

Red $\text{NAD}^+ + \text{H}^+ (\text{H}^+ + 2\text{e}^-) = \text{NADH}$; $\text{E}^{\circ} = -0,4095 \text{ V}$; David Harris



Free energy of activate homeostasis products referring to water and $\text{CO}_{2\text{gas}}$ zero $G_{\text{H}_2\text{O}} = G_{\text{CO}_{2\text{gas}}} = 0 \text{ kJ/mol}$ are peroxide, hydroxonium and anion of peroxide: $G_{\text{H}_2\text{O}_2} = 284,25 \text{ kJ/mol}$; $G_{\text{H}_3\text{O}^+} + G_{\text{HOO}^-} = 22,44 + 337,8 = 360,24 \text{ kJ/mol}$;

$\Delta \text{E}^{\circ} = \text{E}^{\circ}_2 - \text{E}^{\circ}_1 = -0,4095 - 0,4495 = -0,859 \text{ V}$, n is 2;

$\Delta G_{\text{eq}} = (\text{E}^{\circ}_2 - \text{E}^{\circ}_1) \cdot F \cdot n = -0,859 \cdot 2 \cdot 96485 \text{ C/mol} = (-0,4095 - 0,4495) \cdot 2 \cdot 96485 \text{ C/mol} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -165,8 \text{ kJ/mol}$;
 $= \text{EXP}(-\Delta G_{\text{eqAerobi}}/R/T) = \text{EXP}(165761/8,3144/298,15) = 1,097 \cdot 10^{29}$;

$K_{\text{eqAerobi}} = \frac{[\text{NAD}^+] \cdot [\text{H}_2\text{O}_2]_{\text{aqua}} \cdot [\text{H}_2\text{O}]}{[\text{NADH}] \cdot [\text{O}_2]_{\text{aqua}} \cdot [\text{H}_3\text{O}^+]}$ $= e^{-\frac{\Delta G_{\text{eqAerobi}}}{R \cdot T}} = e^{-\frac{-165761}{8,314 \cdot 298,15}} = 1,097 \cdot 10^{29}$;

$= 0,0591/2 \cdot \log([\text{H}_2\text{O}]) = 0,0591/2 \cdot \log(55,34573393) = 0,051508 \text{ V}$

$= 0,0591/2 \cdot \log([\text{H}_2\text{O}]^2) = 0,0591/2 \cdot \log(55,34573393^2) = 0,1030 \text{ V}$

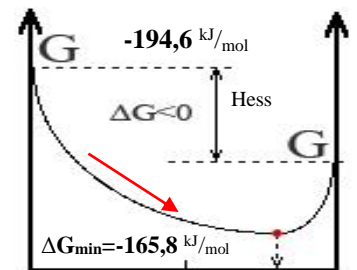
Prigožina atraktors labvēlīgā līdzsvarā Hesa likuma aprēķinos ir eksotermiska un eksoergiska NADH oksidēšanas brīvās enerģijas izmaiņa ir negatīva $\Delta G_{\text{Hess}} = -194,56 \text{ kJ/mol}$, bet minimizējas konstantē brīvās enerģijas izmaiņas vērtība $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -165,8 \text{ kJ/mol}$ sasniedzot līdzsvaru $K_{\text{eqAerobi}} = 1,097 \cdot 10^{29}$;

Lešateljē princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma

ΔG_{min} sasniegšana. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas

līdzsvars.

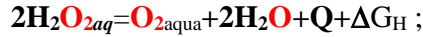
reactanti $\text{H}_3\text{O}^+ + \text{O}_{2\text{aqua}} + \text{NADH}$
 un produkti $\text{H}_2\text{O}_{2\text{aqua}} + \text{H}_2\text{O} + \text{NAD}^+$;



A+B+C 50% D+E+F
 $\text{H}_2\text{O}_{2\text{aqua}} + \text{H}_2\text{O} + \text{NAD}^+$;

TERMODINAMIKA VINGRINĀJUMS XVII Peroksīda $2\text{H}_2\text{O}_2(aq)$ pārvēršana par $\Rightarrow \text{O}_2(aq) + 2\text{H}_2\text{O} + \text{Q}$

Liela ātruma protolīzē peroksīda anjonu $\text{H}^+ + \text{HOO}^- \rightleftharpoons \text{OOH} + \text{H}^+$ sadursmes aktivācijas enerģija ir liela $E_a = 79000 \text{ J/mol}$ pretēji $\text{HOO}^- \Rightarrow \text{Fe}^{3+}$ sadursmes aktivācijas enerģijai $E_a = 29 \text{ J/mol}$ katalāzē ir neliela. Pārvēršot izejvielas $2\text{H}_2\text{O}_2$ produktos:



$$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{O}_2} + 2\Delta G^\circ_{\text{H}_2\text{O}} - 2\Delta G^\circ_{\text{H}_2\text{O}_2} = 16,40 + 2*(-237,191) - (2*(-134,03)) = -189,9 \dots \text{kJ/mol}$$
 eksoerģiski

$$\Delta G_{\text{AlbertyHomeostasis}} = G_{\text{O}_2\text{Biochem}_\text{arteriaj}} + 2*G_{\text{H}_2\text{O}\text{BioChemistry}} - 2*G_{\text{H}_2\text{O}_2} = 88,04 + 2*85,64 - 2*284,25 = -309,18 \text{ kJ/mol};$$
 Alberty

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_3O^+	-285,81	-3,854	-213,275
$\text{O}_2(aq)$	-11,715	110,876	16,4
$\text{O}_2(aq)$	-11,70	-94,2	16,40
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
$\text{H}_2\text{O}_2(aq)$	-191,99	-481,688	-48,39
$\text{H}_2\text{O}_2(aq)$	-191,17	143,9	-134,03
$\text{H}_2\text{O}_2(l)$	-237,129	69,91	-237,129

Mischenko 1972, Himia, Leningrad [26]

$$\Delta H_{\text{Hess}} = 2\Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{O}_2} - 2\Delta H^\circ_{\text{H}_2\text{O}_2} = -202,66 \dots \text{kJ/mol}$$
 exothermic

$$= -11,7 - 2*286,65 - (2*(-191,17)) = -202,66 \text{ kJ/mol}$$

$$\text{CRC 2010}; 2.\Delta S_{\text{dispersed}} = -\Delta H_H/T = -(-202,66)/298,15 = 679,725 \text{ J/mol/K}$$

Biochem Thermodynamic 2006 Masachusetts Technology institute

$$\Delta S_{\text{Hess}} = 2\Delta S^\circ_{\text{H}_2\text{O}} + \Delta S^\circ_{\text{O}_2} - 2\Delta S^\circ_{\text{H}_2\text{O}_2} =$$

$$= 110,876 + 2*69,9565 - (2*481,688) = 1214 \text{ J/mol/K}$$

$$3. \Delta S_{\text{total}} = \Delta S_{\text{Hess}} + \Delta S_{\text{dispersed}} = 1214 + 679,725 = 1893,7 \dots \text{J/mol/K}$$

$$4. \Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T*\Delta S_{\text{Hess}} = -202,66 - 298,15*1,214165 = -564,66 \dots \text{kJ/mol}$$
 exoergic

$$T*\Delta S_{\text{total}} = 1,893725*298,15 = +564,6 \dots \text{kJ/mol};$$
 bound $T\Delta S_{\text{total}} \leftarrow$ dispersed energy ΔG_{Hess} .

Red: $\text{H}_2\text{O}_2 + 2\text{H}_2\text{O} = \text{O}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^-$; absolute standard potential $E^\circ_{\text{RedH}_2\text{O}_2} = 0,5278 \text{ V}$ Alberta Univ. $E_{\text{oclassic}} = 0,694 \text{ V}$;

Ox: $\text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2\text{e}^- = 4\text{H}_2\text{O}$; inverse absolute standard potential $E^\circ_{\text{OxH}_2\text{O}_2} = 1,7123 \text{ V}$ Suhotina $E_{\text{oclassic}} = 1,776 \text{ V}$



Pusreakcijas RedOks Nernsta vienādojumi reducētai un oksidētai formai: elektronu balansēšana 2e^-

$[\text{H}_2\text{O}_2] = 1; 10^{-(10)} \text{ M}$ Biochemistry concentrations $[\text{O}_2(aq)] = 6*10^{-5} \text{ M}$, $[\text{H}_3\text{O}^+] = 10^{-7,36} \text{ M}$, $[\text{H}_2\text{O}] = 55,3 \text{ M}$.

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

$$\text{Ox: } E_{\text{OxH}_2\text{O}_2} = E^\circ_{\text{H}_2\text{O}_2} + 0,0591/2 * \lg([\text{H}_2\text{O}_2] * [\text{H}_3\text{O}^+]^2 / [\text{H}_2\text{O}]^4) = 1,7123 + 0,0591/2 * \lg(1*10^{-(7,36*2)} / 55,3^4) = 1,0713 \text{ V}$$

$$\text{Homeostāze: } \Delta G_{\text{eqBioChem}} = (E_{\text{Red}} - E_{\text{Ox}}) * F * n = (-0,1349 - 1,0713) * 96485 * 2 = (-1,2062) * 96485 * 2 = -232,76 \text{ kJ/mol};$$

$$\Delta G_{\text{AlbertyHomeostasis}} = G_{\text{O}_2\text{Biochem}_\text{arteriaj}} + 2*G_{\text{H}_2\text{O}\text{BioChemistry}} - 2*G_{\text{H}_2\text{O}_2} = 88,04 + 2*85,64 - 2*284,25 = -309,18 \text{ kJ/mol};$$
 Alberty

$$2G_{\text{H}_2\text{O}_2} = G_{\text{O}_2(aq)} + 2*G_{\text{H}_2\text{O}} + \Delta G_{\text{eqAlbertyStandart}} = 330 + 2*0 + 228,57 = 2*284,25 = 548,9 \text{ kJ/mol};$$

Free energy of activate homeostasis products referring to water and CO_2 gas zero $G_{\text{H}_2\text{O}} = G_{\text{CO}_2\text{gas}} = 0 \text{ kJ/mol}$ are

peroxide, hydroxonium and anion of peroxide: $G_{\text{H}_2\text{O}_2} = 284,25 \text{ kJ/mol}$; $G_{\text{H}_3\text{O}^+} + G_{\text{HOO}^-} = 22,44 + 337,8 = 360,24 \text{ kJ/mol}$

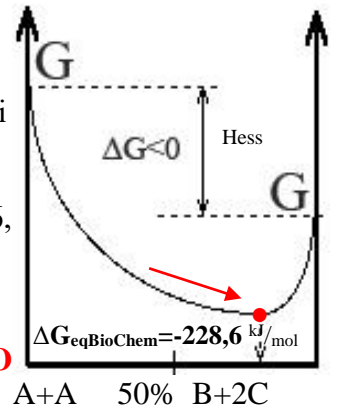
$$\Delta G_{\text{eqAlbertyStandart}_\text{H}_2\text{O}_2} = (E_{\text{Red}} - E_{\text{Ox}}) * F * n = (0,5278 - 1,7123) * 96485 * 2 = (-1,1845) * 96485 * 2 = -228,57 \text{ kJ/mol};$$

$$K_{\text{eqStandart}} = \frac{[\text{O}_2]_{\text{aqua}} * [\text{H}_2\text{O}]^2}{[\text{H}_2\text{O}_2]_{\text{aqua}}^2} = K_{\text{H}_2\text{O}_2} = \exp(-\Delta G_{\text{eq}}/R/T) = \exp(238510/8.3144/298.15) = 10^{41,75} \dots$$

Eksotermiskas un eksoerģiska $\text{H}_2\text{O}_2(aq)$ dismutēšanās Hesa brīvās enerģijas izmaiņa $\Delta G_{\text{Alberty}}$ ir negatīva $-242,7 \text{ kJ/mol}$, bet minimizējas $\Delta G_{\text{qBioChem}} = -238,5 \text{ kJ/mol}$ sasniedzot līdzsvara maisījuma konstanti $K_{\text{qBioChem}} = 10^{41}$. Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana. Liela ātruma protolīzes atraktori $\text{pH} = 7,36$, skābeklis gaisā 20,95% atrodas līdzsvara stāvoklī, kamēr homeostāze neatgriezeniski turpinās, jo ir ne līdzsvara stāvoklis. Prigožina atraktors Nobela prēmija ķīmijā 1977. gadā. KATALĀZE dzēš peroksīda molekulas H_2O_2 simts procentīgā $\omega = 6$, $\omega = 3$ iznākumam taukskābju C20:4 elongācijas sintēzei peroksisomās. KATALĀZES reaktivitāte ir neatgriezeniskas homeostāzes nepieciešams Brauna molekulārais dzinējs evolūcijai un izdzīvošanai.

izejvielas $2\text{H}_2\text{O}_2(aq)$ produkti $\text{O}_2(aq) + 2\text{H}_2\text{O}$

$$\Delta G_{\text{AlbertyHomeostasis}} = -309,18 \text{ kJ/mol}$$



OTHERMODYNAMICS Exercise VII a sukcināta $\text{S}^-\text{CoA}^4- \text{O}_2 \text{H}_2\text{O}_2$ fumarāta dehidrogenēšanas reakcija

Succinat $\text{S}^-\text{CoA}^4- \text{O}_2 \text{H}_2\text{O}_2$ fumarāta dehidrogenēšanas reakcija! Ir eksoerģiska vai endoerģiska! $I=0,25 \text{ M}$;

Biochemistry thermodynamic data 2006; Succinat $^{2-} + \text{O}_2\text{aq} \Rightarrow$ fumarate $^{2-} + \text{H}_2\text{O}_2\text{aq} + \Delta G$; $\text{pH}=7,36$

Red: Succinate $^{2-} + 2\text{H}_2\text{O} =$ Fumarate $^{2-} + 2\text{H}_3\text{O}^+ + 2\text{e}^-$; $E^\circ_{\text{Red}} = 0,2512 \text{ V}$ Lehninger 2000; Univ. Alberta 1997;

Ox: $\text{O}_2\text{aq} + 2\text{H}_3\text{O}^+ + 2\text{e}^- = \text{H}_2\text{O}_2\text{aq} + 2\text{H}_2\text{O}$; $E^\circ_{\text{Ox}} = 0,4495 \text{ V}$; $\Delta E = (E^\circ_{\text{Red}} - E^\circ_{\text{Ox}}) = (0,2512 - 0,4495) = -0,1983 \text{ V}$;

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

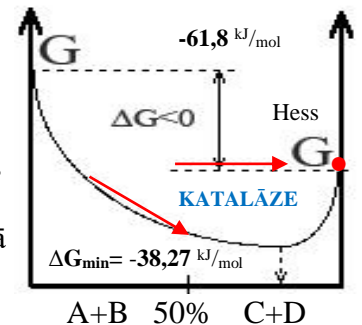
$K_{\text{eq}} = \exp(-\Delta G_{\text{eq}}/R/T) = \exp(38270/8,3144/298,15) = 5065991$ labvēlīgs līdzsvars.

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

Viela	$\Delta H^\circ_{\text{Hess}}$, kJ/mol	$\Delta S^\circ_{\text{Hess}}$, J/mol/K	$\Delta G^\circ_{\text{Hess}}$, kJ/mol
H_3O^+	-285,81	-3,854	-213,275
H_2O	-286,65	-453,188	-151,549
$\text{H}_2\text{O}_2\text{aq}$	-191,99	-481,688	-48,39
O_2aq	-11,70	-94,2	16,4
Succinat $^{2-}$	-908,69	-1295,576	-522,414
SuccinatCoA $^{4-}$	-	-	-339,2476
HSCoA $^{3-}$	-	-	-5,6616
Fumarate $^{2-}$	-776,56	-862,288	-519,4688
Ubiquinol	-	-	3849,60
Ubiquinone	-	-	3853,88

$\Delta G_{\text{H}} = \Delta H_{\text{H}} - T * \Delta S_{\text{H}} = -48,16 - 298,15 * 0,0458 = -61,815 \text{ kJ/mol}$ exoergic

Eksotermiska un eksoerģiska taukskābju C20:4 etil grupas -CH $_2$ -CH $_2$ - dehidrogenēšana par cis dubultsaiti $\text{H} > \text{C} = \text{C} < \text{H}$ peroksisomās Hesa brīvā enerģijas izmaiņa ΔG_{Hess} ir -61,8 kJ/mol negatīva, bet minimizējas līdzsvarā $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = -38,27 \text{ kJ/mol}$.



Reaktanti etil grupas -CH $_2$ -CH $_2$ - dehidrogenēšana Succinat $^{2-} + \text{O}_2\text{aq} \Rightarrow$ produkti cis $\text{H} > \text{C} = \text{C} < \text{H}$ fumarate $^{2-} + \text{H}_2\text{O}_2$
Lešateljē princips Prigožina atraktora kā brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana

$$\text{līdzsvara maisījuma: } K_{\text{eq}} = \frac{[\text{Fumarate}^{2-}] \cdot [\text{H}_2\text{O}_2] \cdot \text{KATALĀZE}}{[\text{Succinate}^{2-}] \cdot [\text{O}_2]} = 5065991.$$

Neatgriezeniskums secībā komplekso enzimatisko reakciju kartībā nodrošina KATALĀZSE reaktivitāte, kura dzēš peroksīdu līdz nullei $[\text{H}_2\text{O}_2] = 0 \text{ mol/liter}$ un procesa ātrumu limitē vienīgi dehidrogenāzes enzīms. KATALĀZE komplekso reakciju secībā nodrošina stabīlu iznākumu • 100% neaizstājamo taukskābju $\omega=6$ un $\omega=3$ sintēzes produktos peroksisomās, jo dzēš peroksīda molekulas H_2O_2 .

Ubihinola oksidēšanas – dehidrogenēšanas iznākumu • 100% nodrošina KATALĀZES reaktivitāte



$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{UbiQuinOx}} + \Delta G^\circ_{\text{H}_2\text{O}_2} - \Delta G^\circ_{\text{O}_2} - \Delta G^\circ_{\text{UbiQuinRed}} = -3853,8792 - 48,39 - (16,4 - 3849,6004) = -69,07 \text{ kJ/mol}$

Ox: $\text{O}_2\text{aq} + 2\text{H}_3\text{O}^+ + 2\text{e}^- = \text{H}_2\text{O}_2\text{aq} + 2\text{H}_2\text{O}$; $E^\circ_{\text{Ox}} = 0,4495 \text{ V}$ University Alberta

Red: Ubiquinol $+2\text{H}_2\text{O} =$ Ubiquinone $+2\text{H}_3\text{O}^+ + 2\text{e}^-$; $E^\circ_{\text{Red}} = 0,2656 \text{ V}$ Lehninger 2000 ;

$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = (E^\circ_{\text{Red}} - E^\circ_{\text{Ox}}) * F * n = (0,2656 - 0,4495) * 96485 * 2 = (-0,1839) * 96485 * 2 = -35,49 \text{ kJ/mol}$;

$K_{\text{eq}} = \exp(-\Delta G_{\text{eq}}/R/T) = \exp(35490/8,3144/298,15) = 90471395 = 1650539$ labvēlīgs līdzsvars .

????

Red: Ubiquinol $6+2\text{H}_2\text{O} =$ Ubiquinone $6+2\text{H}_3\text{O}^+ + 2\text{e}^-$; absolūtais potenciāls $E^\circ_{\text{Red}} = -1,2435 \text{ V}$; $E^\circ_{\text{klasika}} = -1,05 \text{ V}$ CRC 2012 ;

$\Delta G_{\text{min}} = \Delta G_{\text{eq}} = (E^\circ_{\text{Red}} - E^\circ_{\text{Ox}}) * F * n = (-1,2435 - 0,4495) * 96485 * 2 = (-1,693) * 96485 * 2 = -336,6 \text{ kJ/mol}$;

$K_{\text{eq}} = \exp(-\Delta G_{\text{eq}}/R/T) = \exp(336628/8,3144/298,15) = 90471395 = 10^{58,975}$ labvēlīgs līdzsvars .

THERMODYNAMICS Exercise XVII b Malate to Fumarate conversion dehydration **H₂O** BioThermod2006

Malate to fumarate conversion dehydration **H₂O** at temperatures 298,15 K, using the data table! Mention whether the reaction will be **eksoerģiskas** or **endoerģiska**! Malate²⁻+Q+ΔG =>Fumarate²⁻+H₂O; 2000 ΔG_{Lehninger}= 3,1 kJ/mol;

Substance	ΔH ^o _H kJ/mol	ΔS ^o _H J/mol/K	ΔG ^o _H kJ/mol
H ₃ O ⁺	-285,81	-3,854	-213,275
H ₂ O	-286,65	-453,188	-151,549
H ₂ O	-285,85	69,9565	-237,191
O ₂ aqua	-11,70	-94,2	16,4
Succinat ²⁻	-908,69	-1295,576	-522,414
SuccinatSCoA ⁴⁻	-	-	-339,2476
HSCoA ³⁻	-	-	-5,6616
Malate ²⁻	-1079,796	-1358,976	-674,624
Fumarate ²⁻	-776,56	-862,288	-519,4688
Ubiquinol	-	-	3849,60
Ubiquinone	-	-	3853,88

$$1. \Delta H_{Hess} = \Delta H^o_{produkti} - \Delta H^o_{Reaktanti}$$

$$2. \Delta S_{Hess} = \Delta S^o_{produkti} - \Delta S^o_{Reaktanti}; 3. \Delta G_H = \Delta H_H - T \cdot \Delta S_H;$$

$$\Delta H_H = \Delta H^o_{H_2O} + \Delta H^o_{Fumarate} - \Delta H^o_{Malate} = 16,586 \text{ kJ/mol}; \text{Endotermiska}$$

$$= -286,65 - 776,56 - (-1079,796) = 16,586 \text{ kJ/mol}$$

$$\Delta S_{izhklidēta} = -\Delta H_{Hess} / T = -16,586 / 298,15 = -55,63 \text{ J/mol/K}$$

$$\text{BioThermod06}; \Delta S_H = \Delta S^o_{H_2O} + \Delta S^o_{Fumarate} - \Delta S^o_{Malate} = 43,5 \text{ J/mol/K}$$

$$= -453,188 - 862,288 - (-1358,976) = 43,5 \text{ J/mol/K}$$

$$\Delta S_{kopēja} = \Delta S_{Hess} + \Delta S_{izhklidēta} = -55,63 + 43,5 = -12,3 \text{ J/mol/K}$$

$$\Delta G_H = \Delta H_H - T \cdot \Delta S_H = 16,586 - 298,15 \cdot 0,0435 = 3,6165 \text{ kJ/mol};$$

$$\Delta G_H = \Delta G^o_{H_2O} + \Delta G^o_{fumarat} - \Delta G^o_{Malate} = 3,606 \text{ kJ/mol}$$

$$3,606 \text{ kJ/mol} = -151,549 - 519,4688 - (-674,624)$$

$$T \cdot \Delta S_{kopēja} = -0,01214 \cdot 298,15 = -3,6195 \text{ kJ/mol saistīta produkta}$$

TΔSn akumulēta enerģija.

$$\frac{[Fumarat^{2-}] \cdot [H_2O]}{[Malat^{2-}]} = K_{eq} = K_{Leninge} = \exp(-\Delta G_{eq} / R/T) = \exp(-3100 / 8,3144 / 298,15) = 0,28635 = 10^{-0,543} \text{ nelabvēlīga}$$

Hesa dehidratācija produkti mīnus reactanti nelabvēlīga brīvās enerģijas izmaiņa

$$\Delta G_{Hess} = \Delta H_{Hess} - T \cdot \Delta S_{Hess} = 3,62 \text{ kJ/mol}.$$

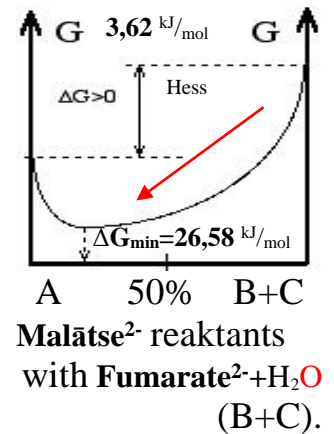
Endotermiska un endoerģiska dehidratācijas brīvās enerģijas izmaiņa ΔG_{Hess} pozitīva 3,62 kJ/mol, bet minimizējas sasniedzot minimumu

$$\Delta G_{min} = \Delta G_{eq} = 3,1 \text{ kJ/mol kā Prigožina atraktors}$$

$$\text{konstante maisījuma attiecībā } K_{eq} = \frac{[Fumarat^{2-}] \cdot [H_2O]}{[Malat^{2-}]} = 0,28635. \text{ Lešatelje}$$

princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana. Brīvās enerģijas

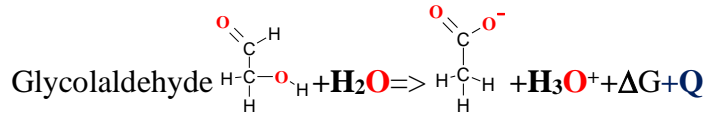
izmaiņas minimuma sasniegšanā iestājas līdzsvars.



THERMODYNAMICS Exercise XVIII Glycolaldehyde $\text{H}_2\text{C}(\text{OH})\text{CHO}$ conversion to $\text{H}_3\text{CCOO}^- + \text{H}_3\text{O}^+ + \text{Q}$

Glycolaldehyde $\text{H}_2\text{C}(\text{OH})\text{CHO}$ conversion to acetate $\text{H}_3\text{CCOO}^- + \text{H}_3\text{O}^+ + \text{Q}$ (25 C) 298.15 K, using the data table!
Mention whether the reaction will be **eksoergiskas** or **endoergiska**! Reaktanti Glyoxal => produkti acetate + $\text{H}_3\text{O}^+ + \text{Q}$

Viela	$\Delta H^\circ_{\text{H}}, \text{kJ/mol}$	$\Delta S^\circ_{\text{H}}, \text{J/mol/K}$	$\Delta G^\circ_{\text{H}}, \text{kJ/mol}$
$\text{H}_2\text{C}(\text{OH})\text{CHO}$	-212	272,5	-313,83
H_2O	-286,65	-453,188	-151,549
$\text{H}_2\text{O}_{(aq)}$	-285,85	69,9565	-237,191
$\text{H}_3\text{O}^+_{(aq)}$	-285,81	-3,854	-213,275
H_3CCOOH	-484,3	159,8	-389,9
H_3CCOO^-	-486,84	82,23	-247,83
H_3CCOO^-	-485,64	87,58	-369,37
H_3CCOO^-	-486	85,3	-240,963



$$\text{H}_2\text{C}(\text{OH})\text{CHO} + \text{H}_2\text{O} \Rightarrow \text{H}_3\text{CCOO}^- + \text{H}_3\text{O}^+ + \text{Q} + \Delta G$$

$$\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{H}_3\text{CCOO}^-} + \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{H}_2\text{O}} + \Delta H^\circ_{\text{H}_2\text{C}(\text{OH})\text{CHO}} = \text{kJ/mol}$$

$$= -485,64 - 285,81 - (-212 - 285,85) = -273,32 \text{ kJ/mol} \text{ exothermic}$$

$$= -486 - 285,81 - (-212 - 286,65) = -273,16 \text{ kJ/mol} \text{ exothermic}$$

$$\Delta S_{\text{dispersed}} = -\Delta H_{\text{H}}/T = 273,16/298,15 = 916,2 \text{ J/K/mol}$$

$$\Delta G_{\text{H}} = \Delta G^\circ_{\text{H}_3\text{CCOO}^-} + \Delta G^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{\text{H}_2\text{O}} - \Delta G^\circ_{\text{H}_2\text{C}(\text{OH})\text{CHO}} = -31,624 \text{ kJ/mol}$$

$$\Delta G_{\text{Hess}} = 369,37 - 213,275 - (-237,191 - 313,83) = -31,624 \text{ kJ/mol};$$

$$\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{H}_3\text{CCOO}^-} + \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{H}_2\text{C}(\text{OH})\text{CHO}} = 87,58 - 3,854 - (69,9565 + 272,5) = -258,73 \text{ J/mol/K};$$

$$\Delta S_{\text{kopējā}} = \Delta S_{\text{H}} + \Delta S_{\text{izkliede}} = 918,966 - 261,014 = 660,236 \text{ J/mol/K};$$

$$\Delta G_{\text{H}} = \Delta H_{\text{H}} - T \cdot \Delta S_{\text{H}} = -273,16 - 298,15 \cdot (-0,25873) = -196 \text{ kJ/mol} \text{ eksoergiska}$$

$$T \cdot \Delta S_{\text{kopējā}} = 660,236 \cdot 298,15 \text{ K} = +196 \text{ kJ/mol};$$

bound $T \Delta S_{\text{H}} \leftarrow \text{izkliede-lost energy } \Delta G_{\text{HeveHseHess}} \leftarrow \text{Q} = 273,96 \text{ kJ/mol} \dots \text{spontaneous } \Delta G_{\text{Hess}} = -196,14 \text{ kJ/mol} \dots$

Formation in space. UV-irradiation of methanol ices containing CO yielded organic compounds such as glycolaldehyde un methyl formate, the more abundant isomer of glycolaldehyde.

Ethylene Glycol un glycolaldehyde require temperatures above 30 K.^{[12][13]} The most consistent formation reactions seems to be on the surface of ice in cosmic dust. Glycolaldehyde has been identified in gas un dust near the center of the Milky Way galaxy,^[16] in a star-forming region 26000 light-years from Earth^[17] un around a protostellar binary staH IRAS 16293-2422, 400 light years from Earth.^{[18][19]} Observation of in-falling glycolaldehyde spectra 60 AU from IRAS 16293-2422 suggests that complex organic molecules may form in stellar systems prior to the formation of planets, eventually arriving on young planets early in their formation.^[13]

Detection in space. The interior region of a dust cloud is known to be relatively cold. With temperatures as cold as 4 Kelvin the gases within the cloud will freeze un fasten themselves to the dust, which provides the reaction conditions conducive for the formation of complex molecules such as glycolaldehyde. When a star has formed from the dust cloud, the temperature within the core will increase. This will cause the molecules on the dust to evaporate un be released. The molecule will emit radio waves that can be detected un analyzed. The Atacama Large Millimeter/submillimeter Array (ALMA) first detected glycolaldehyde. ALMA consists of 66 antennas that can detect the radio waves emitted from cosmic dust.^[20] On October 23, 2015, researchers at the Paris Observatory announced the discovery of glycolaldehyde un ethyl alcohol on Comet Lovejoy, the first such identification of these substances in a comet.^{[21][22]}

Glycolaldehyde is formed from many sources, including the amino acid glycine un from purone catabolism. It can form by action of ketolase on fructose 1, 6-bisfosfāts in an alternate glycolysis pathway. This compound is transferred by thiamin pyrofosfāts during the pentose fosfāts shunt. In Tissue neurons; Mitochondria;

Solar-type protostar with ALMA. Glycolaldehyde (HCOCH_2OH) is the simplest sugar un an important intermediate in the path toward forming more complex biologically relevant molecules. First detection of 13 transitions of glycolaldehyde around a solar-type young staH through Atacama Large Millimeter Array (ALMA) observations of the Class 0 protostellar binary IRAS 16293-2422 at 220 GHz (6 transitions) un 690 GHz (7 transitions). Glycolaldehyde co-exists with its isomeH methyl formate (HCOOCH_3), which is a factor 10-15 more abundant toward the two sources. The data also show a tentative detection of ethylene glycol, the reduced alcohol of glycolaldehyde. In the 690 GHz data, the seven transitions predicted to have the highest optical depths based on modeling of the 220 GHz lines all show red-shifted absorption profiles toward one of the components in the binary (IRAS16293B) indicative of infall un emission at the systemic velocity offset from this by about $0.2''$ (25 AU). We discuss the constraints on the chemical formation of glycolaldehyde un other organic species - in particulaH in the context of laboratory experiments of photochemistry of methanol-containing ices. The relative abundances appear to be consistent with UV photochemistry of a $\text{CH}_3\text{OH-CO}$ mixed ice that has undergone mild heating. The order of magnitude increase in line density in these early ALMA data illustrate its huge potential to reveal the full chemical complexity associated with the formation of solar system analogs.

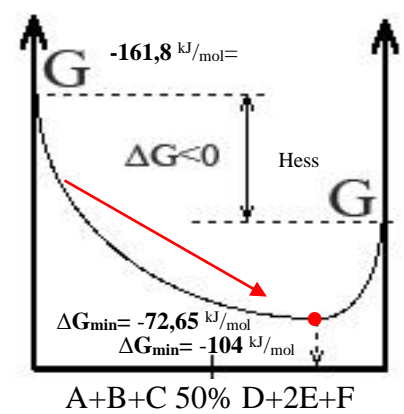
TERMODINAMIKA VINGRINĀJUMS XIX Glikolskābes $\text{H}_2\text{COH-COOH}$ pārvēršana $\text{H}_3\text{C-COOH} + \text{Q}$
 Glycolic acid Formation 61st page $2\text{C} + 2*\text{H}_2\text{gas} + 1,5*\text{O}_2\text{gas} \Rightarrow \text{H}_2\text{COHC(O)OH}$; $\Delta\text{G}_{\text{H}_2\text{COHC(O)OH}} = -403,2968 \text{ kJ/mol}$ [8];
 $\Delta\text{G}_{\text{H}_2\text{COHC(O)OH}} = \text{G}_{\text{H}_2\text{COHC(O)OH}} - (2\text{G}_{\text{Cgraph}} + 2\text{G}_{\text{H}_2\text{gas}} + 1,5*\text{G}_{\text{O}_2\text{gas}}) = -403,2968 \text{ kJ/mol}$;
 $\text{G}_{\text{H}_2\text{COHC(O)OH}} = -403,2968 + (2*91,26 + 2*85,6 + 1,5*303) = 404,9232 \text{ kJ/mol}$;
 Glycolic acid $\text{H}_2\text{COHC(O)OH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{COHC(O)O}^- + \text{H}_3\text{O}^+$; $\text{pK}_{\text{a}1} = 3,83$; Wikipedia
 $\text{K}_{\text{eq}} = [\text{H}_2\text{COHC(O)O}^-] * [\text{H}_3\text{O}^+] / [\text{H}_2\text{COHC(O)OH}] / [\text{H}_2\text{O}] = \text{K}_{\text{a}} / [\text{H}_2\text{O}] = 10^{-(3,83)} / 55,3 = 2,675 * 10^{(-6)} = 10^{(-5,573)}$;
 $\Delta\text{G}_{\text{eqOHCCOOH}} = -\text{R} \cdot \text{T} \cdot \ln(\text{K}_{\text{aeq}}) = -8,3144 * 298,15 * \ln(10^{(-5,573)}) / 1000 = 31,81 \text{ kJ/mol}$.

$\Delta\text{G}_{\text{eqOHCCOOH}} = \text{G}_{\text{OHCCOO}} + \text{G}_{\text{H}_3\text{O}^+} - (\text{G}_{\text{OHCCOOH}} + \text{G}_{\text{H}_2\text{O}}) = \text{G}_{\text{OHCCOO}} + 22,44 - (404,9232 + 0) = 31,81 \text{ kJ/mol}$;
 $\text{G}_{\text{OHCCOO}} = \Delta\text{G}_{\text{eqOHCCOOH}} - \text{G}_{\text{H}_3\text{O}^+} + (\text{G}_{\text{OHCCOOH}} + \text{G}_{\text{H}_2\text{O}}) = 31,81 - 22,44 + (404,9232 + 0) = 414,3 \text{ kJ/mol}$;

Viela	$\Delta\text{H}^\circ_{\text{Hess}}$ kJ/mol	$\Delta\text{S}^\circ_{\text{Hess}}$ J/mol/K	$\Delta\text{G}^\circ_{\text{Hess}}$ kJ/mol
Glyoxylate			
OHCCOO⁻	-	-	-426,588
H₂COHC(O)O⁻	-	-	-403,2968
H₂COHC(O)OH	-651	318,6	-
NADH(aq)	-1036,66	-140,5	-
NAD⁺(aq)	-1041,41	-4081,784	1175,5732
H₃O⁺(aq)	-285,81	-3,854	-213,2746
NAD⁺(aq)	-1007,48	-183	-
NAD⁺(aq)	-1010,3	-3766,008	1112,534
H₃CCOOH	-484,09	159,83	-531,743
H₃CCOO⁻	-486,84	82,23	-247,83
H₃CCOO⁻	-486	85,3	-240,963
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549

$\text{H}_2\text{COHC(O)OH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{COHC(O)O}^- + \text{H}_3\text{O}^+$; $\text{pK}_{\text{a}} = 3,83$
 $\text{G}_{\text{OHCCOO}} = \Delta\text{G}_{\text{eqOHCCOOH}} - \text{G}_{\text{H}_3\text{O}^+} + (\text{G}_{\text{OHCCOOH}} + \text{G}_{\text{H}_2\text{O}}) = 414,3 \text{ kJ/mol}$;

Eksotermiska, eksoergiska
 reducēšana Hesa brīvās
 enerģijas izmaiņa negatīva
-161,8 kJ/mol, bet minimizējas
 par $\Delta\text{G}_{\text{min}} = \Delta\text{G}_{\text{eq}} = -72,65 \text{ kJ/mol}$
 vai **-104 kJ/mol** sasniedzot
 līdzsvara maisījumu. Lešatēje
 princips ir Prigožina atraktora
 brīvās enerģijas
 $\text{G}_{\text{H}_3\text{CCOOH}} = -415,8 \text{ kJ/mol}$;
 $\text{G}_{\text{H}_3\text{CCOO}^-} = 430,46 \text{ kJ/mol}$;
 izmaiņas minimuma $\Delta\text{G}_{\text{min}}$
 sasniegšana.



Acetic acid Formation 61st page $2\text{C} + 2\text{H}_2\text{gas} + \text{O}_2\text{gas} \Rightarrow \text{H}_3\text{CCOOH}$; $\Delta\text{G}_{\text{OHCCOOH}} = -240,963 \text{ kJ/mol}$ [8];

$\Delta\text{G}_{\text{H}_3\text{CCOOH}} = \text{G}_{\text{H}_3\text{CCOOH}} - (2\text{G}_{\text{Cgraph}} + 2\text{G}_{\text{H}_2\text{gas}} + 1*\text{G}_{\text{O}_2\text{gas}}) = -240,963 \text{ kJ/mol}$;
 $\text{G}_{\text{H}_3\text{CCOOH}} = -240,963 + (2*91,26 + 2*85,6 + 1*303) = 415,8 \text{ kJ/mol}$;

Acetic acid $\text{H}_3\text{CCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{OHCCOO}^- + \text{H}_3\text{O}^+$; $\text{pK}_{\text{a}1} = 4,76$; Wikipedia

$\text{K}_{\text{eq}} = [\text{H}_3\text{CCOO}^-] * [\text{H}_3\text{O}^+] / [\text{H}_3\text{CCOOH}] / [\text{H}_2\text{O}] = \text{K}_{\text{a}} / [\text{H}_2\text{O}] = 10^{-(4,76)} / 55,3 = 3,1425 * 10^{(-7)} = 10^{(-6,5)}$;
 $\Delta\text{G}_{\text{eqH}_3\text{CCOO}} = -\text{R} \cdot \text{T} \cdot \ln(\text{K}_{\text{aeq}}) = -8,3144 * 298,15 * \ln(10^{(-6,5)}) / 1000 = 37,1 \text{ kJ/mol}$.

$\Delta\text{G}_{\text{eqOHCCOOH}} = \text{G}_{\text{OHCCOO}} + \text{G}_{\text{H}_3\text{O}^+} - (\text{G}_{\text{OHCCOOH}} + \text{G}_{\text{H}_2\text{O}}) = \text{G}_{\text{OHCCOO}} + 22,44 - (296,032 + 0) = 37,1 \text{ kJ/mol}$;

$\text{G}_{\text{OHCCOO}} = \Delta\text{G}_{\text{eqOHCCOOH}} - \text{G}_{\text{H}_3\text{O}^+} + (\text{G}_{\text{OHCCOOH}} + \text{G}_{\text{H}_2\text{O}}) = 37,1 - 22,44 + (415,8 + 0) = 430,46 \text{ kJ/mol}$;

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

$\Delta\text{G}_{\text{eq}} = \text{E}^\circ_{\text{OxH}_2\text{COHC(O)O}^-} * \text{F} * \text{n} = (-0,033) * 96485 * 2 = -6,368 \text{ kJ/mol}$;

$\Delta\text{G}_{\text{eq}} = \text{G}_{\text{H}_3\text{CCOO}} + 2\text{G}_{\text{H}_2\text{O}} - (\text{G}_{\text{OHCCOO}} + \text{G}_{\text{H}_3\text{O}^+} + \text{G}_{\text{H}^-}) = 430,46 + 2*0 - (414,3 + 22,44) = 6,28 \text{ kJ/mol}$;

$\Delta\text{G}_{\text{eq}} = \text{G}_{\text{H}_3\text{CCOO}} + 2\text{G}_{\text{H}_2\text{O}} - (\text{G}_{\text{OHCCOO}} + \text{G}_{\text{H}_3\text{O}^+} + \text{G}_{\text{H}^-}) = 430,46 + 2*85,6 - (414,3 + 22,44) = 164,92 \text{ kJ/mol}$;

$\text{G}_{\text{H}^-} = \text{G}_{\text{H}_3\text{CCOO}} + 2\text{G}_{\text{H}_2\text{O}} - (\text{G}_{\text{OHCCOO}} + \text{G}_{\text{H}_3\text{O}^+} + \Delta\text{G}_{\text{eq}}) = 430,46 + 2*0 - (414,3 + 22,44 + 6,368) = -12,648 \text{ kJ/mol}$;

$\text{G}_{\text{H}^-} = \text{G}_{\text{H}_3\text{CCOO}} + 2\text{G}_{\text{H}_2\text{O}} - (\text{G}_{\text{OHCCOO}} + \text{G}_{\text{H}_3\text{O}^+} + \Delta\text{G}_{\text{eq}}) = 430,46 + 2*85,6 - (414,3 + 22,44 + 6,368) = 158,55 \text{ kJ/mol}$;

Glycolate $\text{H}_2\text{COHC(O)O}^- + \text{NADH} + \text{H}_3\text{O}^+ \Rightarrow$ acetate $\text{H}_3\text{CCOO}^- + 2\text{H}_2\text{O} + \text{NAD}^+$

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

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

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

Red: $\text{NADH} = \text{NAD}^+ + \text{H}(\text{H}^+ + 2\text{e}^-)$; $\text{E}^\circ_{\text{Red}} = -0,4095 \text{ V}$ David Harris absolute

Glyoxylate **Oks:** $\text{OHCCOO}^- + \text{H}(\text{H}^+ + 2\text{e}^-) + \text{H}_3\text{O}^+ \Rightarrow$ Glycolate $\text{H}_2\text{COHC(O)O}^- + \text{H}_2\text{O}$; $\text{E}^\circ_{\text{Ox}} = 0,1305 \text{ V absolute}$

Glyoxylate $\text{OHCCOO}^- + \text{NADH} + \text{H}_3\text{O}^+ \Rightarrow \text{H}_2\text{COHC(O)O}^- + \text{NAD}^+ + \text{H}_2\text{O}$ Glycolate

$\Delta\text{G}_{\text{eq}} = (\text{E}^\circ_{\text{Red}} - \text{E}^\circ_{\text{OxH}_2\text{O}}) * \text{F} * \text{n} = (-0,4095 - 0,1305) * 96485 * 2 = (-0,54) * 96485 * 2 = -104,2 \text{ kJ/mol}$;

$\Delta\text{G}_{\text{Hess}} = \Delta\text{G}^\circ_{\text{H}_2\text{COHC(O)O}^-} + \Delta\text{G}^\circ_{\text{NAD}^+} + \Delta\text{G}^\circ_{\text{H}_2\text{O}} - \Delta\text{G}^\circ_{\text{H}_2\text{COHC(O)O}^-} - \Delta\text{G}^\circ_{\text{NADH}} - \Delta\text{G}^\circ_{\text{H}_3\text{O}^+} = -63,66 \text{ kJ/mol}$;

$= -403,2968 + 1112,534 - 151,549 - (-426,588 + 1175,5732 - 213,2746) = 21,98 \text{ kJ/mol}$;

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

$= -403,2968 + 1112,534 + 0 - (-426,588 + 1175,5732 + 22,44) = -62,2 \text{ kJ/mol}$ **exoergic**.....;

TERMODINAMIKA VINGRINĀJUMS XX Piruvāta $\text{H}_3\text{CC}=\text{O}\text{COO}^-$ dekarboksilēšana $\text{H}_3\text{CCHO} + \text{HCO}_3^-$

Piruvāta $\text{H}_3\text{CC}=\text{O}\text{COO}^-$ pārvēršana acetaldehīdā $\text{H}_3\text{CCHO} + \text{HCO}_3^-$ (25 C) 298.15 K., pielietojiet tabulas datus!

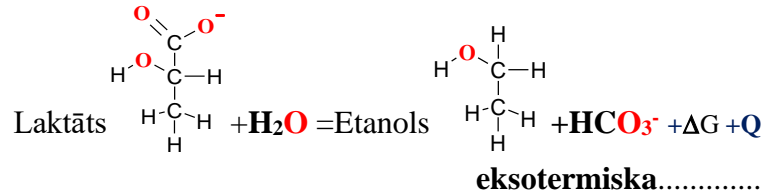
Izejviela Pyruvic acid+Q => produkti acetaldehyde bicarbonate + H_3O^+

Viela	$\Delta H^\circ_{\text{H}} \text{ kJ/mol}$	$\Delta S^\circ_{\text{H}} \text{ J/mol/K}$	$\Delta G^\circ_{\text{H}} \text{ kJ/mol}$
$\text{H}_3\text{CCH}(\text{OH})\text{COO}^-$	-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
$\text{H}_3\text{CCH}_2\text{OH}_l$	-277,6	160,7	62,96
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
HCO_3^-	-689,93	98,324	-586,94
HCO_3^-	-692,4948	-494,768	-544,9688



BioThermodynamics06;

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

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

$\Delta S_{\text{izkļiedēta}} = -\Delta H_{\text{Hess}}/T = 8,325/298,15 = 27,9 \text{ J/K/mol}$;

BioThermodynam06 $\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{H}_3\text{CCH}_2\text{OH}} + \Delta S^\circ_{\text{HCO}_3^-} - \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{H}_3\text{CCH}_2\text{OHCoo}} = 21,51 \text{ J/mol/K}$;

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

$\Delta S_{\text{kopēja}} = \Delta S_{\text{Hess}} + \Delta S_{\text{izkļiedēta}} = 21,51 + 27,9 = 49,41 \text{ J/mol/K}$;

$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = -8,325 - 298,15 \cdot 0,02151 = -14,738 \text{ kJ/mol}$ eksoergiska.....

$T \cdot \Delta S_{\text{kopēja}} = 0,04941 \cdot 298,15 \text{ K} = 14,73 \text{ kJ/mol}$; saistīta $T \Delta S_n$; izkļiedēta-zaudēta enerģija patvaļīga

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

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

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

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

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

$K_{\text{eqAerobi}} = \frac{[\text{NADH}] \cdot [\text{piruvāts}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{NAD}^+] \cdot [\text{laktāts}^-] \cdot [\text{H}_2\text{O}]} = e^{-\frac{\Delta G_{\text{eqAerobic}}}{R \cdot T}} = e^{-\frac{75955}{8,314 \cdot 298,15}} = 10^{-13,3}$;

$\text{NAD}^+ + \text{laktāts}^- + \text{H}_2\text{O} = \text{NADH} + \text{piruvāts}^- + \text{H}_3\text{O}^+$;

$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{NADH}} + \Delta G^\circ_{\text{H}_3\text{CC}=\text{O}\text{COO}^-} + \Delta G^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{\text{NAD}^+} - \Delta G^\circ_{\text{H}_3\text{CCH}_2\text{OHCoo}} - \Delta G^\circ_{\text{H}_2\text{O}} = 45,764 \text{ kJ/mol}$

$\Delta G_{\text{Hess}} = 1175,5732 - 344,6168 - 213,275 - (1112,534 - 303,4256 - 237,191) = 45,764 \text{ kJ/mol}$

$\Delta H_{\text{Hess}} = \Delta H^\circ_{\text{NADH}} + \Delta H^\circ_{\text{H}_3\text{CC}=\text{O}\text{COO}^-} + \Delta H^\circ_{\text{H}_3\text{O}^+} - \Delta H^\circ_{\text{NAD}^+} - \Delta H^\circ_{\text{H}_3\text{CCH}_2\text{OHCoo}} - \Delta H^\circ_{\text{H}_2\text{O}} = 60,18 \text{ kJ/mol}$

$\Delta H_{\text{Hess}} = -1041,41 - 597,04 - 285,81 - (-1010,3 - 1290,852 - 285,85) = 60,18 \text{ kJ/mol}$

$\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{NADH}} + \Delta S^\circ_{\text{H}_3\text{CC}=\text{O}\text{COO}^-} + \Delta S^\circ_{\text{H}_3\text{O}^+} - \Delta S^\circ_{\text{NAD}^+} - \Delta S^\circ_{\text{H}_3\text{CCH}_2\text{OHCoo}} - \Delta S^\circ_{\text{H}_2\text{O}} = -547,9605 \text{ kJ/mol}$

$\Delta S_{\text{Hess}} = -4081,784 - 846,664 - 3,854 - (-3766,008 - 688,29 + 69,9565) = -547,9605 \text{ kJ/mol}$

$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = 45,764 - 298,15 \cdot (-0,5479605) = 209,14 \dots \text{ kJ/mol}$ endoeressgic.....

Aeroba endoergiska laktāta oksidēšanas Hesa brīvās enerģijas izmaiņa pozitīva

$\Delta G_{\text{Hess}} = 209,14 \dots \text{ kJ/mol}$ inversi piruvāta anaeroba reducēšanai negatīva $\Delta G_{\text{Hess}} = -209,14 \dots \text{ kJ/mol}$, bet

minimizējas inversi aerobā oksidēšanā $\Delta G_{\text{min}} = \Delta G_{\text{eqAerobi}} = 76 \dots \text{ kJ/mol}$ un $\Delta G_{\text{min}} = \Delta G_{\text{eqAnaerobi}} = -76 \dots \text{ kJ/mol}$

reducēšanā sasniedzot līdzsvara maisījuma konstantes $4,9336 \cdot 10^{-14} = K_{\text{eqAerobi}}$ vērtību.

Prigožina atraktors ir brīvās enerģijas izmaiņas absolūts minimums ΔG_{min} sasniedzot līdzsvaru.

$\Delta G_{\text{min}} = 76 \dots \text{ kJ/mol} = |\Delta G_{\text{eq}}| < |\Delta G_{\text{Hess}}| = 209 \dots \text{ kJ/mol}$.

Homeostāzē saistīta O_2aqua NADH oksidāze ar aerobo attiecību $[\text{NADH}]/[\text{NAD}^+] = 10^{-6}$ labvēlīga laktāta

dehidrogenāzes iznākumam $\Delta G_{\text{aerobi}} = 75,955 + RT \ln(1/10^6 \cdot 1/1 \cdot 10^{-7,36/55,3}) = 75,955 - 86,2 = -10,245 \text{ kJ/mol}$.

TERMODINAMIKA VINGRINĀJUMS XXI Laktāta $\text{H}_3\text{CCH}(\text{OH})\text{COO}^-_{\text{aq}}$ dekarboksilēšana $\text{H}_3\text{CCH}_2\text{OH} + \text{HCO}_3^-$

Piruvāta $\text{H}_3\text{CC}=\text{O}\text{COO}^-$ pārvēršana acetātā $\text{H}_3\text{CCHO} + \text{HCO}_3^-$ (25 C) 298.15 K, pielietojiet tabulas datus!

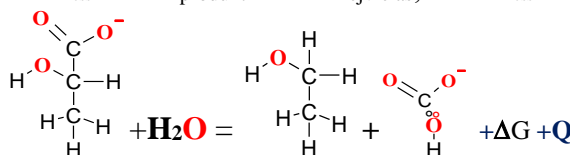
Izejviela laktāts=> produkti etanols + bikarbonāts

Viela	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ 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
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
HCO_3^-	-689,93	98,324	-586,94
HCO_3^-	-692,4948	-494,768	-544,9688



BioThermodynam06; 1. $\Delta H^\circ_{\text{Hess}} = \sum \Delta H^\circ_{\text{produkti}} - \sum \Delta H^\circ_{\text{izejvielas}}$
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2. $\Delta S^\circ_{\text{Hess}} = \sum \Delta S^\circ_{\text{produkti}} - \sum \Delta S^\circ_{\text{izejvielas}}$; 3. $\Delta G^\circ_{\text{Hess}} = \Delta H^\circ_{\text{Hess}} - T \cdot \Delta S^\circ_{\text{Hess}}$



Laktāts Etanols eksotermiska.....

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

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

$\Delta S_{\text{izkļiedēta}} = -\Delta H_{\text{Hess}}/T = 8,325/298,15 = 27,9 \text{ J/K/mol}$;

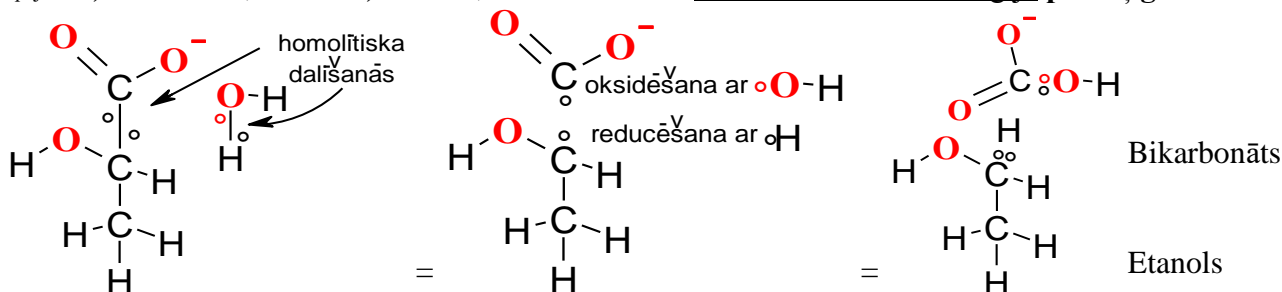
BioThermodynam06 $\Delta S_{\text{Hess}} = \Delta S^\circ_{\text{H}_3\text{CCH}_2\text{OH}} + \Delta S^\circ_{\text{HCO}_3^-} - \Delta S^\circ_{\text{H}_2\text{O}} - \Delta S^\circ_{\text{H}_3\text{CCH}_2\text{OHC(O)O}^-} = 21,51 \text{ J/mol/K}$;

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

$\Delta S_{\text{kopēja}} = \Delta S_{\text{Hess}} + \Delta S_{\text{izkļiedēta}} = 21,51 + 27,9 = 49,41 \text{ J/mol/K}$;

$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = -8,325 - 298,15 \cdot 0,02151 = -14,738 \text{ kJ/mol}$ eksoergiska.....

$T \cdot \Delta S_{\text{kopēja}} = 0,04941 \cdot 298,15 \text{ K} = 14,73 \text{ kJ/mol}$; saistīta $T \Delta S_{\text{net}} \leftarrow$ izkļiedēta-zaudēta enerģija patvaļīgi



Homolītiska dalīšanās ir molekulārās ķīmiskās saites disociācijas process, kurā katrs fragmenta atoms vai molekula iegūst vienu no oriģinālajiem kovalentās saites pāra elektroniem.

Decarboksilēšanās ar karboksilāta molekulas un ūdens molekulas homolītisku dalīšanos karboksilāts oksidējas ar $\text{HO}\bullet$ radikāli par bikarbonāta jonu HCO_3^- un karboksilāta molekulas otrs fragments reducējas ar ūdeņraža radikāli $\text{H}\bullet$ (Etanols).

THERMODYNAMICS Exercise XXII alanine $\text{H}_3\text{CCHNH}_3^+\text{COO}^-$ deamination piruvāts $\text{H}_3\text{CC=OCOO}^-$

Fizioloģiski apstākļi pH=7,36 T=310,15 K (37° C)

Alanīns deaminēšana par pirovīnogskābi un piruvātu $\text{H}_3\text{CC=OCOO}^-$ (37 C) 310.15 K!

Izejviela alanīns + $\text{O}_{2\text{aqua}}$ => produkts 2piruvāts+ 2NH_4^+ + H_3O^+ +Q+ΔG

Viela	$\Delta H^\circ_{\text{H}} \text{ kJ/mol}$	$\Delta S^\circ_{\text{H}} \text{ J/mol/K}$	$\Delta G^\circ_{\text{H}} \text{ kJ/mol}$
$\text{H}_3\text{CC=OCOOH}_{(\text{aq})}$	-607,82	179,91	-
$\text{H}_3\text{CC=OCOO}^-$	-603,7	-433,54	-
$\text{H}_3\text{CC=OCOO}^-$	-597,04	-846,664	-344,6168
$\text{H}_3\text{CCHNH}_3^+\text{COO}^-$	-554,80	-616,47	-
$\text{NH}_4^+_{(\text{aq})}$	-132,5	113,4	-79,3
NH_3_{gas}	-45,94	192,77	-16,4
NH_3_{aq}	-132,5608	-739,2922	91,1056
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549
$\text{H}_3\text{O}^+_{(\text{aq})}$	-285,81	-3,854	-213,27
$\text{O}_{2\text{aqua}}$	-11,715	110,876	16,4
$\text{O}_{2\text{aqua}}$	-11,7	-94,2	16,4

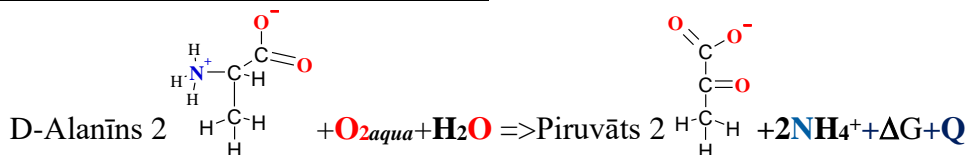
CRC10 1. $\Delta H^\circ_{\text{Hess}} = \sum \Delta H^\circ_{\text{produkti}} - \sum \Delta H^\circ_{\text{izejvielas}}$
vāja skābe $\text{NH}_4^+_{(\text{aq})} + \text{H}_2\text{O} + \Delta G + Q \Rightarrow \text{H}_3\text{O}^+ + \text{NH}_3_{(\text{aq})}$

BioThermodynamics 2006; MassachusettsTinsitute

pKa=9,245 ; $\Delta G_{\text{H}} = -RT \ln(10^{-\text{pKa}}) = 52,77 \text{ kJ/mol}$

$\Delta G_{\text{eq}} = -8,3144 * 298,15 * \ln(10^{-9,245}) = 52,77 \text{ kJ/mol}$

$\Delta G_{\text{Hess}} = \Delta G^\circ_{\text{NH}_3} + \Delta G^\circ_{\text{H}_3\text{O}} - \Delta G^\circ_{\text{NH}_4} - \Delta G^\circ_{\text{H}_2\text{O}} = 151,5 \text{ kJ/mol}$
 $= 91,1056 - 213,27 - (-79,3 + (-151,549 - 237,19)/2) = 151,5 \text{ kJ/mol}$



Sārmainā vidē pH>10: $\text{H}_3\text{CCHNH}_3^+\text{COO}^-_{\text{aq}} + \text{O}_{2\text{aqua}} + 2\text{H}_2\text{O} + Q \Rightarrow \text{H}_3\text{CC=OCOO}^-_{\text{aq}} + 2\text{NH}_3_{(\text{aq})} + \text{H}_3\text{O}^+ + \Delta G$

pH=7,36 bioķīmiskā vidē: $2\text{H}_3\text{CCHNH}_3^+\text{COO}^-_{\text{aq}} + \text{O}_{2\text{aqua}} + \text{H}_2\text{O} \Rightarrow 2\text{H}_3\text{CC=OCOO}^-_{\text{aq}} + 2\text{NH}_4^+_{(\text{aq})} + \Delta G + Q$

1. $\Delta H_{\text{Hess}} = 2\Delta H^\circ_{\text{H}_3\text{CC=OCOO}^-} + 2\Delta H^\circ_{\text{NH}_4} - 2\Delta H^\circ_{\text{alanine}} - \Delta H^\circ_{\text{O}_2} - \Delta H^\circ_{\text{H}_2\text{O}} = -51,13 \text{ kJ/mol}$ eksotermiska.....
 $= 2 * -597,04 + 2 * -132,5 - (2 * -554,8 - 11,7 - 286,65) = -51,135 \text{ kJ/mol}$

2. $\Delta S_{\text{izkliede}} = -\Delta H_{\text{Hess}}/T = 51,135/298,15 = 171,51 \text{ J/K/mol}$;

2. $\Delta S_{\text{Hess}} = 2\Delta S^\circ_{\text{H}_3\text{CC=OCOO}^-} + 2\Delta S^\circ_{\text{NH}_4} - 2\Delta S^\circ_{\text{alanine}} - \Delta S^\circ_{\text{O}_2} - \Delta S^\circ_{\text{H}_2\text{O}} = 313,8 \text{ J/mol/K}$;
 $= 2 * -846,664 + 2 * 113,4 - (2 * -616,47 - 94,2 - 453,188) = 313,8 \text{ J/mol}$

3. $\Delta S_{\text{kopējs}} = \Delta S_{\text{H}} + \Delta S_{\text{izkliede}} = 313,8 + 171,51 = 485,31 \text{ J/mol/K}$

4. $\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T * \Delta S_{\text{Hess}} = -51,13 - 298,15 * 0,3138 = -144,7 \text{ kJ/mol}$ eksoergiska.....

$T * \Delta S_{\text{kopējs}} = 485,31 \text{ J/K/mol} * 298,15 \text{ K} = 144,7 \text{ kJ/mol}$; saistītā TΔSn izkliedes enerģija ΔGpretreakc patvaļīga ΔG_{Hess}

THERMODINAMIKA vingrinājums XXIV sukcināts $\cdot\text{OOCCH}_2\text{CH}_2\text{COO}\cdot$ malāts $\cdot\text{OCHCOHCH}_2\text{COO}\cdot$

Fizioloģiskā vidē pH=7,36 T=310,15 K (37° C)

Ssukcināts $\cdot\text{OOCCH}_2\text{CH}_2\text{COO}\cdot$ par malātu $\cdot\text{OCHCOHCH}_2\text{COO}\cdot$ (37 C) 310.15 K, pielietojiet datu tabulu!

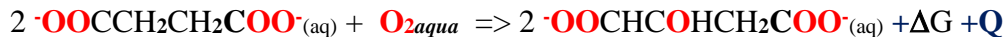
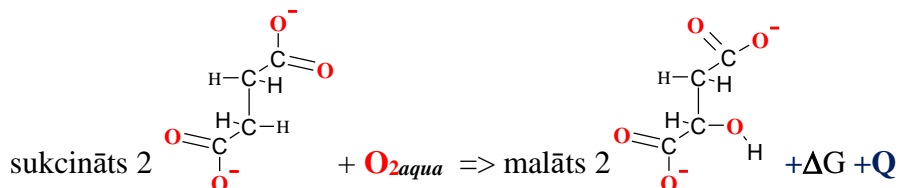
Izejviela sukcināts + $\text{O}_2\text{aqua} \Rightarrow$ produkts malāts, jonu spēks ir nulle I=0.

Viela	$\Delta H^\circ, \text{kJ/mol}$	$\Delta S^\circ, \text{J/mol/K}$	$\Delta G_H \text{kJ/mol}$	$\Delta H_H \text{kJ/mol}$	$\Delta S_H \text{J/mol/K}$	pK
$\text{HOOCCH}_2\text{CH}_2\text{COO}^- \text{(aq)}$	-	-	24.02	3.36	-69.29	pK2=
$\cdot\text{OOCCH}_2\text{CH}_2\text{COO}\cdot \text{(aq)}$	-908,7	-1,268	32.18	0.16	-107.40	pK1=
$\cdot\text{OCHCOHCH}_2\text{COO}\cdot \text{(aq)}$	-1079,8	-1,3314	30.02	0.16	-100.15	pK1=
O_2aqua	-11,715	110,876	-	-	-	-

1. $\Delta H_H = 2\Delta H^\circ_{\cdot\text{OCHCOHCH}_2\text{COO}\cdot} - 2\Delta H^\circ_{\cdot\text{OOCCH}_2\text{CH}_2\text{COO}\cdot} - \Delta H^\circ_{\text{O}_2} = \dots \text{kJ/mol} \dots$

$= 2 \cdot (-1079,8) - 2 \cdot (-908,7) - (-11,715) = -2159,6 + 1829,115 = -330,485 \text{ eksotermiska} \dots \text{kJ/mol} \dots$

2. $\Delta S_{\text{izkļiedēta}} = -\Delta H_H / T = 330,485 / 310,15 = 1065,565 \dots \text{J/K/mol}$



2. $\Delta S_H = 2\Delta S^\circ_{\cdot\text{OCHCOHCH}_2\text{COO}\cdot} - 2\Delta S^\circ_{\cdot\text{OOCCH}_2\text{CH}_2\text{COO}\cdot} - \Delta S^\circ_{\text{O}_2} = \dots \text{J/mol/K} \dots$

$\dots = 2 \cdot (-1,3314) - 2 \cdot (-1,268) - 110,876 = -2,6628 - 108,34 = -111,0 \dots \text{J/mol/K}$

3. $\Delta S_{\text{kopējā}} = \Delta S_H + \Delta S_{\text{izkļiedēta}} = 1065,565 - 111 = 954,565 \dots \text{J/mol/K}$

4. $\Delta G_H = \Delta H_H - T \cdot \Delta S_H = -330,485 - 310,15 \cdot 0,111 = -296,06 \text{ kJ/mol} \dots \text{eksoergiski}$

$T \cdot \Delta S_{\text{kopējā}} = 954,565 \text{ J/K/mol} \cdot 310,15 \text{ K} = 296,06 \dots \text{kJ/mol} \dots$

saistīta $T\Delta S_n \leftarrow$ izkļiedēta enerģija $\Delta G_{\text{pretreakc}} Q = 330,485 \text{ kJ/mol}$ **patvaļīga** $\Delta G_{\text{Hess}} = -296 \text{ kJ/mol} \dots$

$\text{pK}_{\text{eq}} = -\log(K_{\text{eq}}) = -\ln(10) \cdot (-\Delta G_{\text{eq}} / R / T) = -\ln(10) \cdot (296,06 \cdot 1000 / 8,3144 / 310,15) = -\ln(10) \cdot 79,9081 = -4,38088 \dots$

$K_{\text{eq}} = \text{EXP}(-\Delta G_{\text{eq}} / R / T) = 10^{-\text{pK}_{\text{eq}}} = 10^{4,38088} = 2,4 \cdot 10^4 \text{ temperatūra } 310,15 \text{ K (37° C)}$

CRC Viela	$\Delta H^\circ, \text{kJ/mol}$	$\Delta S^\circ, \text{J/mol/K}$	$\Delta G_H \text{kJ/mol}$	$\Delta H_H \text{kJ/mol}$	$\Delta C_H \text{J/mol/K}$	pK	pK
$\text{HOOCCH}_2\text{CH}_2\text{COO}^- \text{(aq)}$	-	-	-	3,0	-121	4,207	pK1=
$\cdot\text{OOCCH}_2\text{CH}_2\text{COO}\cdot \text{(aq)}$	-	-	-	-0,5	-217	5,636	pK2=
$\cdot\text{OCHCOHCH}_2\text{COO}\cdot \text{(aq)}$	-	-	-	-3,6	-31	6,27	pK2=
$\text{HOCHCOHCH}_2\text{COO}^- \text{(aq)}$	-	-	-	1,1	-21	1,92	pK1=

TERMODINAMIKA VINGRINĀJUMS XXIV ksantīns $C_5H_4N_4O_2$ ureāts $C_5H_4N_4O_3^{(s)}$

Fizioloģiskā vidē pH=7,36 T=310,15 K (37° C)

Ksantīns $\cdot C_5H_4N_4O_2^{(s)}$ par ureātu $\cdot C_5H_4N_4O_3^{(s)}$ (37 C) 310.15 K, pielietojiet datu tabulu!

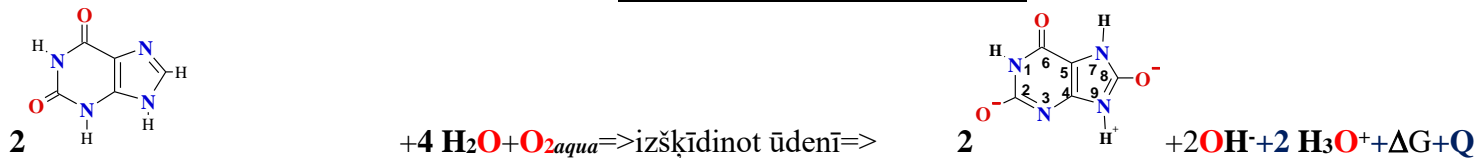
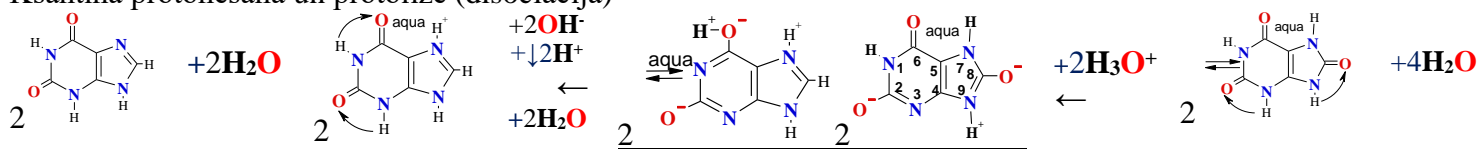
Izejviela ksantīns + $O_{2aqua} \Rightarrow$ produkti ureats jonu spēks I=0,25 .

pK_a Alberty, Robert A.Q 2006.

CRC 2010 viela	ΔH° , kJ/mol	ΔS° , J/mol/K	ΔG_H , kJ/mol	ΔH_H , kJ/mol	ΔC_H , J/mol/K	pK	pKa
urīnskābe $C_5H_5N_4O_3^+$ (aq)	-	-	-193,84	3,0	-121	pK2=	4,207
ureāts $C_5H_4N_4O_3$ (aq)	-	-	-	-0,5	-217	pK1=	5,636
ureāts $C_5H_3N_4O_3^-$ (s)	-618,80	173,20	-204,41	-	-	pK0=	11,3
ksantīns $C_5H_5N_4O_2^+$ (aq)	-	-	-	1,1	-21	pK2=	1,92
ksantīns $C_5H_4N_4O_2$ (s)	-379,60	161,10	-429,565	-3,6	-31	pK1=	6,27
ksantīns $C_5H_3N_4O_2^-$ (aq)	-	-	-	-	-	pK0=	11,1
O_{2aqua}	-11,715	110,876	16,4	-	-	-	-
H_2O (aq)	-285,85	69,96	-237,191	-	-	-	-
H_3O^+ (aq)	-285,81	-3,854	-213,275	-	-	-	-

- $\Delta H_H = 2\Delta H^\circ_{C_5H_3N_4O_3} + 2\Delta H^\circ_{H_3O} - 2\Delta H^\circ_{H_2O} - 2\Delta H^\circ_{C_5H_4N_4O_2} - \Delta H^\circ_{O_2} = -466,605$ eksotermiska.....kJ/mol...
 $\dots = 2 \cdot -618,80 + 2 \cdot -285,81 - (-11,715 + 2 \cdot -285,85 - 2 \cdot 379,6) - (-1809,22 + 1342,615) = -466,605$kJ/mol...
- $\Delta S_{izklydēta} = -\Delta H_H / T = 466,605 / 310,15 = 1504,449$J/K/mol

Ksantīna protonēšana un protolīze (disociācija)



Izejvielas 2 $C_5H_4N_4O_2(aqua)$ + 2 H_2O + $O_{2aqua} \Rightarrow$ 2 $C_5H_3N_4O_3^{(s)}$ + 2 H_3O^+ + $\Delta G + Q$ produkti
 ksantīns_{aqua} ureāts_{aqua}

$$2. \Delta S_H = 2\Delta S^\circ_{C_5H_3N_4O_3} + 2\Delta S^\circ_{H_3O} - 2\Delta S^\circ_{H_2O} - 2\Delta S^\circ_{C_5H_4N_4O_2} - \Delta S^\circ_{O_2} = \dots J/mol/K \dots$$

$$\dots = 2 \cdot 173,2 + 2 \cdot -3,854 - 110,876 - 2 \cdot 69,96 - 2 \cdot 161,1 = 338,692 - 572,996 = -234,304 \dots J/mol/K \dots$$

$$3. \Delta S_{kopējā} = \Delta S_H + \Delta S_{izklydēta} = 1504,449 - 234,304 = 1270,145 \text{ J/mol/K};$$

$$4. \Delta G_H = \Delta H_H - T \cdot \Delta S_H = -466,605 - 310,15 \cdot -0,234304 = -393,936 \text{ kJ/mol eksotermiska.}$$

$$T \cdot \Delta S_{kopējā} = 1270,145 \text{ J/K/mol} \cdot 310,15 \text{ K} = \mathbf{393,94} \dots \text{kJ/mol} \dots$$

saistītā TΔSn ← izklydēta enerģija Q = 466,685 kJ/mol patvaļīga ΔG_{Hess} = -393,936 kJ/mol...

$$pK_{eq} = -\log(K_{eq}) = -\ln(10) \cdot (-\Delta G_H / R/T) = -\ln(10) \cdot (466,605 \cdot 1000 / 8,3144 / 310,15) = -\ln(10) \cdot 180,945 = -5,19819 \dots$$

$$K_{eq} = \text{EXP}(-\Delta G_H / R/T) = 10^{-pK_{eq}} = 10^{5,19819} = 1,58 \cdot 10^5 \text{ temperature } 310,15 \text{ K } (37^\circ \text{ C})$$

$$5. \Delta G_H = 2\Delta G^\circ_{C_5H_3N_4O_3} + 2\Delta G^\circ_{H_3O} - 2\Delta G^\circ_{H_2O} - 2\Delta G^\circ_{C_5H_4N_4O_2} - \Delta G^\circ_{O_2} = -846,205 \text{ eksotermiska} \dots \text{kJ/mol} \dots$$

$$\dots = 2 \cdot -204,41 + 2 \cdot -213,275 - (16,4 + 2 \cdot -237,191 - 2 \cdot -429,565) = -835,37 - 401,148 = -1236,52 \dots \text{kJ/mol} \dots$$

1. Alberty, Robert A.Q 2006©, p463, John Wiley & Sons, Biochemical Thermodynamics Applications of Mathematica

2. David R. Lide, CRC Handbook of Chemistry un Physics, 2010, ©, p.2760

THERMODYNAMICS Exercise XXV $\text{CH}_3\text{CH}_2\text{-O-OCCH}_3$ hidrolīze to $\text{CH}_3\text{CH}_2\text{OH}+\text{HOOCCCH}_3$



$$K_{\text{Lehninger}} = \exp(19600/8,3144/298,15) = \frac{[\text{CH}_3\text{COOH}] \cdot [\text{CH}_3\text{CH}_2\text{OH}]}{[\text{H}_2\text{O}] \cdot [\text{CH}_3\text{CH}_2\text{OOCCH}_3]} = 2715,172$$



$$I=0,25 \text{ M, BioTherm06, pH}=7,36, \Delta G_{\text{Hess}} = \Delta G^\circ_{\text{CH}_3\text{CH}_2\text{OH}} + \Delta G^\circ_{\text{CH}_3\text{COOH}} + \Delta G^\circ_{\text{H}_3\text{O}^+} - \Delta G^\circ_{\text{CH}_3\text{CH}_2\text{-O-OCCH}_3} - 2 \cdot \Delta G^\circ_{\text{H}_2\text{O}} = 89,8 \text{ kJ/mol};$$

Viela	$\Delta H^\circ_{\text{kJ/mol}}$	$\Delta S^\circ_{\text{J/mol/K}}$	$\Delta G^\circ_{\text{kJ/mol}}$
H_3CCOO^-	-486,84	82,23	-247,83
H_3CCOO^-	-485,64	87,58	-369,37
H_3CCOOH	-484,3	159,8	-389,9
H_3CCOO^-	-486,836	-813,043	-241,663
$\text{C}_2\text{H}_4\text{OOCCH}_3$	-485,3	-1644,15	4,9176
$\text{C}_2\text{H}_4\text{OOCCH}_3$	-	-	-11,52
$\text{CH}_3\text{CH}_2\text{OH}$	-	-	62,96
$\text{CH}_3\text{CH}_2\text{OH}$	-277,6	160,7	-174,8
$\text{CH}_3\text{CH}_2\text{OH}$	-290,77	-1227,76	75,2864
H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	-286,65	-453,188	-151,549

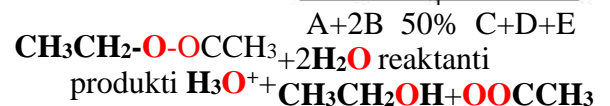
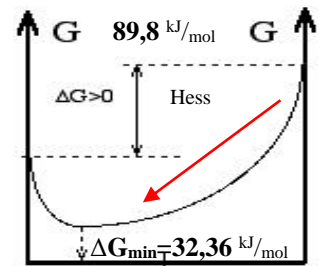
$$K_{\text{eqLehninger}} = K_{\text{Lehninger}} \frac{[\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]} = 2715,172/55,34573 \cdot 10^{(-7,36)} = \frac{[\text{CH}_3\text{COO}^-] \cdot [\text{CH}_3\text{CH}_2\text{OH}] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2 \cdot [\text{CH}_3\text{CH}_2\text{OOCCH}_3]} = 10^{(-5,67)} \text{ At pH}=7,36$$

$$\Delta G_{\text{eq}} = -R \cdot T \cdot \ln(K_{\text{eq}}) = -R \cdot T \cdot \ln(10^{(-5,67)}) = -8,3144 \cdot 298,15 \cdot \ln(10^{(-5,67)}) = 32,36 \text{ kJ/mol};$$

Endoerģiska, eksotermiska $\text{CH}_3\text{CH}_2\text{OOCCH}_3$ hidrolīzes Hesa brīvās enerģijas

Izmaiņa pozitīva $\Delta G_{\text{hydrolise}} = 89,8 \text{ kJ/mol}$, bet minimizējas $\Delta G_{\text{min}} = \Delta G_{\text{eq}} = 32,36 \text{ kJ/mol}$

$$\text{sasniedzot līdzsvara maisījumu } K_{\text{eq}} = 10^{(-5,67)} = \frac{[\text{CH}_3\text{COO}^-] \cdot [\text{CH}_3\text{CH}_2\text{OH}] \cdot [\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2 \cdot [\text{CH}_3\text{CH}_2\text{OOCCH}_3]}$$



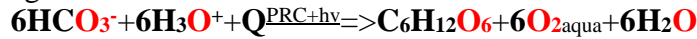
Lešateljē princips ir

Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā.

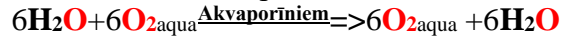
Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

TERMODINAMIKA VINGRINĀJUMS XXVI Osmo molārs koncentrācijas gradients $11 = C_{osm}$ zaļajos augos

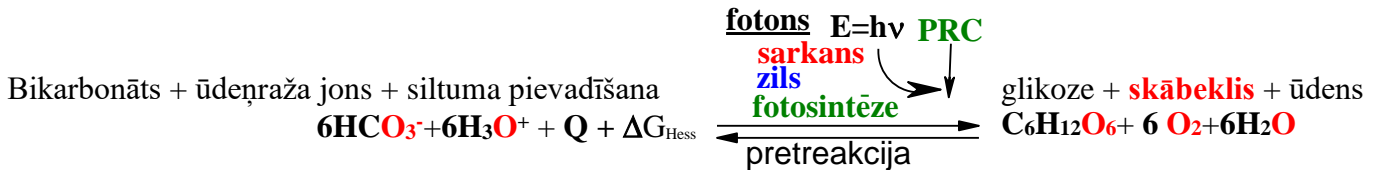
Aprēķināt ΔH_H ΔS_H ΔG_H un siltuma daudzumu **eksotermiska, atermiska vai endotermiska** reakcija standarta apstākļos 298.15 K. (**PRC**) foto sintētiskajā reakcijas centrā **zaļo augu** enzīmu kompleksa produkti glikoze **C₆H₁₂O₆** un skābeklis **6O₂_{aqua}** ar +fotonu **E=h•v** absorbciju akvaporīnu substrāti skābeklis **6O₂** un ūdens **6H₂O** palielina **osmotisko** spiedienu uz šūnu ārpusi 11 reizes, jo samazinās **osmo** molārā koncentrācija šūnā no sākuma reizes $12 = C_{osm} = 6 + 6$ līdz vienai glikozes **C₆H₁₂O₆** molekulai $C_{osm} = 1$.



Tā pēc plūsma uz āru cauri akvaporīniem palielinās 11 reizes. Skābeklis **6O₂** un ūdens **6H₂O** izspiežas ārā no šūnas pretēji koncentrācijas gradientam 1/12 cauri akvaporīniem :



atermiskā $\Delta H_{kanāls} = 0 \text{ kJ/mol}$ veidā bez siltuma zudumiem, pielietojiet **PRC** foto sintētiskā reakcijas centra enerģiju $\Delta G_{\text{PCH}} = 3040,1 \text{ kJ/mol}$ (vingrinājums III)::[lpp.4](#)



Miniet vai reakcija ir **eksoerģiska** vai **endoerģiska**! Universālā gāzu konstante $R = 8,3144 \text{ J/mol/K}$.

Eksoerģiska $\Delta G_{kanāls} = -RT \ln(C_{osm}[\text{O}_{2\text{aqua}} + \text{H}_2\text{O}]_{\text{labā}} / C_{osm}[\text{O}_{2\text{aqua}} + \text{H}_2\text{O}]_{\text{kheisā}}) = -12RT \ln(12/1) = -36.96 \text{ kJ/mol} \dots \dots \dots$

Viela	izejviela	produkts
O₂_{aqua}	$[\text{O}_2] = 6 \cdot 10^{-5} \text{ M}$	$[\text{O}_2] = 6 \cdot 10^{-5} \text{ M}$
H₂O	55,3 M	55,3 M

$$\Delta G_{\text{O}_2} = -RT \ln([\text{O}_2]_{\text{palabi}} / [\text{O}_2]_{\text{pa_kheisi}}) = -RT \ln(K_{\text{līdzsvara}}) = -6.1599 \text{ kJ/mol} \dots$$

$$\dots \dots \dots = -8,3144 \cdot 298,15 \cdot \ln(12/1) = -8,3144 \cdot 298,15 \cdot -2.4849 = -6.1599 \text{ kJ/mol} \dots \dots \dots$$

$$6\text{O}_{2\text{aqua}} \text{ molekulām } \Delta G_{6\text{O}_2} = -6.1599 \cdot 6 = -36.9596 \dots \dots \dots / \text{mol}$$

$$\Delta G_{6\text{H}_2\text{O}} = -6RT \ln([\text{H}_2\text{O}]_{\text{pa_labi}} / [\text{H}_2\text{O}]_{\text{pa_kheisi}}) = -6 \cdot 8,3144 \cdot 310,15 \cdot \ln(1/12) = -36.9596 \dots \dots \dots / \text{mol}$$

eksoerģiska.....

$$\Delta S_{6\text{O}_2} = -6R \ln([\text{O}_2]_{\text{palabi}} / [\text{O}_2]_{\text{pa_kheisi}}) = -8,3144 \cdot \ln(1/12) = 20,66 \cdot 6 = 123.96 \dots \dots \dots \text{ mol/K} \dots$$

$$\Delta S_{6\text{H}_2\text{O}} = -6R \ln([\text{H}_2\text{O}]_{\text{palabi}} / [\text{H}_2\text{O}]_{\text{pa_kheisi}}) = -8,3144 \cdot \ln(1/12) = 123.96 \dots \dots \dots \text{ J/mol/K} \dots$$

$$\Delta H_{kanāls} = 0 \dots \dots \text{ kJ/mol} \dots \dots \dots \text{ bez siltuma zudumiem} \dots \dots \dots$$

$$T \cdot \Delta S_{6\text{O}_2} = -0,12396 \cdot 298,15 = 36.9596 \dots \dots \text{ kJ/mol}$$
 saistīta **PRC** $T \Delta S_n$ izlietotā enerģija $T \Delta S_n = 3040,1 \text{ kJ/mol}$ izplūst O₂

$$T \cdot \Delta S_{6\text{H}_2\text{O}} = -0,12396 \cdot 298,15 = 36.9596 \dots \dots \text{ kJ/mol}$$
 saistīta **PRC** $T \Delta S_n$ izlietotā enerģija $T \Delta S_n = 3040,1 \text{ kJ/mol}$ izplūst H₂O

$$\text{Molekulām } 6\text{O}_{2\text{aqua}} + 6\text{H}_2\text{O} \text{ } T \cdot \Delta S_{6\text{H}_2\text{O} + 6\text{O}_2} = 36.9596 + 36.9596 = 73.919 \dots \dots \text{ kJ/mol}$$
 saistīta **PRC** $T \Delta S_n = 3040,1 \text{ kJ/mol}$

atermiska $\Delta H^\circ_{\text{Hess}} = +0 \text{ kJ/mol}$; $Q = -0 \text{ kJ/mol}$**patvaļīga** $\Delta G^\circ_{\text{Hess}} = -73.919 \text{ kJ/mol}$

Fotosintēze ar producētu no bikarbonāta un ūdeņraža joniem **6HCO₃⁻ + 6H₃O⁺** skābekli un ūdeni **6O₂_{aqua} + 6H₂O** atšķaida osmolāro koncentrāciju. Skābekļa un ūdens plūsma ārā no **PRC** šūnas cauri membrānu akvaporīniem pretēji koncentrācijas gradientam 12/1 virza standarta brīvā enerģija $\Delta G_{6\text{H}_2\text{O} + 6\text{O}_2} = -73.919 \text{ kJ/mol}$ uz vienu glikozes **C₆H₁₂O₆** molu!

TERMODINAMIKA VINGRINĀJUMS IV. vitamīns B₃ oksidē **RetinolCH₂-OH** par **RetinalCH=O**
 Vitamīn 3 B₃ oksidē etanolu alkohola dehidrogenāzes enzīmā par etanālu!



Viela	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol
RetinalCH=O			1141,45
RetinalCH=O	-	-	1198,9852
RetinolCH ₂ OH			1195,07
RetinolCH ₂ OH	-	-	1256,7164
NADH	-41,41	-4465,708	1175,5732
NADH	-1036,66	-140,50	1120,09
H ₃ O ⁺	-285,81	-3,854	-213,275
NAD ⁺	-10,30	-3766,008	1112,534
NAD ⁺	-1007,48	-183	1059,11
H ₂ O	-285,85	69,9565	-237,191
H ₂ O	-286,65	-453,188	-151,549

I=0 M; I=0,1 M

1118,78;1135,91;

Thermodynamic $E^{\circ}_{\text{Retinol}} = 0,2415 + 0,10166 = 0,34316 \text{ V}$;

1170,78;1189,14;

Absolute $E^{\circ}_{\text{Retinol}} = 0,34316 - 0,3982 = -0,05504 \text{ V}$;

Biochemistry Thermodynamic 2006, Alberty Massachusetts

CRC Handbook of Chemistry un Physics 2010 90th David R. Lide

Red $\text{RetinolOH} + 2\text{H}_2\text{O} = \text{RetinalCH=O} + 2\text{H}_3\text{O}^+ + \text{H}^-(2e^-)$;

$E^{\circ}_{\text{H}_2\text{O}} = 0,190 + 0,0591/2 * \log([\text{H}_2\text{O}]^2) = 0,2415 \text{ V}$;

Ox $\text{NAD}^+ + \text{H}^-(2e^-) = \text{NADH}$; $E^{\circ} = -0,4095 \text{ V}$;

Standarta potenciāli E° voltos David Harris; KortlyShucha datos

$\Delta G_{\text{Hess}} = \Delta G^{\circ}_{\text{RetinalCHO}} + \Delta H^{\circ}_{\text{NADH}} + \Delta G^{\circ}_{\text{H}_3\text{O}^+} - \Delta G^{\circ}_{\text{RetinolOH}} - \Delta H^{\circ}_{\text{NAD}^+} - \Delta H^{\circ}_{\text{H}_2\text{O}} =$

$\Delta G_{\text{Hess}} = 1198,9852 + 1175,5732 - 151,549 - (1256,7164 + 1059,11 - 237,191) = 144,4 \text{ kJ/mol}$ endoergiskac;

Sumāri **Red** + **Ox**: $\text{RetinolCH}_2\text{-OH} + \text{NAD}^+ + \text{H}_2\text{O} + \Delta G + Q \Rightarrow \text{RetinalCH=O} + \text{NADH} + \text{H}_3\text{O}^+$;

Novērtētajā balansā $n = 2 = m$ ar elektronu skaitu $2e^- \Delta E^{\circ}$ izteiksmē $E^{\circ}_{\text{H}_2\text{O}}$ elektronu donors mīnus E° elektronu akceptors, jo NAD^+ akceptē elektronus no etanola dotajā piemērā:

Absolute $E^{\circ}_{\text{Retinol}} = 0,34316 - 0,3982 = -0,05504 \text{ V}$

$\Delta E^{\circ} = E^{\circ}_{\text{H}_2\text{O}} - E^{\circ} = -0,05504 - (-0,4095) = 0,3545 \text{ V}$, n is 2;

$\Delta G_{\text{eqAerobic}} = \Delta E^{\circ} \cdot F \cdot n = (-0,05504 - (-0,4095)) * 2 * 96485 = (0,3545) * 2 * 96485 = -R \cdot T \cdot \ln(K_{\text{eq}}) = 68,4 \text{ kJ/mol}$

$$K_{\text{eqAerobi}} = \frac{[\text{NADH}] \cdot [\text{RetinalCHO}] \cdot [\text{H}_3\text{O}^+]}{[\text{NAD}^+] \cdot [\text{RetinolOH}] \cdot [\text{H}_2\text{O}]} = e^{\frac{\Delta G_{\text{eqAerobi}}}{R \cdot T}} = e^{\frac{68408}{8,314 \cdot 298,15}} = 1,036 \cdot 10^{-12} = 10^{-11,985}$$
; Homeostāzē saistīta

$\text{O}_{2\text{aqua}}$ NADH oksidāze ar alkohola dehidrogenāzes attiecību $[\text{NADH}]/[\text{NAD}^+] = 10^{-6}$ labvēlīga $\Delta G_{\text{aerobi}} = 68,4 + RT \ln(1/10^6 * 1/1 * 10^{-7,36}/55,3) = 68,4 - 86,2 = -17,8 \dots \text{kJ/mol}$.

$[\text{NAD}^+]/[\text{NADH}] = 10^3$; $\Delta G_{\text{Homeostāze}} = 68,4 - 69,08 = -0,676 \dots \text{kJ/mol}$.

Aeroba endotermiska un endoergiska RetinolaOH oksidēšanas Hesa brīvā enerģija pozitīva $\Delta G_{\text{Hess}} = 144,4 \dots \text{kJ/mol}$ inversi Retinala=O anaeroba reducēšana negatīva $\Delta G_{\text{Hess}} = -144,4 \dots \text{kJ/mol}$, bet minimizējas inversi aerobā oksidēšanā

$\Delta G_{\text{min}} = \Delta G_{\text{eqAerobi}} = 68,4 \dots \text{kJ/mol}$ un anaerobā $\Delta G_{\text{min}} = \Delta G_{\text{eqAnaerobi}} = -68,4 \dots \text{kJ/mol}$

reducēšanā sasniedzot līdzsvara maisījuma konstantes $10^{-11,985} = K_{\text{eqAerobi}}$ etanola oksidēšanai un etanāla reducēšanai anaerobi $10^{11,985} = K_{\text{eqAnaerobi}}$.

Prigožina atraktors ir brīvās enerģijas izmaiņas absolūts minimums ΔG_{min} sasniedzot līdzsvaru. $\Delta G_{\text{min}} = 68,4 \dots \text{kJ/mol} = |\Delta G_{\text{eq}}| < |\Delta G_{\text{Hess}}| = 144,9 \dots \text{kJ/mol}$.

Anaerobi labvēlīgi $\Delta G_{\text{eq}} = \Delta E^{\circ} \cdot F \cdot n = -0,3545 \text{ V} \cdot 2 \text{ mol} \cdot 96485 \text{ C/mol} = -68,4 \dots \text{kJ/mol}$.

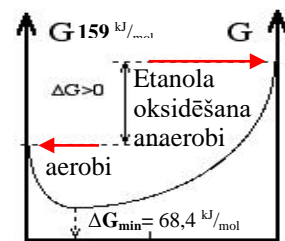
Niecīgā $\text{O}_{2\text{aqua}}$ koncentrācijā hipoksijā anaerobi spirta oksidēšana nelabvēlīga, bet etanāla reducēšana par etanolu labvēlīga attiecībai $[\text{RetinolOH}]/[\text{Retinal=O}] = 1/10$ homeostāzē kopā ar NADH reduktāzes enzīmu kā negatīva brīvās enerģijas izmaiņa

$\Delta G_{\text{anaerobi}} = -27,86 \dots \text{kJ/mol}$. Anaerobi homeostāzes attiecība $[\text{NAD}^+]/[\text{NADH}] = 1/10$ virs $[\text{NADH}]$ labvēlīga reducēšanai.

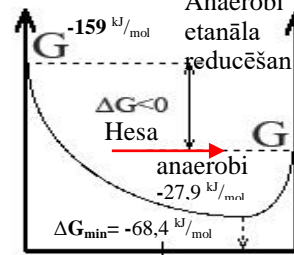
$$\Delta G_{\text{anaerobic}} = -68,4 + 8,3144 * 298,15 * \ln\left(\frac{1}{10} \frac{1}{10} \frac{55,333}{10^{-7,36}}\right) = -27,86 \text{ kJ/mol}$$
;

$$K_{\text{eqAnaerobi}} = \frac{[\text{NAD}^+] \cdot [\text{RetinolOH}] \cdot [\text{H}_2\text{O}]}{[\text{NADH}] \cdot [\text{RetinalCHO}] \cdot [\text{H}_3\text{O}^+]}$$
; K_{eq} vāji Aerobi = $\frac{[\text{NADH}] \cdot [\text{RetinalCHO}] \cdot [\text{H}_3\text{O}^+]}{[\text{NAD}^+] \cdot [\text{RetinolOH}] \cdot [\text{H}_2\text{O}]}$; $[\text{NADH}]/[\text{NAD}^+] = 770/1$;

$\Delta G_{\text{aerobi}} = 68,4 + 8,3144 * 298,15 * \ln(770/1 * 1/1 * 55,3457/10^{-7,36}) = 0,028 \text{ kJ/mol}$.



A+B+C50%D+E+F
 $\text{NAD}^+ + \text{H}_3\text{CCH}_2\text{OH} + \text{H}_2\text{O}$
 $\text{NADH} + \text{H}_3\text{CCHO} + \text{H}_3\text{O}^+$
 Anaerobi



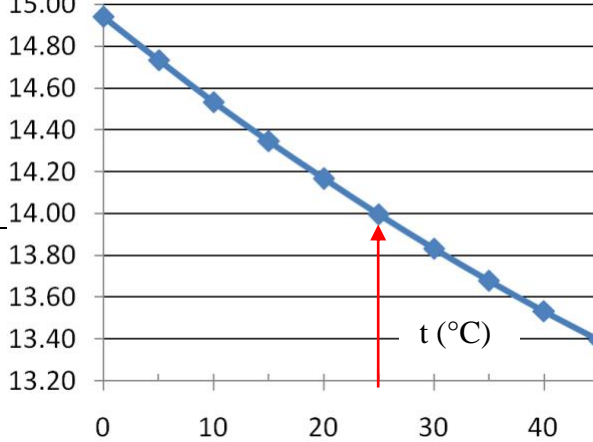
D+E+F 50% A+B+C
 $\text{NADH} + \text{H}_3\text{CCHO} + \text{H}_3\text{O}^+$
 $\text{NAD}^+ + \text{H}_3\text{CCH}_2\text{OH} + \text{H}_2\text{O}$
 Anaerobi

Table 1.6 Ion product of water at different temperatures. (According to B. E. Conway)

t (°C) ; pK_w

t (°C)	pK _w
-1	15,00
0	14,9435
5	14,7338
10	14,5346
15	14,3463
20	14,1669
25	13,9965
30	13,8330
35	13,6801
40	13,5348
45	13,3960
50	13,2617
55	13,1369
60	13,0171

25° C (298,15 K) pK_w=13,9965



$$K_{eq1} = \frac{[OH^-] \cdot [H_3O^+]}{[H_2O] \cdot [H_2O]} = 3.26 \cdot 10^{-18};$$

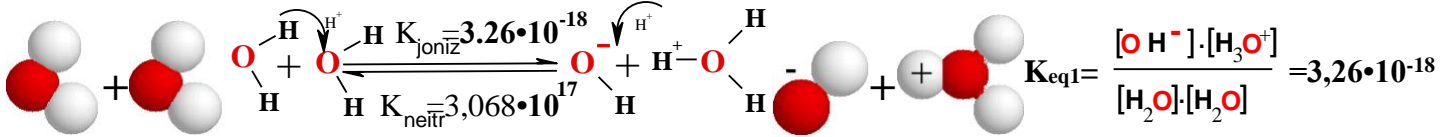
$$= 10^{(-13,9965)/55,34573^2} = 3,291 \cdot 10^{(-18)};$$

$$\Delta G_{Hess} = \Delta H_{Hess} - T \cdot \Delta S_{Hess} = 101,8967 \text{ kJ/mol}$$

$$= 55,89 + 298,15 \cdot 0,154305 = 101,8967 \text{ kJ/mol};$$
endoergiska.....
 Līdzsvarā tiek sasniegts brīvās enerģijas starpības minimums atbilstoši vielu maisījuma sastāvam izteiksmē:
 Termodinamiski nelabvēlīgs
[Alberty](#) [8] free energy for hydrogen gas
 $G^{\circ}_{H2gas} = 85.64 \text{ kJ/mol}$ lets [appreciate](#) oxygen

free energy for gas and aqua $G_{O2gas} = 303.1 \text{ kJ/mol}$; $G_{O2aqua} = 329.68 \text{ kJ/mol}$, relative to homeostasis products zero
 $G_{H2O} = G_{CO2gas} = 0 \text{ kJ/mol}$ and for hydroxonium and hydroxide ions :

$$G_{H3O++OH-} = G_{H3O++} + G_{OH-} = 22.44 + 77.36 = G_{H3O++} + G_{OH-} - G_{2H2O} = -R \cdot T \cdot \ln(K_{H3O++OH-}) + 2 \cdot 0 = 99.8 \text{ kJ/mol.} \quad [1,8,14]$$



$$\Delta G_{eq1} = -R \cdot T \cdot \ln(K_{eq1}) = -R \cdot T \cdot \ln\left(\frac{[OH^-] \cdot [H_3O^+]}{[H_2O] \cdot [H_2O]}\right) = 99,8 \text{ kJ/mol,}$$

Endotermiskas un endoergiskas ūdens jonizācijas reakcijas Hesa brīvās enerģijas izmaiņa
 $\Delta G_{Hess} = \Delta G_{jonizācija} = 101,9 \text{ kJ/mol}$ pozitīva,
 bet minimizējas maisījumā $\Delta G_{min} = \Delta G_{eq} = 99,8 \text{ kJ/mol}$

sasniedzot līdzsvaru $K_{eq1} = \frac{[OH^-] \cdot [H_3O^+]}{[H_2O] \cdot [H_2O]} = 3.26 \cdot 10^{-18};$

vielu maisījumā brīvās enerģijas izmaiņa minimizējas
 $99,8 \text{ kJ/mol} = |\Delta G_{eq2}| < |\Delta G_{Hess2}| = 101,9 \text{ kJ/mol};$

Visas reakcija tiecas uz līdzsvara maisījumu Prigožina atraktoru brīvās enerģijas izmaiņas minimumu $\Delta G_{min} = \Delta G_{eq}$ ar darbīgo masu inverso reakciju konstantēm

$$3.26 \cdot 10^{-18} = \frac{[OH^-] \cdot [H_3O^+]}{[H_2O] \cdot [H_2O]} = K_{eq1} = \frac{1}{K_{eq2}} = \frac{1}{\frac{[H_2O] \cdot [H_2O]}{[OH^-] \cdot [H_3O^+]}} = \frac{1}{3,068 \cdot 10^{17}}.$$

Lešatelje princips ir Prigožina atraktora brīvās enerģijas izmaiņas minimuma ΔG_{min} sasniegšana līdzsvara maisījumā. Brīvās enerģijas izmaiņas minimuma sasniegšanā iestājas līdzsvars.

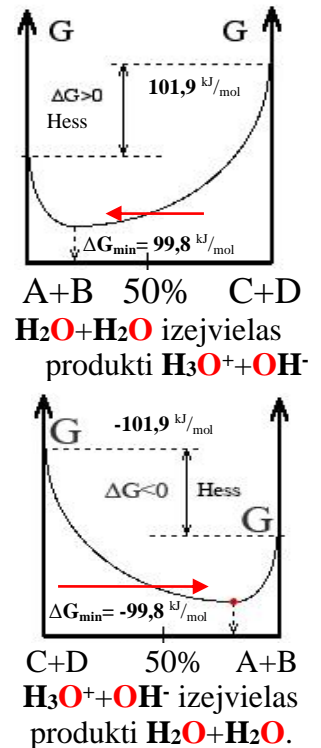
Pareiznot ar ūdens konstanto koncentrācijas kvadrātu

$$K_{eq1} \cdot [H_2O]^2 = 3.26 \cdot 10^{-18} \cdot 55,33^2 = 10^{-14} = K_w,$$

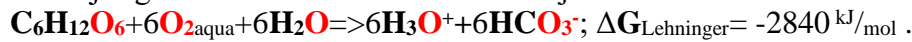
aprēķina ūdens jonu reizinājuma konstanti $K_w = [H_3O^+][OH^-] = 10^{-14},$

Ilja Prigožina 1977. gadā deklarētie atraktori rada kārtību šķietamā visuma haosā.

Tie nosaka, ka visums ir perfekts un precīzi parāda, ka katrs process tiecas uz Prigožina atraktoru - enerģijas izmaiņas minimumu disipatīvās struktūrās.



Glikozes (Glc) C₆H₁₂O₆, bioķīmiskā ūdens **6H₂O** un skābekļa **6O₂**_{aqua} enerģija $\Delta G_{\text{Lehninger}} = +2840 \text{ kJ/mol}$ oksidējot generē koncentrācijas gradientus no **6HCO₃⁻** un **6H₃O⁺** joniem:



Generētie **6HCO₃⁻** + **6H₃O⁺** joni virza **6O₂**_{aqua} + **6H₂O** cauri membrānu akvaporīnu kanāliem osmozē pretēji koncentrācijas gradientiem, bet transportē jonus **6HCO₃⁻** + **6H₃O⁺** lejup pa gradientiem cauri membrānu bikarbonāta un protonu kanāliem.

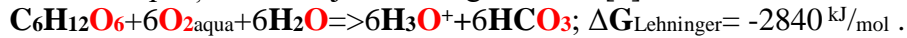
Glc veidošanās 6. lpp. $6\text{C} + 6\text{H}_{2\text{gas}} + 3\text{O}_{2\text{gas}} \Rightarrow \text{C}_6\text{H}_{12}\text{O}_6$; $\Delta G^\circ_{\text{Alberty}} = -402,05 \text{ kJ/mol}$; $\Delta G^\circ_{\text{HessCRC}} = -919 \text{ kJ/mol}$;

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

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

$$\Delta G^\circ_{\text{HessCRC}} + (6G_{\text{Cgraph}} + 6G_{\text{H}_2\text{gas}} + 3G_{\text{O}_2\text{gas}}) = -919 + (6 \cdot 91,26 + 6 \cdot 85,6 + 3 \cdot 303) = G_{\text{C}_6\text{H}_{12}\text{O}_6} = 1051 \text{ kJ/mol};$$

Brīvā enerģija kvazi līdzsvaram aprēķināta lietojot Lehningera datus [6] oksidēšanai -2840 kJ/mol :



$$-2840 = G_{\text{C}_6\text{H}_{12}\text{O}_6} - 6G_{\text{O}_2\text{Homeostasis_arterial}} - 6G_{\text{H}_2\text{O_Biochem}} + (6G_{\text{H}_3\text{O}^+} + 6G_{\text{HCO}_3^-})$$

$$G_{\text{C}_6\text{H}_{12}\text{O}_6} = 2840 - 6G_{\text{O}_2\text{Homeostasis_arterial}} - 6G_{\text{H}_2\text{O_Biochem}} + (6G_{\text{H}_3\text{O}^+} + 6G_{\text{HCO}_3^-})$$

Brīvā glikozes enerģija $G_{\text{C}_6\text{H}_{12}\text{O}_6} = 2840 - 6 \cdot 78,08 - 6 \cdot 85,64 + 6 \cdot (22,44 + 46,08) = 2268,8 \text{ kJ/mol}$,

Brīvā glikozes enerģija $G_{\text{C}_6\text{H}_{12}\text{O}_6} = 2840 - 6 \cdot 330 - 6 \cdot 0 + 6 \cdot (22,44 + 46,08) = 1271 \text{ kJ/mol}$,

Brīvā glikozes enerģija $G_{\text{C}_6\text{H}_{12}\text{O}_6} = 2840 - 6 \cdot 330 - 6 \cdot 85,64 + 6 \cdot (22,44 + 46,08) = 757 \text{ kJ/mol}$,

Free energy of glucose $G_{\text{C}_6\text{H}_{12}\text{O}_6} = 2840 - 6 \cdot 78,08 - 6 \cdot 0 + 6 \cdot (22,44 + 46,08) = 2782,6 \text{ kJ/mol}$.

Glikozes brīvā enerģija pēc Alberty $G_{\text{C}_6\text{H}_{12}\text{O}_6} = 1568 \text{ kJ/mol}$ un Alberty - Lehningera $G_{\text{C}_6\text{H}_{12}\text{O}_6} = 2268,8 \text{ kJ/mol}$. [8,6]

Skābekļa absolūtais standarta potenciāls $E^\circ_{\text{O}_2} = 1,0868 \text{ V}$ rada arteriālu absolūto potenciālu $0,4349 \text{ V}$ pie homeostāzes atraktoriem $[\text{H}_3\text{O}^+] = 10^{-(7,36)} \text{ M}$, $[\text{HCO}_3^-] = 0,0154 \text{ M}$, $[\text{C}_6\text{H}_{12}\text{O}_6] = 5 \cdot 10^{-(3)} \text{ M}$ un $[\text{H}_2\text{O}] = 55,3 \text{ M}$. Tas relatīvi iekļaujas Alberty datus izveidotā skalā ar ūdeņraža absolūto standarta potenciālu $E^\circ_{\text{H(Pt)}} = -0,2965 \text{ V}$. Piezīme: Klasiskā potenciālu skala ir pieņemta ūdeņraža klasiskā atskaites nulle $E^\circ_{\text{H(Pt)klasika}} = 0 \text{ V}$.

Nernsta pus reakcija: $6\text{H}_2\text{O} \rightleftharpoons \text{O}_{2\text{aqua}} + 4\text{H}_3\text{O}^+ + 4\text{e}^-$; $E^\circ_{\text{O}_2} = 1,0868 \text{ V}$; $\Delta G_{\text{eqO}_2} = E^\circ_{\text{O}_2\text{aq}} \cdot F \cdot n_e = 419,3 \text{ kJ/mol}$.

$$\Delta G_{\text{O}_2\text{aqAlberty}} = G_{\text{O}_2\text{aq}} + 4G_{\text{H}_3\text{O}^+} - 6G_{\text{H}_2\text{O}} = 330 - 4 \cdot 22,44 - 6 \cdot 0 = 419,76 \text{ kJ/mol}$$

$$\Delta G_{\text{eqO}_2} = 1,0865 \cdot 96485 \cdot 4 = 419,3 \text{ kJ/mol};$$

$$E_{\text{O}_2} = E^\circ_{\text{O}_2} + 0,0591/4 \cdot \log([\text{O}_{2\text{aqua}}] \cdot [\text{H}_3\text{O}^+]^4 / [\text{H}_2\text{O}]^6) = 1,0868 + 0,0591/4 \cdot \log(6 \cdot 10^{-5} \cdot 10^{-(7,36 \cdot 4)} / 55,346^6) = 0,4346 \text{ Volts}.$$

Skābekļa homeostāzes enerģijas izmaiņa $\Delta G_{\text{eqHomeostasisO}_2} = E^\circ_{\text{O}_2} \cdot F \cdot 1 \cdot 4 = 0,4346 \cdot 96485 \cdot 4 = 167,7 \text{ kJ/mol}$

kā reduktants ar sešām skābekļa molekulu pus reakcijām producē Lehningera enerģiju $\Delta G_{\text{Lehninger}} = -2840 \text{ kJ/mol}$.

Potenciāla starpība ir $\Delta E = \Delta G_{\text{Lehninger}} / F \cdot n = (E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} - E^\circ_{\text{O}_2}) \cdot F \cdot n = -2840000 / 96485 / 24 = -1,2264 \text{ V}$.

Absolūtais standarta potenciāls glikozei no Lehningera datiem ir $E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} = \Delta E + E_{\text{O}_2} = -1,226 + 1,0868 = -0,1392 \text{ V}$

Nernsta pus reakcija ir $\text{C}_6\text{H}_{12}\text{O}_6 + 42\text{H}_2\text{O} \rightleftharpoons 30\text{H}_3\text{O}^+ + 6\text{HCO}_3^- + 24\text{e}^-$ ar potenciālu $E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} = -0,1392 \text{ V}$:

$$\Delta G_{\text{AlbertyAbsoluteC}_6\text{H}_{12}\text{O}_6} = E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} \cdot F \cdot 1 \cdot 24 = -0,1392 \cdot 96485 \cdot 24 = -322 \text{ kJ/mol}$$

$$\Delta G_{\text{AlbertyC}_6\text{H}_{12}\text{O}_6} = 30G_{\text{H}_3\text{O}^+} + 6G_{\text{HCO}_3^-} - (G_{\text{C}_6\text{H}_{12}\text{O}_6} + 6G_{\text{O}_2\text{Homeostasis_arterial}} + 42G_{\text{H}_2\text{O_Biochem}}) = -1086,8 \text{ kJ/mol}$$

$$\text{brīvās enerģijas izmaiņa } \Delta G_{\text{AlbertyHessC}_6\text{H}_{12}\text{O}_6} = 30 \cdot 22,44 + 6 \cdot 46,08 - (1568 + 6 \cdot 78,08 + 42 \cdot 0) = -1086,8 \text{ kJ/mol}.$$

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

$$= -0,1392 + 0,0591/24 \cdot \log(0,0154^6 \cdot 10^{-(7,36 \cdot 30)} / 5 / 10^{-(3)} / 55,346^{42}) = -0,8843 \text{ Volti}$$

un brīvā enerģijas izmaiņa ir eksoergiska, negatīva $\Delta G_{\text{HomeostasisC}_6\text{H}_{12}\text{O}_6} = E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} \cdot F \cdot 1 \cdot 24 = -0,88427 \cdot 96485 \cdot 24 = -2047,65 \text{ kJ/mol}$.

$$\Delta G_{\text{Lehninger}} = \Delta E \cdot F \cdot n = (E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} - E^\circ_{\text{O}_2}) \cdot F \cdot n = (-0,1392 - 1,0868) \cdot F \cdot n = -1,226 \cdot 96485 \cdot 24 = -2840 \text{ kJ/mol}.$$

$$\Delta G_{\text{Homeostasis}} = \Delta E \cdot F \cdot n = (E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} - E^\circ_{\text{O}_2}) \cdot F \cdot n = (-0,88427 - 0,4349) \cdot F \cdot n = -1,31917 \cdot 96485 \cdot 24 = -3054,7 \text{ kJ/mol}.$$

Glikozes Nernsta pus reakcija $\Delta G_{\text{eqC}_6\text{H}_{12}\text{O}_6} = E^\circ_{\text{C}_6\text{H}_{12}\text{O}_6} \cdot F \cdot 1 \cdot 24 = -0,1392 \cdot 96485 \cdot 24 / 1000 = -322,34 \text{ kJ/mol}$

un aprēķināts Hess no Alberty datiem $\Delta G_{\text{AlbertyC}_6\text{H}_{12}\text{O}_6} = 30 \cdot 22,44 + 6 \cdot 46,08 - (1271 + 6 \cdot 78,1 + 42 \cdot 0) = -789,9 \text{ kJ/mol}$ un

bioķīmijas nosacījumu Hesa vērtība $\Delta G_{\text{HessC}_6\text{H}_{12}\text{O}_6} = 30 \cdot 22,44 + 6 \cdot 46,08 - (2268,8 + 6 \cdot 78,1 + 42 \cdot 0) = -1787,7 \text{ kJ/mol}$.

Skābekļa reducēšanas $6 \cdot (\text{O}_{2\text{aqua}} + 4\text{H}_3\text{O}^+ + 4\text{e}^- \rightleftharpoons 6\text{H}_2\text{O})$; standarta potenciāls $E^\circ_{\text{O}_2} = 1,0868 \text{ Volti}$ un glikozes homeostāzes konstante ar vērtībām $[\text{H}_3\text{O}^+] = 10^{-7,36} \text{ M}$, $[\text{HCO}_3^-] = 0,0154 \text{ M}$, $[\text{C}_6\text{H}_{12}\text{O}_6] = 5 \cdot 10^{-3} \text{ M}$, ūdeni $[\text{H}_2\text{O}] = 55,3 \text{ M}$ un $\Delta G_{\text{Lehninger}} = 2840 \text{ kJ/mol}$ ir lielāka par vienu $K_{\text{eqHomeostasis}} = 10^{498}$:

$$K_{\text{eqHomeostasis}} = \frac{[\text{HCO}_3^-]^6 [\text{H}_3\text{O}^+]^6}{[\text{C}_6\text{H}_{12}\text{O}_6] \cdot [\text{O}_2]^6 [\text{H}_2\text{O}]^6} = \text{EXP}(-\Delta G_{\text{eqHomeostasis}} / R / T) = \text{EXP}(2840000 / 8,3144 / 298,15) = 10^{498}.$$

Kvazi līdzsvara stāvoklis virzīts neatgriezeniski kā fotosintēzes dzinējs akumulē brīvo enerģiju produktos:



Using Hess law $2840 \text{ kJ/mol} = G_{\text{C}_6\text{H}_{12}\text{O}_6} + 6G_{\text{O}_2\text{Homeostasis_arterial}} + 6G_{\text{H}_2\text{O_Biochem}} - (6G_{\text{H}_3\text{O}^+} + 6G_{\text{HCO}_3^-})$.

Free energy content of one mol glucose is Hess law calculates referring Alberty [8,15] data:

TERMODINAMIKA VINGRINĀJUMS V h **Pyruvate** Nernst's lactate $\text{H}_3\text{CHC}(\text{OH})\text{COO}^-$.



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

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

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

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

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

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

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

PyruvEnolP³⁻	-1400	-1100	-1189,73	$G_{\text{H}_2\text{O}} = 0 \text{ kJ/mol}$; $G_{\text{H}^-} = -3,068 - 534,2 - 22,44 + (668,8 + 0) = 109,092 \text{ kJ/mol}$
H₃CC=OCOO⁻	-597,4	-850	-350,78	$G_{\text{H}_2\text{O}_{\text{Biochem}}} = 85,64 \text{ kJ/mol}$; $G_{\text{H}^-} = -3,068 - 534,2 - 22,44 + (668,8 + 85,64) = 194,7 \text{ kJ/mol}$
H₃CC=OCOO⁻	-603,7	-433,54	-474,44	
H₃CC=OCOO⁻	-597,04	-846,66	-344,62	$G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} = 534,2 \text{ kJ/mol}$;
H₃O⁺	-285,81	-3,854	-213,275	
H₂O	-285,85	69,9565	-237,191	
H₂O	-286,65	-453,188	-151,549	
H₃CHC(OH)COO⁻	-688,29	-1290,9	-303,4	$G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} = 668,8 \text{ kJ/mol}$;
H₃CHC(OH)COOH				$G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} = 3G_{\text{CO}_2\text{gas}} + 3G_{\text{H}_2\text{O}} - (3G_{\text{O}_2\text{gas}}) = 2271 \text{ kJ/mol}$;

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

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

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

Lactic acid Formation 71st 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 $\text{H}_3\text{CHC}(\text{OH})\text{COOH} + \text{H}_2\text{O} \Leftrightarrow \text{H}_3\text{CHC}(\text{OH})\text{COO}^- + \text{H}_3\text{O}^+$; $\text{pK}_{a1} = 3,86$;

$K_{\text{eq}} = [\text{H}_3\text{CHC}(\text{OH})\text{COO}^-] \cdot [\text{H}_3\text{O}^+] / [\text{H}_3\text{CHC}(\text{OH})\text{COOH}] \cdot [\text{H}_2\text{O}] = K_a / [\text{H}_2\text{O}] = 10^{-(3,86)} / 55,3 = 2,5 \cdot 10^{(-6)} = 10^{(-5,603)}$;

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

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

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

Pyruvic acid Formation 71st page $3\text{C} + 2\text{H}_2\text{gas} + 1,5\text{O}_2\text{gas} \Rightarrow \text{H}_3\text{CC}=\text{OCOOH}$; $\Delta G_{\text{Succinat}} = -344,62 \text{ kJ/mol}$ [8];

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

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

Pyruvic acid $\text{H}_3\text{CC}=\text{OCOOH} + \text{H}_2\text{O} \Leftrightarrow \text{H}_3\text{CHC}(\text{OH})\text{COO}^- + \text{H}_3\text{O}^+$; $\text{pK}_{a1} = 2,5$;

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

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

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

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

NADPH = NADP⁺ + H⁺(H⁺ + 2e⁻); $E^\circ_{\text{NADH}} = -0,41135 \text{ V}$; absolute Lehninger; [6]-

H₂O₂ veidošanās 41st page **H₂gas+O₂gas=>H₂O₂** ; $\Delta G^{\circ}_{\text{UnivAlberta}}=-134,03 \text{ kJ/mol}$; $\Delta G^{\circ}_{\text{Alberty}}=-48,39 \text{ kJ/mol}$;
 $\Delta G_{\text{Alberty}}=G_{\text{H}_2\text{O}_2}-(G_{\text{O}_2\text{gas}}+G_{\text{H}_2\text{gas}})=\underline{284,25-(85,64+303)}=-114,14 \text{ kJ/mol}$ (-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
H₂O₂ aqua	-191,99	-481,688	-48,39
H ₂ O ₂ aqua	-191,17	143,9	-134,03
Succinat²⁻	-908,69	-1295,576	-522,414
Fumarate²⁻	-776,56	-862,288	-519,4688

Alberty nulles $G_{\text{H}_2\text{O}}=0 \text{ kJ/mol}$; atskaitē bāzēti $G_{\text{H}_2\text{O}_2}=\underline{284,25} \text{ kJ/mol}$
 University Alberta
 $G_{\text{Succinat}}=650,8 \text{ kJ/mol}$; $G_{\text{SuccinatFor}}=-522,4+(4*91,26+2*85,6+2*303)=\underline{619,8} \text{ kJ/mol}$
 $G_{\text{Fumarat}}=554,75 \text{ kJ/mol}$; $G_{\text{FumaricFor}}=-519,5+(4*91,26+85,6+2*303)=\underline{537,1} \text{ kJ/mol}$

Succinat²⁻ Formation 41st page **4C+2H₂gas+2O₂gas=>(CH₂)₂(CO₂⁻)(CO₂⁻)** ; $\Delta G_{\text{Succinat}}=-522,4 \text{ kJ/mol}$ Alberty;
 $\Delta G_{\text{SuccinatFor}}=G_{\text{SuccinatFor}}-(4G_{\text{Cgraph}}+2G_{\text{H}_2\text{gas}}+2G_{\text{O}_2\text{gas}})=-522,4 \text{ kJ/mol}$;
 $G_{\text{SuccinatFor}}=-522,4+(4*91,26+2*85,6+2*303)=\underline{619,8} \text{ kJ/mol}$;

Fumarate²⁻ Formation 41st page **4C+H₂gas+2O₂gas=>(CH)₂(CO₂⁻)(CO₂⁻)** ; $\Delta G_{\text{Fumarat}}=-519,5 \text{ kJ/mol}$ Alberty;
 $\Delta G_{\text{Fumarat}}=G_{\text{FumaratFor}}-(4G_{\text{Cgraph}}+G_{\text{H}_2\text{gas}}+2G_{\text{O}_2\text{gas}})=-519,5 \text{ kJ/mol}$;
 $G_{\text{FumaratFor}}=-519,5+(4*91,26+85,6+2*303)=\underline{537,1} \text{ kJ/mol}$;

Succinic acid (CH₂)₂(CO₂H)₂+H₂O<=>(CH₂)₂(CO₂H)(CO₂⁻)+H₃O⁺; pK_{a1}=4,2;
 $K_{a1\text{eq}}=[(\text{CH}_2)_2(\text{CO}_2\text{H})(\text{CO}_2^-)]*[\text{H}_3\text{O}^+]/[(\text{CH}_2)_2(\text{CO}_2\text{H})_2]/[\text{H}_2\text{O}]=K_{a1}/[\text{H}_2\text{O}]=10^{-(4,2)}/55,3=1,14*10^{-6}=10^{-(5,94)}$;
Succinat²⁻ (CH₂)₂(CO₂H)(CO₂⁻)+H₂O<=>(CH₂)₂(CO₂⁻)(CO₂⁻)+H₃O⁺; pK_{a2}=5,6;
 $K_{a2\text{eq}}=[(\text{CH}_2)_2(\text{CO}_2^-)(\text{CO}_2^-)]*[\text{H}_3\text{O}^+]/[(\text{CH}_2)_2(\text{CO}_2\text{H})(\text{CO}_2^-)]/[\text{H}_2\text{O}]=K_{a2}/[\text{H}_2\text{O}]=10^{-(5,6)}/55,3=4,54*10^{-8}=10^{-(7,34)}$;
 (CH₂)₂(CO₂H)₂+2H₂O<=>(CH₂)₂(CO₂⁻)(CO₂⁻)+2H₃O⁺; K_{aeq}=K_{a1eq}*K_{a2eq}=1,14*10⁻⁽⁶⁾*4,54*10⁻⁽⁸⁾=10^{-(13,3)};
 $\Delta G_{\text{eqSuccinat}}=-R*T*\ln(K_{\text{aeq}})=-8,3144*298,15*\ln(10^{-(13,3)})/1000=\underline{75,9} \text{ kJ/mol}$.

$\Delta G_{\text{Succinat}}=G_{\text{Succinat}}+2G_{\text{H}_3\text{O}^+}-(G_{\text{SuccinicAc}}+2G_{\text{H}_2\text{O}})=G_{\text{Succinat}}+2*22,44-(619,8+2*0)=\underline{75,9} \text{ kJ/mol}$;
 $G_{\text{Succinat}}=\Delta G_{\text{Succinat}}-2G_{\text{H}_3\text{O}^+}+(G_{\text{SuccinicAc}}+2G_{\text{H}_2\text{O}})=\underline{75,9}-2*22,44+(619,8+2*0)=\underline{650,8} \text{ kJ/mol}$;

Fumaric acid (CH)₂(CO₂H)₂+H₂O<=>(CH)₂(CO₂H)(CO₂⁻)+H₃O⁺; pK_{a1}=3,03 ;
 $K_{a1\text{eq}}=[(\text{CH})_2(\text{CO}_2\text{H})(\text{CO}_2^-)]*[\text{H}_3\text{O}^+]/[(\text{CH})_2(\text{CO}_2\text{H})_2]/[\text{H}_2\text{O}]=K_{a1}/[\text{H}_2\text{O}]=10^{-(3,03)}/55,3=1,69*10^{-5}=10^{-(4,77)}$;
Fumarate²⁻<=>(CH)₂(CO₂H)(CO₂⁻)+H₂O<=>(CH)₂(CO₂⁻)(CO₂⁻)+H₃O⁺; pK_{a2}=4,44;
 $K_{a2\text{eq}}=[(\text{CH})_2(\text{CO}_2^-)(\text{CO}_2^-)]*[\text{H}_3\text{O}^+]/[(\text{CH})_2(\text{CO}_2\text{H})(\text{CO}_2^-)]/[\text{H}_2\text{O}]=K_{a2}/[\text{H}_2\text{O}]=10^{-(4,44)}/55,3=6,57*10^{-7}=10^{-(6,18)}$;
 (CH)₂(CO₂H)₂+2H₂O<=>(CH)₂(CO₂⁻)(CO₂⁻)+2H₃O⁺; K_{aeq}=K_{a1eq}*K_{a2eq}=1,69*10⁻⁽⁵⁾*6,57*10⁻⁽⁷⁾=10^{-(10,955)};
 $\Delta G_{\text{eqFumarat}}=-R*T*\ln(K_{\text{aeq}})=-8,3144*298,15*\ln(10^{-(10,955)})/1000=\underline{62,53} \text{ kJ/mol}$.

$\Delta G_{\text{Fumarat}}=G_{\text{Fumarat}}+2G_{\text{H}_3\text{O}^+}-(G_{\text{FumaricAc}}+2G_{\text{H}_2\text{O}})=G_{\text{Fumarat}}+2*22,44-(537,1+2*0)=\underline{62,53} \text{ kJ/mol}$;
 $G_{\text{Fumarat}}=\Delta G_{\text{Fumarat}}-2G_{\text{H}_3\text{O}^+}+(G_{\text{FumaricAc}}+2G_{\text{H}_2\text{O}})=\underline{62,53}-2*22,44+(537,1+2*0)=\underline{554,75} \text{ kJ/mol}$;

Ox **O₂ aqua+2H₃O⁺+2e⁻=H₂O₂ aqua+2H₂O**; E^o_{OxO₂H₂O₂}=-0,4495 V absolute University Alberta ;
 $\Delta G_{\text{AlbertyOxO}_2\text{H}_2\text{O}_2}=G_{\text{H}_2\text{O}_2}+2G_{\text{H}_2\text{O}}-(G_{\text{O}_2\text{aqua}}+2G_{\text{H}_3\text{O}^+})=\underline{284,25+2*0-(330+2*22,44)}=-100,4 \text{ kJ/mol}$;
 $\Delta G_{\text{eqAlbertyAbsoluteOxO}_2\text{H}_2\text{O}_2}=E^{\circ}_{\text{eqOxO}_2\text{H}_2\text{O}_2}*F*1*2=-0,4495*96485*2=-\underline{86,7} \text{ kJ/mol}$;

Nernst's half Red **Succinate²⁻+2H₂O = Fumarate²⁻+2H₃O⁺+2e⁻** ; E^o_{RedSuccinate}=0,2512 V; absolute potential ;
 Alberty $\Delta G_{\text{eqSuccinat}_\text{Fumarat}}=G_{\text{Fumarat}}+2G_{\text{H}_3\text{O}^+}-(G_{\text{Succinat}}+2G_{\text{H}_2\text{O}})=\underline{554,75+2*22,44-(650,8+2*0)}=-\underline{51,2} \text{ kJ/mol}$;
 $\Delta G_{\text{eqAlbertyNernstRedSuccinat}_\text{Fumarat}}=E^{\circ}_{\text{eqNernstHalfSuccinat}_\text{Fumarat}}*F*1*2=0,2512*96485*2=\underline{48,47} \text{ kJ/mol}$;
 Standard equilibrium state attractor for non equilibrium states

Succinat²⁻+O₂ aqua=>fumarate²⁻+H₂O₂ aqua+Q+ΔG; $\Delta G_{\text{min}}=\Delta G_{\text{eqSuccinat}_\text{H}_2\text{O}_2}=-\underline{38,3} \text{ kJ/mol}$;
 Alberty Hess $\Delta G_{\text{Succinat}_\text{H}_2\text{O}_2}=G_{\text{Fumarat}}+G_{\text{H}_2\text{O}_2}-(G_{\text{Succinat}}+G_{\text{O}_2\text{aqua}})=\underline{554,75+284,25-(650,8+330)}=-\underline{151,55} \text{ kJ/mol}$;
 $\Delta G_{\text{min}}=\Delta G_{\text{eq}}=(E^{\circ}_{\text{RedSuccinate}}-E^{\circ}_{\text{OxO}_2})*F*n=(0,2512-0,4495)*96485*2=(-0,1983)*96485*2=-\underline{38,3} \text{ kJ/mol}$;

Nernst's half Red **Succinate²⁻+2H₂O = Fumarate²⁻+2H₃O⁺+2e⁻** ; E^o_{RedSuccinate}=0,2512 V; absolute potential ;
 $\Delta G_{\text{eqSuccinat}_\text{Fumarat}}=G_{\text{FumaratFor}}+2G_{\text{H}_3\text{O}^+}-(G_{\text{SuccinatFor}}+2G_{\text{H}_2\text{O}})=\underline{537,1+2*22,44-(619,8+2*0)}=-\underline{37,82} \text{ kJ/mol}$;
 $\Delta G_{\text{eqSuccinat}_\text{Fumarat}}=G_{\text{FumaratFor}}+2G_{\text{H}_3\text{O}^+}-(G_{\text{SuccinatFor}}+2G_{\text{H}_2\text{O}})=\underline{537,1+2*22,44-(619,8+2*85,64)}=-\underline{209,1} \text{ kJ/mol}$;
 $\Delta G_{\text{eqAlbertyNernstRedSuccinat}_\text{Fumarat}}=E^{\circ}_{\text{eqNernstHalfSuccinat}_\text{Fumarat}}*F*1*2=0,2512*96485*2=\underline{48,47} \text{ kJ/mol}$;
 Standard equilibrium state attractor for non equilibrium states

Succinat²⁻+O₂ aqua=>fumarate²⁻+H₂O₂ aqua+Q+ΔG; $\Delta G_{\text{min}}=\Delta G_{\text{eqSuccinat}_\text{H}_2\text{O}_2}=-\underline{38,3} \text{ kJ/mol}$;
 Alberty Hess $\Delta G_{\text{Succinat}_\text{H}_2\text{O}_2}=G_{\text{Fumarat}}+G_{\text{H}_2\text{O}_2}-(G_{\text{Succinat}}+G_{\text{O}_2\text{aqua}})=\underline{537,1+284,25-(619,8+330)}=-\underline{151,55} \text{ kJ/mol}$;
 $\Delta G_{\text{min}}=\Delta G_{\text{eq}}=(E^{\circ}_{\text{RedSuccinate}}-E^{\circ}_{\text{OxO}_2})*F*n=(0,2512-0,4495)*96485*2=(-0,1983)*96485*2=-\underline{38,3} \text{ kJ/mol}$;

CH₃CH₂OH etanola veidošanās no elementiem:

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

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

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

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

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

CH₃CHO acetaldehīda veidošanās no elementiem: $2\text{C}+2\text{H}_{2\text{gas}}+1/2\text{O}_{2\text{gas}}\Rightarrow\text{CH}_3\text{CHO};$

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

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

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

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

$$\text{CH}_3\text{CH}_2\text{OH}+\text{H}_2\text{O}=\text{CH}_3\text{CHO}+\text{H}_3\text{O}^++\text{H}^-(\text{H}^++2\text{e}^-); \text{absolūtais potenciāls } E^\circ_{\text{CH}_3\text{CH}_2\text{OH}}=-0,055 \text{ V}; [19]$$

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

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

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

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

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

Viela	$\Delta H^\circ_{\text{H}} \text{ kJ/mol}$	$\Delta S^\circ_{\text{H}} \text{ J/mol/K}$	$\Delta G^\circ_{\text{H}} \text{ kJ/mol}$	CRC Handbook of Chemistry and Physics 2010 90th David R. Lide
H₃C-CH=O	-212,23	-281,84	24,06	$G_{\text{CH}_3\text{CHO}}=529,28 \text{ kJ/mol};$
H₃C-CH=O	-213,88	-825,64	32,2824	$G_{\text{CH}_3\text{CHO}}=537,5 \text{ kJ/mol};$
NADH	-41,41	-4465,708	1175,5732	BioThermodynam06;
NADH	-1036,66	-140,50	1120,09	
H₃O⁺	-285,81	-3,854	-213,275	
NAD ⁺	-10,30	-3766,008	1112,534	BioThermodynamic,2006,Massachusetts Tecnology Institute,Alberty
NAD ⁺	-1007,48	-183	1059,11	
H₃CCH₂OH	-290,77	-1227,764	75,2864	Alberty $G_{\text{CH}_3\text{CH}_2\text{OH}}=666,106 \text{ kJ/mol};$
H₃CCH₂OH_{aq}	-288,3	-357,7394	-181,64	CRC $G_{\text{CH}_3\text{CH}_2\text{OH}}=409,82 \text{ kJ/mol};$
H₂O	-285,85	69,9565	-237,191	$G_{\text{H}_2\text{O}}=0 \text{ kJ/mol}; G_{\text{H}^-}=-10,6-537,5-22,44+(409,82+0)=-160,7 \text{ kJ/mol}.$
H₂O	-286,65	-453,188	-151,549	$G_{\text{H}_2\text{O}_{\text{Biochem}}}=85,64 \text{ kJ/mol}. G_{\text{H}^-}=-10,6-537,5-22,44+(409,82+85,64)=-75,08 \text{ kJ/mol}$

$\text{NADH} = \text{NAD}^+ + \text{H}^-(\text{H}^++2\text{e}^-); E^\circ_{\text{NADH}}=-0,4095 \text{ V};$ absolute David Harris; [22]

$\text{NAD}^++\text{H}^-(\text{H}^++2\text{e}^-)+\text{CH}_3\text{CH}_2\text{OH}+\text{H}_2\text{O}=\text{NADH}+\text{CH}_3\text{CHO}+\text{H}_3\text{O}^++\text{H}^-(\text{H}^++2\text{e}^-);$

$\text{NAD}^++\text{CH}_3\text{CH}_2\text{OH}+\text{H}_2\text{O}=\text{NADH}+\text{CH}_3\text{CHO}+\text{H}_3\text{O}^+;$

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

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

$$=1112,534+22,44+537,5-(1175,5+666,106+0)=-169,1 \text{ kJ/mol}.$$

$$=1112,534+22,44+32,282-(1175,5+75,2864+0)=-83,53 \text{ kJ/mol}.$$

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

$$=1112,534+22,44+32,282-(1175,5+75,2864+85,64)=-169,2 \text{ kJ/mol}.$$



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

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

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

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

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

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

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

	$\Delta H^\circ_{\text{H}}$ kJ/mol	$\Delta S^\circ_{\text{H}}$ J/mol/K	$\Delta G^\circ_{\text{H}}$ kJ/mol
PyruvEnolP³⁻	-1400	-1100	-1189,73
H₃CC=OCOO⁻	-597,4	-850	-350,78
H₃CC=OCOO⁻	-603,7	-433,54	-474,44
H₃CC=OCOO⁻	-597,04	-846,66	-344,62
H₃O⁺	-285,81	-3,854	-213,275
H₂O	-285,85	69,9565	-237,191
H₂O	-286,65	-453,188	-151,549
H₃CHC(OH)COO⁻	-688,29	-1290,9	-303,4

$$G_{\text{H}_2\text{O}} = 0 \text{ kJ/mol}; G_{\text{H}^-} = -3,068 - 534,2 - 22,44 + (668,8 + 0) = 109,092 \text{ kJ/mol}$$

$$G_{\text{H}_2\text{O}}_{\text{Biochem}} = 85,64 \text{ kJ/mol}; G_{\text{H}^-} = -3,068 - 534,2 - 22,44 + (668,8 + 85,64) = 194,7 \text{ kJ/mol}$$

$$G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} = 534,2 \text{ kJ/mol}; pK_a = 2,5;$$

$$G_{\text{H}_3\text{CHC}(\text{OH})\text{COO}^-} = 668,8 \text{ kJ/mol}; pK_a = 3,86;$$

$$pK_a = 3,86; \Delta H_c^\circ = 1361,9 \text{ kJ/mol}; G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} = 2271 \text{ kJ/mol}; \text{H}_3\text{CHC}(\text{OH})\text{COOH} + 3\text{O}_2_{\text{gas}} = 3\text{CO}_2_{\text{gas}} + 3\text{H}_2\text{O};$$

$$\Delta H_c^\circ = 3G_{\text{CO}_2_{\text{gas}}} + 3G_{\text{H}_2\text{O}} - (G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} + 3G_{\text{O}_2_{\text{gas}}}) = 3 \cdot 0 + 3 \cdot 0 - (G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} + 3 \cdot 303) = 1361,9 \text{ kJ/mol};$$

$$G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} + 3G_{\text{CO}_2_{\text{gas}}} + 3G_{\text{H}_2\text{O}} - (3G_{\text{O}_2_{\text{gas}}}) = 3 \cdot 0 + 3 \cdot 0 - (+3 \cdot 303) - 1361,9 = G_{\text{H}_3\text{CHC}(\text{OH})\text{COOH}} = 2271 \text{ kJ/mol};$$

Lactic acid Formation 71st page 3C+3H₂gas+1,5O₂gas=>H₃CHC(OH)COOH ; G_{H₃CHC(OH)COOH} = -303,4 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 H₃CHC(OH)COOH+H₂O<=>H₃CHC(OH)COO⁻+H₃O⁺; pK_a=3,86;

$$K_{\text{eq}} = [\text{H}_3\text{CHC}(\text{OH})\text{COO}^-] \cdot [\text{H}_3\text{O}^+] / [\text{H}_3\text{CHC}(\text{OH})\text{COOH}] \cdot [\text{H}_2\text{O}] = K_a / [\text{H}_2\text{O}] = 10^{-(3,86)} / 55,3 = 2,5 \cdot 10^{-(6)} = 10^{-(5,603)};$$

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

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

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

Pyruvic acid Formation 71st page 3C+2H₂gas+1,5O₂gas=>H₃CC=OCOOH; ΔG_{Succinat} = -344,62 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 H₃CC=OCOOH+H₂O<=>H₃CHC(OH)COO⁻+H₃O⁺; 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 = NAD⁺ + H⁺(H⁺+2e⁻); E^o_{NADH} = -0,4095 V; absolute Lehninger; [6]

Red lactate+H₂O<=>pyruvate⁻+H₃O⁺+H⁺(H⁺+2e⁻); absolute potential E^o_{H₃CHC(OH)COO⁻} = -0,0159 V;

Ox NAD⁺+H⁺(2e⁻)=NADH ; E^o₁ = -0,4095 V; OksRed NAD⁺+lactate⁻+H₂O=NADH+ pyruvate⁻+H₃O⁺;

Balanced n=2=m with 2e⁻ electrons ΔE^o NAD⁺ accept electrons from lactate:

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

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

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

$$\Delta G_{\text{Hess}} = \Delta H_{\text{Hess}} - T \cdot \Delta S_{\text{Hess}} = 45,764 - 298,15 \cdot 0,5479605 = 209,14 \dots \text{ kJ/mol endoergic; formation 62nd page}$$