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ΔH_H ΔS_H ΔG_H at standard conditions 298.15 K. Reaction is **exothermic** , **athermic**, **endothermic**? $6HCO_3^-$, $6H_3O^+$assimilation reaction in green plants with blue and red photons **E=h•ν** absorption in photosynthetic reaction center PRC+**h•ν** for production $6O_{2aqua}$ and $C_6H_{12}O_6$ using the data table!
Mention whether the reactio6n will be **exoergic** or **endoergic**! <u>Reactants</u> => <u>products</u> glucose + oxyge

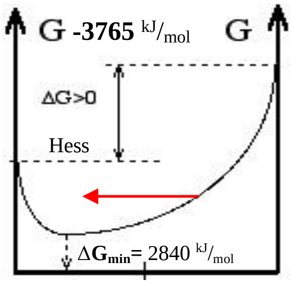
$6HCO_3^-+6H_3O^++\Delta G+Q \Rightarrow C_6H_{12}O_6+6O_{2aqua}+6H_2O$; $\Delta G_{Lehninger}=2840$ kJ/mol

Substance	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$ kJ/mol
$C_6H_{12}O_{6aq}$	-1263,78	269,45	-919,96
Glc	**-1267,13**	**-2901,49**	**-402,05**
O_{2aqua}	-11,715	110,876	16,4
O_{2aqua}	**-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	-213,275
$CO_2\uparrow_{gas}$	-393,509	213,74	-394,359
CO_{2aq}	-413,798	117,5704	-385,98
CO_{2aq}	–413,26	-119,36	-
HCO_3^-	-689,93	98,324	-586,93988
HCO_3^-	**-692,4948**	**-494,768**	**-544,9688**

$\Delta G_H=\Delta G°_{C6H12O6}+6\Delta G°_{O2}+6\Delta G°_{H2O}-6\Delta G°_{H3O}-6\Delta G°_{HCO3}=\mathbf{3336.5}$ kJ/mol
$=\mathbf{-402,05}+6*\mathbf{16,4}+6*\mathbf{-151,549}-(6*\mathbf{-544,9688}+6*-213,274599)=\mathbf{3336.5}$ kJ/mol
Biothermodynamic 2006; data recalculate for pH=7.36. [8]
$\Delta H_H=\Delta H°_{C6H12O6}+6\Delta H°_{O2}+6\Delta H°_{H2O}-6\Delta H°_{H3O}-6\Delta H°_{HCO3}=$kJ/mol
$=\mathbf{-1267,13}+6*\mathbf{-11,7}+6*\mathbf{-286,65}-(6*\mathbf{-692,4948}+6*-285,81)=\mathbf{2812.6}$
$\Delta S_H=\Delta S°_{C6H12O6}+6\Delta S°_{O2}+6\Delta S°_{H2O}-6\Delta S°_{H3O}-6\Delta S°_{HCO3}=\mathbf{-3194.1}$J/mol/K
$=\mathbf{-2901,49}+6*\mathbf{-94,2}+6*\mathbf{-453,188}-(6*\mathbf{-494,768}+6*-3,854)=\mathbf{-3194.\ 1}$J/mol/K
$\Delta G_{Hess}=\Delta H_H-T*\Delta S_H=\mathbf{2812,6}-298,15*\mathbf{-3,1941}=\mathbf{3764.92}$ kJ/mol;
CRC102. $\Delta S_{dispersed}=-\Delta H_{Hess}/T=\mathbf{-2812,6}/298,15=\mathbf{9433.5}$ J/mol/K;
$\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=\mathbf{3194,1+9433,5=12627.6}$ J/mol/K;
$T•\Delta S_{total}=\mathbf{-12,6276}*298,15=\mathbf{-3764.9}$ kJ/mo accumulate <u>energy</u> .
$\Delta G_{Hess}=\mathbf{3764.92}$ kJ/mol > $\Delta G_{Lehninger}=2840$ kJ/mol;
page 3:. Photosynthesis accumulate in products $C_6H_{12}O_6+6H_2O$ and oxygen $6O_{2aqua}$ Bio-Fuel free energy for homeostasis: $6H_3O^++6HCO_3 \Rightarrow C_6H_{12}O_6+6O_{2aqua}+6H_2O$; $6H_2O$; $\Delta G_{Lehninger}=+2840$ kJ/mol;
are used by oxidation to generating concentrations gradients of $6HCO_3^-+6H_3O^+$ ions:
$C_6H_{12}O_6+6O_{2aqua}+6H_2O \Rightarrow 6H_3O^++6HCO_3$; $\Delta G_{Lehninger}=-2840$ kJ/mol;
for osmosis against and transportation down the gradients through membrane channels.

$6CO_{2gas}\uparrow+12H_2O \Rightarrow 6CO_{2aqua}+12H_2O \Rightarrow 6H_3O^++6HCO_3 \Rightarrow C_6H_{12}O_6+6O_{2aqua}+6H_2O \Rightarrow C_6H_{12}O_6+6O_{2\,gas}\uparrow+6H_2O$
$\Delta G_H=\Delta G°_{C6H12O6}+6\Delta G°_{O2}+6\Delta G°_{H2O}-6\Delta G°_{CO2aqua}-12\Delta G°_{H2O}=\mathbf{2921.5}$ kJ/mol;
$=\mathbf{-402,05}+6*\mathbf{16,4}+6*\mathbf{-151,549}-(6*-385,98+12*\mathbf{-151,549})=\mathbf{2921.5}$ kJ/mol;
$\Delta G_H=\Delta G°_{C6H12O6}+6\Delta G°_{O2}+6\Delta G°_{H2O}-6\Delta G°_{CO2gas}-12\Delta G°_{H2O}=\mathbf{2971.8}$ kJ/mol;
$=\mathbf{-402,05}+6*\mathbf{16,4}+6*\mathbf{-151,549}-(6*-394,359+12*\mathbf{-151,549})=\mathbf{2971.8}$ kJ/mol;
$\Delta G_H=\Delta G°_{C6H12O6}-6\Delta G°_{O2\,gas}-6\Delta G°_{H2O}-6\Delta G°_{CO2gas}+12\Delta G°_{H2O}=\mathbf{2873.4}$ kJ/mol;
$=\mathbf{-402,05}+6*\mathbf{0}+6*\mathbf{-151,549}-(6*-394,359+12*\mathbf{-151,549})=\mathbf{2873.4}$; $\Delta G_{BioChem}=\mathbf{2873.4}$ kJ/mol;
$\Delta G_{Hess}=\Delta H_H-T*\Delta S_H=\mathbf{2812,6}-298,15*\mathbf{-3,1941}=\mathbf{3764.92}$ kJ/mol;
$\Delta G_{Hess}=\mathbf{3764.92}$ kJ/mol > $\Delta G_{Lehninger}=2840$ kJ/mol;
$\Delta G_{Lehninger}=\Delta G_{eq}=-R•T•\ln(K_{eq})=-8,3144•298,15•\ln(10^{-497,55})=2840$ kJ/mol;

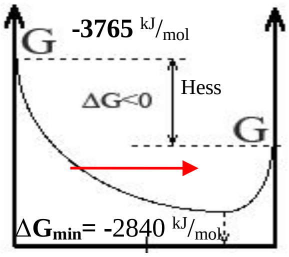
Exothermic and endoergic photosynthesis Hess free energy change positive for gas gas $6O_2$, $6CO_2$ $\Delta G_{photosynthesis}=\mathbf{2873}$ kJ/mol so $\Delta G_{photosynthesis}=\mathbf{2971.8}$ kJ/mol more positive for aqua $6O_{2aqua}$ and $\Delta G_{photosynthesis}=\mathbf{2921.5}$ kJ/mol for both aqua $6O_{2aqua}$, $6CO_{2aqua}$, CA Carbonic Anhydrase driven $\Delta G_{photosynthesis}=\mathbf{3336,5}$ kJ/mol $6O_{2aqua}$, $6H_3O^+$, $6HCO_3^-$, but minimizes $\Delta G_{min}=\Delta G_{eq}=2840$ kJ/mol reaching quasi equilibrium homeostasis mixture for 12 reactants $6H_3O^++6HCO_3^-$ and 13 products



6A+6B 50% 6C+6D
$C_6H_{12}O_6+6O_{2aqua}+6H_2O$

$$K_{eq1}=EXP(-\Delta G_{Lehninger1}/R/T)=EXP(-2840/8,3144/298,15)=10^{-498}=\frac{[C_6H_{12}O_6]\cdot[O_{2\,aqua}]^6[H_2O]^6}{[HCO_3^-]^6_{aqua}\cdot[H_3O^+]^6}$$

$$K_{eq2}=EXP(-\Delta G_{Lehninger2}/R/T)=EXP(2840/8,3144/298,15)=10^{498}=\frac{[HCO_3^-]^6_{aqua}\cdot[H_3O^+]^6}{[C_6H_{12}O_6]\cdot[O_{2\,aqua}]^6\cdot[H_2O]^6}$$



Homeostasis Quasi Equilibrium is Prigogine attractor free energy change minimum ΔG_{min}. Free energy minimum reaching estabilishes homeostasis quasi equilibrium mixture K_{eq}.

13 reactants $C_6H_{12}O_6+6O_{2aqua}+6H_2O$ A+6B+6C
12 products $6H_3O^++6HCO_3^-$ 6D+6E

THERMODYNAMICS Exercise 1a $6CO_2\uparrow$gas photosynthesis to $6O_2\uparrow_{gas}$ and $C_6H_{12}O_6$

Calculate ΔH_H ΔS_H ΔG_H at standard conditions 298.15 K. Reaction is **exothermic** , **athermic**, **endothermic**? CO_2 gas assimilation reaction in green plants with blue and red photons **E=h•v** absorption in photosynthetic reaction center PRC+**h•v** for production $6O_2\uparrow_{gas}$ and $C_6H_{12}O_6$ using the data table! Mention whether the reaction will be **exoergic** or **endoergic**!

Reactants => products glucose + oxygen

Substance	$\Delta H°_H$ $^{kJ}/_{mol}$	$\Delta S°_H$ $^{J}/_{mol/K}$
$O_2\uparrow_{gas}$	0	205,04

$6CO_2\uparrow_{gas}+6H_2O+\Delta G+Q\xrightarrow{PRC+hv}C_6H_{12}O_6+6O_2\uparrow_{gas}$

1. $\Delta H_H=\Delta H°_{C6H12O}+6\Delta H°_{O2}-6\Delta H°_{H2O}-6\Delta H°_{CO2}$=.............$^{kJ}/_{mol}$ ....= -1263,78-6*0-(6*-285,85+6*-393,509)= -1263,78+4076,154= +2812.37 $^{kJ}/_{mol}$ **endothermic**....

2. $\Delta S_{dispersed}=-\Delta H_H/T$ = -2812,37 /298.15= -9432.59 $^{J}/_{mol/K}$.

$\Delta S_H=\Delta S°_{C6H12O}+6\Delta S°_{O2}-6\Delta S°_{H2O}-6\Delta S°_{CO2}$=269,45+6*205,04-(6*69,9565+6*213,74)= -202.489 $^{J}/_{mol/K}$.

3. $\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}$=-202,489-9432,59 = -9635.079 $^{J}/_{mol/K}$.

$\Delta G_H=\Delta H_H-T^*\Delta S_H$ = +2812,37-298,15*-0,202489 =2812,37+60,3721= +2872.74 $^{kJ}/_{mol}$ **endoergic** .

$T\bullet\Delta S_{total}$=-9635,079*298,15= **-2872.7** $^{kJ}/_{mol}$ bound TΔSn← accumulate energy

$C_6H_{12}O_6+6O_2\uparrow_{gas}\xrightarrow{BioOxv}6CO_2\uparrow_{gas}+6H_2O+\Delta G+Q$

1. $\Delta H_H=6\Delta H°_{H2O}+6\Delta H°_{CO2}-\Delta H°_{C6H12O}-6\Delta H°_{O2}$= 6*-285,85+6*-393,509-(-1263,78-6*0)= -2812.37 $^{kJ}/_{mol}$

2. $\Delta S_{dispersed}=-\Delta H_H/T$ = --2812,37 /298.15= +9432.59 $^{J}/_{mol/K}$. **exothermic** .

$\Delta S_H=6\Delta S°_{H2O}+6\Delta S°_{CO2}-\Delta S°_{C6H12O}-6\Delta S°_{O2}$=6*69,9565+6*213,74-(269,45+6*205,04)=+202.489 $^{J}/_{mol/K}$.

3. $\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}$=202,489+9432,59 = 9635.079.. $^{J}/_{mol/K}$....

$\Delta G_H=\Delta H_H-T^*\Delta S_H$= -2812,37-298,15*0,202489= -2812,37-60,3721= -2872.74..................... $^{kJ}/_{mol}$ **exoergic**....

$T\bullet\Delta S_{total}$=9635,079*298,15= **+2872.7**.. $^{kJ}/_{mol}$ bound TΔSn←lost free energy

The molecules O_2, CO_2, $2H_2O$ protolytic functional activation for Biochemistry.

$G_{O2Biochem\_arterial}=G_{O2gas}+G_{O2sp}+\Delta G_{arterial}$=303.1+26.58-251.6=78.08 $^{kJ}/_{mol}$ decreases;

The oxygen O_{2aqua} free energy content in water G_{O2aqua}=330 $^{kJ}/_{mol}$ decreases to $G_{O2Biochem}$=78.08 $^{kJ}/_{mol}$.

Solubility $O_{2gas\ AIR}+H_2O+\Delta G\xrightarrow{Aquaporins}O_{2aqua\text{-}Blood}+Q$ constant:

$$\frac{[O_{2\,aqua}]}{[O_{2\,gas}]\cdot[H_2O]}$$

$=K_{sp}=2.205*10^{-5}$. $G_{O2aqua}=-R\bullet T\bullet\ln(K_{sp})=-8.3144*298.15*\ln(2.205*10^{-5})=26.58$ $^{kJ}/_{mol}$.

$O_{2aqua}+4H_3O^++4e^-=5H_2O$; -E°=**-1,0868** V inverse absolute standard potential.

$E=E°+^{0,0591}/_4\bullet\lg([O_{2aqua}]\bullet[H_3O^+]^4/_{[H2O]}{}^6)$=**1,0868**+$^{0,0591}/_4$*log(6*10^(-5)*10^(-7,36*4)/$_{55,346}$^5)=**0,46068** Volts .

$\Delta E_{H2O}=-E°+E_o$=**-1,0868**+**0,46068**=**-0,62612** Volts; $\Delta G_{arterial}=\Delta E_{H2O}*F*n$=**-0,62612***96485*4/1000=-251.6 $^{kJ}/_{mol}$.

$G_{O2Biochem\_arterial}=G_{O2gas}+G_{O2sp}+\Delta G_{arterial}$=303.1+26.58-251.6=78.08 $^{kJ}/_{mol}$ decreases;

Carbonic Anhydrase CA accumulates free energy to $G_{H3O+HCO3}=G_{H3O+}+G_{HCO3-}$=22.44+46.08=68.52 $^{kJ}/_{mol}$ referring to zero water and CO_{2gas} $G_{CO2+2H2O}$=0 $^{kJ}/_{mol}$. Solubility $CO_{2gas}+H_2O+\Delta G$<=>$CO_{2aqua}+Q$ product :

$K_{spCO2aqua}=[CO_{2aqua}]/[CO_{2gas}]/[H_2O]=EXP(-\Delta G_{sp}/R/T)$=EXP(-8379/8,3144/298,15)=0.034045.

$\Delta G_{spCO2aqua}=-R\bullet T\bullet\ln(K_{spCO2aqua})$=-8.3144*298.15*ln(0.034045)/1000=8.379 $^{kJ}/_{mol}$.

$CO_{2aqua}+2H_2O+\Delta G+Q=v1\xrightarrow{CA}H_3O^++HCO_3^-$ velocity constant $k_{1CO2aqua}=1.5\times10^8\ M^{-1}s^{-1}$. [9]

$$\frac{[HCO_3^-]_{aqua}\cdot[H_3O^+]}{[CO_2]_{aqua}\cdot[H_2O]^2}$$

$=K_{eqCAHCO3aqua}=K_{a\_CO2aqua}/[H_2O]^2=10^{-7.0512}/55.3^2=2.906*10^{-11}$. Equilibrium constant.

$\Delta G_{eqCO2aqua}=-R\bullet T\bullet\ln(K_{eqCO2aqua})$=-8,3144*298,15*ln(2,906*10^(-11))/1000=60.14 $^{kJ}/_{mol}$.

$G_{H3O+}+G_{HCO3-}=22.44+46.08=G_{H3O+HCO3-}=\Delta G_{spCO2aqua}+\Delta G_{eqCO2aqua}$=8.379+60.14=68.52 $^{kJ}/_{mol}$.

Water protolysis increases free energy content from zero G_{2H2O}=0 $^{kJ}/_{mol}$ to G_{H3O+OH}=99.8 $^{kJ}/_{mol}$.

H_2O+H_2O<=>$H_3O^++OH^-$;

$$\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}$$

$=K_{H3O++OH-}=[H_3O^+]*[OH^-]/[H_2O]^2=3.26\bullet10^{-18}$;

$\Delta G_{H3O++OH-}=-R\bullet T\bullet\ln(K_{H3O++OH-})$=-8,3144*298,15*ln(3,26•10^(-18))/1000=99.8 $^{kJ}/_{mol}$.

Distilled protolytic water free energy content in organism increases from zero to $G_{H2O\_Biochemistry}$=**85.65** $^{kJ}/_{mol}$. [1,8].

$H_2O\xrightarrow{Biochemistry}H_2O$;

$G_{H2O\_Biochemistry}=\Delta G°_{H2O\_Biochemistry}-\Delta G°_{H2O\_distilled}$=**-151.549**-(-237.191)=**85.64** $^{kJ}/_{mol}$.

Endothermic and endoergic free energy accumulation in biochemical medium:
osmolar concentration C_{osm}=0.305 M, ionic strength I=0.2 M, temperature 298.15 K
for water create positive $G_{H2O\_Biochemistry}$=**85.64** $^{kJ}/_{mol}$ aktivation as selforganization Homeostasis.

$6C_{gr}+6O_2\uparrow_{gas}\xrightarrow{Power_Staition} 6CO_2\uparrow_{gas}+\Delta G+Q$1. $\Delta H_H=6\Delta H^{\circ}_{CO2}-6\Delta H^{\circ}_{Cgr}+6\Delta H^{\circ}_{O2}=6*-393{,}509\ ^{kJ}/_{mol}$ **exothermic.**

Substance	$\Delta H^{\circ}_H\ ^{kJ}/_{mol}$	$\Delta S^{\circ}_H\ ^{J}/_{mol/K}$	$\Delta G^{\circ}_H\ ^{kJ}/_{mol}$
C_{gr}	0	5.74	G_{Cgr}=**91,26**
C_{gas}	716.7	158.1	**671.3**

$=6*-393{,}509-(6*0-6*0)=-2361{,}05-0=-2361.05\ ^{kJ}/_{mol}$

2. $\Delta S_{dispersed}=-\Delta H_H/T=--2361{,}05/298{,}15=7919\ ^{J}/_{K/mol}$

3. $\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=17{,}76+7919=7936.76\ ^{J}/_{mol/K}$

$\Delta S_H=6\Delta S^{\circ}_{CO2}-6\Delta S^{\circ}_{Cgr}-6\Delta S^{\circ}_{O2}=6*213{,}74-(6*5{,}74+6*205{,}04)=1282{,}44-1264{,}68=17.76\ ^{J}/_{mol/K}$.

$\Delta G_H=\Delta H_H-T*\Delta S_H=-2361{,}05-298{,}15*0{,}01776=+2361{,}05-5{,}295=-2366.35\ ^{kJ}/_{mol}$ **exoergic**.

$T\bullet\Delta S_{total}=7936{,}76\ ^*298{,}15=$**+2366.35** $^{kJ}/_{mol}$ bound $T\Delta Sn\leftarrow$ lost free energy; $G^{\circ}_{Cgr}=-671{,}3\ ^{kJ}/_{mol}$;

$C_{gas}+O_{2gas}\longrightarrow CO_{2gas}$. $\Delta G_H=\Delta G^{\circ}_{CO2gas}-(\Delta G^{\circ}_{Cgas}+\Delta G^{\circ}_{O2})=-394{,}4-(\mathbf{671{,}3}+0)=-1065.7\ ^{kJ}/_{mol}$

$C_{gr}+O_{2gas}\longrightarrow CO_{2gas}$. $\Delta G_H=G^{\circ}_{CO2gas}-(G^{\circ}_{Cgr}+G^{\circ}_{O2})=G^{\circ}_{CO2gas}-(\mathbf{-671{,}3}+\underline{237{,}19})=\mathbf{-394.5}\ ^{kJ}/_{mol}$;

$G^{\circ}_{CO2gas}=\mathbf{-394{,}4}+(\mathbf{-671{,}3}+\underline{237{,}19})=-828.51\ ^{kJ}/_{mol}$; $G_{O2Air}=\underline{237{,}19}\ ^{kJ}/_{mol}$.

$\Delta H_H=\Delta H^{\circ}_{CO2gas}-\Delta H^{\circ}_{Cgas}+\Delta H^{\circ}_{O2}=-393{,}509-(0+716{,}7)=-1110.209\ ^{kJ}/_{mol}$ **exothermic**.

$O_{2gas\ AIR}+H_2O\xrightarrow{Aquaporins}O_{2Blood}$; $G_{O2aqua}=G_{O2Air}+G_{O2sp}=\underline{237{,}19}+26{,}58=263.77\ ^{kJ}/_{mol}$.

$C_{gr}+2H_{2gas}\longrightarrow CH_{4gas}$; $\Delta G_H=G^{\circ}_{CH4gas}-(G^{\circ}_{Cgr}+2G^{\circ}_{H2})=G^{\circ}_{CH4gas}-(\mathbf{-671{,}3}+2*\underline{237{,}19/2})=-50{,}5\ ^{kJ}/_{mol}$;

$G^{\circ}_{CH4gas}=-50{,}5+(\mathbf{-671{,}3}+2*\underline{237{,}19/2})=-484.61\ ^{kJ}/_{mol}$; If biochemistry background level is $G^{\circ}_{CO2gas}=\mathbf{0}\ ^{kJ}/_{mol}$ Hess law give absolute free energy content $G_{Cgr}=-\Delta G^{\circ}_{Hess\_CO2gas}-G^{\circ}_{O2gas0}=\mathbf{394{,}36}-\underline{303{,}1}=\mathbf{91{,}26}\ ^{kJ}/_{mol}$,

$32H_{atomic}+15C_{gr}+23O_2\uparrow_{gas}\xrightarrow{Power\_Staition}15CO_2\uparrow_{gas}+16H_2O+\Delta G+Q$

Substance	$\Delta H^{\circ}_H\ ^{kJ}/_{mol}$	$\Delta S^{\circ}_H\ ^{J}/_{mol/K}$	$\Delta G^{\circ}_H\ ^{kJ}/_{mol}$
H_{atomic}	218.0	114.7	203.3

1.$\Delta H_H=15\Delta H^{\circ}_{CO2}+16\Delta H^{\circ}_{H2O}-32\Delta H^{\circ}_{H}-15\Delta H^{\circ}_{Cgr}-23\Delta H^{\circ}_{O2}=-17452.2$

$=15*-393{,}509+16*-285{,}85-(32*218+15*0+23*0)=-10476-6976=..\ ^{kJ}/_{mol}$

$\Delta S_H=15\Delta S^{\circ}_{CO2}+16\Delta S^{\circ}_{H2O}-32\Delta S^{\circ}_{H}-15\Delta S^{\circ}_{Cgr}-23\Delta S^{\circ}_{O2}=.........\ ^{J}/_{mol/K}$;

$=15*213{,}74+16*69{,}9565-(32*114{,}7+15*5{,}74+23*205{,}04)=4325{,}4-8472.42=-4147............\ ^{J}/_{mol/K}$;

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

$\Delta G_H=\Delta H_H-T*\Delta S_H=-17452{,}2-298{,}15*-4{,}147=-17452{,}2+1236{,}43=-16215.8..........\ ^{kJ}/_{mol}$ **exoergic**............

$T\bullet\Delta S_{total}=54388\ ^*298{,}15=$**+16215.8**........... $^{kJ}/_{mol}$ bound $T\Delta Sn\leftarrow$ lost free energy

Generator gas $\mathbf{6CO}\uparrow+\mathbf{6H_{2gas}}$ is home heating, street lightning fuel of 19th as 20th century beginning in Riga city.

$\mathbf{6\ CO}\uparrow_{gas}+\mathbf{6\ H_{2gas}}+\mathbf{6\ O_2}\uparrow_{gas}\xrightarrow{generator\text{-}gas}\mathbf{6CO_2}\uparrow_{gas}+6\ \mathbf{H_2O}\uparrow_{gas}+\Delta G+Q$ **exothermic**................

Substance	$\Delta H^{\circ}_H\ ^{kJ}/_{mol}$	$\Delta S^{\circ}_H\ ^{J}/_{mol/K}$	$\Delta G^{\circ}_H\ ^{kJ}/_{mol}$
$CO\uparrow_{gas}$	-110,525	197,674	-137,2
H_{2gas}	0	130,68	0
$O_2\uparrow_{gas}$	0	205,152	0
$H_2O\uparrow_{gas}$	-241,8352	188,74024	-228,6

$\Delta H_H=6\Delta H^{\circ}_{CO2}+6\Delta H^{\circ}_{H2O}-6\Delta H^{\circ}_{H2gas}-6\Delta H^{\circ}_{COgas}-6\Delta H^{\circ}_{O2gas}=\ ^{kJ}/_{mol}$

$=6*-393{,}509+6*-241{,}8352-(6*-110{,}53+6*0+6*0)=-3148.89\ ^{kJ}/_{mol}$

$=-3812{,}07+663{,}18=-3148.89$ **exothermic**........... $^{kJ}/_{mol}$

$\Delta S_{dispersed}=-\Delta H_H/T=--3148{,}89/298{,}15=10561.4........\ ^{J}/_{K/mol}$

$\Delta S_H=6\Delta S^{\circ}_{CO2}+6\Delta S^{\circ}_{H2O}-6\Delta S^{\circ}_{H2gas}-6\Delta S^{\circ}_{COgas}-6\Delta S^{\circ}_{O2gas}=\ ^{J}/_{K/mol}$

$...........=6*213{,}74+6*188{,}74024-(6*130{,}68+6*197{,}66+6*205{,}04)=2414{,}88-3200{,}28=-785.399\ ....\ ^{J}/_{mol/K}$.

3. $\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=-785{,}399+10561{,}4=9776...........\ ^{J}/_{mol/K}$

$\Delta G_H=\Delta H_H-T*\Delta S_H=-3148{,}89-298{,}15*-0{,}785399=-3148{,}89+234{,}16=-2914.72...........\ ^{kJ}/_{mol}$ **exoergic**....

$T\bullet\Delta S_{total}=9776^*298{,}15=$**+2914.7**........ $^{kJ}/_{mol}$ bound $T\Delta Sn\leftarrow$ dispersed-lost energy; 3. $\Delta G_{Hess}=\Delta H_{Hess}-T\bullet\Delta S_{Hess}$

Substance	$\Delta H^{\circ}_H\ ^{kJ}/_{mol}$	$\Delta S^{\circ}_H\ ^{J}/_{mol/K}$	$\Delta G^{\circ}_H\ ^{kJ}/_{mol}$
$C_{16}H_{32Liq}$	-328.7	587.9	-
CH_{4gas}	-74.6	186.3	-50.5
H_2O	-285.85	69.9565	-237,191
$CO_2\uparrow_{gas}$	-393.509	213.74	**-394.4**

hexadekene $\mathbf{C_{16}H_{32liq}}+24O_2\uparrow_{gas}\xrightarrow{burm}16CO_{2gas}+16H_2O+\Delta G+Q$

1. $\Delta H_{Hess}=\Sigma\Delta H^{\circ}_{products}-\Sigma\Delta H^{\circ}_{Reactants}$;2. $\Delta S_{Hess}=\Sigma\Delta S^{\circ}_{products}-\Sigma\Delta S^{\circ}_{Reactants}$

1.$\Delta H_H=16\Delta H^{\circ}_{CO2}+16\Delta H^{\circ}_{H2O}-\Delta H^{\circ}_{C16H32}-24\Delta H^{\circ}_{O2}=.........\ ^{kJ}/_{mol}$

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

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

2.$\Delta S_H=16\Delta S^{\circ}_{CO2}+16\Delta S^{\circ}_{H2O}-\Delta S^{\circ}_{C16H32}-24\Delta S^{\circ}_{O2}=.-969.716..........\ ^{J}/_{mol/K}$

$=16*213{,}74+16*69{,}9565-(24*205{,}04+587{,}9)=4539{,}14-5508{,}86=-969.716.........\ ^{J}/_{mol/K}$;

3. $\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=33050-969{,}716=32080.7...........\ ^{J}/_{mol/K}$;

3.$\Delta G_H=\Delta H_H-T*\Delta S_H=-10541-298{,}15*-0{,}969716=-10541+289{,}121=-10251.9..........\ ^{kJ}/_{mol}$ **exoergic**.............

$T\bullet\Delta S_{total}=34385*298{,}15=$**10251.9**............$^{kJ}/_{mol}$....bound $T\Delta Sn\leftarrow$ lost free energy

$\mathbf{C_{16}H_{32liq}}\ ^{kJ}/_{mol}/C/12=10251.9/16/12=53.4\ ^{kJ}/_{gC}$; C 12 $^{g}/_{mol}$ 1 Gt=$1*10^9*10^6$ g=$1*10^{15}$ g;

9.55 Gt=$9.55*10^9*10^6$ g=$9.55*10^{15}$ g; 9.55 Gt/12 Gkmol=$9.55/12*10^9*10^6$ mol=$9.55/12*10^{15}$ mol C;

$G_{Hess}=53.4\ ^{kJ}/_{gC}*9.55*10^{15}$ gC=53.4 *9.55*10^15= 510*10^15 kJ

Reakcija is lēna at pOH=5.9.okeānā ar hidroksīda anjonu

$\mathbf{CO_{2aqua}}+\mathbf{OH^-}+\mathbf{\Delta G}\Leftrightarrow\mathbf{HCO_3^-}+\mathbf{\Delta G}(\mathbf{-39.67}\ ^{kJ}/_{mol})+\mathbf{Q}$ ($\Delta H_{Hess}=\mathbf{-48.68}\ ^{kJ}/_{mol}$)

$\mathbf{CO_2}\uparrow_{gas}+\mathbf{\Delta G}(8.379\ ^{kJ}/_{mol})\Leftrightarrow\mathbf{CO_{2aqua}}+\mathbf{Q}(\Delta H_{Hess}=-20.3\ ^{kJ}/_{mol})$; Sum $\Delta H_{Hess}=-20{,}3\mathbf{-48{,}68}=-68.98\ ^{kJ}/_{mol}$;

THERMODYNAMICS Exercise II $\mathbf{CO_2}$ gas assimilation in water $\mathbf{CO_{2aqua}}$ reaction

$\mathbf{CO_2}\uparrow_{\mathbf{gas}}+\mathbf{H_2O}$ $+\mathbf{\Delta G}$ <=>$\mathbf{CO_{2aqua}}$ $\mathbf{+Q}$; $\mathbf{CO_2}\uparrow_{\mathbf{gas}}$ no act with $\mathbf{H_2O}$ but water soluble. (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? E3 class enzyme CA protolysis drive $\mathbf{CO_{2aqua}}$ with water $2\mathbf{H_2O}$ using table data! Will be **exoergic** or **endoergic**! $\mathbf{CO_2}\uparrow_{\mathbf{gas}}+\mathbf{\Delta G}$<=>$\mathbf{CO_{2aqua}+Q}$; $\mathbf{CO_{2aqua}}+2\mathbf{H_2O}+\mathbf{\Delta G+Q} \overset{CA}{=\!=}> \mathbf{H_3O^+ + HCO_3^-}$.

Substance	ΔH°_H $^{kJ}/_{mol}$	ΔS°_H $^{J}/_{mol/K}$	ΔG°_H $^{kJ}/_{mol}$
$\mathbf{CO_2}\uparrow_{gas}$	-393.509	213,74	-394,359
$\mathbf{H_2O}$	-285,85	69,9565	-237,191
$\mathbf{CO_{2aqua}}$	-413,7976	117,5704	-385,98

$\mathbf{CO_2}\uparrow_{gas}\mathbf{+H_2O+\Delta G} \xrightarrow{\text{Stomata\_Cell\_Membranes}} \mathbf{CO_{2aqua}+Q}$

$\Delta H_{hydratation}= -17{,}9$ $^{kJ}/_{mol}$; **hydratation** CRC 2010

$\Delta G_{sp}=\mathbf{\Delta G^\circ_{CO_2aqua}-\Delta G^\circ_{CO_2gas}-\Delta G^\circ_{H_2O}}=8.379$ $^{kJ}/_{mol}$

$\Delta G_{sp}=-385{,}98-(-394{,}359)=8.379$ $^{kJ}/_{mol}$ **endoergic**.........

$G_{\text{šķ}\mathbf{CO_2}}=\Delta G^\circ_{\mathbf{CO_2}aq}-\Delta G^\circ_{\mathbf{CO_2}gas}-\Delta G^\circ_{\mathbf{H_2O}}=-385{,}98+394{,}359+237{,}191=245{,}57$ $^{kJ}/_{mol}$;

$\mathbf{\Delta H_H=\Delta H^\circ_{CO_2aq}-\Delta H^\circ_{CO_2gas}-\Delta H^\circ_{H_2O}}=-413{,}7976-(-393{,}509-285{,}85)=$ -20.2886.......$^{kJ}/_{mol}$ **exothermic**...........

$\Delta S_{dispersed}= -\ \Delta H_H/\ T ==20{,}288/298.15= 67.746436$..........$^{J}/_{mol/K}$

$\Delta S_{dispersedHydratation}= -\Delta H_{hydratation}/\ T =17{,}9/298.15= 60.04$ ....$^{J}/_{mol/K}$

$\mathbf{\Delta S_H=\Delta S^\circ_{CO_2aqua}-\Delta S^\circ_{CO_2gas}}=117{,}57+69{,}9565-(213{,}74+69{,}9565)=-96.17$...........$^{J}/_{mol/K}$

$\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=-96{,}17+68{,}046 = -28.424$.....$^{J}/_{mol/K}$;

$\Delta S_{total}=\Delta S_{Hydratation}+\Delta S_{dispersed}=-96{,}17+60{,}04= -36.13$.....$^{J}/_{mol/K}$

$\mathbf{\Delta G_{Hess}=\Delta H_{Hess}-T^*\Delta S_{Hess}}=-20{,}1986-298.15^*-0{,}09617=8.3845$........ $^{kJ}/_{mol}$........**endoergic**...........

$\mathbf{\Delta G_{hydratationHess}=\Delta H_{hydratationHess}-T^*\Delta S_{hydratationHess}}=-17{,}9-298.15^*-96{,}17=+10.77$......... $^{kJ}/_{mol}$...**hydratation**..............

$T\bullet\Delta S_{total}=-28{,}124^*298{,}15K=$ **-8.385**....... $^{kJ}/_{mol}$; $T\bullet\Delta S_{total}=-36{,}13^*298{,}15K=$ **-10.77**....... $^{kJ}/_{mol}$

bound $T\Delta Sn\leftarrow$ $\underline{\text{accumulate energy } \Delta G_{reversereaction}}$ **not spontaneous** $\Delta G_{Hess}=8.3845$ $^{kJ}/_{mol}$. Mol fraction $\mathbf{X}^{\mathbf{CO_2}aqua}$:

solubility $\mathbf{K_{sp}}=\dfrac{X^{CO_2aqua}}{[CO_2\ gas]}=\dfrac{[CO_2\ aqua]}{[CO_2\ gas]\cdot[H_2O]}$ $=EXP(-\Delta \mathbf{G_{sp}}/R/T)=EXP(-8379/8{,}3144/298{,}15)=0.034045=1/29.375$;

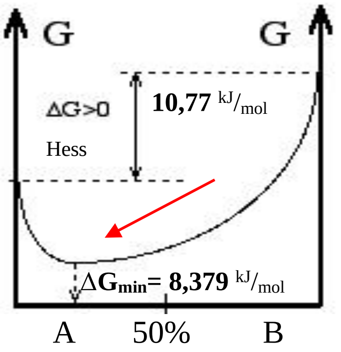
Unfavored $\mathbf{\Delta G_{sp}=-R\bullet T\bullet ln(K_{sp})}=-8{,}3144^*298{,}15^*\mathbf{ln}(0{,}034045)=8.379$ $^{kJ}/_{mol}$.

Exothermic and endoergic $[\mathbf{CO_2}\uparrow_{gas}]=1$ mol fraction 100% dissolution in to water $\mathbf{CO_{2aqua}}$ product Hess free energy change positive $\Delta_{\mathbf{Hess}}=10.77$........$^{kJ}/_{mol}$, but minimized $\mathbf{\Delta G_{min}=\Delta G_{sp}}=8.379$..... $^{kJ}/_{mol}$ reaching equilibrium mixture

Pure 100% $[\mathbf{CO_2}\uparrow_{gas}]$ gas; $[\mathbf{CO_{2aqua}}]=\mathbf{K_{sp}}^*1^*[\mathbf{H_2O}]=0.034045^*55.3=1.882$ M;

Equilibrium reaching is Prigogine attractor free energy change minimum $\mathbf{\Delta G_{min}}$. Air 0.04% mol fraction $[CO_2\uparrow_{\mathbf{air}}]=0.0004$ as 400 ppm units per milion air molecules, disolutes in water $[CO_{2\mathbf{aqua}}]$ as molarity $[CO_{2\mathbf{aqua}}]= 0.00075125$ M;

$[CO_{2aqua}]=K_{sp}^*[CO_2\uparrow_{\mathbf{air}}]^*[H_2O]=0{,}034045^*0{,}0004^*55{,}346=0.00075125$........M ;



$\mathbf{CO_2}\uparrow_{gas}$ reactants
produkti $\mathbf{CO_{2aqua}}$

CA carbonicanhydrase drive irreversible carbon dioxide reaction with two water molecules so increase ratio

$\mathbf{CO_{2aqua}}+2\mathbf{H_2O+\Delta G+Q} \overset{CA}{=\!=}> \mathbf{H_3O^+ + HCO_3^-}$:

$\dfrac{[HCO_3^-]_{aqua}\cdot[H_3O^+]}{[CO_2]_{aqua}\cdot[H_2O]^2}=\mathbf{K_{eq}}_{CAHCO_3aqua}=\mathbf{K_{a\_CO_2aqua}}/[\mathbf{H_2O}]^2=10^{-7.0512}/55.3^2=2.906^*10^{-11}$. CA equilibrium constant accumulate energy: $\mathbf{\Delta G_{eqCO_2aqua}=-R\bullet T\bullet ln(K_{eqCO_2aqua})}=-8{,}3144^*298{,}15^*ln(2{,}906^*10^\wedge(^{-11}))/1000=60.14$ $^{kJ}/_{mol}$.

$G_{\mathbf{H_3O+HCO_3}}=G_{\mathbf{H_3O+}}+G_{\mathbf{HCO_3-}}=22.44+46.08=\Delta \mathbf{G}_{spCO_2aqua}+\Delta\mathbf{G}_{eqCO_2aqua}=8.379+60.14=68.52$ $^{kJ}/_{mol}$. [1,8,14]

$K_{CO_2aqua}=[CO_{2aqua}+HCO_3^-]/[CO_2\uparrow_{air}]=0{,}023/0{,}00075125=30.6$ times.

Limestone, dolomite, chalk and marble bulk of rocks formation posible if $CO_2\uparrow_{air}$ carbonic dioxide from air 0.04% react with water by carbonic anhydrase CA.

On Earth this reaction drive E3 class enzyme hydrolases carbonic anhydrases CA .

THERMODYNAMICS Exercise III Bicarbonate $\mathbf{6HCO_3^-}$ $\mathbf{+6H_3O^+}$ photosynthesis to $\mathbf{6O_2}$ and $\mathbf{C_6H_{12}O_6}$

Calculate ΔH_H ΔS_H ΔG_H. Reaction is **exothermic** , **athermic**, **endothermic**? From water, Bicarbonate assimilation reaction in green plants with blue and red photon **E=h•v** absorption photosynthesis in photosynthetic reaction center PRC+**h•v** for $\mathbf{6O_{2}}_{aqua}$ and $\mathbf{C_6H_{12}O_6}$ at standard conditions 298.15 K! Will be **exoergic** or **endoergic**!

Substance	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$ kJ/mol
$\mathbf{C_6H_{12}O_6}$***aq***	-1263,78	269,45	-919,96
Glc	**-1267,13**	**-2901,49**	**-402,05**
$\mathbf{O_2}$***aqua***	-11,715	110,876	16,4
$\mathbf{O_2}$***aqua***	**-11.7**	**-94,2**	**16,4**
$\mathbf{H_2O}$	-285,85	69,9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{H_3O^+}$	-285,81	-3,854	-213,275
$\mathbf{HCO_3^-}$	-689,93	98,324	-586,94
$\mathbf{HCO_3^-}$	**-692,4948**	**-494,768**	**-544,9688**

$$6HCO_3^- + 6H_3O^+ + \Delta G + Q \xrightarrow{PRC+hv} C_6H_{12}O_6 + 6O_{2aqua} + 6H_2O$$

CRC 2010

2006, Maschusett’s Technology Inst. Alberty [8]

$\Delta H_H=\Delta H°_{C6H12O6}+6\Delta H°_{O2}+6\Delta H°_{H2O}-6\Delta H°_{H3O}-6\Delta H°_{HCO3}=\mathbf{2812.6}$ kJ/mol

$=\mathbf{-1267{,}13}+6*\mathbf{-11{,}7}+6*\mathbf{-286{,}65}-(6*\mathbf{-692{,}4948}+6*-285{,}81)=\mathbf{2812.6}$ kJ/mol

$\Delta G_H=\Delta G°_{C6H12O6}+6\Delta G°_{O2}+6\Delta G°_{H2O}-6\Delta G°_{H3O}-6\Delta G°_{HCO3}=\mathbf{3336.52}$ kJ/mol

$=\mathbf{-402{,}05}+6*\mathbf{16{,}4}+6*\mathbf{-151{,}549}-(6*\mathbf{-544{,}9688}+6*-213.275)=\mathbf{3336.5}$ kJ/mol

$\Delta S_H=\Delta S°_{C6H12O6}+6\Delta S°_{O2}+6\Delta S°_{H2O}-6\Delta S°_{H3O}+6\Delta S°_{HCO3}=\mathbf{-3194.1}$ J/mol/K

$=\mathbf{-2901{,}49}+6*\mathbf{-94{,}2}+6*\mathbf{-453{,}188}-(6*\mathbf{-494{,}768}+6*-3{,}854)=\mathbf{-3194.1}$ J/mol/K

$\Delta G_H=\Delta H_H-T*\Delta S_H=\mathbf{2812{,}6}-298{,}15*\mathbf{3{,}1941}=\mathbf{-3765}$ kJ/mol **endoergic**....

$\Delta S_{dispersed}=-\Delta H_H/T=\mathbf{-2812{,}6}*1000/298{,}15=\mathbf{-9433.51}$ J/mol/K; $\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=\mathbf{-3194{,}1-9433{,}51}=\mathbf{-12627.6}$ J/mol/K;

$T\bullet\Delta S_{total}=\mathbf{-12627{,}6}*298{,}15K=\mathbf{-3764.9}$ kJ/mol; bound $T\Delta S_{total}$accumulate energy in products .

page 3:. **not spontaneous, unfavored**.

Accumulate energy $T\Delta S_{total}=\mathbf{-3764.9}$ kJ/mol is bound in products: $\mathbf{C_6H_{12}O_6+6O_{2aqua}+6H_2O}$.....

BioFuel $\mathbf{C_6H_{12}O_6+6H_2O+6O_{2aqua}}$! $\mathbf{C_6H_{12}O_6+6O_{2aqua}+6H_2O \xrightarrow{Biooxidation} 6HCO_3^-+6H_3O^++\Delta G+Q}$

$\Delta H_H=6\Delta H°_{H3O}+6\Delta H°_{HCO3}-\Delta H°_{C6H12O6}-6\Delta H°_{O2}-6\Delta H°_{H2O}=6*\mathbf{-692{,}4948}+6*-285{,}81-(\mathbf{-1267{,}13}+6*\mathbf{-11{,}7}+6*\mathbf{-286{,}65})=\mathbf{-2812.6}$ kJ/mol

$\Delta G_H=6\Delta G°_{H3O}+6\Delta G°_{HCO3}-\Delta G°_{C6H12O6}-6\Delta G°_{O2}-6\Delta G°_{H2O}=6*\mathbf{-544{,}9688}+6*-213{,}275-(\mathbf{-402{,}05}+6*\mathbf{16{,}4}+6*\mathbf{-151{,}549})=\mathbf{-3336.5}$ kJ/mol

$\Delta S_H=6\Delta S°_{H3O}+6\Delta S°_{HCO3}-\Delta S°_{C6H12O6}-6\Delta S°_{O2}-6\Delta S°_{H2O}=6*\mathbf{-494{,}768}+6*-3{,}854-(\mathbf{-2901{,}49}+6*\mathbf{-94{,}2}+6*\mathbf{-453{,}188})=\mathbf{3194.1}$ J/mol/K

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

$\Delta S_{dispersed}=-\Delta H_H/T=\mathbf{2812{,}6}*1000/298{,}15=\mathbf{9433.51}$ J/mol/K; $\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=\mathbf{3194{,}1+9433{,}51=12627.6}$ J/mol/K;

$T\bullet\Delta S_{total}=\mathbf{12627{,}6}*298{,}15K=\mathbf{3764.9}$ kJ/mol; bound $T\Delta S_{total}$ dispersed energy to environment .

page 3:. Bio-Fuel $\mathbf{C_6H_{12}O_6+6O_{2aqua}+6H_2O}$ bound, dispersed energy $T\Delta S_{total}=\mathbf{3764.9}$ kJ/mol spent generating of $\mathbf{6HCO_3^-+6H_3O^+}$ in products concentration.

Generator gas $\mathbf{6CO}\uparrow\mathbf{+6H_{2}}_{gas}$ is home heating, street lightning fuel of 19th as 20th century beginning in Riga city.

$$6\,CO\uparrow_{gas} + 6\,H_{2gas} + 6\,O_2\uparrow_{gas} \xrightarrow{generator\text{-}gas} 6CO_2\uparrow_{gas} + 6\,H_2O\uparrow_{gas} + \Delta G + Q$$ **exothermic**................

Substance	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$ kJ/mol
$\mathbf{CO}\uparrow$***gas***	-110,525	197,674	-
$\mathbf{H_{2}}_{gas}$	0	130,68	0
$\mathbf{O_2}\uparrow$***gas***	0	205,04	**-61.166**
$\mathbf{H_2O}\uparrow$***gas***	-241,8352	188,74024	-

$\Delta H_H=6\Delta H°_{CO2}+6\Delta H°_{H2O}-6\Delta H°_{H2gas}-6\Delta H°_{COgas}-6\Delta H°_{O2gas}=$....... kJ/mol

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

$=-3812{,}07+663{,}18=-3148.89$ **exothermic**.................................. kJ/mol

2.$\Delta S_{dispersed}=-\Delta H_H/T=--3148{,}89/298{,}15=10561.4$......................... J/K/mol

2.$\Delta S_H=6\Delta S°_{CO2}+6\Delta S°_{H2O}-6\Delta S°_{H2gas}-6\Delta S°_{COgas}-6\Delta S°_{O2gas}=$.......... J/K/mol

...........$=6*213{,}74+6*188{,}74024-(6*130{,}68+6*197{,}66+6*205{,}04)=2414{,}88-3200{,}28=-785.399$ J/mol/K......................

3. $\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=-785{,}399+10561{,}4=9776$... J/mol/K

$\Delta G_H=\Delta H_H-T*\Delta S_H=-3148{,}89-298{,}15*-0{,}785399=-3148{,}89+234{,}16=-2914.72$..................kJ/mol **exoergic**....

$T\bullet\Delta S_{total}=9776*298{,}15=\mathbf{+2914.7}$.. kJ/mol bound $T\Delta Sn\leftarrow$ dispersed-lost energy

$$\mathbf{H_2O \xrightarrow{Biochemistry} H_2O};$$

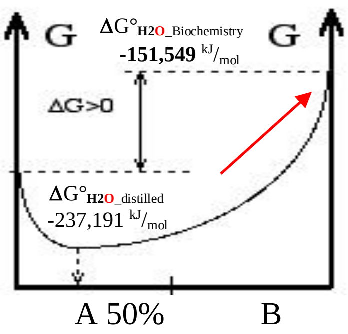
$G_{H2O\_Biochemistry}=\Delta G°_{H2O\_Biochemistry}-\Delta G°_{H2O\_distilled}=\mathbf{-151{,}549}-(-237{,}191)=\mathbf{85.64}$ kJ/mol.

Endothermic and endoergic free energy accumulation from biochemical medium:

osmolar concentration $C_{osm}=0.305$ M, ionic strength I=0.2 M, temperature 298.15 K

in water is positive $G_{H2O\_Biochemistry}=\mathbf{85.64}$ kJ/mol aktivation as selforganization for

Homeostasis. reactant H_2O =>produkt H_2O.



THERMODYNAMICS Exercise III B Glucose $\mathbf{C_6H_{12}O_6}$ oxidation by $\mathbf{6O_{2aqua}}$ to $\mathbf{6HCO_3^-}$ $\mathbf{+6H_3O^+}$

Calculate ΔH_H ΔS_H ΔG_H. Reaction is **exothermic** , **athermic**, **endothermic**? Glucose $\mathbf{C_6H_{12}O_6}$ oxidation by $\mathbf{6O_{2aqua}}$ to $\mathbf{6HCO_3^-}$ $\mathbf{+6H_3O^+}$ at standard conditions 298.15 K using the data table! Mention whether the reaction will be **exoergic** or **endoergic**! $\mathbf{C_6H_{12}O_6+6O_2 => 6CO_2+6H_2O}$ $\mathbf{+\Delta G+Q}$; $\Delta\mathbf{G}_{Lehninger}$=-2840 $^{kJ}/_{mol}$

Substance	$\Delta H°_H$ $^{kJ}/_{mol}$	$\Delta S°_H$ $^{J}/_{mol/K}$	$\Delta G°_H$ $^{kJ}/_{mol}$
$\mathbf{C_6H_{12}O_{6aq}}$	-1263,78	269,45	-919,96
Glc	**-1267,13**	**-2901,49**	**-402,05**
$\mathbf{O_{2aqua}}$	-11,715	110,876	16,4
$\mathbf{O_{2aqua}}$	**-11.7**	**-94,2**	**16,4**
$\mathbf{O_2}\uparrow_{gas}$	0	205,152	**-61.166**
$\mathbf{H_2O}$	-285,85	69,9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{H_3O^+}$	-285,81	-3,854	-213,274599
$\mathbf{CO_2}\uparrow_{gas}$	-393,509	213,74	-394,359
$\mathbf{CO_{2aq}}$	-413,798	117,5704	-385,98
$\mathbf{CO_{2aq}}$	–413.26	-119,36	-
$\mathbf{HCO_3^-}$	-689,93	98,324	-586,93988
$\mathbf{HCO_3^-}$	**-692,4948**	**-494,768**	**-544,9688**

$\mathbf{C_6H_{12}O_6+6O_{2aqua}+6H_2O => 6HCO_3^-+6H_3O^++\Delta G+Q}$

$\Delta G_H=6\Delta G°_{H3O}+6\Delta G°_{HCO3}-\Delta G°_{C6H12O6}-6\Delta G°_{O2}-6\Delta G°_{H2O}=^{kJ}/_{mol}$

=6*-586,93988+6*-213,274599-(-919,96+6*16,4+6*-237,191)=-2556.6

=6***-544,9688**+6*-213,274599-(**-402,05**+6***16,4**+6***-151,549**)=**-3336.5**

$\Delta H_H=6\Delta H°_{H3O}+6\Delta H°_{HCO3}-\Delta H°_{C6H12O6}-6\Delta H°_{O2}-6\Delta H°_{H2O}=^{kJ}/_{mol}$

=6*-689,93+6*-285,81-(-1263,78+6*-11,715+6*-285,85)=-2805.3

=6***-692,4948**+6*-285,81-(**-1267,13**+6***-11,7**+6***-286,65**)=**-2812.6**

$\Delta S_H=6\Delta S°_{H3O}+6\Delta S°_{HCO3}-\Delta S°_{C6H12O6}-6\Delta S°_{O2}-6\Delta S°_{H2O}$=-787 $^{J}/_{mol/K}$

=6*98,324+6*-3,854-(269,45+6*110,876+6*69,9565)=-787.625 $^{J}/_{mol/K}$

=6***-494,768**+6*-3,854-(**-2901,49**+6***-94,2**+6***-453,188**)=**3194.1**

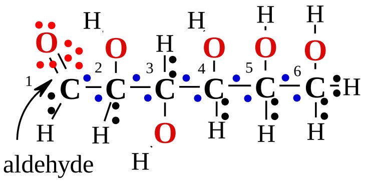
Alb$\Delta G_H=\Delta H_H-T*\Delta S_H$=-2805,27-298,15*-0,787625=-2570.4 $^{kJ}/_{mol}$

$\Delta G_H=\Delta H_H-T*\Delta S_H$=**-2812,6**-298,15***-3,1941**=**-3764.92** $^{kJ}/_{mol}$

CRC102. $\Delta S_{dispersed}=-\Delta H_H/T$=-2805,3/298,15=9409 $^{J}/_{mol/K}$

B06; $\Delta S_{dispersed}=-\Delta H_H/T$=**2812,6**/298,15=**9433.5** $^{J}/_{mol/K}$

page 1:. Bio-Fuel ($\mathbf{C_6H_{12}O_6+6H_2O}$) $\mathbf{+6O_{2aqua}}$ photosynthesis bound energy $T\Delta S_{total}=\Delta\mathbf{G}_{Lehninger}$=+2840 $^{kJ}/_{mol}$ produce life resources $\mathbf{C_6H_{12}O_6+6H_2O}$ $\mathbf{+6O_{2aqua}}$ and are used by oxidation to generating concentrations gradients of $\mathbf{6HCO_3^-}$ $\mathbf{+6H_3O^+}$ in products for osmosis against and transportation down the gradients through membranes.



$\mathbf{C_6H_{12}O_6}+6\mathbf{O_{2aqua}}+6\mathbf{H_2O}$=>$6H_3O^++6HCO_3^-$=>$6\mathbf{CO_{2aqua}}+12\mathbf{H_2O}$=>$6\mathbf{CO_{2gas}}\uparrow+12\mathbf{H_2O}$.

Glucose 7 C:-H, 5 C●-●C: 7*2+5*2=24 electrons Reduction potential:

$\mathbf{E°_{C6H12O6}}$=0.1392 V 4th page $24H_3O^++6H_3O^++6HCO_3^-+24\ e^-$<=>$\mathbf{C_6H_{12}O_6+42H_2O}$;

-2840 $^{kJ}/_{mol}$=$\Delta\mathbf{G}_{Lehninger}$=$\mathbf{\Delta G_{eq}=\Delta E°•F•n=(E°_{C6H12O6}-E°_{O2})•F•n=}$(0.1392-1.0868)**•F•n**;

$\mathbf{\Delta G_{eq}/F/n=(E_{C6H12O6}-E_{O2})=\Delta E=}$-2840000/96485/24=($\mathbf{E_{C6H12O6}}$-1,0868)=-0,9476 V;

Attractors pH=7,36 and $[O_{2aqua}]=6*10^{-5}$ M reduction potential is strong $\mathbf{E_{C6H12O6}=\Delta E+E_{O2}}$=-0,9476+1.0868=**0.1392** V;

$[H_3O^+]=10^{-7,36}$ M, $[O_{2aq}]=6*10^{-5}$M; $E_{O2}=E°+^{0,0591}/_4•\log([O_{2aqua}]•[H_3O^+]^4/_{[H2O]^5})=$

=**0,1392**+$^{0,0591}/_{24}$*log(6*10^(-5)*10^(-7,36*4)/55,3^5)=**0,03485** V

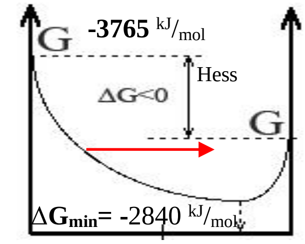
Oxidised form: 6*($\mathbf{O_{2aqua}+4H_3O^++4e=5H_2O}$) Suchotin absolute inverse standard potential $\mathbf{-E°_{O2}}$=-1,0868 V; [17]

$\Delta G_{Hess}=\Delta H_H-T*\Delta S_H$=**-2812,6**-298,15***3,1941**=**-3764.92** $^{kJ}/_{mol}$;

│ΔG_{Heas}=**-3764.92** $^{kJ}/_{mol}$ │>│ $\Delta\mathbf{G}_{Lehninger}$=-2840 $^{kJ}/_{mol}$ │;

$\mathbf{\Delta G_{eq}=-R•T•ln(K_{eq})}$=-8,3144•298,15•**ln**($10^{497,55}$)=-2840 $^{kJ}/_{mol}$

Exothermic and exoergic oxidation Hess free energy change negative for gas $6\mathbf{O_2}$, $6\mathbf{CO_2}$ $\Delta\mathbf{G_{oxidation}}$=**-2873** $^{kJ}/_{mol}$ so $\Delta\mathbf{G_{oxidation}}$=**-2921.5** $^{kJ}/_{mol}$ more for aqua both $6\mathbf{O_{2aqua}}$, $6\mathbf{CO_{2aqua}}$, $\Delta\mathbf{G_{oxidation}}$=**-2971.8** $^{kJ}/_{mol}$ for $6\mathbf{O_{2aqua}}$, $6\mathbf{CO_{2gas}}$, $\Delta\mathbf{G_{oxidation}}$=**-3765** $^{kJ}/_{mol}$ for $6H_3O^+$,$6HCO_3$, but minimizes $\Delta\mathbf{G_{min}}=\Delta\mathbf{G_{eq}}$= -2840 $^{kJ}/_{mol}$ reaching quasi equilibrium mixture for 13 reactants $\mathbf{C_6H_{12}O_6+6O_{2aqua}+6}H_2O$ and 12 products $\mathbf{6H_3O^++6HCO_3^-}$



A+6B+6C 50%   6D+6E

$\mathbf{C_6H_{12}O_6+6O_{2aqua}}+6\mathbf{H_2O}$

reactants products

$6\mathbf{H_3O^+}+6\mathbf{HCO_3^-}$

$$EXP(-\Delta\mathbf{G}_{Lehninger}/R/T)=EXP(2840/8,314/298,15)=10^{498}=\mathbf{K_{eq}}=\frac{[HCO_3^-]^6_{aqua}\cdot[H_3O^+]^6}{[C_6H_{12}O_6]\cdot[O_{2\,aqua}]^6\cdot[H_2O]^6}$$

Homeostasis Quasi Equilibrium is Prigogine attractor free energy change $\Delta\mathbf{G_{min}}$. minimum Free energy minimum reaching establishes homeostasis quasi equilibrium mixture. $\mathbf{K_{eq}}$.

Photosynthesis 1st page. accumulate free energy in life resources $\mathbf{C_6H_{12}O_6}+6\mathbf{O_{2aqua}}+6\mathbf{H_2O}$ $\Delta\mathbf{G}_{Lehninger}$ =2840 $^{kJ}/_{mol}$; from zero level protolysis products create $6*G_{H3O+HCO3-}$=6*68,38 $^{kJ}/_{mol}$ =411.12 $^{kJ}/_{mol}$ with protolytic activate reach quasi state equilibrium $\Delta\mathbf{G}_{Lehninger}=\mathbf{G_{C6H12O6}+6}G_{O2Biochem\_arterial}\mathbf{+6}G_{H2O\_Bioķīmija}-6G_{H3O+HCO3-}$=2840 $^{kJ}/_{mol}$ and generate glucose free energy content $\mathbf{G_{C6H12O6}}$=2840-6*78.08-6***85.64**+6*68.52=2840-468,48-513,84+411,12=2268.8 $^{kJ}/_{mol}$ to glucose with reduction potential $\mathbf{E_{C6H12O6}}$=-0.**884** V at attractor values $[H_3O^+]=10^{-7,36}$ M, $[O_{2aq}]=6*10^{-5}$M.

Calculate ΔH_H ΔS_H ΔG_H at standard conditions 298.15 K. Reaction is **exothermic** , **athermic**, **endothermic**?
Beta oxidation in mitochondria, peroxysomes of palmitic acid with $\mathbf{O_2}_{aqua}$ standard conditions (25°C) 298.15 K, using data on table! Will reaction **exoergic** or **endoergic**! Reactants =>products bicarbonate +hydronium ions

$\mathbf{C_{16}H_{32}O_{2s}}+16\mathbf{H_2O}+23\mathbf{O_2}_{aqua}=16\mathbf{HCO_3^-}\ |+16\mathbf{H_3O^+}=16\mathbf{CO_2}_{aqua}+32\mathbf{H_2O}=16\mathbf{CO_2}_{gas}\uparrow+32\mathbf{H_2O}$; $\Delta\mathbf{G}_{Lehninger}=-9770\ ^{kJ}/_{mol}$

Substance	$\Delta H°_H\ ^{kJ}/_{mol}$	$\Delta S°_H\ ^{J}/_{mol/K}$	$\Delta G°_H\ ^{kJ}/_{mol}$
$\mathbf{C_{16}H_{32}O_2}$	-	-	**1067,2384**
$\mathbf{C_{16}H_{32}O_{2s}}$	-891,5	452,4	-
$\mathbf{C_{16}H_{32}O_{2liq}}$	-838,1	-	1003,54
$\mathbf{O_2}_{aqua}$	-11,715	110,876	16,4
$\mathbf{O_2}_{aqua}$	**-11,7**	**-94,2**	**16,4**
$\mathbf{O_2}\uparrow_{gas}$	0	205,152	**-61.166**
$\mathbf{H_2O}$	-285,85	69,9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{H_3O^+}$	-285,81	-3,854	-213,2746
$\mathbf{CO_2}\uparrow_{gas}$	-393,509	213,74	-394,359
$\mathbf{CO_2}_{aq}$	-413,798	117,5704	-385,98
$\mathbf{CO_2}_{aq}$	–413.26	-119,36	-
$\mathbf{HCO_3^-}$	-689,93	98,324	-586,93988
$\mathbf{HCO_3^-}$	**-692,4948**	**-494,768**	**-544,9688**

<u>biooxidation</u> mitochondria, peroxysomes
1. $\Delta H_{Hess}=\Sigma\Delta H°_{products}-\Sigma\Delta H°_{Reactants}$
2. $\Delta S_{Hess}=\Sigma\Delta S°_{products}-\Sigma\Delta S°_{Reactants}$; 3. $\Delta G_H=\Delta H_H-T\bullet\Delta S_H$

2. $\Delta S_{dispersed}=-\Delta H_H/T=9930{,}7/298{,}15=3337.7\ ^{J}/_{mol/K}$;**33224.5**
$\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=33307{,}7-2610{,}33=30697.47\ ^{J}/_{mol/K}$;
$\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=\mathbf{33224{,}5+987{,}26=34211.76}\ ^{J}/_{mol/K}$;
$\Delta G_H=\Delta H_H-T*\Delta S_H=-9930{,}7-298{,}15*-2{,}61933=-9152.5\ ^{kJ}/_{mol}$;
$\Delta G_H=\Delta H_H-T*\Delta S_H=\mathbf{-9905{,}9}-298{,}15*\mathbf{0{,}987256}=\mathbf{-10200.2}\ ^{kJ}/_{mol}$;
$T\bullet\Delta S_{total}=30{,}69747^{*}298{,}15=9152.5\ ^{kJ}/_{mol}$ <u>lost free energy</u>
$T\bullet\Delta S_{total}=\mathbf{34{,}21173}^{*}298{,}15=\mathbf{10200.2}\ ^{kJ}/_{mol}$ <u>lost free energy</u>
CRC102.
B06;

$\Delta G_H=16\Delta G°_{HCO3}+16\Delta G°_{H3O}-\Delta G°_{C16H32O2}-16\Delta G°_{H2O}-23\Delta G°_{O2}=\ ^{kJ}/_{mol}$;
$=16*-586{,}93988+16*-213{,}2746-(16*-237{,}191+23*16{,}4+1003{,}54)=-10389\ ^{kJ}/_{mol}$;
$=16*\mathbf{-544{,}9688}+16*-213{,}2746-(16*\mathbf{-151{,}549}+23*\mathbf{16{,}4}+\mathbf{1067{,}2384})=\mathbf{-11151{,}55}\ ^{kJ}/_{mol}$;
$\Delta G_H=16\Delta G°_{CO2aqua}+32\Delta G°_{H2O}-\Delta G°_{C16H32O2}-16\Delta G°_{H2O}-23\Delta G°_{O2}=\ ^{kJ}/_{mol}$;
$=16*-385{,}98+32*-213{,}2746-(16*-237{,}191+23*16{,}4+1003{,}54)=-10386\ ^{kJ}/_{mol}$;
$=16*-385{,}98+32*-213{,}2746-(16*\mathbf{-151{,}549}+23*\mathbf{16{,}4}+\mathbf{1067{,}2384})=\mathbf{-12020}\ ^{kJ}/_{mol}$;
$\Delta G_H=16\Delta G°_{CO2gas}+32\Delta G°_{H2O}-\Delta G°_{C16H32O2}-16\Delta G°_{H2O}-23\Delta G°_{O2}=\ ^{kJ}/_{mol}$;
$=16*-394{,}359+32*-213{,}2746-(16*-237{,}191+23*16{,}4+1003{,}54)=-10720\ ^{kJ}/_{mol}$;
$=16*-394{,}359+32*-213{,}2746-(16*\mathbf{-151{,}549}+23*\mathbf{16{,}4}+\mathbf{1067{,}2384})=\mathbf{-12154}\ ^{kJ}/_{mol}$;
$\Delta H_H=16\Delta H°_{HCO3}+16\Delta H°_{H3O}-\Delta H°_{C16H32O2}-16\Delta H°_{H2O}-23\Delta H°_{O2}=\ ^{kJ}/_{mol}$;
$=16*-689{,}93+16*-285{,}81-(16*-285{,}85+23*-11{,}715-838{,}1)=-9930{,}7\ ^{kJ}/_{mol}$ exothermic;
$=16*\mathbf{-692{,}4948}+16*-285{,}81-(16*\mathbf{-286{,}65}+23*\mathbf{-11{,}7}-891.5)=\mathbf{-9905{,}9}\ ^{kJ}/_{mol}$ exothermic;
$\Delta S_H=16\Delta S°_{HCO3}+16\Delta S°_{H3O}-\Delta S°_{C16H32O2}-16\Delta S°_{H2O}-23\Delta S°_{O2}=\ ^{J}/_{mol/K}$;
$=16*98{,}324+16*-3{,}854-(16*69{,}9565+23*110{,}876+452{,}4)=-2619{,}33\ ^{J}/_{mol/K}$;
$=16*\mathbf{-494{,}768}+16*-3{,}854-(16*\mathbf{-453{,}188}+23*\mathbf{-94{,}2}+452{,}4)=\mathbf{987{,}256}\ ^{J}/_{mol/K}$;

$$\Delta\mathbf{G}_{eq}=\mathbf{-R\bullet T\bullet ln(K_{eq})}=-8{,}3144\bullet298{,}15\bullet\mathbf{ln}(10^{1711{,}6428})=-9770\ ^{kJ}/_{mol}$$

Exothermic and exoergic palmitate oxidation Hess free energy change negative for aqua

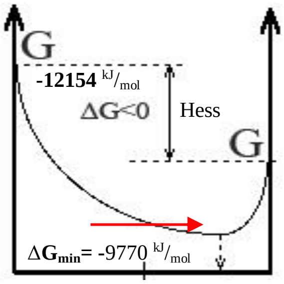
$\mathbf{O_2}_{aqua}$ > for gas $\mathbf{CO_2}_{gas}\uparrow$ $\Delta\mathbf{G}_{oxidation}=\mathbf{-12154}\ ^{kJ}/_{mol}$ and

$\Delta\mathbf{G}_{oxidation}=\mathbf{-12020}\ ^{kJ}/_{mol}$ for both aqua $\mathbf{O_2}_{aqua}$ and $\mathbf{CO_2}_{aqua}$, but minimizes

$\Delta\mathbf{G}_{min}=\Delta\mathbf{G}_{eq}=-9770\ ^{kJ}/_{mol}$ reaching equilibrium mixture

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

$\mathbf{C_{16}H_{32}O_2}+23\mathbf{O_2}$ A+23B reactants



A+23B 50%
16C+16D
products 16C+16D
$16\mathbf{CO_2}+16\mathbf{H_2O}$

Equilibrium reaching is Prigogine attractor free energy change minimum $\Delta\mathbf{G}_{min}$.

Free energy minimum reaching establishes equilibrium mixture.

THERMODYNAMICS IV Vitamin B3 ethanol $\mathbf{H_3C\text{-}CH_2\text{-}OH}$ oxidation to ethanal $\mathbf{H_3C\text{-}CH{=}O}$ aerobic Calculate ΔH_H ΔS_H ΔG_H at standard conditions 298.15 K . Reaction is **exothermic** , **athermic**, **endothermic**? Vitamin B3 for anaerobic ethanal reduction to ethanol product with alcohol dehydrogenase using the data table! Mention whether will be **exoergic** or **endoergic**! $\mathbf{H_3C\text{-}CH_2\text{-}OH}+NAD^+\mathbf{+H_2O}+\Delta\mathbf{G+Q}$ => $\mathbf{H_3C\text{-}CH{=}O}+NAD\mathbf{H+H_3O^+}$

Substance	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
$\mathbf{H_3C\text{-}CH{=}O}$	-212,23	-281,84	24,06
$\mathbf{H_3C\text{-}CH{=}O}$	**-213,88**	**-825,64**	**32,2824**
NAD**H**	**-41,41**	**-4465,708**	**1175,5732**
NAD**H**	-1036,66	-140,50	1120,09
$\mathbf{H_3O^+}$	-285.81	-3.854	-213,275
NAD^+	**-10,30**	**-3766,008**	**1112,534**
NAD^+	-1007,48	-183	1059,11
$\mathbf{H_3CH_2OH}$	**-290,77**	**-1227,764**	**75,2864**
$H_3CH_2OH_{aq}$	-288,3	-357,7394	-181,64
$\mathbf{H_2O}$	-285.85	69.9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**

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$\Delta H_{Hess}=\Delta H^\circ_{\mathbf{H3O}}+\Delta H^\circ_{\mathbf{CH3CHO}}+\Delta H^\circ_{\mathbf{NADH}}-\Delta H^\circ_{\mathbf{CH3CH2OH}}-\Delta H^\circ_{\mathbf{H2O}}-\Delta H^\circ_{\mathbf{NAD+}}=$

$=\mathbf{-213{,}88}-1036{,}66-285{,}81-(-288{,}3-1007{,}48-285.85)=45{,}28$ kJ/mol

BioThermodyn06;$\Delta S_{dispersed}=-\Delta H_H/T=-45{,}28/298.15=-151{,}9$ J/mol/K

$\Delta S_{Hess}=\Delta S^\circ_{\mathbf{H3O}}+\Delta S^\circ_{\mathbf{CH3CHO}}+\Delta S^\circ_{\mathbf{NADH}}-\Delta S^\circ_{\mathbf{CH3CH2OH}}-\Delta S^\circ_{\mathbf{H2O}}-\Delta S^\circ_{\mathbf{NAD+}}=$

$=\mathbf{-825{,}64}-140{,}50-3{,}854-(-357{,}7394-183+69{,}9565)=-499{,}211$ J/mol/K

BioThermodynamic,2006,Massachusetts Tecnology Institute,Alberty

$\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=-151{,}9-499{,}211=-651{,}111$ J/mol/K

$\Delta G_H=\Delta H_H-T^*\Delta S_H=45{,}28-298{,}15^*-0{,}499211=194{,}12$ kJ/mol endoergic

pH=7,36 $T\bullet\Delta S_{total}=0{,}651111^*298{,}15=\mathbf{-194{,}1}$ kJ/mol

$\Delta G_{Hess}=\Delta G^\circ_{\mathbf{H3O}}+\Delta G^\circ_{\mathbf{CH3CHO}}+\Delta G^\circ_{\mathbf{NADH}}-\Delta G^\circ_{\mathbf{CH3CH2OH}}-\Delta G^\circ_{\mathbf{H2O}}-\Delta G^\circ_{\mathbf{NAD+}}=$

The standard **E°** in **Volts** from David Harris; KortlyShucha

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

Red NADH <=> $\mathbf{NAD^+}$ + $\mathbf{H^-(2e^-)}$; absolute potential $\mathbf{E^\circ_{NADH}}=-0{,}4095$ V; David Harris; [22];

Ox $\mathbf{CH_3CHO+2H_3O^++H^-(2e^-)}$<=>$\mathbf{CH_3CH_2OH+2H_2O}$; absolute potential $\mathbf{E^\circ_{CH3CH2OH}}=-0{,}055$ V; [19].

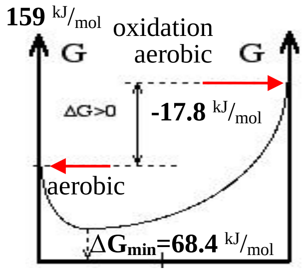
sum $\mathbf{NAD^+}+\mathbf{CH_3\text{-}CH_2\text{-}OH+H_2O{=}{>}NADH+CH_3\text{-}HC{=}O+H_3O^+}$;

By convention balanced **n=2=m** number of electrons $\mathbf{2e^-\Delta E^\circ}$ is expressed as $\mathbf{E^{\circ 2}_{H2O}}$ of the electron **donor** minus $\mathbf{E^{\circ 1}}$ of the electron **acceptor**. Because $\mathbf{NAD^+}$ is **accepting** electrons from **ethanol** in our example

$\mathbf{\Delta G_{min}=\Delta G_{eq}=(\ E^\circ_{NAD+}-E^\circ_{eqNernsCH3CH2OH})^*F^*n}=(-0{,}4095+0{,}055)^*96485^*2=(\mathbf{-0{,}3545})^*\ 96485^*2=\mathbf{-68{,}408}$ kJ/mol;

$$\frac{[\mathrm{NADH}]\cdot[\mathbf{CH_3CHO}]\cdot[\mathbf{H_3O^+}]}{[\mathrm{NAD^+}]\cdot[\mathbf{CH_3CH_2OH}]\cdot[\mathbf{H_2O}]}=\mathbf{K_{eq}}{}_{AerobicOx}=EXP(-\Delta\mathbf{G}_{eq}/R/T)=EXP(-68400/8{,}3144/298{,}15)=\mathbf{19.65\bullet10^{11}=10}^{-12};$$

$\mathbf{O_2}{}_{aqua}$ ratio $[\mathbf{NADH}]/[\mathbf{NAD^+}]=10^{-6}$ with pH=7.36 favored free energy change negative $\Delta\mathbf{G}_{aerobicOx}=68{,}4+8{,}3144^*298{,}15^*\ln(1/10\text{^}6^*1/1^*10\text{^}(^{-7{,}36})/55{,}3457)/1000=-17{,}85$ kJ/mol ; $\Delta\mathbf{G}_{eq}=\mathbf{68{,}4}-86{,}21=-17.85$ kJ/mol, $[\mathbf{NADH}]/[\mathbf{NAD^+}]=10^{-5}$; $\Delta\mathbf{G}_{eq}=\mathbf{68{,}4}-80{,}5=-12.14$ kJ/mol. negative. Aerobic endothermic and endoergic $\mathbf{H_3CCH_2OH}$ **ethanol** oxidation Hess law free energy change positive $\Delta\mathbf{G_{HessOx}}=159$........kJ/mol inverse to $\mathbf{H_3CCH{=}O}$ **ethanal** anaerobic reduction negative $\Delta\mathbf{G_{HessRed}}=-159$........kJ/mol , but minimized inverse in aerobic oxidation $\Delta\mathbf{G_{min}}=\Delta\mathbf{G_{eq}}{}_{Aerobic}\mathbf{_{Ox}}=68{,}4$ kJ/mol , $\Delta\mathbf{G_{min}}=\Delta\mathbf{G}_{eqAnaerobic}\mathbf{_{Red}}=-68{,}4$ kJ/mol reduction reaching equilibrium mixture constants $\mathbf{10}^{-12}=\mathbf{K_{eq}}{}_{Aerobic}$ **ethanol** oxidation and **ethanal** reduction anaerobic $\mathbf{10}^{12}=\mathbf{K_{eq}}{}_{Anaerobic}$.



A+B+C50%D+E+F

$NAD^++H_3CCH_2OH+H_2O$

$NADH+H_3CCHO+H_3O^+$

Prigogine attractor is free energy change absolute minimum at Equilibrium

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

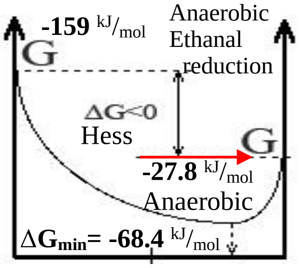
$\mathbf{H_3C\text{-}CH{=}O}+NAD\mathbf{H+H_3O^+}$ =>$\mathbf{H_3C\text{-}CH_2\text{-}OH}+NAD^+\mathbf{+H_2O}+\Delta\mathbf{G+Q}$;

Anaerobic $\mathbf{\Delta G}_{eq}=\mathbf{\Delta}E^\circ\bullet F\bullet n=-0{,}3545\ V\bullet2\ mol\bullet96485$ C/mol$=-68{,}4$ kJ/mol favored.

Insufficient low $\mathbf{O_2}{}_{aqua}$ concentration hypoxia to anaerobic alcohol oxidation unfavored but ethanal reduction to ethanol favored ratio $[\mathbf{H_3CCH_2OH}]/[\mathbf{H_3CCH{=}O}]=1/10$ **homeostasis** anaeirobic ratio $[\mathbf{NAD^+}]/[\mathbf{NADH}]=1/10$ with pH=7,36 negative free energy change :

$\Delta\mathbf{G}_{anaerobic}\mathbf{_{Red}=}-68{,}4+8{,}3144^*298{,}15^*\ln(1/10^*1/10^*55{,}3457/10\text{^}(^{-7{,}36}))/1000=\mathbf{-27.8}$ **kJ/mol**

$$\Delta\mathbf{G}_{Anaerobic}\mathbf{_{Red}=-68{,}4}+8{,}3144^*298{,}15^*\mathbf{ln}\left(\frac{1}{10}\,\frac{10}{1}\,\frac{55.333}{10^{-7.36}}\right)=\mathbf{-16.4}\ \mathbf{kJ/mol}\ ;$$



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

$NADH+H_3CCHO+H_3O^+$

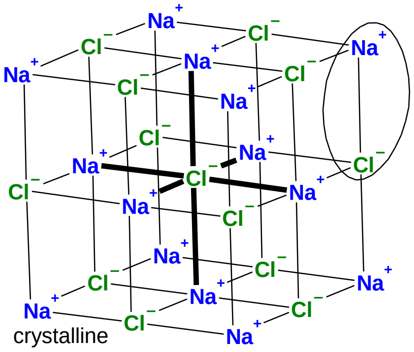
$NAD^++H_3CCH_2OH+H_2O$

$$\mathbf{K}_{Anaerobic}\mathbf{_{Red}}=10^{12}=\frac{[\mathrm{NAD^+}]\cdot[\mathbf{CH_3CH_2OH}]\cdot[\mathbf{H_2O}]}{[\mathrm{NADH}]\cdot[\mathbf{CH_3CHO}]\cdot[\mathbf{H_3O^+}]}\ ;\ \mathbf{K}_{Aerobic}\mathbf{_{Ox}}=10^{-12}=\frac{[\mathrm{NADH}]\cdot[\mathbf{CH_3CHO}]\cdot[\mathbf{H_3O^+}]}{[\mathrm{NAD^+}]\cdot[\mathbf{CH_3CH_2OH}]\cdot[\mathbf{H_2O}]}\ ;\ \text{favored oxidation}$$

$[NADH]/[NAD^+]=1/7700$; $\Delta\mathbf{G}_{Aerobic}\mathbf{_{Red}}=68{,}4+8{,}3144^*298{,}15^*\ln(1/7700^*1/10^*10^{-7{,}36}/55{,}3457)/1000=\mathbf{-11.5}$ kJ/mol.

THERMODYNAMICS Exercise V For crystalline salt $\mathbf{Na}^{+}\mathbf{Cl}^{-}$ $^{\mathbf{and}}$ dissociation reaction with water

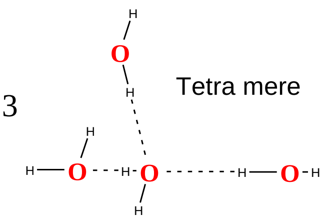
Salt $\mathbf{Na}^{+}\mathbf{Cl}^{-}$ hydration with 36 $^{g}/_{100g}$ solubility in 100 g water, density of solution 1,203 $^{g}/_{mL}$; w%=26,4706 %:
$\mathbf{Na}^{+}\mathbf{Cl}^{-}+3\ (\mathbf{H_2O})_4 \Rightarrow [6\mathbf{H_2O{:}{=}{>}Na}^{+}]_{aqua} + [\mathbf{Cl}^{-}{<}{=}6\mathbf{H_2O}]_{aqua}$ resource account nc=49,142/12=4,0952 .M.
1. First factor **coordination** sodium and chloride ions consume 12 water molecules: products $\mathbf{Na}^{+}_{aq}+\mathbf{Cl}^{-}_{aq}$

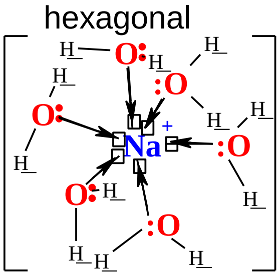


Water molecules

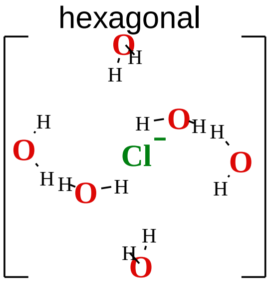
three tetra meres

$+\ 3\ (\mathbf{H_2O})_4 \ \Rightarrow$





+



$[6\mathbf{H_2O{:}{=}{>}Na}^{+}]_{aqua} \quad + \quad [\mathbf{Cl}^{-}{<}{=}6\mathbf{H_2O}]_{aqua}$

1. $\mathbf{Na}^{+}\mathbf{Cl}^{-}\Rightarrow\mathbf{Na}^{+}+\ \mathbf{Cl}^{-}$; energy $\Delta G_{\mathbf{Na+Cl-}} = 700\ ^{kJ}/_{mol}$; Ionu crystalline destruction.
2. $3(\mathbf{H_2O})_4\Rightarrow 12\mathbf{H_2O}$; energy $3{*}\Delta G_{(\mathbf{H_2O})_4}=3{*}90=270\ ^{kJ}/_{mol}$; Tetra mer destruction.
3. $\mathbf{Na}^{+}+6\mathbf{H_2O}\Rightarrow[6(\mathbf{H_2O{:}}\rightarrow\square)\text{-}\mathbf{Na}^{+}]$ energy $6{*}\Delta G_{[\mathbf{H_2O{:}{=}{>}Na+}]}=6{*}{-400}={-2400}\ ^{kJ}/_{mol}$; Coordination hexagonal.
4. $\mathbf{Cl}^{-}+6\mathbf{H_2O} \Rightarrow [\mathbf{Cl}^{-}\text{-}(....6\mathbf{H_2O})]$ energy $6{*}\Delta G_{[\mathbf{Cl}\text{--}(....\mathbf{H_2O})]}=6{*}{-30}={-180}\ ^{kJ}/_{mol}$; Six hydrogen bons creation.

$$\Delta G_{reaction}=\Delta G_{\mathbf{Na+Cl-}}+3{*}\Delta G_{(\mathbf{H_2O})_4}+6{*}\Delta G_{[\mathbf{H_2O{:}{=}{>}Na+}]}+6{*}\Delta G_{[\mathbf{Cl}\text{--}(....\mathbf{H_2O})]}=700+270-2400-180= -1610\ ^{kJ}/_{mol}\ ;$$

Dissociation degree $\boldsymbol{\alpha}$=4,0952/5,4434=75,2 % crystalline $\mathbf{NaCl}_{aqua}+\mathbf{Q}\Rightarrow\mathbf{Na}^{+}_{aqua}+\mathbf{Cl}^{-}_{aqua}+\Delta G$; and solubility product $\mathbf{K_{sp}}=\mathbf{K_{eq}}=[\mathbf{Na}^{+}{}_{aq}]{*}[\mathbf{Cl}^{-}{}_{aq}]/[\mathbf{NaCl}_{aq}]= =4{,}0952{*}4{,}0952/1{,}3482=12{,}4393$ reactants and products free emergy change negative: $\Delta\mathbf{G_{sp}}=\mathbf{-R{\bullet}T{\bullet}ln(K_{sp})}=-8{,}3144{\bullet}298{,}15{\bullet}\mathbf{ln}(12{,}44)=-6{,}25\ ^{kJ}/_{mol}$, **;**

$$\Delta G_{Hess}=\Delta H_{Hess}-T{*}\Delta S_{Hess}=3{,}82-298{,}15{*}0{,}0435 = -9{,}15.......\ ^{kJ}/_{mol}\ \textbf{exoergic}..$$

Substance	$\Delta H°_H$ $^{kJ}/_{mol}$	$\Delta S°_H$ $^{J}/_{mol/K}$	$\Delta G°_H$ $^{kJ}/_{mol}$
$\mathbf{Na}^{+}\mathbf{Cl}^{-}$	-411,12	72,00	-
$\mathbf{Na}^{+}_{aqua}$	-240,10	59,00	-261,9
$\mathbf{Cl}^{-}_{aqua}$	-167,2	56,50	-
$\mathbf{H_2O}$	-285.85	69,9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{H_3O}^{+}$	-285,81	-3,854	-213,275
$\mathbf{HCl}_{gas}$	-92,31	186,902	-95,3
$\mathbf{HCl}_{aqua}$	-167,2	56,5	-131,2

crystalline $\mathbf{NaCl}+\mathbf{Q}=\mathbf{Na}^{+}_{aqua}+\mathbf{Cl}^{-}_{aqua}+\Delta G$;

1. $\Delta H_H=\Delta H°_{\mathbf{Na}}+\Delta H°_{\mathbf{Cl}}-\Delta H°_{\mathbf{NaCl}}$ =.........$^{kJ}/_{mol}$. **endothermic**..........
$= -240.1-167.2-(-411.12) =-407.3+411.12= +3.82.........\ ^{kJ}/_{mol}$
2. $\Delta S_{dispersed}= -\ \Delta H_H/\ T = -3.82\ /298.15= -12.812.........\ ^{J}/_{(mol\ K)}$

$\Delta S_H=\Delta S°_{\mathbf{Na}}+\Delta S°_{\mathbf{Cl}}-\Delta S°_{\mathbf{NaCl}}=59+56.5-72= 43.5......\ ^{J}/_{mol/K}$;

$\Delta S_{total}= \Delta S_H+ \Delta S_{dispersed}= -12.812+43.5= +30.688.......\ ^{J}/_{mol/K}$

$\Delta G_H=\Delta H_H-T{*}\Delta S_H=3{,}82-298{,}15{*}0{,}0435 = -9{,}15.......\ ^{kJ}/_{mol}$exoergic....

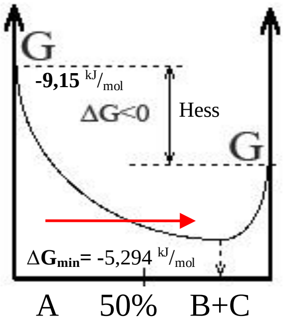
$T{\bullet}\Delta S_{total}=30{,}688{\bullet}298{,}15=\mathbf{9.15}$ ....$^{kJ}/_{mol}$ bound free energy

Non dissociated salt neutral molecules form in two ways:

1. **Electrostatic** atraction ions *Debye - Hückels'* physiology 0,9% solution forms osmolar $C_{osm}=0{,}305$ M concentration with sodium chloride ions and salt neutral molecules : $\mathbf{NaCl} \rightleftarrows \mathbf{Na}^{+}+\mathbf{Cl}^{-}$ in litre 1000 mL .
$C_{osm}=[\mathbf{Na}^{+}]+[\mathbf{Cl}^{-}]+[\mathbf{NaCl}] =i{*}C_M=0{,}305$ M. $m_{\mathbf{NaCl}}/m_{šķ}= m_{\mathbf{NaCl}}\ /1000{*}100\% =w\%=0{,}9\%$, jo blīvums is 1 $^{g}/_{mL}$.
Sodium chloride mas $m_{\mathbf{NaCl}}=0{,}9\%{*}1000/100\% =9\ ^{g}/_{L}$ and mol number $n_{\mathbf{NaCl}}=m_{\mathbf{NaCl}}/M_{\mathbf{NaCl}}=9/58{,}5=0{,}15385\ ^{mol}/_{L}$;
$C_{osm}=[\mathbf{Na}^{+}]+[\mathbf{Cl}^{-}]+[\mathbf{NaCl}]=i{*}C_M=(1+ \boldsymbol{\alpha}(m-1)){*}C_M=(1+\boldsymbol{\alpha}(2-1)){*}0{,}15385=0{,}305$ M. Dissociation degree alpha is:
$\boldsymbol{\alpha} =(0{,}305/0{,}15385-1)=0{,}98245$ with fraction of $[\mathbf{NaCl}]= C_M -C_M{*}\boldsymbol{\alpha}=0{,}15385-0{,}15385{*}0{,}98245=0{,}0027$ M
Physiology 0,9% solution $\mathbf{K}_{0,9\%}=\mathbf{K}_{0,9\%}=[\mathbf{Na}^{+}]{*}[\mathbf{Cl}^{-}]/[\mathbf{NaCl}]=0{,}15115{*}0{,}15115/0{,}0027=8{,}4616$;

$$\Delta\mathbf{G}_{0,9\%}=\mathbf{-R{\bullet}T{\bullet}ln(K}_{0,9\%}\mathbf{)}=-8{,}3144{\bullet}298{,}15{\bullet}\mathbf{ln}(8{,}4616)=-5{,}294\ ^{kJ}/_{mol},$$

Endothermic and exoergic solubility Hess free energy change $\Delta\mathbf{G}_{Hess}= -9{,}15\ ^{kJ}/_{mol}$ is negative, but minimized $\Delta\mathbf{G_{min}} =\Delta\mathbf{G}_{0,9\%}= -5{,}294\ ^{kJ}/_{mol}$ in physiologic 0,9 % mixture reached equilibrium $\mathbf{K}_{0,9\%}=\mathbf{K}_{0,9\%}=[\mathbf{Na}^{+}{}_{aq}]{*}[\mathbf{Cl}^{-}{}_{aq}]/[\mathbf{NaCl}\ _{aq}]= 8{,}46$ or solubility product $\Delta\mathbf{G_{sp}}= -6{,}25\ ^{kJ}/_{mol}$ reached $\mathbf{K}_{sp}=\mathbf{K}_{eq}=12{,}44$. Le Chatelier principle is Prigogine attractor free energy change minimum $\Delta\mathbf{G_{sp}}$ for crystalline sodium chloride $\mathbf{Na}^{+}\mathbf{Cl}^{-}$ **solubility** product. At free energy minimum $\Delta\mathbf{G_{min}}$ reaching establishes equilibrium.



$\mathbf{Na}^{+}\mathbf{Cl}^{-}{}_{ciets}$ reactant.

Note: Strong electrolytes are soluble with negative $\Delta\mathbf{G<0}$ and greater one $\mathbf{K_{eq}} \mathbf{>>1}$;
Weak electrolytes with positive $\Delta\mathbf{G}_{eq}\mathbf{>0}$ and $0 < \mathbf{K_{eq}} < \mathbf{1}$ **endoergic** are water insoluble.

THERMODYNAMICS Exercise V For crystalline salt Na^+OH^- dissociation reaction with water

Crystalline Na^+OH^- hydration reaction with water 100 $^g/_{100g}$ solubility in 200 g water solution of density 1,5217 $^g/_{mL}$; w%=50 % M_{NaOH}=$Na+O+H$=23+16+1=40 .$^g/_{mol}$; $n_{NaOH}=m_{NaOH}/M_{NaOH}$=760,85/40=19,02 mol; $n_{H2O}=m_{\ H2O}/M_{H2O}$=760,85/18=42,27 mol; nc=42,27/9=4,697 M; Double water mols number are enough for sodium ions coordination . Hydroxide ions repuls from water molecules stai alone.

Substance	$\Delta H°_H$ $^{kJ}/_{mol}$	$\Delta S°_H$ $^{J}/_{mol/K}$	$\Delta G°_H$ $^{kJ}/_{mol}$
$NaOH_{aq}$	-44,51	solution-	-
$NaOH.H_2O$	-21,41	solution	-
$NaOH_{lattic}$	-	lattice	-887
$NaOH_{Cryst}$	-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
$Na+_{aqua}$	-240,10	59,00	-261,9
OH^-	-230.00	-10,539	-157,2

$\Delta H_{Hes}=\Delta H°_{Na}+\Delta H°_{OH}-\Delta H°_{NaOH}-2*\Delta H°_{H2O}$=527,4 $^{kJ}/_{mol}$;

=-240,1-230-(-425,8-2*285.85)=527,4 $^{kJ}/_{mol}$;

$\Delta S_{dispersed}=-\Delta H_H/T$=-527,4/298,15= -1768,908 $^J/_{(mol\ K)}$

$\Delta S_{Hess}=\Delta S°_{Na}+\Delta S°_{OH}-\Delta S°_{NaOH}-2*\Delta H°_{H2O}$=59-10.539-64,4-2*69,9565=-155,852 $^J/_{mol/K}$;

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

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}$=527,4-298,15*-0,155852=573,867 $^{kJ}/_{mol}$;

$T\bullet\Delta S_{total}$=-1,92476*298,15= **-573,867** $^{kJ}/_{mol}$ bound free energy

$\Delta G_H=\Delta G°_{Na}+\Delta G°_{OH}-\Delta G°_{NaOH}$=467,9 $^{kJ}/_{mol}$. **exoergic**.

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

Non dissociated hydroxide neutral molecules not forming:

I) Crystalline Na^+OH^- sodium hydroxide complete dissociates into ions coordinates two water H_2O w%=50 %.

$2Na^+OH^-+(H_2O)_4=>2[2H_2O:=>Na^+]_{aqua}+2OH^-$; solubility constant is ions factorial at equilibrium:

Crystal sodium hydroxide dissociation solubility product: $Na^+OH^-+2H_2O=>[1.0469H_2O:=>Na^+]_{aqua}+OH^-$;

$\Delta G_{Hess}=\Delta G°_{Na}+\Delta G°_{OH}-\Delta G°_{NaOH}-2*\Delta G°_{H2O}$=-261,9-157,2-(-379,7-2*237,191)=435 $^{kJ}/_{mol}$;

Total concentration $n_{total}=[H_2O]+[[2H_2O:=>Na^+]_{aqua}]+[OH^-]$=4,23+19,02+19,02=**42.27** M;

Solubility product in mol fractions $K_{sp}=[Na^+_{aqua}]*[OH^-]_{aqua}/[Na^+OH^-]/n_{kop\bar{a}}$^2=19,02*19,02/1/**42,27**^2=**0,2025**.

$\Delta G_{min}=\Delta G_{sp}=-R\bullet T\bullet\ln(K_{sp})$=-8,3144*298,15*ln(0,**2025**)=**3,959** $^{kJ}/_{mol}$.

Solubility 100 $^g/_{100g}$ solution density 1,5217 $^g/_{mL}$; w%=50 %; One liter solution contain

$n_{\ NaOH}=m_{NaOH}/M_{NaOH}$ = 760,85/40 = 19,02 mol; $n_{H2O}=m_{\ H2O}/M_{H2O}$ = 760,85/18 = 42,27 mol;

Two 2 water molecules coordinates linear at Na^+ ions, but OH^-ions repel water.

Hess change positive $\Delta G_{Hess}=\Delta G_{NaOH}+\Delta G_{(H2O)4}/2+2*\Delta G_{[H2O:=>Na+]}$=887+45-800=132 $^{kJ}/_{mol}$ endoergic, but minimied in mixture reached solubility equilibrium:$\Delta G_{eq}=\Delta G_{sp}=-8,3144\bullet 298,15\bullet\ln(0,2025)$=**3,959** $^{kJ}/_{mol}$.

Solubility equilibrium is Prigogine attractor free energy change minimum ΔG_{min} . At free energy chsnge minimum reachibg establishes crystalline sadium hydroxide Na^+OH^- **solubility** equilibrium .

1. Ions lattice destruction: $NaOH=>Na^++OH^-$ energy: ΔG_{NaOH}=887 $^{kJ}/_{mol}$.

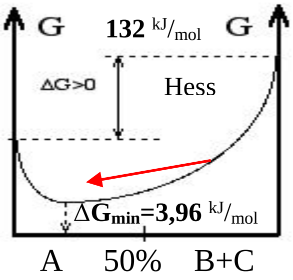
2. Tetra mer destruction: $(H_2O)_4=>4H_2O$ energy $\Delta G_{(H2O)4}$=90 $^{kJ}/_{mol}$. w%=50 %

3.a Two H_2O coordination in cation energy $2*\Delta G_{[H2O:=>Na+]}$=2*-400=-800 $^{kJ}/_{mol}$:

$\Delta G_{Hess}=\Delta G_{NaOH}+\Delta G_{(H2O)4}/2+2*\Delta G_{[H2O:=>Na+]}$=887+45-800=132 $^{kJ}/_{mol}$.

Notice: Strong electrolytes are soluble with negative **$\Delta G<0$** and greater one **$K_{eq}>>1$** ;

Weak electrolytes with positive **$\Delta G_{eq}>0$** and 0 < **$K_{eq}<1$ endoergic** are water insoluble .

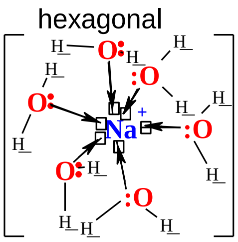


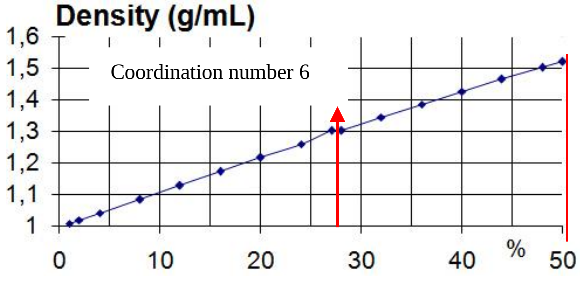
$Na^+OH^-_{Cryst}$=>products Na^++OH^-

At 0% < w% < 27 % $NaOH_{Cryst}$ solution density 1,301 $^g/_{mL}$ $2Na^+OH^-+3(H_2O)_4=>2[6H_2O:=>Na^+]_{aqua}+2OH^-$;

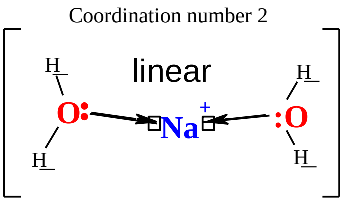
3.b Six H_2O molecules coordinate symetrical around cation $6*\Delta G_{[H2O:=>Na+]}$=6*-400=-2400 $^{kJ}/_{mol}$:

$\Delta G_{reactions}=\Delta G_{NaOH}+3/2*\Delta G_{(H2O)4}+6*\Delta G_{[H2O:=>Na+]}$=887+270/2-2400= -1378 $^{kJ}/_{mol}$.





w%=27%



THERMODYNAMICS Exercise Va hydrogen chloride **HCl** solubility and reaction

$\Delta H_{\text{hydration}\mathbf{HCl}}=\Delta H°_{\mathbf{HCl}\text{aqua}}-\Delta H°_{\mathbf{HCl}\text{gas}}$=-167,2-(-92,31)= -74,89.......... $^{\text{kJ}}/_{\text{mol}}$ **exothermic**..................

CRC 2010 Reaction is **exothermic** , **athermic**, **endothermic**,**exoergic**, **endoergic**! ?$\mathbf{HCl}_{\text{gas}}$**=>**$\mathbf{HCl}_{\text{aqua}}$+ΔG+**Q**;

Substance	$\Delta H°_H$ $^{\text{kJ}}/_{\text{mol}}$	$\Delta S°_H$ $^{\text{J}}/_{\text{mol/K}}$	$\Delta G°_H$ $^{\text{kJ}}/_{\text{mol}}$
$\mathbf{Na^+Cl^-}$	-411,12	72,00	-
$\mathbf{Na^+}_{\text{aqua}}$	-240,10	59,00	-
$\mathbf{Cl^-}_{\text{aqua}}$	-167,08	56,50	-
$\mathbf{H_2O}_{aq}$	-285,85	69,956	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{H_3O^+}$	-285,81	-3,854	-213,275
$\mathbf{HCl}_{\text{gas}}$	-92,31	186,902	-95,3
$\mathbf{HCl}_{\text{aqua}}$	-167,2	56,5	-131,2

$\Delta G_H=\Delta G°_{\mathbf{HCl}\text{aqua}}-\Delta G°_{\mathbf{HCl}\text{gas}}$=-131,2-(-95,3)= -35,9............ $^{\text{kJ}}/_{\text{mol}}$

1. $\Delta H_{\text{Hess}}=\Sigma\Delta H°_{\text{products}}-\Sigma\Delta H°_{\text{Reactants}}$; **exoergic**..................

$\Delta H_{\text{hydration}\mathbf{HCl}}=\Delta H°_{\mathbf{HCl}\text{aqua}}-\Delta H°_{\mathbf{HCl}\text{gas}}$=-167,2-(-92,31)= -74,89.......... $^{\text{kJ}}/_{\text{mol}}$

2. $\Delta S_{\text{Hess}}=\Sigma\Delta S°_{\text{products}}-\Sigma\Delta S°_{\text{Reactants}}$; **exothermiska**..................

$\Delta S_{\text{total}}=\Delta S_H+\Delta S_{\text{dispersed}}$=251,182-130,4=120,78...... $^{\text{J}}/_{\text{mol/K}}$;

$\Delta S_{\text{Hess}}=\Delta S°_{\mathbf{HCl}\text{aqua}}-\Delta S°_{\mathbf{HCl}\text{gas}}$=56,5-186,902=-130,402....... $^{\text{J}}/_{\text{mol/K}}$;

$\Delta S_{\text{dispersed}}$= - ΔH_{Hess}/ T =74,89 /298,15=251,182....... $^{\text{J}}/_{\text{mol/K}}$;

3. $\Delta G_{\text{Hess}}=\Delta H_{\text{Hess}}-T\bullet\Delta S_{\text{Hess}}$ =-74,89-298,15*-0,130=-36,01...... $^{\text{kJ}}/_{\text{mol}}$

Bound T•ΔS_{total}=120,78 $^{\text{J}}/_{\text{K/mol}}$•298,15 K=**36,01**..... $^{\text{kJ}}/_{\text{mol}}$;exoergic........

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

$\mathbf{HCl}+\mathbf{H_2O}\mathbf{=>}\mathbf{H_3O^+}+\mathbf{Cl^-}_{\text{aqua}}$ +**Q** +ΔG; $\mathbf{HCl}\mathbf{=>}\mathbf{H^+}+\mathbf{Cl^-}_{\text{aqua}}$; $[\mathbf{H_3O^+}]^2+[\mathbf{H_2O}]*\mathbf{K_{dis}}*[\mathbf{H_3O^+}]-\mathbf{K_{dis}}*[\mathbf{H_2O}]$*11,978=0

$\Delta H_{\text{Hess}}=\Delta H°_{\mathbf{H3O}}+\Delta H°_{\mathbf{Cl-}}-\Delta H°_{\mathbf{HCl}\text{aq}}-\Delta H°_{\mathbf{H2O}}$= -285,81-167,08-(-167,2-285,85)=0,16....... $^{\text{kJ}}/_{\text{mol}}$; **athermic**..............

2. $\Delta S_{\text{dispersed}}$= - ΔH_{Hess}/ T = -0,16 /298,15= -0,537........... $^{\text{J}}/_{\text{mol/K}}$

$\Delta S_{\text{Hess}}=\Delta S°_{\mathbf{H3O}}+\Delta S°_{\mathbf{Cl-}}-\Delta S°_{\mathbf{HCl}}-\Delta S°_{\mathbf{H2O}}$=-3,854+56,60-(69,96+56,5)= 52,64-126,46=-73,714......... $^{\text{J}}/_{\text{mol/K}}$

$\Delta S_{\text{total}}=\Delta S_{\text{Hess}}+\Delta S_{\text{dispersed}}$= -0,537-73,714= -74,251....... $^{\text{J}}/_{\text{mol/K}}$;

$\Delta G_{\text{Hess}}=\Delta H_{\text{Hess}}-T*\Delta S_{\text{Hess}}$=0,16-298.15*-0,073714=22,1378.............. $^{\text{kJ}}/_{\text{mol}}$ **endoergic**...........................

T•ΔS_{total}=-74,251 $^{\text{J}}/_{\text{K/mol}}$•298,15 K=**-22,14**..... $^{\text{kJ}}/_{\text{mol}}$;

$m_{\mathbf{H2O}}$=1180-436,6=743,4 g; $n_{\mathbf{H2O}}$=743,4/18=41,3 $^{\text{mol}}/_{\text{L}}$, First solution:

$[\mathbf{H_2O}]=41,3-[\mathbf{H_3O^+}]$=41,3-0,25235=41,04765 $^{\text{mol}}/_{\text{L}}$' $C_{\mathbf{HCl}}=[\mathbf{HCl}_{\text{aqua}}]+[\mathbf{Cl^-}]$=11,978 M ;

$[\mathbf{HCl}_{\text{aqua}}]=(11,978-[\mathbf{Cl^-}])$=(11,978-0,25235)=11,725664 $^{\text{mol}}/_{\text{L}}$; $[\mathbf{HCl}_{\text{aqua}}]\ [\mathbf{H_2O}]*\mathbf{K_{dis}}=[\mathbf{H_3O^+}]*[\mathbf{Cl^-}_{\text{aqua}}]$;

As equal $[\mathbf{Cl^-}_{\text{aqua}}]=[\mathbf{H_3O^+}]$ and replased $[\mathbf{Cl^-}_{\text{aqua}}]$ with $[\mathbf{H_3O^+}]$ square equation is solved as: $ax^2+bx+c=0$.

$(11,978-[\mathbf{Cl^-}])\ [\mathbf{H_2O}]*\mathbf{K_{dis}}=[\mathbf{H_3O^+}]*[\mathbf{Cl^-}_{\text{aqua}}]$; $(11,978-[\mathbf{H_3O^+}])\ [\mathbf{H_2O}]*\mathbf{K_{dis}}=[\mathbf{H_3O^+}]*[\mathbf{H_3O^+}]$;

$[\mathbf{H_3O^+}]^2+[\mathbf{H_2O}]*\mathbf{K_{dis}}*[\mathbf{H_3O^+}]-\mathbf{K_{dis}}*[\mathbf{H_2O}]$* 11,978=0

Square equation $ax^2+bx+c=0$ solves real root of two mathematic $\mathbf{x}=\left(\frac{-b+\sqrt{b^2-4ac}}{2a}\right)$;

$$[\mathbf{Cl^-}_{aq}]=[\mathbf{H_3O^+}]=\frac{-K_{dis}\cdot[H_2O]+\sqrt{(K_{dis}*[H_2O])^2-4*-K_{dis}*[H_2O]*11{,}7257}}{2}=0{,}25235\text{ M}$$

$[\mathbf{Cl^-}_{aq}]=[\mathbf{H_3O^+}]$=(-Kdis*41,04765+SQRT((Kdis*41,04765)^2-4*-Kdis*41,04765*11,978))/2=0,25235.............M

Dissociation degree **α=0,021**=$\mathbf{C_{dis}/C_M}$=0,25236/11,978; $\mathbf{C_M}=\mathbf{C_{dis}}+\mathbf{C_{nedis}}$=0,25235 + 11,725664=11,978 $^{\text{mol}}/_{\text{L}}$;

Dissociation degree **α%=2,1**%;pH=0,6 ; Equilibrium constant : $\mathbf{K_{dis1}}$=0,000132306:

$$\frac{[H_3O^+]\cdot[Cl^-]_{aqua}}{[HCl]_{aqua}\cdot[H_2O]}$$

=$\mathbf{K_{eq}}$=(0,25235*0,25235)/(41,04765*11,725664)=0,000132306=$10^{-3,878}$;

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

Ja sālsskābes koncentrācija is $C_{\mathbf{HCl}}=[\mathbf{HCl}_{\text{aqua}}]+[\mathbf{Cl^-}]$=0,1 M ; $[\mathbf{H_2O}]=55,33-[\mathbf{H_3O^+}]$=55,33-0,1=55,23 $^{\text{mol}}/_{\text{L}}$

0,04728863 M=$[\mathbf{Cl^-}_{aq}]=[\mathbf{H_3O^+}]$=(-Kdis1*55,23+SQRT((Kdis1*55,23)^2-4*-Kdis1*55,23*0,1))/2;

$$\frac{[H_3O^+]\cdot[Cl^-]_{aqua}}{[HCl]_{aqua}\cdot[H_2O]}$$

=$\mathbf{K_{eq}}$=(0,04728863*0,04728863)/(55,23*0,05271137)=0,000768129= $\mathbf{K_{dis1}}$; $\mathbf{C_M}$ = 0,1 M

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

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

Protolysis Hess llaw positiv1 22,138 $^{\text{kJ}}/_{\text{mol}}$, but minimized reaching equilibrium 17,8 $^{\text{kJ}}/_{\text{mol}}$.

0,04728863 M =$[\mathbf{H_3O^+}]=10^{-\text{pH}}=10^{-1,325}$; pH= -log$[\mathbf{H_3O^+}]$ = -log(0,04728863)= 1,325=pH;

Dissociation degree $\boldsymbol{\alpha}_{0,1}$=$\mathbf{C_{dis}/C_M}$=0,0472886/0,1=0,047 , **α%**= 4,7%; $\boldsymbol{\alpha}_{0,01}$=0,008343/0,01=0,8343, **α%**=83,43%;

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

0,008343 M=$[\mathbf{Cl^-}_{aq}]=[\mathbf{H_3O^+}]$=(-Kdis2*55,32+SQRT((Kdis2*55,32)^2-4*-Kdis2*55,32*0,01))/2;

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

ΔG_{Hess}=22,138........... $^{\text{kJ}}/_{\text{mol}}$ **endoergic**.............Prigogine minimum $\Delta\mathbf{G_{eq}}$=17,8.......... $^{\text{kJ}}/_{\text{mol}}$, THERMODYNAMICS Exercise V b For crystalline $CH_3COO^-Na^+$ solubility and reaction

$$CH_3COONa_s+8H_2O=>[6H_2O:=>Na^+]_{aq} +[2H_2O=>^-OOCCH_{3aq}]$$

Solubility 50.4 $^g/_{100g}$ H_2O, density 1.26 $^g/_{mL}$, $C_{CH3COONa}$= 5.1493 $^{mol}/_L$; w%= 36.1 %

Litre solution mas with density 1.26 $^g/_{mL}$ is $m_{solution}$ = 1260 $^g/_L$.

What times 150.4 g included 1260 grams solution 1260/150.4= 8.7766............times .

Sodium acetate mas in litre $m_{CH3COONa}$ =8.7766*50.4 g/100g =442.34..........$^g/_L$..

Molar mas calculates as sum of atomic mases: $M_{CH3COONa}=M_{Na}+M_{CH3COO}$=23+24+32+3= 82 $^g/_{mol}$.

Salt number of mols in one litre is mas of salt over it's molar mas:

$n_{CH3COONa}= m_{CH3COONa} / M_{CH3COONa}$= 442.34 / 82= 5.1493 $^{mol}/_L$; $C_{CH3COONa}$ = 5.1493 $^{mol}/_L$;

Water $m_{H2O}=m_s-m_{CH3COONa}$ =1260-442.34= 817.76 g; $n_{H2O}= m_{H2O} / M_{H2O}$ 817.76/18=45.431 moli..

Mas fraction in perocents : $m_{CH3COONa}/m_{šķ}$=442.34 /1260*100% =w%= 36.1;

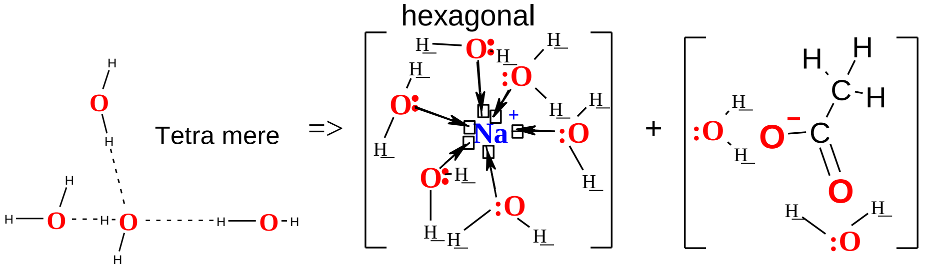
Complete dissociation in ideal solution coordinate 6 H_2O , 2 H_2O sodium ions and acetate ions crystalline $CH_3COONa_s \rightleftarrows Na^++CH_3COO^-$ solie, poore compound mol fraction is one $[CH_3COONa]_{solid}$ = 1 and solubility product constant: $K_{sp}= K_{eq} =[Na^+]*[CH_3COO^-]$=5.1493*5.1493=26.515 is ions factorial reaching Prigogine attractor at equilibrium free emergy change minimum negative::

Thermodynamic favored solubilty product constant: for favored equilibrium:

$$\Delta G_{min}=\Delta G_{eq}=-R\bullet T\bullet \ln(K_{eq}) =-8.3144\bullet 298.15\bullet \ln(26.515)= -8.125\ ^{kJ}/_{mol}.$$

Saturated solution water coordination resorces 8 are indispensible: nc= n_{H2O} /8=45.431/8= 5.6789..........moli.

$CH_3COONa_{aqua} + 2(H_2O)_4$



+ Q + ΔG;

CRC 2010 reactant => products

Substance	ΔH°Hess, $^{kJ}/_{mol}$	ΔS°Hess, $^J/_{mol/K}$	ΔG°Hess, $^{kJ}/_{mol}$
Na^+_{aqua}	-240.1	59	-
$CH_3COO^-_{aq}$	-486	85.3	-247.83
$CH_3COO^-_{aq}$	**-486.836**	**-822.3**	**-241.663**
CH_3COONa_s	-708.8	123.0-	-607.7-

$CH_3COONa_s => Na^+_{aqua}+CH_3COO^-_{aqua}$ +**Q** +ΔG;

1. $\Delta H_{Hess}= \Sigma\Delta H°_{products}- \Sigma\Delta H°_{Reactants}$;

2. $\Delta S_{Hess}= \Sigma\Delta S°_{products}- \Sigma\Delta S°_{Reactants}$;3.$\Delta G_{Hess}=\Delta H_{Hess}-T\bullet\Delta S_{Hess}$

2. $\Delta S_{dispersed}=-\Delta H_{Hess}/T$=17.3/298.15=58.02448...........$^J/_{mol/K}$;

$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}$=58.02448+21.3=79.32448...........$^J/_{mol/K}$;

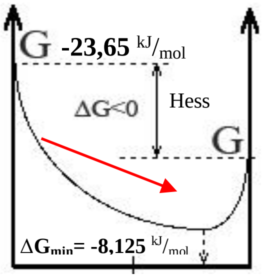
1. $\Delta H_{Hess}=\Delta H°_{H3CCOO-}+\Delta H°_{Na}-\Delta H°_{H3CCOO\ Na}$=-486-240.1-(-708.8)= -17.3 $^{kJ}/_{mol}$ **eksotermiska**..................

2. $\Delta S_{Hess}=\Delta S°_{H3CCOO-}+\Delta S°_{Na+aqua}-\Delta S°_{H3CCOO\ Na}$=59+85.3-123= 144.3-123=21.3.......$^J/_{mol/K}$ **exoergic**............

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}$=-17.3-298.15*0.0213=-23.65........$^{kJ}/_{mol}$;$T\bullet\Delta S_{total}$=79.32448•298.15=**23.65**...........$^{kJ}/_{mol}$;

Exothermic and exoergic CH_3COONa_s solubility product Hess free energy change ΔG_{Hess} negative -23.65 $^{kJ}/_{mol}$, but minimizes up to $\Delta G_{min} = \Delta G_{eq}$ =-8.125 $^{kJ}/_{mol}$ in mixture reaching solubility product $K_{sp}=K_{eq}=[Na^+]*[CH_3COO^-_{aqua}]$=5.1493*5.1493=26.515 . Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium



reactant crystalline CH_3COONa_s_A 50% B+C

and products_ $Na^+_{aq}+CH_3COO^-_{aq}$

THERMODYNAMICS Exercise V aa For crystalline **$NH_4Cl_{(s)}$** electrolyte solubility in water

Data from tables: solubility 39.5 $^{g}/_{100g}$ H_2O, pKa=9.25, density 1.3536 $^{g}/_{mL}$,

Litre solution mas with density 1.3536 $^{g}/_{mL}$ is $m_{\mathbf{solution}}$ = 1353.6 ....$^{g}/_{L}$.

What times 139.5 g include 1353.6 grams solution 1353.6/139.5= 9.7032............times

Amonium chloride mas in litre m_{NH4Cl} = 9.7032 *39.5 g/100g = 383.2764..........$^{g}/_{L}$..

Molar mas is sum of atomic mases: $M_{\mathbf{NH4Cl}}=M_{\mathbf{NH4}}+M_{Cl}$=16+24+35.5= 75.5...........$^{g}/_{mol}$.

Salt number of mols in litre is salt mas over it's molar mas:

n_{NH4Cl}= m_{NH4Cl} / M_{NH4Cl}= 383.2764 / 75.5= 5.07651 $^{mol}/_{L}$; C_{NH4Cl}= 5.07651.........$^{mol}/_{L}$;

Water $m_{\mathbf{H2O}}=m_{\mathbf{šķ}}-m_{NH4Cl}$ = 1353.6-383.2764=970.32 g $n_{\mathbf{H2O}}$= $m_{\mathbf{H2O}}$ / $M_{\mathbf{H2O}}$ =970.32/18=53.907.........moli.

Mas fratio in percents is mas of salt over solution mas :

$m_{NH4Cl}/m_{\mathbf{šķ}}$=383.2764/1353.6*100% =w%=28.32...........%;

Thermodynamic favored complete dissolution reaction by Hes law and solubility constant .

Substance	$\Delta H°_{Hess}$, $^{kJ}/_{mol}$	$\Delta S°_{Hess}$, $^{J}/_{mol/K}$	$\Delta G°_{Hess}$, $^{kJ}/_{mo}$
Cl-$_{aqua}$	-167.2	56.50	-
NH_4^+ $_{(aq)}$	-132.5	113.4	-
$NH_4Cl_{(s)}$	-314.4	94.6-	-202.97

reactants **$NH_4Cl_{(s)}$** +**Q => NH_4^++ Cl^-**$_{aqua}$ +ΔG products;

1. $\Delta H_{Hess}= \Sigma\Delta H°_{products}- \Sigma\Delta H°_{Reactants}$;
2. $\Delta S_{Hess}= \Sigma\Delta S°_{products}- \Sigma\Delta S°_{Reactants}$;

CRC 2010 3. $\Delta G_{Hess}= \Delta H_{Hess}-T\bullet\Delta S_{Hess}$

1. $\mathbf{\Delta H_{Hess}=\Delta H°_{NH4}+\Delta H°_{Cl}-\Delta H°_{NH4Cls}}$= -132.5-167.2-(-314.4)=-299.7+314.4=14.7.........$^{kJ}/_{mol}$ **endothermic**............
2. $\Delta S_{dispersed}=-\Delta H_{Hess}/T$=-14.7/298.15=-49.3........$^{J}/_{mol/K}$;
2. $\mathbf{\Delta S_{Hess}=\Delta S°_{NH4}+\Delta S°_{Cl}-\Delta S°_{NH4Cl}}$= 113.4 +56.50-(94.6)= 169.9-94.6=75.3..........$^{J}/_{mol/K}$
3. $\Delta S_{total}= \Delta S_{Hess}+ \Delta S_{dispersed}$=-49.3+75.3= 26........$^{J}/_{mol/K}$;

$\mathbf{\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}}$=14.7-298.15*0.0753=-7.75..........$^{kJ}/_{mol}$; **exoergic**.............................

$T\bullet\Delta S_{total}$=26 $^{J}/K/_{mol}$•298.15 K=**7.75**........$^{kJ}/_{mol}$;

$$\frac{[NH_4^+]_{aqua}\cdot[Cl^-]_{aqua}}{[NH_4Cl]_{aqua}}=\mathbf{K_{sp}}_{Hess}=\mathbf{exp(-\Delta G_{Hess}/R/T)}=\exp(7.75/8.3144/298.15)=22.8.......$$

Thermodynamic favored Hess solubility product in water .

Complete dissociation solubility product constant $\mathbf{K_{dis}}=[\mathbf{NH_4^+}]*[\mathbf{Cl^-}_{aqua}]$= 5.07651*5.07651=25.771..........

Amonium chloride $\mathbf{K_{sp}}_{Hess}$=22.8 non dissociated concentration is calculated in expression :

$[\mathbf{NH_4Cl}_{aqua}]= [\mathbf{NH_4^+}]*[\mathbf{Cl^-}_{aqua}]/ \mathbf{K_{sp}}_{Hess}$=25.771/22.8= 1.13.......$^{mol}/_{L}$,

including equal dissociated ions concentration in subtraction solubility concentration minus non dissociated salt concentration: $[\mathbf{NH_4^+}]=[\mathbf{Cl^-}_{aqua}]$= 5.07651-1.13=3.97651 ....$^{mol}/_{L}$,

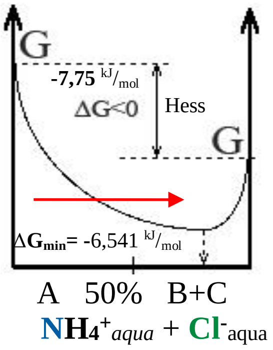
Favored solubility product constant: $\mathbf{K_{eq}}=\dfrac{[NH_4^+]_{aqua}\cdot[Cl^-]_{aqua}}{[NH_4Cl]_{aqua}}$ =3.97651*3.97651/1.13= 13.9935...........

$\mathbf{\Delta G_{eq}=-R\bullet T\bullet ln(K_{eq})}$=-8.3144•298.15•**ln**(13.9935)= -6. 541 ....$^{kJ}/_{mol}$, Endothermic and exoergic **$NH_4Cl_{(s)}$** dissociation Hess free energiy change $\Delta\mathbf{G_{dis}}_{Hess}$=-7.75 ....$^{kJ}/_{mol}$ negative, but minimized reaching $\Delta\mathbf{G_{min}}=\Delta\mathbf{G_{eq}}$= -6. 541.........$^{kJ}/_{mol}$ equilibrium mixture

$$\mathbf{K_{eq}}=\frac{[NH_4^+]_{aqua}\cdot[Cl^-]_{aqua}}{[NH_4Cl]_{aqua}}$$ =13.9935....... Le Chatelier principle is

Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium.

reactant non dissociated amonium chloride **NH_4Cl_{aqua}**_ and products



Free energy change minimum reaching establishes equilibrium

THERMODYNAMICS Exercise V.b acetic acid $\mathbf{CH_3COOH}$ in protolytic reaction

Calculate ΔH_H, ΔS_H, ΔG_H at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? For the $\mathbf{CH_3COOH}$ protolytic reaction with water! Will be **exoergic** or **endoergic**!

Viela	$\Delta H°_H$ $^{kJ}/_{mol}$	$\Delta S°_H$ $^{J}/_{mol/K}$	$\Delta G°_{Hess}$, $^{kJ}/_{mo}$
$\mathbf{H_3O^+}$	-285.81	-3.854	-213,275
$\mathbf{H_3CCOO^-}$	-486	85.3	85.3
$\mathbf{CH_3COO^-_{aq}}$	**-486,836**	**-822,3**	**-241,663**
$\mathbf{H_2O}$	-285.85	69.9565	69.9565
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{H_3C\text{-}COOH}$	-484,09	159,83	-531,743

Reactants => products

$\mathbf{CH_3COOH+H_2O}+\Delta G \Leftrightarrow \mathbf{H_3O^+ + CH_3COO^{-\,-} + Q}$

1. $\Delta H_{Hess} = \Delta H°_{products} - \Delta H°_{reactants}$
2. $\Delta S_{Hess} = \Delta S°_{products} - \Delta S°_{reactants}$
3. $\Delta G_{Hess} = \Delta H_{Hess} - T \bullet \Delta S_{Hess}$

1. $\mathbf{\Delta H_H = \Delta H°_{H3CCOO-} + \Delta H°_{H3O} - \Delta H°_{H2O} - \Delta H°_{H3CCOOH}} = -486-285,81-(-285,85-484,09) = -1,87$ $^{kJ}/_{mol}$ **exothermic**.

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

2. $\mathbf{\Delta S_H = \Delta S°_{H3CCOO-} + \Delta S°_{H3O} - \Delta S°_{H2O} - \Delta S°_{H3CCOOH}} = 85,3-3,854-(69,9565+159,83) = -148,3405$ $^{J}/_{mol/K}$.

3. $\Delta S_{total} = \Delta S_r + \Delta S_{disperse} = -148,3405+6,272011 = -142,0685$……………………………………………………… $^{J}/_{(mol\ K)}$….

$\mathbf{\Delta G_H} = \Delta H_H - T^* \mathbf{\Delta S_H} = -1,87+298,15^*0,1483405 = 42,3577$ $^{kJ}/_{mol}$ **endoergic**.

3. $T \bullet \Delta S_{total} = -142,0685^{J}/K/_{mol} \bullet 298,15\ K =$ **-42,3577** $^{kJ}/_{mol}$.

bound $T\Delta S_n \leftarrow$ <u>accumulated energy $\Delta G_{reverseHess} \leftarrow$</u>$Q = 1,87$ $^{kJ}/_{mol}$..non **spontaneous** $\Delta G_H = 42,4$ $^{kJ}/_{mol}$.

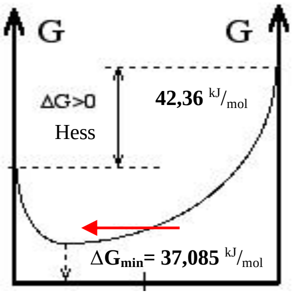
Equilibrium reached by free energy minimum at compounds mixture ratio in expression:

Thermodynamic unfavored equilibrium constant $\mathbf{K_{eq}} = \dfrac{[H^+]\cdot[CH_3COO^-]}{[H_2O]\cdot[CH_3COOH]_{nondis}} = \mathbf{K_a/[H_2O]} = 1,76^*10^{-5}/55,3 = 10^{-6,497}$

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

Endothermic and endoergic acetic acid protolytic reaction Hess free energy change $\mathbf{\Delta G_{protolyse}}_{Hess} = 42,36$ $^{kJ}/_{mol}$ positive, but minimizes up to $\mathbf{\Delta G_{min} = \Delta G_{eq}} = 37,085$ $^{kJ}/_{mol}$ reaching equilibrium mixture :

$$\mathbf{K_{eq}} = \frac{[H^+]\cdot[CH_3COO^-]}{[H_2O]\cdot[CH_3COOH]_{nondis}} = 10^{-6,497}\ .$$



reactants mixture_ A+B 50% C+D

products_$\mathbf{CH_3COOH+H_2O}$

$\mathbf{H_3O^+ + CH_3COO^{--}}$

Classic protolysis constant of acetic acid $\mathbf{K_a = K_{eq}[H_2O]} = \dfrac{[H^+]\cdot[CH_3COO^-]}{[H_2O]\cdot[CH_3COOH]_{nondis}} = 10^{-6,497}{}^*55,3 = 10^{-4,76}$; is

thermodynamic unfavored constsnt $\mathbf{K_{eq}}$ multiplication with water constant concentration $\mathbf{[H_2O]} = 55,3$ **M**

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium.

$\mathbf{[H_3O^+]} = \mathbf{[CH_3COO^-]} = C^*\boldsymbol{\alpha} = 0,2^*0,00931 = 10^{-2,73}$ M $= 1,862^*10^{-3}$ M; $\boldsymbol{\alpha} = 10^{-2,73}/0,2 = 0,00931$;

THERMODYNAMICS Exercise V.c H_2O Water ionization and neutralization inverse attractors of reaction

Calculate ΔH_{Hess}, ΔS_{Hess}, ΔG_{Hess} at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? For the water H_2O protolytic reaction with water! Will be **exoergic** or **endoergic**!

1. equilibrium $H_2O+H_2O+\Delta G^-+Q \Leftrightarrow H_3O^++OH^-$; 2. equilibrium $H_3O^++OH^- \Leftrightarrow H_2O+H_2O+\Delta G^-+Q$;

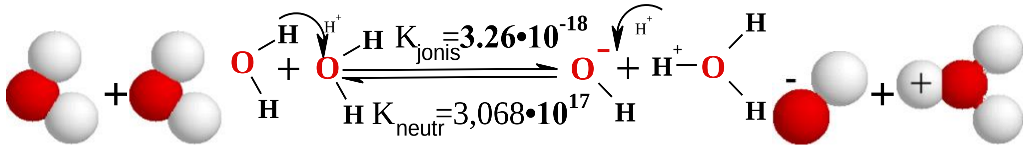
Substance	$\Delta H°_{Hess}$, $^{kJ}/_{mol}$	$\Delta S°_{Hess}$, $^{J}/_{mol/K}$	$\Delta S°_{Hess}$, $^{J}/_{mol/K}$
H_3O^+	-285,81	-3,854	-213,275
OH^-	–230.00	–10.539	-157,2
H_2O	-285.85	69.9565	-237,191
$H_2O_{\uparrow gas}$	-241,8352	188,7402	-228,6

$\Delta G_{Hess}=\Delta G°_{OH}+\Delta G°_{H3O}-2\Delta G°_{H2O}=103.907\ ^{kJ}/_{mol}$;
$=-157,2-213,275-2*-237,191=103.907\ ^{kJ}/_{mol}$;
$\Delta H_{Hess}=\Delta H°_{OH}+\Delta H°_{H3O}-2\Delta H°_{H2O}=55,89\ ^{kJ}/_{mol}$; **endothermic**.
$=-285,81-230-(2*(-285,85))=-515.81+571,7=55,89\ ^{kJ}/_{mol}$;
$\Delta S_{disperse}=-\Delta H_{Hess}/T=-55,89/298,15=-187,456\ ^{J}/_{(mol\ K)}$;

$\Delta S_{Hess}=\Delta S°_{OH}+\Delta S°_{H3O}-2\Delta S°_{H2O}=-3,854-10,539-2*69,956= 14.393-139.912=-154.305\ ^{J}/_{mol/K}$;
$\Delta S_{total}= \Delta S_{Hess}+ \Delta S_{disperse}=-187,456-154,305=-341,761\ ^{J}/_{(mol\ K)}$;
$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=55,89+298,15*0,154305=101,8967\ ^{kJ}/_{mol}$; **endoergic**..................
$T\bullet\Delta S_{total}=-341,761\ ^{J}/K/_{mol}\bullet 298,15\ K=$ **-101,896**............$^{kJ}/_{mol}$;bound TΔSn accumulated energy ; non **spontaneous**

Equilibrium reached by free energy minimum at compounds mixture ratio in expression:

$G_{H3O++OH-}=G_{H3O+}+G_{OH-}=22.44+77.36=G_{H3O+}+G_{OH-}-G_{2H2O}=-R\bullet T\bullet\ln(K_{H3O++OH-})+2*0=99.8\ ^{kJ}/_{mol}$. [1,8,14]



$$K_{eq1}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=3,26\bullet 10^{-18}$$

$$\Delta G_{eq1} = -R\bullet T\bullet\ln(K_{eq1})= -R\bullet T\bullet\ln\left(\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}\right) = 99,8\ ^{kJ}/_{mol},$$

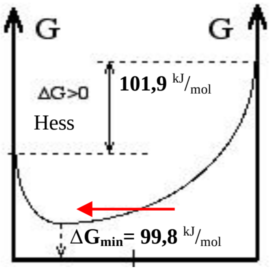
Endothermic and endoergic water protolysis reaction Hess free energy change $\Delta G_{Hess}=\Delta G_{protolyse}=101,9\ ^{kJ}/_{mol}$ positive, but minimizes reached equilibrium

$$K_{eq1}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=3.26\bullet 10^{-18}\ ;\ \text{up to}\ \Delta G_{min} = \Delta G_{eq} = 99,8\ ^{kJ}/_{mol}$$

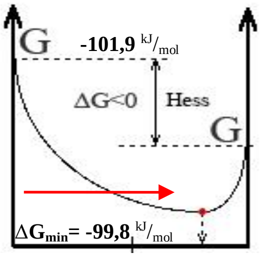
Free energy change ΔG_{Hess} for pure compounds by absolute value in Hess law is greater. Reaching equilibrium mixture of compounds free energy change minimizes: **99,8 $^{kJ}/_{mol}$ = $|\Delta G_{eq}| < |\Delta G_{Hess}|$ =101,9 $^{kJ}/_{mol}$**

All reactions trend to Prigogine attractor minimum of free energy change $\Delta G_{min} = \Delta G_{eq}$ at equilibrium mixture with active mass law inverse reactions constants:

$$3.26\bullet 10^{-18}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=K_{eq1}=\frac{1}{K_{eq2}}=\frac{1}{\frac{[H_2O]\cdot[H_2O]}{[OH^-]\cdot[H_3O^+]}}=\frac{1}{3,068*10^{17}}\ .$$



A+B 50% C+D
H_2O+H_2O reactants
products $H_3O^++OH^-$



C+D 50% A+B
$H_3O^++OH^-$ reactants
products H_2O+H_2O.

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.

Water factorial constant and concentration square K_w water constant. $K_{eq1}*[H_2O]^2=3.26\bullet 10^{-18}*55,33^2=10^{-14}=K_w$, one calculates water ions factorial constant $K_w = [H_3O^+][OH^-] =10^{-14}$, Attractors claim that our Universe is perfect and show that each process trends to energy change minimum in mixture of reacting compounds.

Protolysis $\Delta G_{H3O++OH-}=G_{H3O+}+G_{OH-}= 22,44+77,36= 99,8\ ^{kJ}/_{mol}$ akumulate equal acidic and basic pH= pOH= 7.

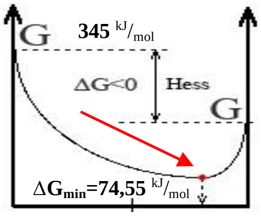
$H_2O+Q\Leftrightarrow H_2O_{gas}+\Delta G$; $\Delta H_{Hess}=\Delta H°_{H2Ogas}-\Delta H°_{H2O}=-241,8352-(-285,85)=44,0148\ ^{kJ}/_{mol}$ is endothermic, endoergic evaporation. $\Delta G_{Hess}=\Delta G°_{H2Ogas}-\Delta G°_{H2O}=-228,6-(-237,191)=G_{gasH2O}+G_{H2O}=8,59+0\ ^{kJ}/_{mol}$. In 101,3 kPa atmosphere partial vapor pressure p_o=3,1699 kPa is solubility product $K_{sp}=X_{H2O}/X_{H2Ogas}=1/0,03129=31,959$ of air mol fraction X_{H2Ogas}=3,1699/101,3=0,03129, but pure water mol fraction is one X_{H2O}=1. Evaporation accumulate energy

$\Delta G_{evaporation}=-R\bullet T\bullet\ln(K_{sp})=-8,3144*298,15*\ln(0,03129)=8,588\ ^{kJ}/_{mol}$ in one mol .

THERMODYNAMICS Exercise V.d solubility NH_{3gas}, NH_4^+ in protolytic reaction and protonation of NH_{3aqua}

For the ammonium $NH_4^+{}_{aq}$ protolytic reaction with water! 1.$NH_{3gas}+H_2O+\Delta G \Rightarrow NH_{3aq}+Q$;

$NH_{3\,(aq)}+H_2O \Rightarrow NH_4^++OH^-$ strong protolytic base $pK_b=4,74 < 9,25=pK_a$ weak $NH_4^++H_2O \Rightarrow NH_{3\,(aq)}+H_3O^+$;



A 50% B

reactants $NH_{3gas}+H_2O$

un produkt NH_{3aq}

$G_{NH3gas}=\Delta G°_{NH3aq}-\Delta G_{Hess\text{-}sp\text{-}NH3gas}-G°_{H2O}=91,1056-(-74,5537)-(-0)=165,7\ ^{kJ}/_{mol}$; **Alberty**

$NH_{3gas}+H_2O \Rightarrow NH_{3aq}$; $\Delta H_{hidratācija}=\Delta H°_{NH3aq}-\Delta H°_{NH3gas}-\Delta H°_{H2O}=-132,5608+45,94-286,65=-373,3\ ^{kJ}/_{mol}$;

$G_{Hydration}+G_{NH3gas}+\Delta G_{H2O}=G_{NH3aq}=107,5+165,7+0=273,2\ ^{kJ}/_{mol}$;

$\Delta G_{Hydration}=\Delta G_{NH3aq}-\Delta G_{NH3gas}-\Delta G_{H2O}=91,1056-(-16,4-0)=107,5\ ^{kJ}/_{mol}$;

$\Delta S_{Hydration}=\Delta S°_{NH3aqua}-\Delta S°_{NH3gas}-\Delta S°_{H2O}=-739,2922-192,77-69,9565=-1002\ ^{J}/_{mol/K}$;

$\Delta G_{Hess\text{-}sp\text{-}NH3gas}=\Delta H_{Hydrations}-T\cdot\Delta S_{Hydration}=-373,3-298,15\cdot-1,002=-74,5537\ ^{kJ}/_{mol}$;

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

Ammonia NH_{3aq} protonation:

2. K_{eq2}; **Ammonia** water $NH_{3aq}+H_2O+Q \Rightarrow NH_4^++OH^-+\Delta G$ strong base;

$\Delta H_{Hess}=\Delta H°_{NH4+}+\Delta H°_{OH}-\Delta H°_{NH3}-\Delta H°_{H2O}=55.8\ ^{kJ}/_{mol}$ endoothermic

$\Delta H_{Hess}=-132.5608-230.015-(-132.5-285.85)=55.8\ ^{kJ}/_{mol}$; $\Delta S_{dispersed}=-\Delta H_H/T=-55.77/298.15\cdot1000=-187\ ^{J}/_{(mol\,K)}$;

Viela	$\Delta H°_H\ ^{kJ}/_{mol}$	$\Delta S°_H\ ^{J}/_{mol/K}$	$\Delta G°_H\ ^{kJ}/_{mol}$
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	–10.539	-157.2

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

CRC 2010; $\Delta S_{Hess}=\Delta S°_{NH4+}+\Delta S°_{OH}-\Delta S°_{NH3}-\Delta S°_{H2O}=771.8\ ^{J}/_{mol/K}$;

$\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=-189.74+1294.98=1105.24\ ^{J}/_{(mol\,K)}$;

$\Delta G_{Hess}=\Delta H_{Hess}-T\cdot\Delta S_{Hess}=55,77-298,15\cdot0,7718=-174,3\ ^{kJ}/_{mol}$.

$T\bullet\Delta S_{tota}=0,5848\cdot298,15=174,4\ ^{kJ}/_{mol.}$; bound energy ;

BioTherm2006; $\Delta G_{Hess}=\Delta G°_{NH4+}+\Delta G°_{OH}-\Delta G°_{NH3}-\Delta G°_{H2O}=-90.415\ ^{kJ}/_{mol}$

$=-79,3-157,2-(91,1056-237,191)=-90.4146\ ^{kJ}/_{mol}$ **exoergic**.

$K_{eq2}=\exp(-\Delta G_{min}/R/T)=\exp(90414.6/8.3144/298.15)=10^{15.84}$; strong

Hesss change negative $\Delta G_{Hess}=-329.4\ ^{kJ}/_{mol}$ minimized at equilibrium mixture $\Delta G_{min}=-R\bullet T\bullet\ln(K_{eq2})=-90.415\ ^{kJ}/_{mol}$;

3. K_{eq3}; protolysis $NH_4^++H_2O+\Delta G+Q \Rightarrow NH_{3aq}+H_3O^+$; $pK_{eq}=10,99$; $NH_4^+=H^++NH_{3aqua}$; $pK_a=9,25$;

1.$\Delta H_H=\Delta H°_{NH3}+\Delta H°_{H3O}-\Delta H°_{NH4+}-\Delta H°_{H2O}=-132.5-285.81-(-132.5608-286.65)=0.901$.........$^{kJ}/_{mol}$ **athermic**......

2.$\Delta S_{dispersed}=-\Delta H_H/T=-0.901/298.15=-3.02$........$^{J}/_{(mol\,K)}$; $\Delta G_{Hess}=\Delta G°_{NH3}+\Delta G°_{H3O}-\Delta G°_{NH4+}-\Delta G°_{H2O}=108.7\ ^{kJ}/_{mol}$

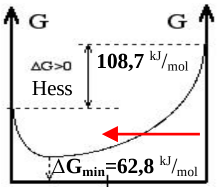
2. $\Delta S_{Hess}=\Delta S°_{NH3}+\Delta S°_{H3O}-\Delta S°_{NH4+}-\Delta S°_{H2O}=-739.2922-3.854-(113.4-453.188)=-403.4$...........$^{J}/_{mol/K}$

$\Delta G_{Hess}=\Delta H_{Hess}-T\cdot\Delta S_{Hess}=0.9008-298.15\cdot-0.4033582=121.2$..........$^{kJ}/_{mol}$.**endoergic**................

$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}=-3.021-403.358=-406.4$....... $^{J}/_{(mol\,K)}$ $T\bullet\Delta S_{total}=-406.4\cdot298.15=-121.2$.........$^{kJ}/_{mol}$;

$$K_{eq2}=\frac{[OH^-]\cdot[NH_4^+]}{[NH_3]aqua\cdot[H_2O]}=10^{15,84};\ K_{eq3}=\frac{[NH_3]aqua\cdot[H_3O^+]}{[NH_4^+]\cdot[H_2O]}=[H_2O]\cdot K_{H2O}/K_{NH4OH}=[H_2O]\frac{3.26\cdot10^{-18}}{1,78\cdot10^{-5}}=1,014\cdot10^{-11};$$

$$\text{Clasic acid value } K_a=\frac{[H^+]\cdot[NH_3]aqua}{[NH_4^+]}=[H_2O]\cdot K_{eq3}=55.3\cdot1.014\cdot10^{-11}=5.61176\cdot10^{-10}=10^{-9.25}=10^{pKa};\ pK_a=9.25;$$



A+B 50% C+D

reactants $NH_4^++H_2O$

products $NH_{3aq}+H_3O^+$

$\Delta G_{eq3}=-R\bullet T\bullet\ln(K_{eq3})=-8.3144\bullet298.15\bullet\ln(1.014\cdot10^{-11})=62.75\ ^{kJ}/_{mol}$, Endothermic and exoergic NH_4^+ protolysis Hess free energy change $\Delta G_{protolysisHess3}=108.7\ ^{kJ}/_{mol}$ is positive, but

minimized $\Delta G_{eq3}=62.8\ ^{kJ}/_{mol}$ at equilibrium mixture $K_{eq3}=\frac{[NH_3]aqua\cdot[H_3O^+]}{[NH_4^+]\cdot[H_2O]}=1.014\cdot10^{-11}$

Endothermic and exoergic NH_{3aq} and H_2O protolysis free energy change $\Delta G_{protolysisHess}$ negative $-174.3\ ^{kJ}/_{mol}$ but minimized to $\Delta G_{eq2}=\Delta G_{min}=-90.4\ ^{kJ}/_{mol}$ reached strong base equilibrium mixture $K_{eq2}=10^{15.84}$;

Prigogine attractor is free energy change minimum. Free energy change minimum establishes equilibrium.

$\Delta G_{eq}=G_{NH3aq}+G_{H3O}-G_{NH4+}-G_{H2O}=273,2+22,44-232,89-0=62,76\ ^{kJ}/_{mol}$,

$G_{NH4+}=G_{NH3aq}+G_{H3O}-\Delta G_{eq}-G_{H2O}=273,2+22,44-62,75-0=232,9\ ^{kJ}/_{mol}$,

Amonia solution concentration C=0.001 M; ax2-bx-c-0NH4-CH3COO

$[OH^-]=[NH_4^+]=C\cdot\alpha=0.001\cdot0.1259=10^{-3.9}\ M=1.259\cdot10^{-4}\ M$; $pOH=3.9$; $\alpha=10^{-3.9}/0.001=0.1259$;

THERMODYNAMICS Exercise V.e diyhidrogenphosphate $\mathbf{H_2PO_4^-}_{aq}$ protolysis in water

Calculate ΔH_H ΔS_H ΔG_H at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? For the diyidrogenphosphate $\mathbf{H_2PO_4^-}_{aq}$ protolysis with water! Will be **exoergic** or **endoergic**!

Data $\mathbf{NaH_2PO_4}$ $2H_2O$ solubility 94,9 $^{g}/_{100g}$ H_2O, density 1,32 $^{g}/_{mL}$, $\mathbf{Na_2HPO_{4s}}$ 11,8 $^{g}/_{100g}$ H_2O, density 1,1 $^{g}/_{mL}$, CRC 2010 ; **BioThermodynamic2006** $\mathbf{H_2PO_4^- + H_2O + \Delta G + Q \Rightarrow HPO_4^{2-} + H_3O^+}$ CRC2020;pH=7,36; I=0,25 M;

Substance	$\Delta H°_H$, $^{kJ}/_{mol}$	$\Delta S°_H$, $^{J}/_{mol/K}$	$\Delta G°_H$, $^{kJ}/_{mol}$
$\mathbf{H_3O^+}$	-285.81	-3.854	-213,275
$\mathbf{H_2O}$	-285.85	69.9565	-237,191
$\mathbf{H_2O}_{\uparrow gas}$	-241,8352	188,7402	-228,6
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{H_3PO_4}$	-1271,7	150,8	-1123,6
$\mathbf{H_2PO_4^-}$	-1302,6	92.5	-1137,3
$\mathbf{HPO_4^{2-}}$	-1292,14	-33,47	-1089,28
$\mathbf{HPO_4^{2-}}$	**-1298,89**	**-810,792**	**-1057,143**
$\mathbf{PO_4^{3-}}$	–1277,4	–220,5	–1018,7

1.$\Delta H_{Hess} = \Delta H°_{products} - \Delta H°_{reactants}$;2.$\Delta S_{Hess} = \Delta S°_{products} - \Delta S°_{reactants}$

CRC 2010; 3.$\Delta G_{Hess} = \Delta H_{Hess} - T \bullet \Delta S_{Hess}$

$=\mathbf{-1057,143}-213,275-(-1137,3\mathbf{-151,549})= \mathbf{18,43}$ $^{kJ}/_{mol}$

$=-228,6-(-237,191)=$; $\Delta H_H=-241,8352-(-285,85)=64,3$ $^{kJ}/_{mol}$

BioTherm2006;$\Delta G_H = \Delta G°_{HPO42-} + \Delta G°_{H3O} - \Delta G°_{H2PO4-} - \Delta G°_{H2O} =$

$=-1089,28-213,275-(-1137,3-237,191)= 71,936$ $^{kJ}/_{mol}$

1.$\Delta H_H = \Delta H°_{HPO42-} + \Delta H°_{H3O} - \Delta H°_{H2PO4-} - \Delta H°_{H2O} = 10,5$ $^{kJ}/_{mol}$ endot

$=-1292,14-285,81-(-1302,6-285,85)= -1577,95-1588,45=10,5$ $^{kJ}/_{mol}$

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

3. $\Delta S_{total} = \Delta S_H + \Delta S_{disperse} = -199,784-35,3= -234,984$ $^{J}/_{(mol\ K)}$;

2. $\Delta S_H = \Delta S°_{HPO42-} + \Delta S°_{H3O} - \Delta S°_{H2PO4-} - \Delta S°_{H2O} = -33,47-3,854-(92,5+69,96)=-199,784$ $^{J}/_{mol/K}$;

$\Delta G_H = \Delta H_H - T*\Delta S_H = 10,5-298,15*-0,199784=70,0$ $^{kJ}/_{mol}$; $=\mathbf{4,55}-298,15*\mathbf{-0,454}=\mathbf{140}$ $^{kJ}/_{mol}$ endoergic...

3. $T \bullet \Delta S_{total} = -234,984$ $^{J}/_{mol/K}$ •298,15 K= -70,0.... $^{kJ}/_{mol}$ bound TΔSn accumulated energy.non **spontaneous**

Equilibrium reached by free energy change minimum Prigogine attractor at compounds mixture ratio in expression

products over reactants: $\frac{[HPO_4^{2-}]\cdot[H_3O^+]}{[H_2PO_4^-]\cdot[H_2O]}$ $=\mathbf{K_{eq2}} = \mathbf{K}_{a2}/[\mathbf{H_2O}]=10^{-7,199}/55,3457339=1,144*10^{-9}$; $pK_{a2}=7,199$

$$\mathbf{\Delta G_{eq2}=-R \bullet T \bullet ln(K_{eq2})}=-8,3144 \bullet 298,15 \bullet \mathbf{ln}(1,143*10^{-9})=51,04\ ^{kJ}/_{mol};$$

Dihydrogenphosphate $\mathbf{H_2PO_4^-}_{aq}$ weak acid $pK_a=7,199$ unfavored protolysis $\mathbf{H_2PO_4^- + H_2O \Rightarrow HPO_4^{2-} + H_3O^+}$.

$$\mathbf{K_a}= \frac{[HPO_4^{2-}]\cdot[H_3O^+]}{[H_2PO_4^-]} =[\mathbf{H_2O}]\ \mathbf{K_{eq}} = 55,3*1,144*10^{-9} =10^{-7,199}=10^{-pKa};\ pK_a=7,199;$$

$\mathbf{HPO_4^{2-} + H_2O \Rightarrow PO_4^{3-} + H_3O^+ = K_{eq3} = K}_{\mathbf{HPO42-}}/[\mathbf{H_2O}]= 10^{-12,35}/55,3457339=8,07*10^{-15}$; $pK_{a3}=12,35$

$\Delta G_H = \Delta G°_{PO43-} + \Delta G°_{H3O} - \Delta G°_{HPO42-} - \Delta G°_{H2O} = -1018,7-213,275-(-1089,28-237,191)= 94,5$ $^{kJ}/_{mol}$;

$$\mathbf{\Delta G_{eq3}=-R \bullet T \bullet ln(K_{eq3})}=-8,3144 \bullet 298,15 \bullet \mathbf{ln}(8,07*10^{-15})=80,44\ ^{kJ}/_{mol},$$

$\mathbf{H_3PO_4 + H_2O \Rightarrow H_2PO_4^- + H_3O^+}$; $\mathbf{K_{eq1} = K}_{\mathbf{H3PO4}}/[\mathbf{H_2O}]= 10^{-2,147975}/55,3457339=7,113*10^{-3}$; $pK_{a1}=2,148$

$\Delta G_H = \Delta G°_{H2PO4-} + \Delta G°_{H3O} - \Delta G°_{H3PO4} - \Delta G°_{H2O} = -1089,28-213,275-(-1123,6-237,191)= 58,24$ $^{kJ}/_{mol}$;

$$\mathbf{\Delta G_{eq1}=-R \bullet T \bullet ln(K_{eq1})}=-8,3144 \bullet 298,15 \bullet \mathbf{ln}(0,0001285)= 22,21\ ^{kJ}/_{mol};$$

Endothermic and endoergic $\mathbf{HPO_4^{2-}}$, $\mathbf{H_2PO_4^-}$, $\mathbf{H_3PO_4}$ protolytic Hess free energy change positive $\mathbf{\Delta G_{protolysis}}=94,5$ $^{kJ}/_{mol}$, 70,0 $^{kJ}/_{mol}$ and 58,24 $^{kJ}/_{mol}$, but minimizes up to $\mathbf{\Delta G_{min}} = \mathbf{\Delta G_{eq}}$ = 80,44 , 51,04 and 22,21 $^{kJ}/_{mol}$ reaching equilibrium

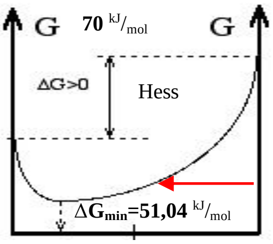
$\mathbf{HPO_4^{2-} + H_2O \Rightarrow PO_4^{3-} + H_3O^+}$; $\mathbf{H_2PO_4^- + H_2O \Rightarrow HPO_4^{2-} + H_3O^+}$;

$\mathbf{H_3PO_{4aq} + H_2O \Rightarrow H_2PO_4^- + H_3O^+}$; $pK_{a3}=12,35$, $pK_{a2}=7,199$, $pK_{a1}=2,148$

$$\frac{[H_2PO_4^-]\cdot[H_3O^+]}{[H_3PO_4]_{aqua}\cdot[H_2O]} = \mathbf{K_{eq1}} = \mathbf{K}_{\mathbf{H3PO4}}/[\mathbf{H_2O}] = 10^{-2,148}/55,3=0,0001285;$$

$$\mathbf{\Delta G_{eq3}=-R \bullet T \bullet ln(K_{eq3})}=-8,3144 \bullet 298,15 \bullet \mathbf{ln}(7,113*10^{-3})=80,44\ ^{kJ}/_{mol},$$

$$\frac{[PO_4^{3-}]\cdot[H_3O^+]}{[HPO_4^{2-}]\cdot[H_2O]} = \mathbf{K_{eq3}} = \mathbf{K}_{\mathbf{HPO42-}}/[\mathbf{H_2O}]= 10^{-12,35}/55,3=8,07*10^{-15};$$



A+B 50% C+D

$H_2PO_4^-{}_{aq} + \mathbf{H_2O}$

reactants products

$\mathbf{HPO_4^{2-}}$ aq + $\mathbf{H_3O^+}$.

Reaction Prigogine attractor is free energy changeminimum $\mathbf{\Delta G_{min}}$
Free energy minimum reaching establishes equilibrium.

THERMODYNAMICS Exercise V f ATP^{4-} adenosine triphosphate hydrolysis reaction

Calculate ΔH_r, ΔS_r, ΔG at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? For the ATP^{4-} adenosine triphosphate hydrolysis reaction with water! Will be **exoergic** or **endoergic**!

$H_2PO_4^- + H_2O + \Delta G + Q \Rightarrow HPO_4^{2-} + H_3O^+$; $\Delta G_{eq} = -R \bullet T \bullet \ln(K_{eq}) = -8{,}3144 \bullet 298{,}15 \bullet \ln(1{,}143 * 10^{-9}) = -51{,}04\ ^{kJ}/_{mol}$;

$K_{H2PO4} = K_{KortlyShuh}/[H_2O] = 10\text{^}(^{-7{,}199})/55{,}3457 = 1{,}143*10^{-9} = \dfrac{[HPO_4^{2-}]\cdot[H_3O^+]}{[H_2PO_4^-][H_2O]}$; $[H_2PO_4^-] = \dfrac{[HPO_4^{2-}]_{aqua}\cdot[H_3O^+]}{1{,}143*10^{-9}\cdot[H_2O]}$;

Equilibrium pH < 7.199 $ATP^{3-} + H_2O \Rightarrow ADP^{2-} + H_2PO_4^-$; $K_{Lehninger} = 3984.1$; $\Delta G_{bl} = -20{,}55\ ^{kJ}/_{mol}$;

$\Delta G_{bLehninger} = -R \bullet T \bullet \ln(K_{Lehninger}) = -8{,}3144 * 298{,}15 * \ln(3984{,}1)/1000 = -20.55\ ^{kJ}/_{mol}$;

$K_{Lehninger} = K_{bLehninger}/[H_2O] = 220500{,}2/55{,}3457 = 3984.1 = \dfrac{[H_2PO_4^-]\cdot[ADP^{3-}]}{[H_2O]\cdot[ATP^{4-}]}$

$\Delta G_H = \Delta G°_{ADP3} + \Delta G°_{HPO42} - \Delta G°_{ATP4} - \Delta G°_{H2O} = -1399{,}9 - 1137{,}3 - (-2267{,}64 - 237{,}191) = -32.4\ ^{kJ}/_{mol}$;

b) $ATP^{4-} + 2H_2O \Rightarrow ADP^{3-} + HPO_4^{2-} + H_3O^+$; $\Delta G_{bLehninger} = -30{,}5\ ^{kJ}/_{mol}$; pH=7,36;

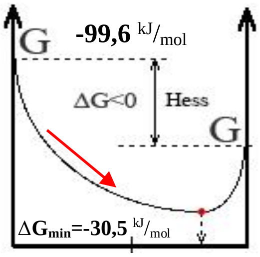
$K_{bLehninger} = \exp(-\Delta G_{bLehninger}/R/T) = \exp(30500/8{,}3144/298{,}15) = \exp(12{,}304) = 220500{,}2 = \dfrac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_2O]^2[ATP^{4-}]}$

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

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

Exothermic and exoergic ATP^{3-} hydrolise reaction Hess free energy change is negative $\Delta G_{Hess} = -99{,}58\ ^{kJ}/_{mol}$, but minimized $\Delta G_{min} = \Delta G_{bLehninger} = -30{,}5\ ^{kJ}/_{mol}$ reaching equilibrium mixture 298,15 K temperature $220500{,}2 = K_{bLehninger}$

Equilibrium reaching is Prigogine attractor free energy change minimum ΔG_{min} . Free energy change minimum reaching establishes equilibrium.



reactants $ATP^{4-} + 2H_2O$

products $ADP^{3-} + HPO_4^{2-} + H_3O^+$

1.$\Delta H_{reaction} = \Delta H°_{products} - \Delta H°_{reactants}$;

Substance $\Delta H°_H\ ^{kJ}/_{mol}$ $\Delta S°_H\ ^{J}/_{mol/K}$ $\Delta G°_H$, $^{kJ}/_{mol}$; 2.$\Delta S_{Hess} = \Delta S°_{products} - \Delta S°_{reactants}$;3.$\Delta G_{Hess} = \Delta H_{Hess} - T \bullet \Delta S_{Hess}$;

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**

Mishcenko; $H\text{-}ATP^{3-} + H_2O = ATP^{4-} + H_3O^+$; pK2=6,71; Alberty

$H_2\text{-}ATP^{2-} + H_2O = H\text{-}ATP^{3-} + H_3O^+$; pK1=3,99

$H\text{-}ADP^{2-} + H_2O = ADP^{3-} + H_3O^+$; pK2=6,496; Alberty

$H_2\text{-}ADP^- + H_2O = H\text{-}ATP^{2-} + H_3O^+$; pK1=3,87

$HGlc6P^- + H_2O \Rightarrow Glc6P^{2-} + H_3O^+$; pK2= 5,89; Alberty

$HFruc6P^- + H_2O \Rightarrow Fruc6P^{2-} + H_3O^+$; pK2= 5,89; Alberty

$H_2Fruc16P^{2--} + H_2O \Rightarrow HFruc6P^{3-} + H_3O^+$; pK1= 6,64; Alberty

$HFruc16P^{3--} + H_2O \Rightarrow Fruc6P^{4-} + H_3O^+$; pK1= 5,92; Alberty

$HGlyc3P^- + H_2O \Rightarrow Glyc3P^{2-} + H_3O^+$; pK1= 5,92; Alberty

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bb) $ADP^{3-} + HPO_4^{2-} + H_3O^+ \Rightarrow ATP^{4-} + 2H_2O$; $\Delta G_{bLehninger} = 30{,}5\ ^{kJ}/_{mol}$;

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

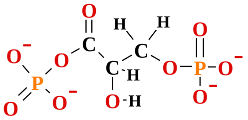
$\Delta G_H = \Delta G°_{ATP4} - 2\Delta G°_{H2O} - \Delta G°_{ADP3} - \Delta G°_{HPO42} - \Delta G°_{H3O} =$

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

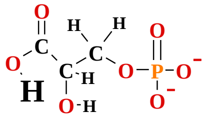
$K_{bbLehninger} = \exp(-\Delta G_{bbLehninger}/R/T) = \exp(-30500/8{,}3144/310{,}15) = 7{,}3*10\text{^}^{(-6)}$;

THERMODYNAMICS Exercise V g **1,3-bis-phospho-glycerate** hydrolysis to **3-phospho-glycerate**

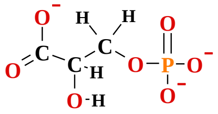
Calculate ΔH_H ΔS_H ΔG_H at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**?
For the phosphate hydrolyse **Glyc31P=>Glyc3P**$^-$ reaction with water! Will be **exoergic** or **endoergic**! CRC 2010



$\Delta G_{aLehninger}=-49,3\ ^{kJ}/_{mol}$;
+2H$_2$O=>
3.$\Delta G_{Hess}=\Delta H_{Hess}-T\bullet\Delta S_{Hess}$



+HPO$_4^{2-}$
+H$_2$O=>



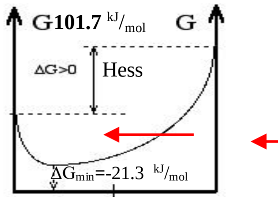
+HPO$_4^{2-}$
+ H$_3$O$^+$

$K_{aLehninger}=\exp(49300/8,3144/298,15)=433562158,5$; **Glycerat31P^{4-}+ 2H$_2$O => Glycerat3P^{3-}+ HPO$_4^{2-}$+ H$_3$O$^+$**;
Mishcenko (**H$_3$O$^+$**) $\Delta H°_{Hess}=-285,81\ ^{kJ}/_{mol}$; $\Delta G_{Hess}=\Delta G°_{H3O+}+\Delta G°_{Glyc3P}+\Delta G°_{HPO42-}-\Delta G°_{Glyc31P}-2\Delta G°_{H2O}$=**-107.75** $^{kJ}/_{mol}$;
Substance $\Delta H°_H\ ^{kJ}/_{mol}$ $\Delta S°_H\ ^{J}/_{mol/K}$ $\Delta G°_H$, $^{kJ}/_{mol}$; 1.$\Delta H_{Hess}=\Delta H°_{products}-\Delta H°_{reactants}$; 2.$\Delta S_{Hess}=\Delta S°_{products}-\Delta S°_{reactants}$;

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**
Glyat3P^{3-}	**-1725,81**	**-2224,26**	**-1347,73**
Glyt31P^{4-}	-1725,76	-2290,6	-2207,30
Glyat2P^{3-}	-	-	-1341.79
Glyat2P^{3-}	-	-	**-1333,2**
Glycerol	-	-	-171,35
Glycerol	**-679,85**	**-1760,65**	**-154,912**
Glycerate$^-$	**Bio**	**Thermo**	**-452,31**
Glyol3P^{3-}	**dynami**	**c 2006**	-1077,13
Glyo13P^{3-}	**-1725,8**	**-2224,26**	**-1062,65**
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**

B06; =-213,275**-1347,73-1057,143**-(-2207,30+2***-151,549**)=**-107.75** $^{kJ}/_{mol}$;
CRC10 **Glyc3P^{2-}+H$_2$O =>Glycerol+HPO$_4^{2-}$+ΔG+Q; $\Delta G_{Lehninger}$= -9,2** $^{kJ}/_{mol}$**;**
CRC10 $\Delta G_{Hess}=\Delta G°_{Glycerol}+\Delta G°_{HPO42-}-\Delta G°_{Glyc3P}-\Delta G°_{H2O}$ =**-46,43** $^{kJ}/_{mol}$
CRC10=-171,35-1089,28-(**-1062,65**+(**-151,549**))=**-46,43** $^{kJ}/_{mol}$;
$K_{aLehninger}=\exp(9200/8,3144/298,15)=40,906$
Glycerol1P$^-$+ADP^{2-}(+H$_2$O)=>Glycerol+ATP^{3-}; **$\Delta G_{Lehninger}$=11.35** $^{kJ}/_{mol}$**;**
$K_{aL}=K_{Lehninger}$*[**H$_2$O**]=0,000185513*55,3457339=0,0102673531329907
$\Delta G_H=\Delta G°_{Glyc}+\Delta G°_{ATP3}-\Delta G°_{Glyc3P}-\Delta G°_{ADP2}$= **40** $^{kJ}/_{mol}$;
=-171,35**-2267,64-(-1062,65-1399,9)**= **39,998** $^{kJ}/_{mol}$;
abb)Glycerol1P^{2-}+ADP^{3-}+H$_3$O$^+$=>Glycerol+ATP^{4-}+H$_2$O; **$\Delta G_{Lehninger}$**=21.3 $^{kJ}/_{mol}$
$K_{abb}=K_aK_{bb}=40,906*0,000004535142=0,000185515$
$K_{abb}=\exp(-21300/8,3144/298,15)=0,000185513$;
$\Delta G_H=\Delta G°_{Glyc}+\Delta G°_{ATP4}+\Delta G°_{H2O}-\Delta G°_{Glyc3P}-\Delta G°_{ADP3}-\Delta G°_{H3O}$=**101.724** $^{kJ}/_{mol}$;
=**-154,912-2267,64-151,549-(-1062,65-1399,9**-213,275)=**101.724** $^{kJ}/_{mol}$;

$\Delta G_{abb}=\Delta G_a+\Delta G_{bb}=-9,2+30,5=21.3\ ^{kJ}/_{mol}$;
Exoergic transfer **HPO$_4^{2-}$** from Glycerol1P^{2-}to ATP^{4-}
positive **$\Delta G_{transfer}$=101.7** $^{kJ}/_{mol}$, but minimizes reaching
ΔG_{abb}=$\Delta G_a+\Delta G_{bb}$=21.3 $^{kJ}/_{mol}$ equilibrium mixture
$K_{abb}=K_aK_{bb}=40,906*0,000004535142=0,000185513$.
ΔG_{aL}=-8,3144*298,15***ln**(0,010267353)= 11,35 $^{kJ}/_{mol}$



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

$\Delta G_{abb}=\Delta G_a+\Delta G_{bb}=-9,2+30,5=21.3\ ^{kJ}/_{mol}$; Reactants Glycerol1P^{2-}+ADP^{3-}+H$_3$O$^+$

$$\frac{[\mathrm{Glycerol}]\cdot[\mathrm{HPO_4^{2-}}]\cdot[\mathrm{ATP^{4-}}]}{[\mathrm{H_2O}]\cdot[\mathrm{Glycerol1P^{2-}}]\cdot[\mathrm{ADP^{3-}}]}=K_{eqL}=\quad K_{abb}=K_aK_{bb}=0,000185513$$

Products Glycerol+ATP^{4--}+H$_2$O;;

Glycerat31P^{2-}+ H$_2$O => Glycerat3P$^-$+ H$_2$PO$_4$;

$\Delta G_{Hess}=\Delta G°_{Glyc3P}+\Delta G°_{H2PO4-}-\Delta G°_{Glyc31P}-\Delta G°_{H2O}$=**-1347,73**-1137,3-(-2207,3+(-237,191))= **-40.54** $^{kJ}/_{mol}$;
ΔG_{eaL}=-R•T•ln(K_{aL})=-8,3144•298,15•**ln**(7833705)=-39,35 $^{kJ}/_{mol}$;

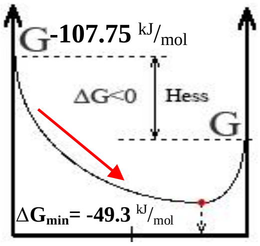
$$K_{aL}=K_{Lehninger}/[\mathrm{H_2O}]=433562158,5/55,3457339=7833705=\frac{[\mathrm{Glycerat3P^{3-}}]\cdot[\mathrm{H_2PO_4^-}]}{[\mathrm{H_2O}]\cdot[\mathrm{Glycerat13P^{4-}}]}$$

$\Delta G_H=\Delta G°_{Glyc3P}+\Delta G°_{HPO42}+\Delta G°_{H3O}-\Delta G°_{Glyc31P}-\Delta G°_{H2O}$=**-1347,73-1057,143**-213,275-(-2207,3+2*(**-151,549**))=**-107.75** $^{kJ}/_{mol}$;

Glycerat31P^{4-}+ 2H$_2$O => Glycerat3P^{3-}+ HPO$_4^{2-}$+ H$_3$O$^+$; 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;
Equilibrium favored pH=7,36. Exothermic and exoergic **1,3-bis-phospho-glycerate** hydrolize reaction free energy change negative **$\Delta G_{hydrolise}$** =**-107.75** $^{kJ}/_{mol}$, but minimizes **ΔG_{eq}**=-49.3 $^{kJ}/_{mol}$

reaching equilibrium mixture: 433562158,5=$K_{aLehninger}$ = $\dfrac{[\mathrm{HPO_4^{2-}}]\cdot[\mathrm{H_3O^+}]\cdot[\mathrm{Glycerat3P^{3-}}]}{[\mathrm{H_2O}]^2\cdot[\mathrm{Glycerat13P^{4-}}]}$;

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



reactants
A+2B 50% C+D+E
Glyc31P^{4-}+2H$_2$O

Free energy change minimum reaching establishes equilibrium.

products **Glyc3P^{3-}+HPO$_4^{2-}$+H$_3$O$^+$**

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

$\mathbf{ADP^{2-}+H_2PO_4^-=>ATP^{3-}+H_2O}$; $\Delta G_{Lehninger}=20,55\ ^{kJ}/_{mol}$; 2,26<pH<6,72

$K_{bL}=[H_2O]K_{Lehninger}=0,000004535142*55,34573393=0,000251001=10^{-3,6004}=\frac{[H_2O]\cdot[ATP^{4-}]}{[H_2PO_4^-]\cdot[ADP^{3-}]}$

$\Delta G_{bLenhinger}=-R\bullet T\bullet\ln(K_{bLehninger})=-8,3144\bullet 298,15\bullet\ln(0,000251001)=20,551\ ^{kJ}/_{mol}$;

bb $\mathbf{ADP^{3-}+HPO_4^{2-}+H_3O^+=>ATP^{4-}+2H_2O}$; $\Delta G_{bbLehninger}=30,5\ ^{kJ}/_{mol}$; pH=7,36

$K_{bb}=K_{Lehninger}=\exp(-30,5/8,3144/298,15)=0,000004535142=\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$

$\Delta G_H=\Delta G°_{ATP4}+2\Delta G°_{H2O}-\Delta G°_{HPO42}-\Delta G°_{ADP3}-\Delta G°_{H3O}=\mathbf{46,015}\ ^{kJ}/_{mol}$;

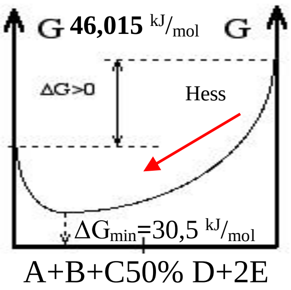
$=\mathbf{-2267,64}-2*\mathbf{151,549-(-1057,143-1399,9}-213,275)=\mathbf{46,015}\ ^{kJ}/_{mol}$;

Biochemistry Thermodyn 2006, Alberty Masachusetts; $\mathbf{H_3O^+}$ Mishchenko 213.275 $^{kJ}/_{mol}$;

Endothermic and endoergic $\mathbf{ADP^{3-}}$ phosphorilation Hess free energy change positive at pH 7,36 $\Delta G_{Hess}=\mathbf{46.015}\ ^{kJ}/_{mol}$, but minimizes $\Delta G_{min}=\Delta G_{eq}=30.5\ ^{kJ}/_{mol}$ reaching

equilibrium mixture : $0,000004535142=K_{bb}=\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}\cdot$ reactants

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



$\mathbf{HPO_4^{3-}+ADP^{3-}+2H_3O^+}$

products $\mathbf{HPO_4^{2-}+ATP^{4-}}$

Free energy change minimum reaching establishes equilibrium.

$Glycerol1P^-+ADP^{2-}=>Glycerol+ATP^{3-}(+\mathbf{H_2O})$;

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

$K_{eqLehninger}=K_{Lehninger}*[H_2O]=0,000185512570561914*55,34573393=0,010267$

$\Delta G_{eqLehninger}=-R\bullet T\bullet\ln(K_{aeLehninger})=-8,3144*298,15*\ln(0,01026732937099)/1000=\mathbf{11.351}\ ^{kJ}/_{mol}$;

$Glycerol1P^{2-}+ADP^{3-}+H_3O^+=>Glycerol+ATP^{4-}+2H_2O$; $\Delta G_{abb}=\Delta G_a+\Delta G_{bb}=\mathbf{-9,2+30,5=21.3}\ ^{kJ}/_{mol}$; $\Delta G_{Lehninger}=21,3\ ^{kJ}/_{mol}$;

$\Delta G_H=\Delta G°_{Glyc}+\Delta G°_{ATP4}+2\Delta G°_{H2O}-\Delta G°_{Glyc3P2}--\Delta G°_{ADP3}-\Delta G°_{H3O}=\mathbf{40}\ ^{kJ}/_{mol}$;

$=\mathbf{-154,912-2267,64+2*-151,549-(-1062,65-1399,9}-213,275)=\mathbf{39.998}\ ^{kJ}/_{mol}$;

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

$\mathbf{Glycerat31P^{4-}}+ADP^{3-}=>\mathbf{Glycerat3P^{3-}+}ATP^{4-}$ $\Delta G_{Lehninger}=-18.8\ ^{kJ}/_{mol}$;

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

$\mathbf{Glycerat31P^{4-}+H_2O=>Glycerat3P^{3-}+H_2PO_4}$; pH<7,199; $G_{aLehninger}=-39,4\ ^{kJ}/_{mol}$;

$K_{aLehninger}=K_{Lehninger}/[H_2O]=433562158,5/55,3457339=7833705,111=\frac{[Glycerat3P^{3-}]\cdot[H_2PO_4^-]}{[H_2O]\cdot[Glycerat13P^{4-}]}$

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

$K_{abbLehninger}=\exp(-\Delta G_{abbLehninger}/R/T)=\exp(18800/8,3144/298,15)=1966.266$

$K_a=K_{Lehninger}=\exp(-\Delta G_{Lehninger}/R/T)=\exp(49300/8,3144/298,15)=433562158,5=\frac{[HPO_4^{2-}]\cdot[H_3O^+]\cdot[Glycerat3P^{3-}]}{[H_2O]^2\cdot[Glycerat13P^{4-}]}$

$\mathbf{Glycerat31P^{4-}+2H_2O=>Glycerat3P^{3-}+HPO_4^{2-}+H_3O^+}$; $\Delta G_{Lehninger}=-49,3\ ^{kJ}/_{mol}$,

$\Delta G_{Hess}=\Delta G°_{H3O+}+\Delta G°_{Glyc3P}+\Delta G°_{HPO42-}-\Delta G°_{Glyc31P}-2\Delta G°_{H2O}=\mathbf{-107.75}\ ^{kJ}/_{mol}$;exothermic

$=-213,275\mathbf{-1347,73-1057,143}-(-2207,30+2*\mathbf{-151,549})=\mathbf{-107.75}\ ^{kJ}/_{mol}$;

$\mathbf{Glyat31P^{4-}}+ADP^{3-}=>\mathbf{Glyat3P^{3-}+}ATP^{4-}$;$\Delta G_{eqtotal}=-49,3+30,5=\mathbf{-18,8}\ ^{kJ}/_{mol}$;$\Delta G_{totalHess}=\mathbf{-33}\ ^{kJ}/_{mol}$

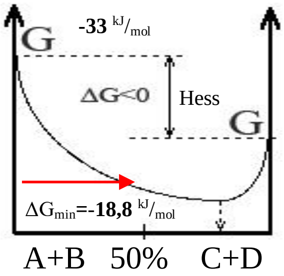
$\Delta G_{Hess}=\Delta G°_{ATP4-}+\Delta G°_{Glyc3P3}-\Delta G°_{Glyc31P4}-\Delta G°_{ADP3}=\mathbf{-33}\ ^{kJ}/_{mol}$; $=-2292,5\mathbf{-1347,73}-(-2207,3\mathbf{-1399,9})=\mathbf{-33}\ ^{kJ}/_{mol}$;

$$K_aK_{bb}=K_{abb}=433562158,5*0,000004535142=1966.266=\frac{[Glycerat3P^{3-}]\cdot[ATP^{4-}]}{[Glycerat13P^{4-}]\cdot[ADP^{3-}]}$$

$\Delta G_{eq}=-R\bullet T\bullet\ln(K_{eq})=-8,3144\bullet 298,15\bullet\ln(1965,363914)=\mathbf{-18,8}\ ^{kJ}/_{mol}$ pH=7,36. Exothermic and exoergic $\mathbf{Glycerat31P^{4-}}$ phosphate transfer free energy change is negative at pH=7,36 negative $\Delta G_{transfer}=\mathbf{-33}\ ^{kJ}/_{mol}$, but minimizes to $\Delta G_{min}=\Delta G_{eq}=\mathbf{-18,8}\ ^{kJ}/_{mol}$ reaching equilibrium mixture :

$$K_{eq}=K_aK_{bb}=\frac{[Glycerat3P^{3-}]\cdot[ATP^{4-}]}{[Glycerat13P^{4-}]\cdot[ADP^{3-}]}=433562158,5*0,000004535142=1966.266;$$

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



Free energy change minimum reaching establishes equilibrium. $\mathbf{Glyc31P^{4-}}+ADP^{3-}$ (A+B) reactants
$\mathbf{Glyc3P^{3-}}+ATP^{4-}$ (C+D) products.

THERMODYNAMICS Exercise V h **PyruvateEnolP^{3-}** hydrolysis to $H_3CC{=}OCOO^-$+**HPO_4^{2-}**

PyruvEnolP^{3-}+H_2O=>$H_3CC{=}OCOO^-$+**HPO_4^{2-}**; $\Delta G_{Lehninger}$=-61,9 $^{kJ}/_{mol}$;pH=7,36;

I=0,25 M, **BioTherm06**, pH=7,36, $\Delta G_{Hess}=\Delta G°_{H3CC=OCOO-}+\Delta G°_{HPO42-}-\Delta G°_{PyruvEnolP3-}-\Delta G°_{H2O}$=**-190,3** $^{kJ}/_{mol}$;

Substance	$\Delta H°_H$ $^{kJ}/_{mol}$	$\Delta S°_H$ $^{J}/_{mol/K}$	$\Delta G°_H$, $^{kJ}/_{mol}$;
PyruvEnolP^{3-}	-1400	-1100	-1189,73
$H_3CC{=}OCOO^-$	-597,4	-850	-350,78
$H_3CC{=}OCOO^-$	-603,7	-433,54	-474,44
$H_3CC{=}OCOO^-$	**-597,04**	**-846,66**	**-344,62**
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**

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

$\Delta H_{Hess}=\Delta H°_{pyruvat}+\Delta H°_{HPO42-}-\Delta H°_{PyruvEnolP3-}-\Delta H°_{H2O}$=**-209** $^{kJ}/_{mol}$;

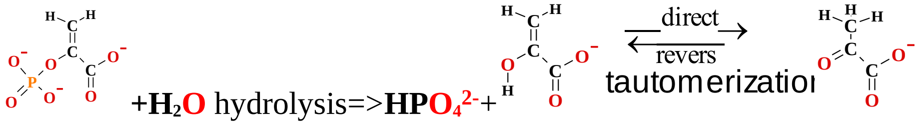
=**-597,04-1298,89**-(-1400-**286,65**)= **-209** $^{kJ}/_{mol}$; **exothermic**

$\Delta S_{Hess}=\Delta S°_{pyruvat}+\Delta S°_{HPO42-}-\Delta S°_{PyruvEnolP3-}-\Delta S°_{H2O}$=**-104,3** $^{J}/K/_{mol}$;

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

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

K$_{LehningeH}$=exp(61900/8,3144/298,15)= 69902464988=$10^{10,84}$



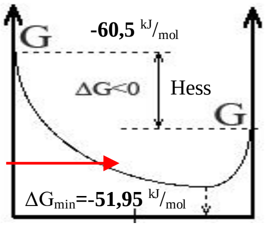
a +H_2O hydrolysis=>**HPO_4^{2-}**+ pyruvate $\Delta G_{Lehninger}$=-61,9 $^{kJ}/_{mol}$;

$$K_a=69902464988=\frac{[CH_3C{=}OCOO^-]\cdot[HPO_4^{2-}]}{[H_2O]\cdot[PyruvEnolP^{3-}]}=10^{10,844};\ pH=7,36..$$

Exothermic and exoergic **PyruvEnolP^{3-}** hydrolize reaction Hess free energy change negative at pH=7,36 Δ**G**$_{hydrolise}$=**-190.3** $^{kJ}/_{mol}$, but minimizes Δ**G**$_{min}$=Δ**G**$_a$= -61,9 $^{kJ}/_{mol}$ reaching equilibrium mixture **K**$_a$= 69902464988= $\frac{[CH_3C{=}OCOO^-]\cdot[HPO_4^{2-}]}{[H_2O]\cdot[PyruvEnolP^{3-}]}$ =$10^{10,844}$;

Equilibrium reaching is Prigogine attractor free energy change minimum **ΔG**$_{min}$.

Free energy change minimum reaching establishes equilibrium.



reactants A+B 50% C+D

PyruvEnolP^{3-}+H_2O

products $H_3CC{=}OCOO^-$+**HPO_4^{2-}**.

PyruvEnolP^{3-}+ADP^{3-}+H_3O^+=>$H_3CC{=}OCOO^-$**+**ATP^{4-}+H_2O; Δ**G**$_{abb}$=Δ**G**$_a$+Δ**G**$_{bb}$=-61,9+30,5= -31,4 $^{kJ}/_{mol}$**;**

$\Delta G_{Hess}=\Delta G°_{ATP4-}+\Delta G°_{H2O}+\Delta G°_{H3CC=OCOO}-\Delta G°_{PyruvEnolP3-}-\Delta G°_{ADP3}-\Delta G°_{H3O\,-}$=**-90.724** $^{kJ}/_{mol}$;

=**-2267,64-151,549**-474,44-(-1189,73-**1399,9**-213,275)=**-90.724** $^{kJ}/_{mol}$;

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}$=**-187.58**-298,15*-0,**3434**=**-85,195** $^{kJ}/_{mol}$;

Δ**G**$_{abb}$**=-R•T•ln(K**$_{abb}$)=-8,3144*298,15***ln**(317017,604870608)/1000=**-31.4** $^{kJ}/_{mol}$;

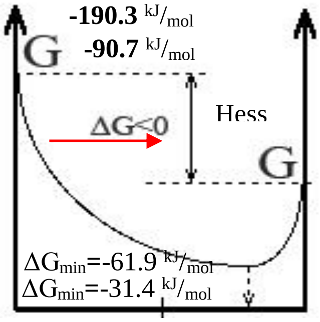
pH=7,36. **K**$_{abb}$=**K**$_a$**K**$_{bb}$=69902464988*0,000004535142=317017,604870608= $\frac{[H_2O]\cdot[ATP^{4-}]\cdot[CH_3C{=}OCOO^-]}{[ADP^{3-}]\cdot[H_3O^+]\cdot[PyruvEnolP^{3-}]}$

Exothermic and exoergic **PyruvEnolP^{3-}** hydrolize reaction Hess free energy change negative at pH=7,36 negative Δ**G**$_{hydrolise}$= **-190.3** $^{kJ}/_{mol}$ and **-90.724** $^{kJ}/_{mol}$, but minimizes Δ**G**$_{min}$=Δ**G**$_{abb}$= **-61.9** $^{kJ}/_{mol}$ and -31,4 $^{kJ}/_{mol}$ reaching equilibrium mixture :

$$69902464988=\frac{[CH_3C{=}OCOO^-]\cdot[HPO_4^{2-}]}{[H_2O]\cdot[PyruvEnolP^{3-}]}=\mathbf{K_a};\ \mathbf{K}_{abb}=\frac{[H_2O]\cdot[ATP^{4-}]\cdot[CH_3C{=}OCOO^-]}{[ADP^{3-}]\cdot[H_3O^+]\cdot[PyruvEnolP^{3-}]}=317017,6.$$

Equilibrium reaching is Prigogine attractor free energy change minimum ΔG$_{\mathbf{min.}}$

Free energy change minimum reaching establishes equilibrium.



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

reactants PyruvEnolP^{3-}_+**ADP^{3-}+H_3O^+**_

products **$H_3CC{=}OCOO^-$+ATP^{4-}+H_2O** _

ADP^{2-}+H$_2$PO$_4^-$=>**ATP**$^{3-}$+**H$_2$O**; ΔG$_{Lehninger}$ = 20,55 $^{kJ}/_{mol}$; 2,26<pH<6,72

ΔG$_{Hess}$=ΔG°$_{ATP3}$+ΔG°$_{H2O}$-ΔG°$_{H2PO4-}$-ΔG°$_{ADP2}$=**-2267,64-151,549-(-1399,9-1057,143)=37,85** $^{kJ}/_{mol}$;

K$_{bL}$=[H$_2$O]K$_{Lehninger}$= 0,000004535142* 55,34573393= 0,000251001=10$^{-3,6004}$= $\frac{[H_2O]\cdot[ATP^{4-}]}{[H_2PO_4^-]\cdot[ADP^{3-}]}$

ΔG$_{bLehninger}$=-R•T•ln(K$_{bLehninger}$)=-8,3144•298,15•**ln**(0,000251001)=20,551 $^{kJ}/_{mol}$;

bb ADP^{3-}+HPO$_4^{2-}$+H$_3$O$^+$=>ATP^{4-} +2H$_2$O; Δ**G$_{bb}$**$_{Lehninger}$=30,5 $^{kJ}/_{mol}$; pH=7,36

K$_{bb}$=**K**$_{Lehninger}$=exp(-30,5/8,3144/298,15)= 0,000004535142= $\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$

ΔG$_{Hess}$=ΔG°$_{ATP4}$+2ΔG°$_{H2O}$-ΔG°$_{HPO42}$-ΔG°$_{ADP3}$-ΔG°$_{H3O}$=**99.58** $^{kJ}/_{mol}$;

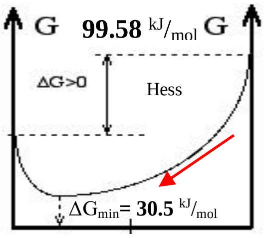
=**-2267,64**-2***151,549-(-1057,143-1399,9**-213,275)=**99.58** $^{kJ}/_{mol}$;**Biothermodynamic** 2006; [**H$_2$O**]/[**H$_3$O$^+$**] CRC 2010

Endothermic and endoergic **ADP^{3-}** phosphorilation reaction at pH 7,36 Hess free energy change negative Δ**G$_{phosphorilation}$** =**99.58** $^{kJ}/_{mol}$, but minimizes

Δ**G$_{min}$**= Δ**G$_{bb}$**=30,5 $^{kJ}/_{mol}$ reaching equilibrium mixture :

0,000004535142=K$_{bb}$= $\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$. Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG$_{min}$.

Free energy change minimum reaching establishes equilibrium. Reactants



ΔG$_H$=ΔG°$_{ATP4-}$+ΔG°$_{H2O}$+ΔG°$_{H3CC=OCOO}$ -ΔG°$_{PyruvEnolP3-}$-ΔG°$_{ADP3}$-ΔG°$_{H3O}$ -=**-90.724** $^{kJ}/_{mol}$; **ADP^{3-}+HPO$_4^{2-}$+H$_3$O$^+$** -

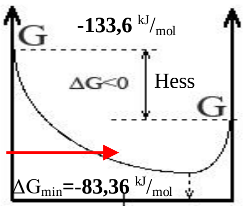
=**-2267,64-151,549**-474,44-(-1189,73-**1399,9**-213,275)=**-90.724** $^{kJ}/_{mol}$; product **ATP^{4-} +2H$_2$O** ;

PyruvEnolP^{3-}+ADP^{3-}+H$_3$O$^+$=>H$_3$CC=OCOO$^-$+ATP^{4-}+H$_2$O; Δ**G**$_{ab}$=Δ**G**$_a$+Δ**G**$_{bb}$=-61,9+30,5=-31,4 $^{kJ}/_{mol}$**;**

K$_{abb}$=exp(31400/8,3144/298,15)= 317017,6

K$_{abb}$= **K$_a$ K$_b$** =69902464988*0,000004535142=317017,6= $\frac{[H_2O]\cdot[ATP^{4-}]\cdot[CH_3C{=}OCOO^-]}{[ADP^{3-}]\cdot[H_3O^+]\cdot[PyruvEnolP^{3-}]}$

Exothermic and exoergic **PyruvEnolP^{3-}** hydrolize reaction Hess free energy change negative at pH=7,36 negative Δ**G$_{hydrolise}$**=**-90.724** $^{kJ}/_{mol}$, but minimizes reaching equilibrium mixture Δ**G**$_{abb}$=-31.4 $^{kJ}/_{mol}$: **K$_{abb}$**= $\frac{[H_2O]\cdot[ATP^{4-}]\cdot[CH_3C{=}OCOO^-]}{[ADP^{3-}]\cdot[H_3O^+]\cdot[PyruvEnolP^{3-}]}$ =317017.6. Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG$_{min}$.



Free energy change minimum establishes equilibrium.

reactants PyruvEnolP^{3-}+**ADP^{3-}+H$_3$O$^+$**

products **H$_3$CC=OCOO$^-$+ATP^{4-}+H$_2$O**

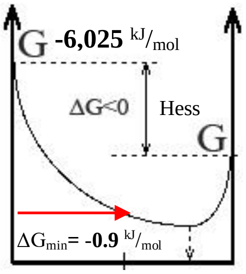
$\frac{[CH_3COO^-]\cdot[HSCoA^{4-}]\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[Acetyl\text{-}CoA^{4-}]}$=1,4381; **HPO$_4^{2-}$**+ADP^{3-}+Acetyl-CoA^{4-}=>ATP^{4-}+CH$_3$COO$^-$+HSCoA^{4-} ;

ΔG$_H$=ΔG°$_{ATP4-}$+ ΔG°$_{CH3COO-}$+ΔG°$_{CoA2-}$-ΔG°$_{HPO42}$-ΔG°$_{ADP3}$-ΔG°$_{Acetyl-CoA2-}$= **-6.025** $^{kJ}/_{mol}$;

=**-2267,64-241,663-5,6616-(-1057,143-1399,9-51,8968)**= **-6.025** $^{kJ}/_{mol}$;

K$_{abTotal}$= **K$_a$ K$_{bb}$** =318243,5442*0,000004535142=1.438142576

Δ**G$_{ab}$**=-8,3144•298,15•**ln**(1,438142576)= **-0.9007** $^{kJ}/_{mol}$ pH=7,36.. Exothermic and exoergic **PyruvEnolP^{3-}** hydrolize reaction Hess free energy change negative at pH=7,36 negative Δ**G$_{hydrolise}$**=**-6** $^{kJ}/_{mol}$, but minimizes Δ**G$_{min}$**=Δ**G$_{eq}$**= **-0.9** $^{kJ}/_{mol}$ reaching equilibrium mixture **K$_{ab}$**= $\frac{[CH_3COO^-]\cdot[HSCoA^{4-}]\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[Acetyl\text{-}CoA^{4-}]}$=1,4381 Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG$_{min}$.



reactants **HPO$_4^{2-}$** +ADP^{3-}+Acetyl-CoA^{4-}

Free energy change minimum reaching establishes equilibrium.

products ATP^{4-}+ CH$_3$COO$^-$ + HSCoA^{4-}

Δ**G$_{total}$=ΔG$_a$+ΔG$_b$=ΔG**$_{ab}$=30,5087-31,409= -0,9003 $^{kJ}/_{mol}$**;**

THERMODYNAMICS Exercise V h **AcylCoA^{4-}** hydrolysis to acid+ **HSCoA^{4}**

AcetylCoA^{2-}+H_2O =>CH_3COOH+HSCoA^{2-}; ΔG_{aL}=-21,45 $^{kJ}/_{mol}$; $K_{aL}=K_{Lehninger}/[H_2O]$=5727,95

$\Delta G_{Hess}=\Delta G°_{CH3COOH}+\Delta G°_{CoA2-}-\Delta G°_{Acetyl\text{-}CoA2-}-\Delta G_{H2O}$=-531,743**-5,6616**-(**-51,8968-151,549**)= -333,96 $^{kJ}/_{mol}$;

$\Delta G_{aL}=-R\bullet T\bullet \ln(K_{aL})$=-8,3144*298,15***ln**(5727,95006026944)/1000= **-**21,45 $^{kJ}/_{mol.}$;

I=0,25 M, **BioTherm06**, CRC10; $\Delta G_{Lehninger}$=-31,4 $^{kJ}/_{mol}$; pH=7,36, Acetyl-CoA^{3-}+2H_2O=>CH_3COO^-+HSCoA^{3-}+H_3O^+

AcetylCoA^{3-}	-	-	**-51,8968**
AcetylCoA^{3-}	-	-	-58,06
HSCoA^{3-}	-	-	-7,26
HSCoA^{3-}	**BioThe**	**rmod**06	**-5,6616**
H_3CCOO^-	**-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_3CCOO^-	-486,84	82,23	-247,83
H_3CCOO^-	-485,64	87,58	-369,37
PalmtylCoA^{3-}	PalmitateCoA	-	**-784,9391**
H_3CCOOH	-484,09	159,83	-531,743
$C_2H_4OOCCH_3$	**-485,3**	**-1644,15**	**4,9176**
$C_2H_4OOCCH_3$	-	-	-11.52
CH_3CH_2OH	-	-	62.96
CH_3CH_2OH	-277.6	160.7	-174.8
CH_3CH_2OH	**-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**

$\Delta G_{Hess}=\Delta G°_{CH3COO-}+\Delta G°_{CoA2-}+\Delta G°_{H3O+}-\Delta G°_{Acetyl\text{-}CoA2-}-2*\Delta G_{H2O}$=**-105,6** $^{kJ}/_{mol}$

=**-241,663-5,6616**-213,275-(**-51,8968**+2***-151,549**)= **-105,6** $^{kJ}/_{mol}$;

$K_a=K_{Leninge}$=exp(31400/8,3144/298,15)=317017,64

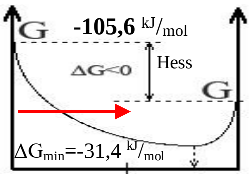
$$K_{aL}=K_{Lehninger}/[H_2O]=317017,6/55,346=5727,95=\frac{[CH_3COOH]\cdot[HSCoA^{2-}]}{[H_2O]\cdot[Acetyl\text{-}CoA^{2-}]}$$

$$K_a=K_{Lehninge}=317017,64=\frac{[CH_3COO^-]\cdot[HSCoA^{3-}].[H_3O^+]}{[H_2O]^2\cdot[Acetyl\text{-}CoA^{3-}]}$$

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

Endoergic **AcylCoA^{3-}** hydrolize Hess free energy change at pH=7,36 positive ΔG_{Hess}=**-105,6** $^{kJ}/_{mol}$, but minimizes $\Delta G_{min}=\Delta G_a$=-31,4 $^{kJ}/_{mol}$ reaching equilibrium mixture Le Chatelier principle is Prigogine attractor free energy minimum ΔG_{min}

Acetyl CoA^{3-}+2H_2O



CH_3COO^-+HSCoA^{3-}+H_3O^+

PalmitCoA^{3-}+2H_2O

reaktanti _

$CH_3(CH_2)_{14}COO^-$+

+HSCoA^{3-}+H_3O^+;

Free energy change minimum reaching establishes equilibrium. A+2B 50% C+D+E produkti.

Hydrolisis equilibrium of PalmitateCoA^{2-}+H_2O=>$CH_3(CH_2)_{14}COOH$+HSCoA^{2-};ΔG_{aLr}=-22.35 $^{kJ}/_{mol}$;at p H<5

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

$$K_{aL}=K_{Lehninger}/[H_2O]=455782,655095979/55,346=8235,15078047156=\frac{[CH_3(CH_2)_{14}COOH][HSCoA^{2-}]}{[Palmitate\text{-}CoA^{2-}][H_2O]}$$

$\Delta G_{Hess}=\Delta G°_{HSCoA2}+\Delta G°_{Palmitate}-(\Delta G_{PalmitateCoA2}+\Delta G_{H2O})$= **-136,4** $^{kJ}/_{mol}$;

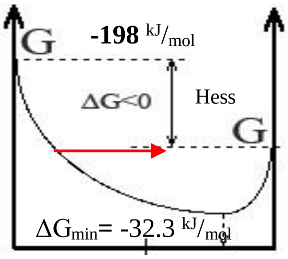
$$K_a=K_{Lehninger}=455782,655095979=\frac{[CH_3(CH_2)_{14}COO^-]\cdot[HSCoA^{3-}].[H_3O^+]}{[H_2O]^2\cdot[Palmitate\text{-}CoA^{3-}]}$$

$\Delta G_{Hess}=\Delta G°_{HSCoA2}+\Delta G°_{Palmitate}-(\Delta G_{PalmitateCoA2}+\Delta G_{H2O})$=**-5,6616-1067,238-(-784,9391-151,549)=-136,4** $^{kJ}/_{mol}$;

PalmitCoA^{3-}+2H_2O=>$CH_3(CH_2)_{14}COO^-$+HSCoA^{3-}+H_3O^+;$\Delta G_{Lehninger}$= -32.3 $^{kJ}/_{mol}$;

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

$K_a=K_{Lehninge}$=exp(32300/8,3144/298,15)=455782,655095979; Endoergic Hydrolysis of Palmit**CoA^{3-}** free energy change negative ΔG_{Hess}=**-198** $^{kJ}/_{mol}$ at pH=7,36 minimizes to $\Delta G_{min}=\Delta G_a$= -32.3 $^{kJ}/_{mol}$ reaching equilibrium mixture $K_a=K_{Lehninger}$=455782,655095979**.** Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.



a) $HP_2O_7^{3-}$+2 H_2O=>HPO_4^{2-}+HPO_4^{2-}+H_3O^+**;** $\Delta G_{aLehninger}$=**-19.2** $^{kJ}/_{mol}$;

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

ATP^{4-}+2H_2O=>AMP^{2-}+ **$HP_2O_7^{3-}$**+H_3O^+; $\Delta G_{bLehninger}$=**-45.6** $^{kJ}/_{mol}$; PalmitCoA^{3-}+2H_2O

A+2B 50% C+D+E

CH_3COO^-+HSCoA^{4-}+H_3O^+=>Acetyl-CoA^{4-}+2H_2O; products $CH_3(CH_2)_{14}COO^-$+HSCoA^{3-}+H_3O^+

$\Delta G_{cLehninger}$**=31.4** $^{kJ}/_{mol}$; $K_c=EXP(-\Delta G_a/R/T)$ =exp(-31400/8,3144/298,15)= 0,0000031544;

ppbc) CH_3COO^-+HSCoA^{4-}+ATP^{4-}+2H_2O=>Acetyl-CoA^{4-}+AMP^{2-}+**HPO_4^{2-}**+**HPO_4^{2-}**+**H_3O^+**; ΔG_{Lehnin}=**-33.4** $^{kJ}/_{mol}$;

ΔG_{abc}=**-45.6-19.2+31.4=-33.4** $^{kJ}/_{mol}$, K_{abc}=2310,5736*97462087,2480605*0,0000031544=710349,826891739:

$\Delta G_{ppbcHess}$= $\Delta G_{ppHess}+\Delta G_{bHess}+\Delta G_{cHess}$ **=-85.6 -111,45+105,6=-91.45** $^{kJ}/_{mol}$.

$\Delta G_{abc}=-R\bullet T\bullet \ln(K)$=-8,3144*298,15***ln**(710349,826891739)=**-33,4** $^{kJ}/_{mol}$;

THERMODYNAMICS Exercise V h Palmtyl**CoA^{4-}** hydrolysis to **HSCoA^{4-}**

Hydrolisis equilibrium of PalmitateCoA^{2-}+H_2O=>$CH_3(CH_2)_{14}COOH$+HSCoA^{2-};**ΔG_{aLr}=**-22.35 $^{kJ}/_{mol}$;at p H<5

ΔG_{aL}=-R•T•ln(K_{aL})=-8,3144*298,15***ln**(8235,15078047156)=-22,35 $^{kJ}/_{mol}$;

K_{aL}=**$K_{Lehninger}$**/[**H_2O**]=455782,655095979/55,346=8235.15078047156= $\dfrac{[CH_3(CH_2)_{14}COOH][HSCoA^{2-}]}{[Palmitate\text{-}CoA^{2-}][H_2O]}$

ΔG_{Hess}=$\Delta G°_{HSCoA2}$+$\Delta G°_{Palmitate}$-($\Delta G_{PalmitateCoA2}$+ΔG_{H2O})= **-136,4** $^{kJ}/_{mol}$;

=**-5,6616-1067,238-(-784,9391-151,549)=-136,4** $^{kJ}/_{mol}$; =**-5,6616-1067,238**-213,275**-(-784,9391+2*(-151,549**-237,191**)/2)=-112.5** $^{kJ}/_{mol}$;

Hydrolisis equilibrium of PalmitCoA^{3-}+2H_2O=>$CH_3(CH_2)_{14}COO^-$+HSCoA^{3-}+H_3O^+;**$\Delta G_{Lehninger}$**=-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_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**
$HP_2O_7^{3-}$	**-2291**,04	**-1181,25**	**-1938,85**
$HP_2O_7^{3-}$	-2247,8	46	-1940,66
$H_2P_2O_7^{2-}$	-	-	**-1952,27**

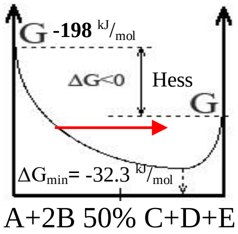
ΔG_{Hess}=$\Delta G°_{HSCoA2}$+$\Delta G°_{Palmitate-}$+$\Delta G°_{H3O+}$-($\Delta G_{PalmitateCoA4}$+2ΔG_{H2O})=**-112.5** $^{kJ}/_{mol}$

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

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

Endoergic Palmitate-**CoA^{3-}** hydrolize Hess free energy change **ΔG_{aHess}=-198** $^{kJ}/_{mol}$ negative, but minimizes reaching **ΔG_{min}**=**ΔG_a**= -32.3 $^{kJ}/_{mol}$ equilibrium mixture 455782,655=**K_a**. Le Chatelier principle is Prigogine attractor free energy change minimum ΔG_{min} **.** Free energy change minimum reaching establishes equilibrium. **ΔG_{mppL}**=-35,651 $^{kJ}/_{mol}$;

ATP^{3-}+H_2O => AMP$^-$+$H_2P_2O_7^{2-}$; pH<6,72



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

ΔG_{mppL}=-R•T•ln(K_{mppL})=-8,3144*298,15***ln**(1760959,91125033)/1000=-35,65 $^{kJ}/_{mol}$;

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

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

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

Exothermic and exoergic transfer Hess free energy change negative at pH=7,36

$\Delta G_{transfer}$=**-111.45** $^{kJ}/_{mol}$, but minimizes reaching equilibrium 97462087=**K_{mpp}** to **ΔG_{min}**=**ΔG_{eq}**= -45.6 $^{kJ}/_{mol}$:

ab ATP^{4-}+2H_2O=>AMP^{2-}+$HP_2O_7^{3-}$+H_3O^+. **$\Delta G_{Leninger}$**=-45,6 $^{kJ}/_{mol}$;

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

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

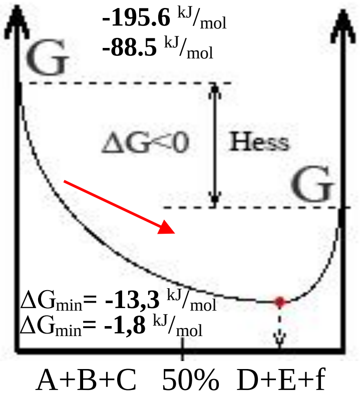
abc) $CH_3(CH_2)_{14}COO^-$+HSCoA^{3-}+**ATP^{4-}** =>**$HP_2O_7^{3-}$+AMP^{2-}**+PalmitateCoA^{3-};

pH=7,36; ΔG_{abc}=**-45,6-19,2+32,3=-32,**5 $^{kJ}/_{mol}$,

K_{abc}=2310,5736*97462087,2480605*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= $\dfrac{[HP_2O_7^{3-}]\cdot[AMP^{3-}]\cdot[Palmitate\text{-}CoA^{3-}]}{[CH_3(CH_2)_{14}COO^-]\cdot[HSCoA^{3-}]\cdot[ATP^{4-}]}$



bba) HPO_4^{2-}+ADP^{3-}+Palmitate-CoA^{3-}=>$CH_3(CH_2)_{14}COO^-$+HSCoA^{3-}+**ATP^{4-}**;

$\Delta G_{bbaLehninger}$=ΔG_{bb}+**ΔG_a**=30,5-32,3= -1.8 $^{kJ}/_{mol}$; reactants_ADP^{3-}+HPO_4^{2-}+Palmitate-CoA^{4-}

=**-1938,85-530,066-1067,238-(-2267,64-5,6616-1067,238)=-195.6** $^{kJ}/_{mol}$;products_$CH_3(CH_2)_{14}COO^-$+HSCoA^{4-}+ATP^{4-}

ΔG_{Hess}=$\Delta G°_{ATP4}$+$\Delta G°_{HSCoA3}$+$\Delta G°_{Palmitat}$**-**$\Delta G°_{HP2O73}$**-**$\Delta G°_{AMP2}$**-**$\Delta G°_{PalmitateCoA3}$=**-195.6** $^{kJ}/_{mol}$;

ΔG_{Hess}=$\Delta G°_{ATP4}$+$\Delta G°_{HSCoA3}$+$\Delta G°_{Palmitat}$**-**$\Delta G°_{HPO42}$**-**$\Delta G°_{ADP3}$**-**$\Delta G°_{PalmitateCoA3}$= **-88.5** $^{kJ}/_{mol}$;

=**-2267,64-5,6616-1067,238-(-1067,238-1399,9-784,9391)=-88.5** $^{kJ}/_{mol}$;**Biothermodynamic** 2006; CRC 2010

$K_{bbaLehninger}$=exp(-$\Delta G_{bbaLehninger}$/R/T)=exp(1800/8,3144/298,15)=2.067= $\dfrac{[CH_3(CH_2)_{14}COO^-]\cdot[HSCoA^{3-}]\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[Palmitate\text{-}CoA^{3-}]}$

ΔG_{bbaL}=-R•T•ln(K_{abbaL})=-8,3144*298,15***ln**(2,0671)=-1,8 $^{kJ}/_{mol}$; Transfer Hess free energy change negative at pH=7,36 Δ**G_{Hess}=-88.5** $^{kJ}/_{mol}$, but minimizes Δ**G_{bbaL}**=-1,8 $^{kJ}/_{mol}$ reaching equilibrium mixture 2,067=**K_{bbaL}** . Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.

cL $CH_3(CH_2)_{14}COOH+HSCoA^{2-}$ => $\text{PalmitateCoA}^{2-}+H_2O$; ΔG_{aL}=22.35 $^{kJ}/_{mol}$;at p H<5

$\Delta G_{Hess}=\Delta G°_{HSCoA2}+\Delta G°_{Palmitate}-(\Delta G_{PalmitateCoA4}+\Delta G_{H2O})$ =**-784,9391-151,549-(-5,6616-1067,238)**=**136,4** $^{kJ}/_{mol}$;

$K_{aLehninger}=K_{Lehninger}$=455782,7*$[H_2O]$=2,194*10^($^{-6}$)*55,34573393=0,000121429

ΔG_{eqLehn}=**-R•T•ln**($K_{eqLehninge}$)=-8,3144*298,15***ln**(0,000121429)=22,35 $^{kJ}/_{mol}$;

c $CH_3(CH_2)_{14}COO^-+HSCoA^{3-}+H_3O^+$=>$\text{PalmitateCoA}^{3-}$+2 H_2O; pH=7,36; ΔG_{Lenin}=32,3 $^{kJ}/_{mol}$;

$\Delta G_{aHess}=\Delta G_{Leninger}+2\Delta G_{H2O}-\Delta G_{H3O}$=**-784,9391+2*-151,549-(-5,6616-1067,238**-213,275)=**198,14** $^{kJ}/_{mol}$;

$K_c=K_{Lehninger}$=EXP(-ΔG_H /R/T)=EXP(-32300/8,3144/298,15)=2,194*10^{-6}= $\frac{[H_2O]^2\cdot[\text{Palmitate-CoA}^{3-}]}{[CH_3(CH_2)_{14}COO^-]\cdot[\text{HSCoA}^{3-}]\cdot[H_3O^+]}$

ΔG_c=**-RTln**(K_c)=-8,3144*298,15***ln**(2,194*10^($^{-6}$))/1000= 32,3 $^{kJ}/_{mol}$;

a$_{Lehninger}$ $H_2P_2O_7^{2-}+H_2O$=>$H_2PO_4^-+H_2PO_4^-$; pH<7,199; $\Delta G_{cLeningeH}$= -29,15 $^{kJ}/_{mol}$;

$\Delta G_{Hess}=2\Delta G°_{H2PO4-}-\Delta G°_{H2P2O72-}-\Delta G°_{H2O}$=2*-1137,3-(**-1952,27-151,549**)= **-170.8** $^{kJ}/_{mol}$;

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

$K_{cLehninger}=K_{Lehninger}*[H_2O]$=2310,5736*55,34573393=127880,391691282= $\frac{[H_2PO_4^-]\cdot[H_2PO_4^-]}{[H_2O]\cdot[H_2P_2O_7^{2-}]}$

a $HP_2O_7^{3-}+2H_2O$=>$HPO_4^{2-}+HPO_4^{2-}+H_3O^+$+ΔG+**Q;** pH=7,36; $\Delta G_{LeningeH}$=-19,2 $^{kJ}/_{mol}$;

$\Delta G_{Hess}=2\Delta G°_{HPO42}+\Delta G°_{H3O}-\Delta G°_{HP2O73}-2\Delta G°_{H2O}$=2***-1057,143**-213,275-(**-1938,85+2*(-151,549)**)=**-85.6** $^{kJ}/_{mol}$

ΔG_a=**-R•T•ln**(K_a)=-8,3144*298,15***ln**(3,2927*10^(-8))/1000=**42,71** $^{kJ}/_{mol}$,

K_c= $K_{Lehninger}$=**exp(-**$\Delta G_{Lehninger}$**/R/T**)=exp(19200/8,3144/298,15)=2310,5736= $\frac{[HPO^{2-}]^2\cdot[H_3O^+]}{[H_2O]^2\cdot[HP_2O_7^{3-}]}$

$\Delta G_{Habb}=\Delta G°_{Glycerol}+\Delta G°_{ATP4}+\Delta G°_{H2O}-\Delta G°_{ADP3}-\Delta G°_{Glyol3P}-\Delta G°_{H3O}$=**101.724** $^{kJ}/_{mol}$;

=**-154,912-2267,64-151,549-(-1399,9-1062,65**-213,275)=**101.724** $^{kJ}/_{mol}$;

=-171,35**-2267,64+(**-237,191**-151,549)**/2-(**-1399,9-1062,65**-213,275)=**42.465** $^{kJ}/_{mol}$;

$\Delta G_{Lehninger}$=-9,2 $^{kJ}/_{mol}$; Glycerol-3-phosphate^{2-}+H_2O+ΔG+**Q**=>Glycerol+HPO_4^{2-} ; pH=7.36;

bb $ADP^{3-}+HPO_4^{2-}+H_3O^+$=>$ATP^{4-}$+2 H_2O; ΔG_{bb}=30,5 $^{kJ}/_{mol}$;

Glycerol1P^{2-}+$ADP^{3-}+H_3O^+$=>Glycerol+ATP^{4-}-+H_2O;ΔG_{abb}=21.3 $^{kJ}/_{mol}$; $\Delta G_{abb}=\Delta G_a+\Delta G_{bb}$=-9,2+30,5=21.3 $^{kJ}/_{mol}$;

Glyc1P$^-$+ ADP^{2-}=>Glycerol+ ATP^{3-}; $\Delta G_{Lehninger}$=11.35 $^{kJ}/_{mol}$**;** K_{aL}=0.010267

$K_{abbL}=K_{abL}*[H_2O]$=0,000185506741578019*55,346=<u>0,010267056119377</u>

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

$\Delta G_{abbLehninger}$=**-R•T•ln**($K_{abbLehninge}$)=-8,3144*298,15***ln**(<u>0,010267056119377</u>)/1000=11,35 $^{kJ}/_{mol}$;

Fruc6P^{2-}+H_2O =>Fruc+HPO_4^{2-}+ΔG+**Q**; $\Delta G_{Lehninger}$=-15,9 $^{kJ}/_{mol}$

$\Delta G_{Hess}=\Delta G°_{Fruc}+\Delta G°_{HPO42-}-\Delta G°_{Fruc6P}-\Delta G°_{H2O}$ = **-70.951** $^{kJ}/_{mol}$

=-426,32-1089,28-(**-1293,1-151,549**)= **-70.951** $^{kJ}/_{mol}$ exoergic

$\Delta H_{Hess}=\Delta H°_{Fruc}+\Delta H°_{HPO42-}-\Delta H°_{Fruc6P}-\Delta H°_{H2O}$=**-8,51** $^{kJ}/_{mol}$

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

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

$\Delta S_{Hess}=\Delta S°_{Fruc}+\Delta S°_{HPO42-}-\Delta S°_{Fruc6P}-\Delta S°_{H2O}$=**19,066** $^{kJ}/_{mol}$

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

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

$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}$=**19,066+28,54=47.606** $^{J}/_{mol/K}$

T•ΔS_{total}=**0,047606** *298,15=**14.194** $^{kJ}/_{mol}$ TΔSn <u>dispersed</u>

Fruc6P^{2-}+$ADP^{3-}+H_3O^+$ =>Fruc+$ATP^{4-}+H_2O$;$\Delta G_{Lehninger}$=14,6 $^{kJ}/_{mol}$; pH=7.36

$\Delta G_{Habb}=\Delta G°_{Fruc}+\Delta G°_{ATP4}+\Delta G°_{H2O}-\Delta G°_{ADP3}-\Delta G°_{Fruc6P}-\Delta G°_{H3O}$=**85.426** $^{kJ}/_{mol}$;

=**-401,66-2267,64-151,549-(-1399,9-1293,1**-213,275)=**85.426** $^{kJ}/_{mol}$;

Fruc6P$^-$+ADP^{2-}=>Fruc+ATP^{3-};$\Delta G_{Lehninger}$=4.65 $^{kJ}/_{mol}$; $K_{Lehninge}$=0,153199602471084

$\Delta G_{Habb}=\Delta G°_{Fruc}+\Delta G°_{ATP4}-\Delta G°_{ADP3}-\Delta G°_{Fruc6P}$=**23.7** $^{kJ}/_{mol}$;

=**-401,66-2267,64-(-1399,9-1293,1)=23.7** $^{kJ}/_{mol}$;

$K_{abbL}=K_{abbL}*[H_2O]$=0,00276803386823048*55,346=0,153199602471084

$\Delta G_{abbLehninger}$=**-R•T•ln**($K_{abbLehninge}$)=-8,3144*298,15***ln**(0,153199602471084)/1000=4.65 $^{kJ}/_{mol}$;

THERMODYNAMICS Exercise V h Glycerol-3-phosphate^{2-} and Fructose-6-phosphate^{2-} hydrolysis .

Calculate ΔH_H ΔS_H ΔG_H at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**?
For the phosphate hydrolyse **Glycerol3P2-** reaction with water! Will be **exoergic** or **endoergic**!

$\Delta\mathbf{G}_{Lehninger}$=-9,2 $^{kJ}/_{mol}$; Glycerol-3-phosphate^{2-}+$\mathbf{H_2O}$+ΔG+**Q**=>Glycerol+$\mathbf{HPO_4^{2-}}$; pH=7.36;

Substance ΔH°_H $^{kJ}/_{mol}$ ΔS°_H $^{J}/_{mol/K}$ ΔG°_H , $^{kJ}/_{mol}$; Glycerol-3-phosphate$^-$+$\mathbf{H_2O}$+ΔG+**Q**=>Glycerol+ $\mathbf{H_2PO_4^-}$;pH<7.199

Substance	ΔH°_H $^{kJ}/_{mol}$	ΔS°_H $^{J}/_{mol/K}$	ΔG°_H , $^{kJ}/_{mol}$
$\mathbf{H_3O^+}$	-285,81	-3,854	-213,275
$\mathbf{H_2O}$	-285,85	69,9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{H_2PO_4^-}$	-1296,3	90,4	-1130,2
$\mathbf{H_2PO_4^-}$	-1302,6	92,5	-1137,3
$\mathbf{HPO_4^{2-}}$	-1292,14	-33,47	-1089,28
$\mathbf{HPO_4^{2-}}$	**-1298,89**	**-810,792**	**-1057,143**
$\mathbf{ADP^{3-}}$	-2627,4	-4010	-1424,7
$\mathbf{ATP^{4-}}$	-3617,15	-4520	-2292,5
$\mathbf{ADP^{3-}}$	**-2627,4**	**-4117,11**	**-1399,9**
$\mathbf{ATP^{4-}}$	**-3617,1**	**-4526,1**	**-2267,64**
Glyat3P^{3-}	-	-	-1347,73
Glyt31P^{4-}	-1725,76	-2290,6	-2207,30
Glyat2P^{3-}	-	-	-1341,79
Glyat2P^{3-}	-	-	**-1333,2**
Glycerol$^-$	-	-	-171,35
Glycerol$^-$	**-679,85**	**-1760,65**	**-154,912**
Glycerate$^-$	-	-	**-452,31**
Glyol3P^{2-}	-	-	-1077,13
Glyol3P^{2-}	**-1725,81**	**-2224,26**	**-1062,65**
Fruc16P^{4-}	-	-	-2206,78
Fruc16P^{4-}	**-3340,81**	**-3872,58**	**-2186,2**
Fruc6P^{2-}	-	-	-1315,74
Fruc6P^{2-}	**-2268,05**	**-3270,06**	**-1293,1**
Fruc	-	-	-426,32
Fruc	**-1264,32**	**-2893,39**	**-401,66**
Glc6P^{2-}	-2260	-3291,56	-1318,92
Glc6P^{2-}	**-2279,314**	**-3297,196**	**-1296,262**

Mishcenko ;$\Delta G_H=\Delta G^\circ_{\mathbf{Glycerol}}+\Delta G^\circ_{\mathbf{HPO42-}}-\Delta G^\circ_{\mathbf{Glyol3P}}$ $-\Delta G^\circ_{\mathbf{H2O}}$=**-14.294** $^{kJ}/_{mol}$
=-171,35**-1057,143-(-1062,65-151,549)=-14.294** $^{kJ}/_{mol}$ exoergic

B06; K$_a$=**K**$_{Lehninger}$=exp(9200/8,3144/298,15)=40,9055659488465

$\Delta G_H=\Delta G^\circ_{\mathbf{Glycerol}}+\Delta G^\circ_{\mathbf{H2PO4-}}-\Delta G^\circ_{\mathbf{Glyol3P}}-\Delta G^\circ_{\mathbf{H2O}}$=**-70.913** $^{kJ}/_{mol}$; exoergic
=**-154,912**-1130,2-(**-1062,65-151,549**)=**-70.913** $^{kJ}/_{mol}$

Glycerol1P^{2-}+ADP^{3-}+$\mathbf{H_3O^+}$=>Glycerol+ATP^{4--}+H$_2$O;$\Delta\mathbf{G}_{abb}$=21.3 $^{kJ}/_{mol}$;
$\Delta\mathbf{G}_{abb}=\Delta\mathbf{G}_a+\Delta\mathbf{G}_{bb}$=-9,2+30,5=21.3 $^{kJ}/_{mol}$;

$\mathbf{K}_{abb}=\mathbf{K}_a\mathbf{K}_{bb}$=40,9055659488465*4,535*10^($^{-6}$)= 0,000185506741578019

$\Delta G_{Habb}=\Delta G^\circ_{\mathbf{Glyc}}+\Delta G^\circ_{ATP4}+\Delta G^\circ_{H2O}-\Delta G^\circ_{ADP3}-\Delta G^\circ_{\mathbf{Glyol3P}}-\Delta G^\circ_{\mathbf{H3O}}$=**101.724** $^{kJ}/_{mol}$
=**-154,912-2267,64-151,549-(-1399,9-1062,65**-213,275)=**101.724** $^{kJ}/_{mol}$;
=-171,35**-2267,64+(**-237,191**-151,549**)/2-(**-1399,9-1062,65**-213,275)=**42.465** $^{kJ}/_{mol}$

Glyc1P$^-$+ ADP^{2-}=>Glycerol+ ATP^{3-}; $\Delta\mathbf{G}_{Lehninger}$=11.35 $^{kJ}/_{mol}$**;** $\mathbf{K}_{aL}$=0.010267
$\mathbf{K}_{abbL}=\mathbf{K}_{abL}$*[$\mathbf{H_2O}$]=0,000185506741578019*55,346=0,010267056119377
$\Delta G_{HabbL}=\Delta G^\circ_{\mathbf{Glyc}}+\Delta G^\circ_{ATP4}-\Delta G^\circ_{ADP3}-\Delta G^\circ_{\mathbf{Glyol3P}}$=**-154,912-2267,64-**(**-1399,9-1062,65**)=**40** $^{kJ}/_{mol}$

BioThe06;

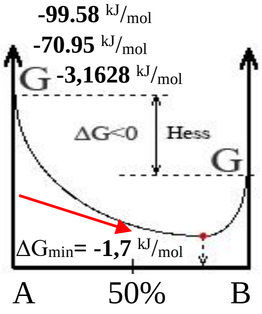
a) Fruc6P^{2-}+$\mathbf{H_2O}$ =>Fruc+$\mathbf{HPO_4^{2-}}$+ΔG+**Q**; $\Delta\mathbf{G}_{Lehninger}$=-15,9 $^{kJ}/_{mol}$;
$\Delta G_{Hess}=\Delta G^\circ_{\mathbf{Fruc}}+\Delta G^\circ_{\mathbf{HPO42-}}-\Delta G^\circ_{\mathbf{Fruc6P}}-\Delta G^\circ_{\mathbf{H2O}}$ = **-70.951** $^{kJ}/_{mol}$; exoergic
=-426,32-1089,28-(**-1293,1-151,549**)=**-70.951** $^{kJ}/_{mol}$ exoergic
$\mathbf{K}_a=\mathbf{K}_{Lehninger}$=exp(15900/8,3144/298,15)=610,3521266

ADP^{2-}+H$_2$PO$_4^-$=>ATP^{3-}+H$_2$O; $\Delta\mathbf{G}_{Lehninger}$ = 20,55 $^{kJ}/_{mol}$; 2,26<pH<6,72
$\mathbf{K}_{Lehninger}$**=exp(-Δ$\mathbf{G}_{Lehninger}$/R/T)**=exp(-30500/8,3144/298,15)=4,535*10^{-6};
$\mathbf{K}_{bL}$**=[H$_2$O]**$\mathbf{K}_{Lehninger}$= 0,000004535142* 55,34573393= 0,000251001
bb ADP^{3-}+HPO$_4^{2-}$+H$_3$O$^+$=>ATP^{4-}+2 H$_2$O; pH=7.36; $\Delta\mathbf{G}_{bb}$**=**30,5 $^{kJ}/_{mol}$;
$\mathbf{K}_{bb}=\mathbf{K}_{Lehninger}$**=exp(-Δ$\mathbf{G}_{Lehning}$/R/T)**=exp(-30500/8,3144/298,15)=4,535*10^{-6}
$\Delta G_{Hess}=\Delta G^\circ_{ATP4}+2\Delta G^\circ_{H2O}-\Delta G^\circ_{HPO42}-\Delta G^\circ_{ADP3}-\Delta G^\circ_{H3O}$=**99.58** $^{kJ}/_{mol}$
=**-2267,64**-2***151,549-(-1057,143-1399,9**-213,275)=**99.58** $^{kJ}/_{mol}$;

Fruc6P^{2-}+ADP^{3-}+$\mathbf{H_3O^+}$=>Fruc+ATP^{4-}+$\mathbf{H_2O}$; $\Delta\mathbf{G}_{Lehninger}$=14,6 $^{kJ}/_{mol}$; $\Delta\mathbf{G}_{abb}=\Delta\mathbf{G}_a+\Delta\mathbf{G}_{bb}$**=**-15,9+30,5=14.6 $^{kJ}/_{mol}$**;**
$\Delta G_{Habb}=\Delta^\circ G_{Fruc}+\Delta^\circ G_{ATP4}+\Delta^\circ G_{H2O}-\Delta^\circ G_{ADP3}-\Delta^\circ G_{Fruc6P}-\Delta^\circ H_{\mathbf{H3O}}$=**-401,66-2267,64-151,549-(-1399,9-1293,1**-213,275)=**85.426** $^{kJ}/_{mol}$;
$\mathbf{K}_{abb}$=exp(-14600/8,3144/298,15)=0,00276803386823048; $\Delta\mathbf{G}_{aHess}+\Delta\mathbf{G}_{bHess}$=**-70,951+99,58=28.6** $^{kJ}/_{mol}$;

Fruk6P^{2-}=>Glc6P^{2-}; $\Delta\mathbf{G}_{Lehninger}$= -1,7 $^{kJ}/_{mol}$; $\Delta G_H=\Delta G^\circ_{\mathbf{Glc6P}}+\Delta G^\circ_{\mathbf{Fruc6P}}$=**-1296,262+1293,1=-3,162** $^{kJ}/_{mol}$;
$\mathbf{K}_{Lehninger}$**=exp(-Δ$\mathbf{G}_{Lehninger}$/R/T)**=exp(1700/8,3144/298,15)=exp(0,29783)=1,98531;
$\Delta\mathbf{G}_{eq}$**=-R•T•ln(K$_{eq}$)**=-8,3144•298,15·**ln**(1,98531)=-1,7 $^{kJ}/_{mol}$ exothermic and exoergic Pi transfer to Glc, Fruc6P, **ATP^{4-}** reaction $\Delta\mathbf{G}_{hydrolise}$=**-3,173**, **-70.95** and **-99.58** $^{kJ}/_{mol}$ Hess free energy change negative, but minimizes $\Delta\mathbf{G}_{min}=\Delta\mathbf{G}_{eq}$=-1,7 , -15,9 and -30.5 $^{kJ}/_{mol}$ reaching equilibrium mixture $\mathbf{K}_{Lehninger}$=1.985= $\frac{[Glc6P^{2-}]}{[Fruc6P^{2-}]}$; $\mathbf{K}_a$= 610,35; $K_{bLehninger}$=220500,2;

ΔG_{min}= -30.5 $^{kJ}/_{mol}$ ΔG_{min}= -15.9 $^{kJ}/_{mol}$



Le Chatelier principle is Prigogine attractor Free energy change minimum ΔG_{min} reaching at equilibrium. Reactants A fructose-6-phosphate=> products glucose-6-phosphate B
Free energy change minimum reaching establishes equilibrium.

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

THERMODYNAMICS Exercise V e **$(H_3CCO)_2O$** hydrolysis to acetate **CH_3COO^-** at pH<4,76 and pH=7,36.

$CH_3COOOCCH_3$+**H_2O**=2**CH_3COOH**; **$CH_3COOOCCH_3$**+3**H_2O**=2**CH_3COO^-**+2**H_3O^+**; $\Delta G_{Lehninger}$=-91,1 $^{kJ}/_{mol}$;

Substance	$\Delta H°_H$ $^{kJ}/_{mol}$	$\Delta S°_H$ $^{J}/_{mol/K}$	$\Delta G°_H$ $^{kJ}/_{mol}$
H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**
$(H_3CCO)_2O$	-624,4	658,853	-728,91
$(H_3CCO)_2O$	$\Delta G°_{(H3CCO)2O}$	-728,91	-728,91
H_3CCOO^-	-	-	-247.83
H_3CCOO^-	**-486,836**	**-822,3**	**-241,663**
$H_3C\text{-}COOH$	-484,09	159,83	-531,743

=2*-531,743-(-728,91-237,191)= -97.385 $^{kJ}/_{mol}$;

CRC10; $\Delta G_H=2\Delta G°_{CH3COOH}-\Delta G°_{(H3CCO)2O}-\Delta G°_{H2O}$=-97.385 $^{kJ}/_{mol}$;

CRC10; $2\Delta G°_{CH3COOH}+91{,}1-\Delta G°_{H2O}=\Delta G°_{(H3CCO)2O}$=-728,91 $^{kJ}/_{mol}$;

B06; ΔH_{Hess}=2*-531,743-(-728,91-237,191)=-97.385 $^{kJ}/_{mol}$;

CRC10; $\Delta H_{Hess}=2\Delta H°_{CH3COOH}-\Delta H°_{(H3CCO)2O}-\Delta H°_{H2O}$=-57.93 $^{kJ}/_{mol}$;

$\Delta S_H=2\Delta S°_{CH3COOH}-\Delta S°_{(H3CCO)2O}-\Delta S°_{H2O}$=113,995 $^{J}/_{mol/K}$;

CRC10; =2*159,83-(658,853-**453,188**)= 113,995 $^{J}/_{mol/K}$;

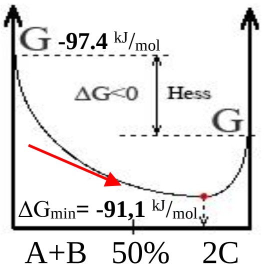
B06; $\Delta S_{dispeHse}=-\Delta H_{Hess}/T$=57130/298,15=191,615 $^{J}/_{mol/K}$;

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

$\Delta S_{total}=\Delta S_H+\Delta S_{dispeHsed}$=191,615+113,995=305,61 $^{J}/_{mol/K}$; $T\bullet\Delta S_{total}$=0,30561*298,15=91,12 $^{kJ}/_{mol}$ TΔSn <u>dispersed</u>

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

Exothermic and exoergic **$(H_3CCO)_2O$** hydrolize Hess free energy change negative at pH<4,76 as **CH_3COOH** **$\Delta G_{hydrolise}$** = **-97.4** $^{kJ}/_{mol}$, but minimizes **ΔG_{min}=ΔG_{eq}**=-91,1 $^{kJ}/_{mol}$ reaching equilibrium mixture



Products 2**CH_3COOH**

$$\underline{9{,}12*10^{15}}=10^{15{,}96}=\mathbf{K_{eq}}=\frac{[CH_3COOH]^2}{[CH_3COOOCCH_3]\cdot[H_2O]}$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium. reaktanti **$(H_3CCO)_2O$+ H_2O**

Free energy change minimum reaching establishes equilibrium.

$CH_3COOOCCH_3$ +3 **H_2O** => 2 **CH_3COO^-**+2 **H_3O^+**; ΔG_H = 217,26 $^{kJ}/_{mol}$; at pH=7,36;

$\Delta G_{Hess}=2\Delta G°_{CH3COO}+2\Delta S°_{H3O}-\Delta G°_{(H3CCO)2O}-3\Delta G°_{H2O}$=2***-241,663+2***-213,275-(-728,91+3***-151,549**)=**273.7** $^{kJ}/_{mol}$;

=2***-241,663+2***-213,275-(-728,91+3***-151,549**)=**273.7** $^{kJ}/_{mol}$ endoergic

$\Delta H_H=2\Delta H°_{CH3COO}+2\Delta S°_{H3O}-\Delta H°_{(H3CCO)\,2O}-3\Delta H°_{H2O}$=**-60,942** $^{kJ}/_{mol}$; $\Delta S_{dispeHse}=-\Delta H_H/T$=**60,942**/298,15=**204,4** $^{J}/_{mol/K}$;

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

$\Delta S_H=2\Delta S°_{CH3COO-}+2\Delta S°_{H3O}-\Delta S°_{(H3CCO)\,2O}-3\Delta S°_{H2O}$= $\Delta S_{total}=\Delta S_H+\Delta S_{dispeHsed}$=**-951,597+204,4=-747,197** $^{J}/_{mol/K}$;

=2***-822,3+2***-3,854-(658,853+3***-453,188**)=**-951.597** $^{J}/_{mol/K}$;

$\Delta G_H=\Delta H_H-T*\Delta S_H$=**-60,942**-298,15*-0,**9516**=**222.777** $^{kJ}/_{mol}$;$T\Delta S_{total}$=-0,747197*298,15=-222.777 $^{kJ}/_{mol}$ TΔSn <u>dispersed</u>

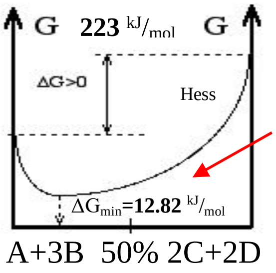
ΔG_{eq} = - R•T•ln(K_{eq})=-8,3144*298,15***ln**(0,0056732)/1000=12,82107402328 $^{kJ}/_{mol}$,,

K_{eq}=$K_{Lehninger}$[H_3O^+]^2/[H_2O]^2=9,12*10^15*10^(-7,36*2)/55,34573393^2=0,0056732= $\dfrac{[CH_3COO^-]^2\cdot[H_3O^+]^2}{[CH_3COOOCCH_3]\cdot[H_2O]^3}$

Endothermic and endoergic anhydride hydrolysis Hess free energy change **$\Delta G_{hydrolyse}$** positive 223 $^{kJ}/_{mol}$, but minimizes up to **ΔG_{min}=ΔG_{eq}**=12.82 $^{kJ}/_{mol}$ reaching equilibrium

mixture K_{eq}= $\dfrac{[CH_3COO^-]^2\cdot[H_3O^+]^2}{[CH_3COOOCCH_3]\cdot[H_2O]^3}$=0,0056732. Le Chatelier principle is

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



Reactants **$(H_3CCO)_2O$**+3**H_2O** products 2**CH_3COO^-**+2 **H_3O^+**

$H_2P_2O_7^{2-}$+H_2O=**H_3O^++$HP_2O_7^{3-}$**; $\Delta G_{Hess}=\Delta G°_{H3O+}+\Delta G°_{HOPO2OPO2O3}-\Delta G°_{H2OPO2OPO2O2-}-\Delta G°_{H2O}$= **25.73** $^{kJ}/_{mol}$;

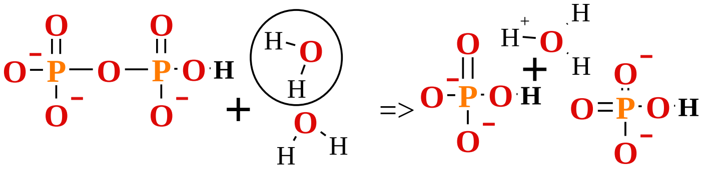
=-213,275-**1938,85**-(-1940,66-237,191)= **25.73** $^{kJ}/_{mol}$;

ΔG_{eq} = -R•T•ln(K_{eq})=-8,3144*298,15***ln**(10^(-8,463))/1000=48,31 $^{kJ}/_{mol}$,

K_{eq}=$K_{H2P2O72}$/[H_2O] =$10^{-6.72}$/55,34573393=3,4436*10^{-9}=$10^{-8,463}$= $\dfrac{[H_3O^+]\cdot[HP_2O_7^{3-}]}{[H_2O]\cdot[H_2P_2O_7^{2-}]}$;

THERMODYNAMICS Exercise V e **Pyrophosphate** hydrolysis to HPO_4^{2-} + HPO_4^{2-}

Calculate ΔH_H, ΔS_H, ΔG_H at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? For the phosphate hydrolyse of pyrophosphate reaction with water! Will be **exoergic** or **endoergic**! pH=7,36;



Pyrophosphate	pKa	ΔH°	C
$H_4P_2O_7=H^++H_3P_2O_7^-$	0,83	-9,2	-90
$H_3P_2O_7^-=H^++H_2P_2O_7^{2-}$ 7	2,26	-5,0	-130
$H_2P_2O_7^{2-}=H^++\mathbf{HP_2O_7^{3-}}$	6,72	0,5	-136
$\mathbf{HP_2O_7^{3-}}=H^++P_2O_7^{4-}$	**9,46**	1,4	-141

1.$\Delta H_{Hess}=\Delta H°_{products}-\Delta H°_{reactants}$; $\mathbf{HP_2O_7^{3-}}+2H_2O \Rightarrow HPO_4^{2-}+HPO_4^{2-}+\mathbf{H_3O^+}$; $\Delta \mathbf{G}_{LehningeHpp}=-19,2$ kJ/mol; pH=7,36

Substance $\Delta H°_H$, kJ/mol $\Delta S°_H$, J/mol/K $\Delta G°_H$, kJ/mol ; $\mathbf{HP_2O_7^{3-}}+ADP^{3-} \Rightarrow HPO_4^{2-}+ATP^{4-}$; $\Delta \mathbf{G}_{abbpp}=11,3$ kJ/mol; pH=7,36;

$\mathbf{H_3O^+}$	-285,81	-3,854	-213,275
$\mathbf{H_2O}$	-285,85	69,9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{H_2PO_4^-}$	-1296,3	90,4	-1130,2
$\mathbf{H_2PO_4^-}$	-1302,6	92,5	-1137,3
$\mathbf{HPO_4^{2-}}$	-1292,14	-33,47	-1089,28
$\mathbf{HPO_4^{2-}}$	**-1298,89**	**-810,792**	**-1057,143**
$\mathbf{H_2P_2O_7^{2-}}$	-	-	**-1952,27**
$\mathbf{HP_2O_7^{3-}}$	-	-	-1940,66
$\mathbf{HP_2O_7^{3-}}$	**-2291,04**	**-1181,25**	**-1938,85**
adenosine	**-626,66**	**-3316,57**	**362,172**
adenosine	-	-	335.46

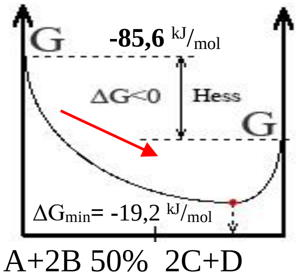
Mishchenko ; $\Delta \mathbf{G}_{abbpp}=\Delta \mathbf{G}_{app}+\Delta \mathbf{G}_{bb}=-19,2+30,5=11,3$ kJ/mol;

$\Delta G_{Hess}=\Delta G°_{H3O}+2\Delta G°_{HPO42}-\Delta G°_{HOPO2OPO2O2}-2\Delta G°_{H2O}=\mathbf{-85,6}$ kJ/mol ;

$=-213,275+2*\mathbf{-1057,143}-(\mathbf{-1938,85}+2*\mathbf{-151,549})=\mathbf{-85,6}$ kJ/mol;

Endothermic and endoergic $\mathbf{HPO_4^{2-}}$ transfer from $\mathbf{HP_2O_7^{2-}}$ Hess free energy change positive at pH=7,36 $\Delta \mathbf{G}_{Hess}=\mathbf{-85,6}$, but minimizes $\Delta \mathbf{G}_{min}=\Delta \mathbf{G}_{eq}=-19,2$ kJ/mol reaching equilibrium

$$\mathbf{K}_{app}=\mathbf{K}_{Lehningepp}=2310,57=\frac{[HPO_4^{2-}]^2\cdot[H_3O^+]}{[H_2O]^2\cdot[HP_2O_7^{3-}]}\cdot$$



reaktanti $\mathbf{HP_2O_7^{3-}}+2H_2O$

produkti $2HPO_4^{2-}+\mathbf{H_3O^{+}}$-

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching. Products. Free energy change minimum reaching establishes equilibrium.

$$\mathbf{K}_{app}=\mathbf{K}_{Lehningerpp}=\mathbf{exp(-\Delta G_{Lehningerpp}/R/T)}=exp(19200/8,3144/298,15)=2310,57=\frac{[HPO_4^{2-}]^2\cdot[H_3O^+]}{[H_2O]^2\cdot[HP_2O_7^{3-}]}$$

$H_2P_2O_7^{2-}+H_2O=\mathbf{H_3O^+}+\mathbf{HP_2O_7^{3-}}$;

$$\mathbf{K}_{eq}=\mathbf{K}_{H2P2O72}/[\mathbf{H_2O}]=10^{-6,72}/55,3457=3,4436*10^{-9}=10^{-8,463}=\frac{[H_3O^+]\cdot[H\ P_2O_7^{3-}]}{[H_2O]\cdot[H_2P_2O_7^{2-}]}$$

$\mathbf{H_2P_2O_7^{2-}}+H_2O \Rightarrow H_2PO_4^-+H_2PO_4^-$; $\Delta \mathbf{G}_{Lehninger}=-19,2$ kJ/mol;without 6,72<pH<7,199;

$$\mathbf{K}_{pp}=\mathbf{K}_{Lehningerpp}/[\mathbf{H_2O}]=2310,57/55,34573393=41,748=\frac{[H_2PO_4^-]\cdot[H_2PO_4^-]}{[H_2O]\cdot[H_2P_2O_7^{2-}]}$$

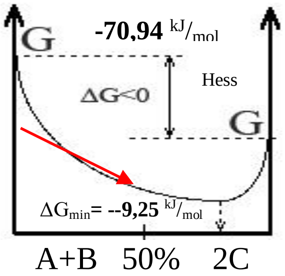
$\Delta \mathbf{G}_{ppL}=\mathbf{-R \bullet T \bullet ln}(\mathbf{K}_{eqL})=-8,3144*298,15*\mathbf{ln}(41,74799819)=\mathbf{-9,251}$ kJ/mol ,

$\Delta G_{Hess}=2\Delta G°_{H2PO4-}-\Delta G°_{H2P2O72-}-\Delta G°_{H2O}=\mathbf{-70,94}$ kJ/mol; $=2*-1130,2-(\mathbf{-1952,27}-237,191)=\mathbf{-70,94}$ kJ/mol;

Exothermic and exoergic $\mathbf{H_2P_2O_7^{2-}}$ hydrolytic Hess free energy change to $H_2PO_4^-$ $+HPO_4^{2-}$ negative $\Delta \mathbf{G}_{Hess}=\mathbf{-70,94}$ kJ/mol , but minimizes reaching equilibrium mixture $\Delta \mathbf{G}_{min}=\Delta \mathbf{G}_{eqL}=\mathbf{-9,251}$ kJ/mol without pH<7,199

$$41,748=\mathbf{K}_{pp}=\frac{[H_2PO_4^-]\cdot[H_2PO_4^-]}{[H_2O]\cdot[H_2P_2O_7^{2-}]}$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min}. Free energy change minimum reaching establishes equilibrium. $\mathbf{K}_{pp}=41,748$;



Reactants $\mathbf{HP_2O_7^{2-}+H_2O}$

produkti $H_2PO_4^-+H_2PO_4^-$

$\mathbf{H_2P_2O_7^{2-}}+\mathbf{ADP^{2-}} \Rightarrow \mathbf{H_2PO_4^-}+\mathbf{ATP^{3-}}$; pH<6,72; $\Delta \mathbf{G}_{abbppPH}=21,25$ kJ/mol;

$\mathbf{K}_{abbppPH}=\mathbf{K}_{abbpp}/[\mathbf{H_2O}]=\underline{0,01047878}/55,3457=0,0001893$

$\Delta \mathbf{G}_{abbppPH}=\mathbf{-R \bullet T \bullet ln}(\mathbf{K}_{abbppPH})=-8,3144*298,15*\mathbf{ln}(0,0001893)/1000=21,25$ kJ/mol;

$\mathbf{K}_{abbppL}=\mathbf{exp(-\Delta G_{Lehninger}/R/T)}=exp(-11300/8,3144/298,15)=\underline{0,01047878}$

$\mathbf{K}_{abL}=\mathbf{K}_{aL}\mathbf{K}_{bL}=41,748*0,000250942=0,010476327$;

$\Delta \mathbf{G}_{abbppL}=\mathbf{-R \bullet T \bullet ln}(\mathbf{K}_{abbppL})=-8,3144 \bullet 298,15 \bullet \mathbf{ln}(\underline{0,01047878})=11,3$ kJ/mol;

$\mathbf{HP_2O_7^{3-}}+\mathbf{ADP^{3-}} \Rightarrow \mathbf{HPO_4^{2-}}+\mathbf{ATP^{4-}}$; pH=7,36; $\Delta \mathbf{G}_{Lehninger}=30,5+(-19,2)=11,3$ kJ/mol;;

$\Delta G_{Hess}=\Delta G°_{HPO42-}+\Delta G°_{ATP4-}-\Delta G°_{HP2O73-}-\Delta G°_{ADP3-}=\mathbf{-1057,143-2267,64-(-1938,85-1399,9)=13,967}$ 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**

$\Delta H_{Hess}=\Delta H^\circ_{Gln}+\Delta H^\circ_{H2O}-\Delta H^\circ_{Glu}-\Delta H^\circ_{NH4+}=\mathbf{19{,}5}$ kJ/mol

$=\mathbf{-809{,}12-286{,}65}-(\mathbf{-982{,}77}-132{,}5)=\mathbf{19{,}5}$ kJ/mol endothermic

$\Delta S_{Hess}=\Delta S^\circ_{Gln}+\Delta S^\circ_{H2O}-\Delta S^\circ_{Glu}-\Delta S^\circ_{NH4+}=\mathbf{-842.48}$ J/mol/K

$=\mathbf{-2379{,}04-453{,}188}-(\mathbf{-2103{,}15}+113{,}4)=\mathbf{-842.478}$ J/mol/K

$\Delta G_{Hess}=\Delta H_{Hess}-T^*\Delta S_{Hess}=\mathbf{-19{,}5}\ -298{,}15^*-0{,}\mathbf{84248}=\mathbf{231.685}$ kJ/mol; endoergic

a)$Glu^-+NH_4^+\Rightarrow Gln+H_2O$; $\Delta G_{bLehninger}=\mathbf{14{,}2}$ kJ/mol; pH=7,36;

$K_{aLehningeH}=\mathbf{exp(-\Delta G_{aLehninger}/R/T)}=exp(14200/8{,}3144/298{,}15)=307.43$

$\Delta G_{Hess}=\Delta G^\circ_{Gln}+\Delta G^\circ_{H2O}-\Delta G^\circ_{Glu}-\Delta G^\circ_{NH4+}=\mathbf{-99{,}8112-151{,}549}-(\mathbf{-355{,}712}-79{,}3)=\mathbf{183.65}$ kJ/mol;

$K_{bLehningeH}=\mathbf{exp(-\Delta G_{bLehninger}/R/T)}=exp(-14200/8{,}3144/298{,}15)=\underline{0{,}003252737}=\frac{[Gln]\cdot[H_2O]}{[Glu^-]\cdot[NH_4^+]}$

Endoergic Glu amination to Gln Hess free energy change ΔG_{Hess} positive **183.65** kJ/mol ,

$Gln+H_2O\Rightarrow Glu^-+NH_4^+$; $\Delta G_{aLehninger}=-14.2$ kJ/mol; $\Delta G_{Hess}=\mathbf{-183.65}$ kJ/mol; $K_{aLehninger}=307.43=\frac{[Glu^-]\cdot[NH_4^+]}{[Gln]\cdot[H_2O]}$

but minimizes up to $\Delta G_{min}=\Delta G_{aLehninger}=\mathbf{14.2}$ kJ/mol reaching equilibrium mixture:

$K_{aLehninger}=\underline{0{,}003252737}=[Glu^-]^*[NH_4^+]/[Gln]^*[H_2O]$. Exoergic Glu amination to Gln with **ATP⁴⁻** free energy change $\Delta G_{Hess}=\mathbf{-40{,}2}$ kJ/mol negative at pH<7,199, but minimizes reaching equilibrium mixture

$\Delta G_{min}=\Delta G_{abL}=\mathbf{-6{,}35}$ kJ/mol

AMP^{2-}	-	-	-554,83
ADP^{3-}	-2627,4	-4010	-1424,7
ATP^{4-}	-3617,15	-4520	-2292,5
AMP^{2-}	**-1638,34**	**-3717,19**	**-530,066**
ADP^{3-}	**-2627,4**	**-4117,11**	**-1399,9**
ATP^{4-}	**-3617,1**	**-4526,1**	**-2267,64**
NH_4^+(aq)	-132,5	113,4	-79,3
Glu^{--}	-	-	-372,16
Glu^-	**-982,77**	**-2103,15**	**-355,712**
Gln^-	-	-	-120,36
Gln	**-809,12**	**-2379,04**	**-99,8112**

$\frac{[H_2PO_4^-]\cdot[ADP^{2-}]\cdot[Gln]}{[Glu^-]\cdot[NH_4^+]\cdot[ATP^{3-}]}=12.959=K_{abLehninger}$.

a $ATP^{3-}+H_2O\Rightarrow ADP^{2-}+H_2PO_4^-$;$\Delta G_{bl}=\mathbf{-20{,}55}$ kJ/mol;

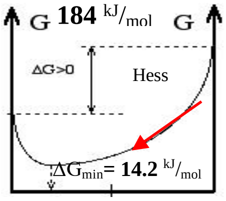
$K_{bLehninger}=exp(20550/8{,}3144/298{,}15)=3984.$

$\Delta G_{aLehninger}=\mathbf{-RTln(K_{aLehninger})}=$

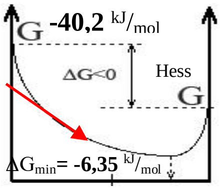
$=-8{,}3144\bullet 298{,}15\bullet \mathbf{ln}(3984)=\mathbf{-20{,}55}$ kJ/mol;

$K_a=K_{Lehninger}=\mathbf{exp(-\Delta G_{Lehninger}/R/T)}=$

$=exp(30500/8{,}3144/298{,}15)=220500$



A+B 50% C+D



$\Delta G_{Hess}=\Delta G^\circ_{H2PO4}+\Delta G^\circ_{Gln}+\Delta G^\circ_{ADP2}-\Delta G^\circ_{NH4}-\Delta G^\circ_{Glu}-\Delta G^\circ_{ATP3}=20.292$ kJ/mol;

$=-1137{,}3-120{,}36-1424{,}7-(-79{,}3\mathbf{-355{,}712-2267{,}64})=20.292$ kJ/mol;

$K_{aLehninger}=K_{Lehninger}/[\mathbf{H_2O}]=220500/55{,}34573393=3984=\frac{[H_2PO_4^-]\cdot[ADP^{2-}]}{[H_2O]\cdot[ATP^{3-}]}$

pH<7,199;$Glu^-+NH_4^++ATP^{3-}\Rightarrow Gln+ADP^{2-}+H_2PO_4^-$;$\Delta G_{abL}=\mathbf{14{,}2-20{,}55=-6{,}35}$ kJ/mol

pH<7,199; $K_{abLehninger}=K_{aLehninger}{}^*K_{bLehninger}=3984^*0{,}003252737=12.959=\frac{[H_2PO_4^-]\cdot[ADP^{2-}]\cdot[Gln]}{[Glu^-]\cdot[NH_4^+]\cdot[ATP^{3-}]}$

$\Delta G_{abL}=\mathbf{-R\bullet T\bullet ln}(K_{abL})=-8{,}3144^*298{,}15^*\mathbf{ln}(12{,}958904208)=\mathbf{-6.35}$ kJ/mol;pH<7,199

$\Delta H_{Hess}=\Delta H^\circ_{H2PO4-}+\Delta H^\circ_{Gln}+\Delta H^\circ_{ADP3}-\Delta H^\circ_{NH4}-\Delta H^\circ_{Glu}-\Delta H^\circ_{ATP4}=\mathbf{-6{,}75}$ kJ/mol;

$=-1302{,}6\mathbf{-809{,}12-2627{,}4}-(-132{,}5\mathbf{-982{,}77-3617{,}1})=\mathbf{-6{,}75}$ kJ/mol exo

$\Delta S_{Hess}=-\Delta S^\circ_{H2PO4-}+\Delta S^\circ_{Sln}+\Delta S^\circ_{ADP3}-\Delta S^\circ_{NH4}-\Delta S^\circ_{Slu}-\Delta S^\circ_{ATP4}=\mathbf{112{,}2}$ J/mol/K;

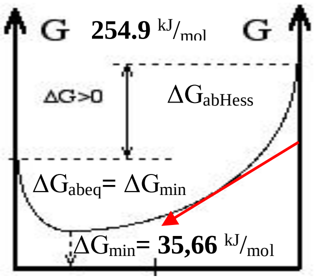
$=92{,}5\mathbf{-2379{,}04-4117{,}11}-(113{,}4\mathbf{-2103{,}15-4526{,}1})=\mathbf{112{,}2}$ kJ/mol exo

$\Delta G_{Hess}=\Delta H_{Hess}-T^*\Delta S_{Hess}=\mathbf{-6{,}75}\ -298{,}15^*0{,}\mathbf{1122}=\mathbf{-40{,}2}$ kJ/mol endoergic;

$Glu^-+NH_4^++ATP^{4-}+H_2O\Rightarrow Gln+ADP^{3-}+HPO_4^{2-}+H_3O^+$; $\Delta G_{ab}=66{,}16-30{,}5=35.66$ kJ/mol;

$\Delta H_{Hess}=\mathbf{-809{,}12-2627{,}4-1298{,}89}-285{,}81-(\mathbf{-982{,}77}-132{,}5\mathbf{-3617{,}1}-285{,}85)=-3$ kJ/mol;

$\Delta G_{Hess}=\Delta H_{Hess}-T^*\Delta S_{Hess}=\mathbf{-3}\ -298{,}15^*-0{,}\mathbf{8649=254.9}$ kJ/mol;



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

$K_{abL}=K_a{}^*K_{bLehninger}=220500^*0{,}003252737=717.23=\frac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[Gln]\cdot[H_3O^+]}{[Glu^-]\cdot[NH_4^+]\cdot[ATP^{4-}]\cdot[H_2O]}$

$\Delta S_{Hess}=\mathbf{-2379{,}04-4117{,}11-810{,}792}-3{,}854-(\mathbf{-2103{,}15+}113{,}4\mathbf{-4526{,}1}+69{,}9565)=\mathbf{-864.9}$ J/mol/K;

$\Delta G_{Hess}=\Delta G^\circ_{Gln}+\Delta G^\circ_{ADP3}+\Delta G^\circ_{HPO42}+\Delta H^\circ_{H3O}-\Delta G^\circ_{Glu}-\Delta G^\circ_{NH4}-\Delta G^\circ_{ATP4}-\Delta G^\circ_{H2O}=\mathbf{84{,}0718}$ kJ/mol;

$\Delta G_H=\mathbf{-99{,}8112-1057{,}143-1399{,}9}-213{,}275-(\mathbf{-355{,}712}-79{,}3\mathbf{-2267{,}64-151{,}549})=\mathbf{84{,}072}$ kJ/mol;

$\Delta G^o_{abHess}=(\Delta G^\circ_{Hess})\ \mathbf{84{,}07}((\Delta H^\circ_{Hess},\Delta S^\circ_{Hess})\mathbf{254.9})$ kJ/mol; $\Delta G_{ab}=66{,}16-30{,}5=35.66$ kJ/mol;

$\mathbf{ATP^{3-}+H_2O=>AMP^{1-}+H_2P_2O_7^{2-}}$; $\Delta\mathbf{G}_{\text{Lehningerppm}}=-35{,}65\ ^{\text{kJ}}/_{\text{mol}}$; $\mathbf{K}_{\text{Lehningerppm}}=\mathbf{K}_{\text{Lehninger}}/[\mathbf{H_2O}]=1760968$; pH<6,72;

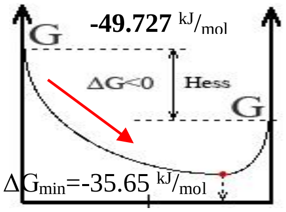
$\Delta\text{G}_{\text{Hess}}=\Delta\text{G}°_{\text{H2P2O73-}}-\Delta\text{G}°_{\text{AMP2-}}-\Delta\text{G}°_{\text{ATP4-}}-\Delta\text{G}°_{\mathbf{H2O}}=\mathbf{-1938{,}85-530{,}066-(-2267{,}64-151{,}549)}=\mathbf{-49.727}\ ^{\text{kJ}}/_{\text{mol}}$;

$\Delta\mathbf{G}_{\text{mppL}}=\mathbf{-R\bullet T\bullet ln(K}_{\text{mppL}})=-8{,}3144*298{,}15*\mathbf{ln}(1760959{,}91125033)/1000=-35{,}65\ ^{\text{kJ}}/_{\text{mol}}$;

Exothermic and exoergic $\mathbf{ATP^{4-}}$ hydrolize Hess free energy change negative as $\mathbf{H_2P_2O_7^{2-}}$ $\Delta\mathbf{G}_{\text{Hess}}=\mathbf{-63.15}\ ^{\text{kJ}}/_{\text{mol}}$, but minimized $\Delta\mathbf{G}_{\mathbf{min}}=\Delta\mathbf{G}_{\text{Lehningerppm}}=-35.65\ ^{\text{kJ}}/_{\text{mol}}$ reaching equilibrium

mixture: $\mathbf{K}_{\text{mppL}}=\mathbf{K}_{\text{Leninger}}/[\mathbf{H_2O}]=1760959{,}91125033=\dfrac{[H_2P_2O_7^{2-}]\cdot[AMP^{1-}]}{[H_2O]\cdot[ATP^{3-}]}$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta\text{G}_{\text{min}}$ reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.



reactants $\text{ATP}^{3-}+\text{H}_2\text{O}$

products $\mathbf{AMP^{1-}+H_2P_2O_7^{2-}}$

ppm) $\mathbf{ATP^{4-}+2H_2O=>AMP^{2-}+HP_2O_7^{3-}+H_3O^+}$; $\Delta\mathbf{G}_{\text{Lehninger}}=-45{,}6\ ^{\text{kJ}}/_{\text{mol}}$;at pH=7,36;

$\Delta\text{G}_{\text{Hess}}=\Delta\text{G}°_{\mathbf{H3O}}+\Delta\text{G}°_{\text{HP2O73}}+\Delta\text{G}°_{\text{AMP2}}-\Delta\text{G}°_{\text{ATP4}}-2\Delta\text{G}°_{\mathbf{H2O}}=-213{,}275\mathbf{-1938{,}85-530{,}066-(-2267{,}64}+2*\mathbf{-151{,}549})=\mathbf{-111{,}45}\ ^{\text{kJ}}/_{\text{mol}}$;

$\mathbf{K}_{\text{ab}}=\mathbf{K}_{\text{Leninger}}=\exp(45600/8{,}3144/298{,}15)=97462087{,}2480605$; $\Delta\text{S}_{\text{dispersed}}=-\Delta\text{H}_{\text{H}}/\text{T}=\mathbf{24{,}79}/298{,}15=\mathbf{83{,}15}\ ^{\text{J}}/_{\text{(mol K)}}$;

$\Delta\text{H}_{\text{Hess}}=\Delta\text{H}°_{\mathbf{H3O}}+\Delta\text{H}°_{\text{HP2O73}}+\Delta\text{H}°_{\text{AMP2}}-\Delta\text{H}°_{\text{ATP4}}-2\Delta\text{H}°_{\mathbf{H2O}}=-285{,}81\mathbf{-2291{,}04-1638{,}34}-(\mathbf{-3617{,}1}+2*\mathbf{-286{,}65})=\mathbf{-24{,}79}\ ^{\text{kJ}}/_{\text{mol}}$;

$\Delta\text{S}_{\text{Hess}}=\Delta\text{S}°_{\mathbf{H3O}}+\Delta\text{S}°_{\text{HP2O73}}+\Delta\text{S}°_{\text{AMP2}}-\Delta\text{S}°_{\text{ATP4}}-2\Delta\text{S}°_{\mathbf{H2O}}=-3{,}854\mathbf{-1181{,}25-3717{,}19-(-4526{,}1}+2*\mathbf{-453{,}188})=\mathbf{530{,}182}\ ^{\text{J}}/_{\text{(mol K)}}$;

$\Delta\text{G}_{\text{Hess}}=\Delta\text{H}_{\text{Hess}}-\text{T}*\Delta\text{S}_{\text{Hess}}=\mathbf{-24{,}79}\ -298{,}15*0{,}\mathbf{530182}=\mathbf{-182{,}9}\ ^{\text{kJ}}/_{\text{mol}}$ exoergic;

$\Delta\text{S}_{\text{total}}=\Delta\text{S}_{\text{H}}+\Delta\text{S}_{\text{dispersed}}=\mathbf{530{,}182+83{,}15=613{,}332}\ ^{\text{J}}/_{\text{mol/K}}$; $\text{T}\bullet\Delta\text{S}_{\text{total}}=\mathbf{0{,}613332}*298{,}15=\mathbf{182{,}86}\ ^{\text{kJ}}/_{\text{mol}}$ TΔSn <u>dispersed</u>

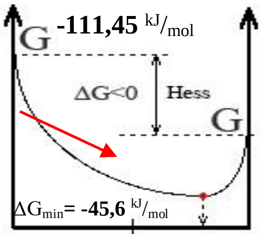
Equilibrium reached by free energy change minimum at compounds mixture ratio in Prigogine attractor expression is favored grater as one

$1<\mathbf{K}_{\text{Lehningeppm}}=\mathbf{exp(-}\Delta\mathbf{G}_{\text{Lehninger}}\mathbf{/R/T})=\exp(45600/8{,}3144/298{,}15)=97462087{,}2480605=\dfrac{[HP_2O_7^{3-}]\cdot[AMP^{2-}]\cdot[H_3O^+]}{[H_2O]^2\ \cdot[ATP^{4-}]}$

Exothermic, exoergic pyrophosphate hydrolysis Hess free energy change $\Delta\mathbf{G}_{\mathbf{Hess}}$ is negative $\mathbf{-111{,}45}\ ^{\text{kJ}}/_{\text{mol}}$, but minimized up to $\Delta\mathbf{G}_{\mathbf{min}}=\Delta\mathbf{G}_{\text{Lehningerppm}}=-45{,}6\ ^{\text{kJ}}/_{\text{mol}}$ reaching

equilibrium mixture $\mathbf{K}_{\text{Lehningeppm}}=\dfrac{[HP_2O_7^{3-}]\cdot[AMP^{2-}]\cdot[H_3O^+]}{[H_2O]^2\ \cdot[ATP^{4-}]}=97462087{,}2480605.$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta\text{G}_{\text{min}}$. Free energy change minimum reaching establishes equilibrium.



reactants $\text{ATP}^{4-}+2\mathbf{H_2O}$

products

$\mathbf{AMP^{2-}+HP_2O_7^{3-}+H_3O^+}$

$\mathbf{H_2P_2O_7^{2-}}+\text{H}_2\text{O}=>\text{H}_2\text{PO}_4^-+\text{H}_2\text{PO}_4^-$; $\Delta\mathbf{G}_{\text{pp}}=\mathbf{-70{,}94}\ ^{\text{kJ}}/_{\text{mol}}$; without 6,72<pH<7,199;

$\Delta\text{G}_{\text{Hess}}=2\Delta\text{G}°_{\text{H2PO4}}-\Delta\text{G}°_{\text{H2P2O72}}-\Delta\text{G}°_{\mathbf{H2O}}=2*-1130{,}2-(\mathbf{-1952{,}27}-237{,}191)=\mathbf{-70{,}94}\ ^{\text{kJ}}/_{\text{mol}}$;

$\mathbf{K}_{\mathbf{pp}}=\mathbf{K}_{\text{Lehningerpp}}/[\mathbf{H_2O}]=2310{,}57/55{,}34573393=41{,}748=\dfrac{[H_2PO_4^-]^2}{[H_2O].[H_2P_2O_7^{2-}]}$;

$\Delta\mathbf{G}_{\mathbf{ppL}}=\mathbf{-R\bullet T\bullet ln(K}_{\mathbf{eqL}})=-8{,}3144*298{,}15*\mathbf{ln}(41{,}74799819)=\mathbf{-9{,}251}\ ^{\text{kJ}}/_{\text{mol}}$,

$\mathbf{HP_2O_7^{3-}}+2\text{H}_2\text{O}+\Delta\text{G}+\mathbf{Q}=>\text{HPO}_4^{2-}+\text{HPO}_4^{2-}+\mathbf{H_3O^+}$**;** $\Delta\mathbf{G}_{\text{LehningeHpp}}=-19{,}2\ ^{\text{kJ}}/_{\text{mol}}$; pH=7,36

$\mathbf{K}_{\mathbf{app}}=\mathbf{K}_{\text{Lehningepp}}=\mathbf{exp(-}\Delta\mathbf{G}_{\text{Lehninger}}\mathbf{/R/T})=\exp(19200/8{,}3144/298{,}15)=2310{,}57=\dfrac{[HPO_4^{2-}]^2\cdot[H_3O^+]}{[H_2O]^2\cdot[HP_2O_7^{3-}]}$

$\Delta\text{G}_{\text{Hess}}=\Delta\text{G}°_{\mathbf{H3O}}+\mathbf{2}\Delta\text{G}°_{\mathbf{HPO42}}-\Delta\text{G}°_{\text{HOPO2OPO2O2}}-2\Delta\text{G}°_{\mathbf{H2O}}=\mathbf{-85{,}6}\ ^{\text{kJ}}/_{\text{mol}}$;
$=-213{,}275+2*\mathbf{-1057{,}143-(-1938{,}85}+2*\mathbf{-151{,}549})=\mathbf{-85{,}6}\ ^{\text{kJ}}/_{\text{mol}}$

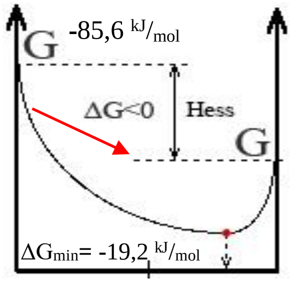
Eksoergic pyrophosphate $\mathbf{HP_2O_7^{3-}}$ hydrolysis Hess free energy change at pH=7,36

$\Delta\mathbf{G}_{\text{Hess}}$ negative $\mathbf{-85{,}6}\ ^{\text{kJ}}/_{\text{mol}}$, but minimized $\Delta\mathbf{G}_{\mathbf{min}}=\Delta\mathbf{G}_{\mathbf{eq}}=-19{,}2\ ^{\text{kJ}}/_{\text{mol}}$ reaching

equilibrium mixture $\mathbf{K}_{\mathbf{a}}=\dfrac{[HPO_4^{2-}]^2\cdot[H_3O^+]}{[H_2O]^2\cdot[HP_2O_7^{3-}]}=2310{,}57$. Le Chatelier principle is

Prigogine attractor for Free energy change minimum $\Delta\text{G}_{\text{min}}$ reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium.



reactants $\mathbf{HP_2O_7^{3-}}+\mathbf{2H_2O}$

products **2** $\text{HPO}_4^{2-}+\text{H}_3\text{O}^+$

pp) $HP_2O_7^{3-}+2\,H_2O \Rightarrow HPO_4^{2-}+HPO_4^{2-}+H_3O^+$; $\Delta G_{ppLehninger}=-19.2$ kJ/mol; $\Delta G_{ppHess}=-85.6$ kJ/mol;

b) $ATP^{4-}+2H_2O \Rightarrow AMP^{2-}+HP_2O_7^{3-}+H_3O^+$; $\Delta G_{bLehninger}=-45.6$ kJ/mol; $\Delta G_{bHess}=-111{,}45$ kJ/mol;

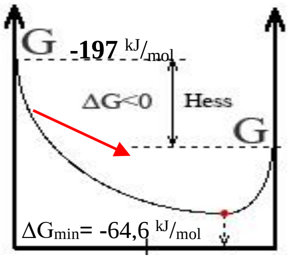
ppb) $ATP^{4-}+4H_2O \Rightarrow AMP^{2-}+HPO_4^{2-}+HPO_4^{2-}+2H_3O^+$; $\Delta G_{ppbL}=-64.6$ kJ/mol; $\Delta G_{ppHess}=-197{,}05$ kJ/mol;

$\Delta G_{ppbH}=\Delta G_{ppH}+\Delta G_{bH}=-85{,}6-111{,}45=-197{,}05$ kJ/mol ;

$\Delta G_{Hess}=\Delta G^\circ_{AMP2-}+2\Delta G^\circ_{H3O}+2\Delta G^\circ_{HPO42}-\Delta G^\circ_{ATP4}-4\Delta G^\circ_{H2O}=-197$ kJ/mol ;

$=-530{,}066-2*213{,}275+2*-1057{,}143-(-2267{,}64+4*-151{,}549)=-197.066$ kJ/mol

Exothermic and exoergic $ATP^{4-}+4H_2O$ hydrolise Hess free energy change negative $\Delta G_{Hess}=-197$ kJ/mol , but $\Delta G_{min}=\Delta G_{ppbL}=-64.6$ kJ/mol; minimizes reaching equilibrium mixture $K_{ppbLehninger}=207737828686$.



A+2B 50% 2C+D

reaktants $ATP^{4-}+4H_2O$

products $AMP^{2-}+HPO_4^{2-}+HPO_4^{2-}+2H_3O^+$;

$K_{ppb}=K_{Leningeppb}=\exp(-\Delta G_{Lehningerppb}/R/T)=\exp(64600/8{,}3144/298{,}15)=207737828686=\frac{[HPO_4^{2-}]^2\cdot[H_3O^+]^2\cdot[AMP^{2-}]}{[H_2O]^4\cdot[ATP^{4-}]}$

bb) $ADP^{3-}+HPO_4^{2--}+H_3O^+\Rightarrow ATP^{4-}+2H_2O$; $\Delta G_{bbLehninger}=30{,}5$ kJ/mol;

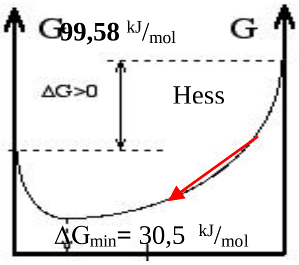
$K_{bbLehningeH}=\exp(-\Delta G_{bbLehningeH}/R/T)=\exp(-30500/8{,}3144/298{,}15)=0.000004535142=\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$

$\Delta G_{Hess}=\Delta G^\circ_{ATP3}-2\Delta G^\circ_{H2O}-\Delta G^\circ_{ADP2}-\Delta G^\circ_{HPO42}-\Delta G^\circ_{H3O}=99{,}58$ kJ/mol;

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

Endothermic and endoergic **ADP^{3-}** phosphorylation at pH = 7,36 Hess free energy change positive $\Delta G_{transfer}=99{,}58$ kJ/mol , but minimizes to $\Delta G_{min}=\Delta G_{eq}=30{,}5$ kJ/mol reaching equilibrium mixture $K_{bbLehningeH}=0.000004535142$: Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium.



A+B+C 50% D+2E

reactants $ADP^{3-}+HPO_4^{2-}+H_3O^+$

products $ATP^{4-}+2H_2O$

$HP_2O_7^{3-}+ADP^{3-}\Rightarrow HPO_4^{2-}+ATP^{4-}$; $\Delta G_{abbpp}=\Delta G_{app}+\Delta G_{bb}=-19{,}2+30{,}5=11{,}3$ kJ/mol; pH=7,36

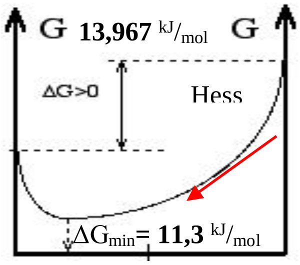
$\Delta G_H=\Delta G^\circ_{HPO42}+\Delta G^\circ_{ATP4}-\Delta G^\circ_{HP2O73}-\Delta G^\circ_{ADP3-}=-1057{,}143-2267{,}64-(-1938{,}85-1399{,}9)=13{,}967$ kJ/mol;

$K_{abpp}=K_{app}K_{bbLehninger}=2310{,}57*0{,}000004535142=0{,}010478763$

$\Delta G_{abpp}=-R\cdot T\cdot\ln(K_{abpp})=-8{,}3144*298{,}15*\ln(0{,}010478763)/1000=11{,}3$ kJ/mol;

Endothermic and endoergic phosphate transfer Hess free energy change positive $\Delta G_{transfer}=13{,}967$ kJ/mol , but minimizes up to $\Delta G_{min}=\Delta G_{eq}=11{,}3$ kJ/mol reaching equilibrium mixture: $K_{abpp}=0{,}010478763=\frac{[HPO_4^{2-}]\cdot[ATP^{4-}]}{[HP_2O_7^{3-}]\cdot[ADP^{3-}]}$. Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium



A+B 50% C+D

reactants $HP_2O_7^{3-}+ADP^{3-}$

products $HPO_4^{2-}+ATP^{4-}$

ADP^{2-}+ $H_2PO_4^-$=>ATP^{3-}+H_2O; $\Delta G_{Lehninger}$ = 20,55 $^{kJ}/_{mol}$; without pH=?;

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

$$\frac{[H_2O]\cdot[ATP^{3-}]}{[H_2PO_4^-]\cdot[ADP^{2-}]}$$

=$\mathbf{K}_{bbLehningeH}$**=exp(-ΔG$_{Lehninger}$/R/T)**=exp(-30500/8,3144/298,15) = 000004535142

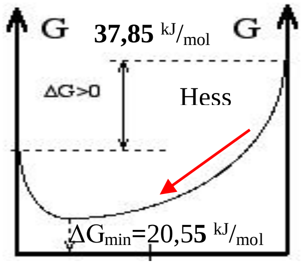
= $\mathbf{K}_{bL}$= $\mathbf{K}_{bbLehninger}$[H_2O] =0,000004535142*55,3457339 =0,000250993.

ΔG_{bL}= **-R•T•ln**(K_{bL})=-8,3144*298,15***ln**(0,000250993)/1000= 20,5512 $^{kJ}/_{mol}$;

Endothermic and endoergic **ADP^{2-}** phosphorylation without pH = 7,36 Hess free energy change negative Δ**G$_{transfer}$=37,85** $^{kJ}/_{mol}$, but minimizes up to Δ**G$_{min}$=ΔG$_{eq}$**=20,55 $^{kJ}/_{mol}$ reaching equilibrium mixture:

$$K_{bL}=K_{bbLehninger}[H_2O]=0{,}000250993=\frac{[H_2O]\cdot[ATP^{3-}]}{[H_2PO_4^-]\cdot[ADP^{2-}]}.$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.



A+B 50% C+D

reactants ADP^{2-}+$H_2PO_4^-$

products **ATP^{3-}**+ H_2O;

bb) ADP^{3-}+HPO_4^{2--}+H_3O^+=>ATP^{4-}+$2H_2O$; Δ**G$_{bLehninger}$**=30,5 $^{kJ}/_{mol}$; **K$_{bbLehn}$**=1/220500,2=0.000004535142;

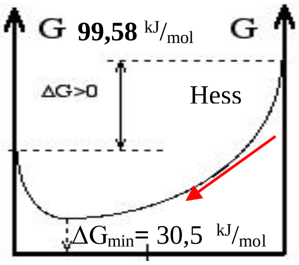
$\Delta G_{Hess}=\Delta G°_{ATP3}-2\Delta G°_{H2O}-\Delta G°_{ADP2}-\Delta G°_{HPO42}-\Delta G°_{H3O}$=**-1399,9-1057,143**-213,275-(**-2267,64+2*-151,549**)=**99,58** $^{kJ}/_{mol}$;

$\mathbf{K}_{bbLehningeH}$**=exp(-ΔG$_{Lehninger}$/R/T)**=exp(-30500/8,3144/298,15) = 0.000004535142 .

$$\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$$ =$\mathbf{K}_{bbLehningeH}$**=exp(-ΔG$_{Lehninger}$/R/T)**=exp(-30500/8,3144/298,15) = 0.000004535142

Endothermic and endoergic **ADP^{3-}** phosphorylation at pH = 7,36 Hess free energy change positive Δ**G$_{transfer}$**= **99,58** $^{kJ}/_{mol}$, but minimizes to Δ**G$_{min}$**= Δ**G$_{eq}$**= 30,5 $^{kJ}/_{mol}$ reaching equilibrium mixture

$$K_{bbLehningeH}=0.000004535142=\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$$: Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.



A+B+C 50% D+2E

reactants_ **ADP^{3-}+HPO_4^{2-}+H_3O^+**

products ATP^{4-}+$2H_2O$

b0) $\mathbf{ATP^{3-}+H_2O \Rightarrow ADP^{2-}+H_2PO_4^-}$; $\Delta G_{b0LehningeH}=-20,55\ ^{kJ}/_{mol}$; $\mathbf{K}_{b0Lehninger}=\mathbf{K}_{\mathbf{b}Lehninger}/[\mathbf{H_2O}]=3984$; without pH=?

$\Delta G_{Hess}=\Delta G°_{\mathbf{ADP3}}+\Delta G°_{\mathbf{HPO42}}-\Delta G°_{\mathbf{ATP4}}-\Delta G°_{\mathbf{H2O}}=\mathbf{-1399,9-1057,143}-(\mathbf{-2267,64-151,549})=\mathbf{-37,854}\ ^{kJ}/_{mol}$;

$$\mathbf{K}_{b0Lehninger}=\mathbf{K}_{\mathbf{b}Lehninger}/[\mathbf{H_2O}]=220500,2/55,3457=3984,1=\frac{[H_2PO_4^-]\cdot[ADP^{3-}]}{[H_2O]\cdot[ATP^{4-}]}$$

$$\Delta\mathbf{G}_{b0LehningeH}=\mathbf{-R\bullet T\bullet ln}(\mathbf{K}_{b0LehningeH})=-8,3144*310,15*\mathbf{ln}(3984,052962)/1000=-21,38\ ^{kJ}/_{mol};$$

b) $\mathbf{ATP^{4-}+2H_2O \Rightarrow ADP^{3-}+HPO_4^{2-}+H_3O^+}$; $\Delta\mathbf{G}_{\mathbf{b}Lehninger}=-30,5\ ^{kJ}/_{mol}$; $\mathbf{K}_{\mathbf{b}Lehninger}=K_{Lehninger}[\mathbf{H_2O}]/[\mathbf{H_3O^+}]=220500,2$;

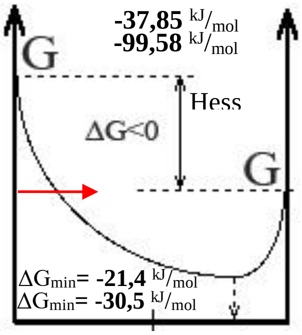
$\Delta G_{Hess}=\Delta G°_{\mathbf{ADP3}}+\Delta G°_{\mathbf{HPO42}}+\Delta G°_{\mathbf{H3O}}-\Delta G°_{\mathbf{ATP4}}-2\Delta G°_{\mathbf{H2O}}=\mathbf{-1399,9-1057,143}-213,275-(\mathbf{-2267,64+2*-151,549})=\mathbf{-99,58}\ ^{kJ}/_{mol}$;

T=298,15 K (25° C);

$$\mathbf{K}_{\mathbf{b}Lehninger}=\mathbf{exp(-\Delta G}_{\mathbf{b}Lehninger}\mathbf{/R/T)}=\exp(30500/8,3144/298,15)=220500,2=\frac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_2O]^2[ATP^{4-}]}$$

T=310,15 K (37° C); $\mathbf{K}_{LehningeH}=\mathbf{exp(-\Delta G}_{Lehninger}\mathbf{/R/T)}=\exp(30500/8,3144/310,15)=136983,2474$;

$$\Delta\mathbf{G}_{bLehningeH}=\mathbf{-R\bullet T\bullet ln}(\mathbf{K}_{bLehningeH})=-8,3144*310,15*\mathbf{ln}(136983,2474)/1000=-30,5\ ^{kJ}/_{mol};$$



Exothermic and exoergic $\mathbf{ATP^{4-}}$ hydrolise Hess free energy change $\Delta G_{Hess}=\mathbf{-37,85}\ ^{kJ}/_{mol}$ $\Delta G_{Hess}=\mathbf{-\ 99,58}\ ^{kJ}/_{mol}$ negative at absence pH = 7,36, but minimizes to $\Delta\mathbf{G}_{\mathbf{min}}=\Delta\mathbf{G}_{\mathbf{eq}}$ -21,38 $^{kJ}/_{mol}$ and -30,5 $^{kJ}/_{mol}$ reaching equilibrium mixture

$$\mathbf{K}_{b0Lehninger}=\mathbf{K}_{\mathbf{b}Lehninger}/[\mathbf{H_2O}]=3984,1=\frac{[H_2PO_4^-]\cdot[ADP^{3-}]}{[H_2O]\cdot[ATP^{4-}]}$$

$$\mathbf{K}_{\mathbf{b}Lehninger}=220500,2=\frac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_2O]^2\cdot[ATP^{4-}]}.$$

reactants $\mathbf{ATP^{4-}+2H_2O}$

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium mixture.

products $ADP^{3-}+HPO_4^{2-}+H_3O^{+-}$

Free energy change minimum reaching establishes equilibrium.

$\Delta\mathbf{G}_{\mathbf{Hess}}=\Delta G°_{\mathbf{cHeatine}}+\Delta G°_{\mathbf{HPO42}}-\Delta G°_{\mathbf{PcHeatine}}-\Delta G°_{\mathbf{H2O}}=107,69-1089,28-(-689,08-237,191)=-55,3\ ^{kJ}/_{mol}$;
$\Delta\mathbf{G}_{\mathbf{Hess}}=107,69-1089,28-(-689,08-237,191)=-55,3\ ^{kJ}/_{mol}$;
$\Delta\mathbf{G}_{\mathbf{Hess}}=\mathbf{126,1868}-1089,28-(\underline{\mathbf{-736,4}}-237,191)=10,5\ ^{kJ}/_{mol}$;

$\Delta G_{CRCHess}=\Delta G°_{\mathbf{cHeatine}}+\Delta G°_{\mathbf{ATP3}}-\Delta G°_{\mathbf{PcHeatine1}}-\Delta G°_{\mathbf{ADP2}}=-71,03\ ^{kJ}/_{mol}$; exoergic CRC2010
$=107,69-2292,5-(-689,08-1424,7)=-71,03\ ^{kJ}/_{mol}$ CRC 2010
$\Delta\mathbf{G}_{CRC}=\mathbf{-R\bullet T\bullet ln}(\mathbf{K}_{CRC})=-8,3144*310,15*\mathbf{ln}(173)/1000=-13,3\ ^{kJ}/_{mol}$;

bd) $ADP^{2-}+H_2O$=>$AMP^{-}+H_2PO_4^{-}$;**ΔG_{bd}=**-22.85 $^{kJ}/_{mol}$; without pH=?

ΔG_{Hess}=ΔG°$_{H2PO4-}$+ΔG°$_{AMP-}$-ΔG°$_{ADP2-}$-ΔG°$_{H2O}$=**-530,066**-1130,2-(**-1399,9-151,549**)= **-108.8** $^{kJ}/_{mol}$;

ΔG_{bd}=-R•T•ln(K$_{bd}$)=-8,3144*298,15***ln**(10075,75322)/1000= -22,85 $^{kJ}/_{mol}$;

K$_{bd}$=**K$_{bd}$**$_{Lehninger}$/[**H$_2$O**]=557649,957/55,34573393=10075,75= $\frac{[H_2PO_4^-]\cdot[AMP^-]}{[H_2O]\cdot[ADP^{2-}]}$

ΔG_{bd}=-R•T•ln(K$_{bd}$)=-8,3144*298,15***ln**(10075,75322)/1000= -22,85 $^{kJ}/_{mol}$;

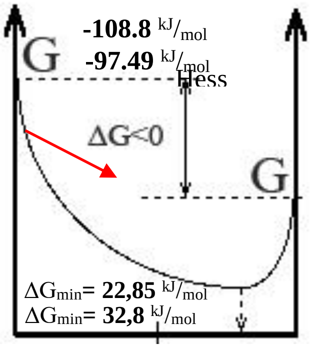
K$_{bd}$ $_{Lehninger}$**=exp(-ΔG$_{Lehninger}$/R/T)**=exp(32800/8,3144/298,15)=557649,957= $\frac{[HPO_4^{2-}]\cdot[H_3O^+]\cdot[AMP^{2-}]}{[H_2O]^2\cdot[ADP^{3-}]}$

bd) $ADP^{3-}+2H_2O$=>$AMP^{2-}+HPO_4^{2-}+H_3O^+$; pH=7,36; **Δ$G_{Lehninger}$**=-32.8 $^{kJ}/_{mol}$;

ΔG_{Hess}=ΔG°$_{H3O+}$+ΔG°$_{HPO42-}$+ΔG°$_{AMP2-}$-ΔG°$_{ADP3-}$-2ΔG°$_{H2O}$=-213,275**-1057,143-530,066-(-1399,9**+2*(**-151,549**))=**-97,49** $^{kJ}/_{mol}$;

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
Adenosin	**-626,66**	**-3316,57**	**362,172**

Exothermic, exoergic ADP^{2-} and **ADP^{3-}** hydrolise without pH=? and at pH=7,36 Hess free energy change negative **Δ$G_{hydrolise}$** = **-108.8** $^{kJ}/_{mol}$ and **-97,49** $^{kJ}/_{mol}$, but minimizes **ΔG_{min}**=**ΔG_{bd}**=-22,85 $^{kJ}/_{mol}$ and -32.8 $^{kJ}/_{mol}$ reaching equilibrium mixture **K$_{bd}$**=10075,75 and **K$_{bd}$**$_{Lehninger}$=557649,957.



reactants **$ADP^{2-}+H_2O$** A+B 50% C+D

products $H_2PO_4^-+AMP^-$

reactants **$ADP^{3-}+2H_2O$** A+2B 50% C+D+E

products $AMP^{2-}+HPO_4^{2-}+H_3O^+$

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

Free energy change minimum reaching establicshes equilibrium.

Am) $AMP^{2-}+H_2O$=>Adenosine+HPO_4^{2-}; **Δ$G_{Lehninger}$**=-14.2 $^{kJ}/_{mol}$; **K$_{Am}$**=exp(14200/8,3144/298,15)=307,43344;

$\frac{[HPO_4^{2-}]\cdot[Adenosin]}{[H_2O]\cdot[AMP^{2-}]}$ **K$_{Am}$**=**K$_{Lehninger}$**=exp(14200/8,3144/298,15)=307,43344 at pH=7,36 .

ΔG_{Hess}=ΔG°$_{adenosin}$+ΔG°$_{HPO42}$-ΔG°$_{AMP2}$-ΔG°$_{H2O}$=**362,172**-1089,28-(**-530,066-151,549**)=**-45.5** $^{kJ}/_{mol}$;

AmL) $AMP^{-}+H_2O$=>Adenosine+$H_2PO_4^{---}$; at les pH<7.199 **ΔG_{AmL}**= -14,2 $^{kJ}/_{mol}$.

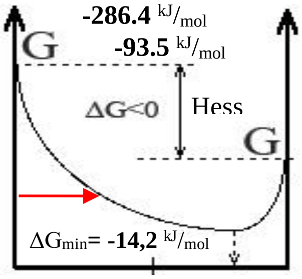
K$_{AmL}$= **K$_{Lehninger}$**=exp(14200/8,3144/298,15)=307,43344= $\frac{[H_2PO_4^-]\cdot[Adenosin]}{[H_2O]\cdot[AMP^-]}$.

Δ$G_{HessAmL}$=ΔG°$_{adenosin}$+ΔG°$_{H2PO4}$-ΔG°$_{AMP}$-ΔG°$_{H2O}$=**362,172**-1137,3-(**-530,066-151,549**)=**-93.5** $^{kJ}/_{mol}$; pH<7.199;

ΔG_{HessAm}=ΔH_{HessAm}–T*ΔS_{HessAm}=**-4,27** -298,15*0,**946308=-286.4** $^{kJ}/_{mol}$ exoergic;

Exothermic and exoergic Hess free energy change negative for AMP^- at les pH<7.199 **Δ$G_{hydrolize}$**=**-286.4** $^{kJ}/_{mol}$ and **AMP^{2-}** hydrolyze **-93.5** $^{kJ}/_{mol}$ at pH=7,36, but minimizes to **ΔG_{min}**=**ΔG_{Am}**= -14,2 $^{kJ}/_{mol}$ at pH=7,36 reaching equilibrium mixture:

K$_{AmL}$=307,4= $\frac{[HPO_4^{2-}]\cdot[Adenosin]}{[H_2O]\cdot[AMP^{2-}]}$. Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium.



A+B 50% C+D

reactants $AMP^{2-}+H_2O$

products Adenosine+HPO_4^{2-} .

Free energy change minimum reaching establishes equilibrium.

ΔH_{HessAm}=ΔH°$_{adenosin}$+ΔH° $_{HPO42}$-ΔH°$_{AMP}$-ΔH°$_{H2O}$=**-626,66**-1302,6-(**-1638,34-286,65**)=**-4.27** $^{kJ}/_{mol}$;

ΔS_{HessAm}=ΔS°$_{adenosin}$+ΔS° $_{HPO42}$-ΔS°$_{AMP}$-ΔS°$_{H2O}$=**-3316,57**+92,5-(**-3717,19-453,188**)=**946.308** $^{kJ}/_{K}/_{mol}$;

$\mathbf{H_2P_2O_7^{2-}}$+ADP^{2-} =>$H_2PO_4^-$ +ATP^{3-}; pH<6,72; $\mathbf{K}_{abbppPH}$=$\mathbf{K}_{abbpp}$/[$\mathbf{H_2O}$]=0,01047878/55,3457=0,0001893

$\Delta G_{Hess}=\Delta G°_{H2PO4-}+\Delta G°_{ATP3-}-\Delta G°_{H2P2O72-}-\Delta G°_{ADP2-}$=**-1057,143-2267,64-(-1952,27-1399,9)=27,39** $^{kJ}/_{mol}$;

$\Delta \mathbf{G}_{abbppPH}$**=-R•T•ln(K**$_{abbppP}$)=-8,3144*298,15***ln**(0,0001893)/1000=21,25 $^{kJ}/_{mol}$

pp) $\mathbf{HP_2O_7^{3-}}$+ADP^{3-} =>HPO_4^{2-} +ATP^{4-}; $^-$;$\Delta \mathbf{G}_{abbppL}$=30,5+(-19,2)=11,3 $^{kJ}/_{mol}$; pH=7,36; $\Delta \mathbf{G}_{Hess}$**=13,967** $^{kJ}/_{mol}$;

$\Delta G_H=\Delta G°_{HPO42-}+\Delta G°_{ATP4-}-\Delta G°_{HP2O73-}-\Delta G°_{ADP3-}$=**-1057,143-2267,64-(-1938,85-1399,9)=13,967** $^{kJ}/_{mol}$;

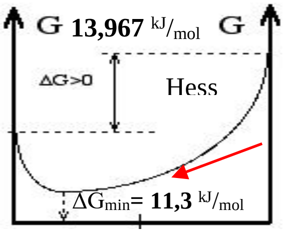
$\Delta H_H=\Delta H°_{HPO42-}+\Delta H°_{ATP4-}-\Delta H°_{HP2O73-}-\Delta H°_{ADP3-}$=**-1298,89-3617,1-(-2291,04-2627,4)=2,45** $^{kJ}/_{mol}$;

2. $\Delta S_{dispeHse}=-\Delta H_H/T$=**-2,45**/298,15=**-8,22** $^{J}/_{(mol\ K)}$; $\Delta S_{total}=\Delta S_H+\Delta S_{dispeHsed}$=**-38,532-8,2173=-46,75** $^{J}/_{mol/K}$

$\Delta S_H=\Delta S°_{HPO42-}+\Delta S°_{ATP4-}-\Delta S°_{HP2O73-}-\Delta S°_{ADP3-}$=**-810,792-4526,1-(-1181,25-4117,11)=-38,53** $^{J}/_{(mol\ K)}$;

$\Delta G_H=\Delta H_H-T*\Delta S_H$=**2,45**-298,15*-0,**038532=13,94** $^{kJ}/_{mol}$ endoergic; $T•\Delta S_{total}$=**-0,0467493**•298,15=**-13,94** $^{kJ}/_{mol}$;

$\mathbf{K}_{abbpp}$**=exp(-**$\Delta \mathbf{G}_{Lehninger}$**/R/T)**=exp(-11300/8,3144/298,15)=0,01047878;



A+B 50% C+D

reactants $HP_2O_7^{3-}$+ADP^{3-}

products $\mathbf{HPO_4^{2-}}$ +**ATP**$^{4--}$

$\Delta \mathbf{G}_{abbppL}$**=-R•T•ln(K**$_{abbppL}$)=-8,3144*298,15***ln**(0,01047878)=11,3 $^{kJ}/_{mol}$. Endothermic and endoergic $\mathbf{H_2P_2O_7^{2-}}$ hydrolysis transfer to ADP^{3-} Hess free energy change positive at pH=7,36 $\Delta \mathbf{G}_{Hess}$=**13,967** $^{kJ}/_{mol}$, but minimizes $\Delta \mathbf{G}_{min}$=11,3 $^{kJ}/_{mol}$ reaching

equilibrium mixture : 0,01047878=$\mathbf{K}_{abbpp}$= $\frac{[H_2PO_4^-]\cdot[ATP^{4-}]}{[H_2P_2O_7^{2-}]\cdot[ADP^{3-}]}$. Le Chatelier principle is

Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium.
Free energy change minimum reaching establishes equilibrium.

Substance $\Delta H°_{Hess}$,$^{kJ}/_{mol}$ $\Delta S°_{Hess}$,$^{J}/_{mol/K}$ $\Delta G°_{Hess}$, $^{kJ}/_{mol}$;

$\mathbf{H_3O^+}$	-285,81	-3,854	-213,275
$\mathbf{H_2O}$	-285,85	69,9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{H_2PO_4^-}$	-1296,3	90,4	-1130,2
$\mathbf{H_2PO_4^-}$	-1302,6	92.5	-1137,3
$\mathbf{HPO_4^{2-}}$	-1292,14	-33,47	-1089,28
$\mathbf{HPO_4^{2-}}$	**-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	$\Delta G°_{Hess}$	-701,4
creatine$^-$	**-537,48**	**189,5**	**126,1868**
creatine$^-$	-	CRC 2010	107,69

$\Delta \mathbf{G}_{CARLSON1963}$**=-41**±2 $^{kJ}/_{mol}$;$\mathbf{K}_{CARLSON1963}$=15238538,96;

Pcreatine^{2-}+H_2O=creatine+$\mathbf{HPO_4^{2-}}$; $\Delta \mathbf{G}_{Lehninger}$=-43 $^{kJ}/_{mol}$;

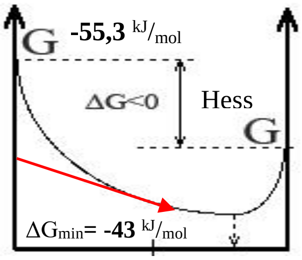
$\Delta G_{\mathbf{Hess}}=\Delta G°_{\mathbf{cHeatine}}+\Delta G°_{\mathbf{HPO42}}-\Delta G°_{\mathbf{PcHeatine}}-\Delta G°_{\mathbf{H2O}}$ = -55,32 $^{kJ}/_{mol}$;

$\Delta G_{\mathbf{Hess}}$ =107,69-1089,28-(-689,08-237,191)= -55,3 $^{kJ}/_{mol}$;

$\mathbf{K}_{Ellington}$=36400000; t=35° C; 308 K

$\Delta G_{Lehninger}$=43+**126,1868-1057,143+151,549**=$\Delta G°_{\mathbf{Pcreatine}}$= **-736,4** $^{kJ}/_{mol}$

Exothermic and exoergic Pcreatin^{2-} hydrolise
Hess free energy change negative at pH=7,36
$\Delta \mathbf{G}_{\mathbf{hydrolise}}$ =-55,3 $^{kJ}/_{mol}$, but minimizes
$\Delta \mathbf{G}_{\mathbf{min}}=\Delta G_{Lehninge}$= -43 $^{kJ}/_{mol}$ reaching
equilibrium mixture



A+B 50% C+D

$\mathbf{K}_{Lehninge}$=34145290,295= $\frac{[creatine]\cdot[HPO_4^{2-}]}{[Pcreatine^{2-}]\cdot[H_2O]}$

$_{CARLSON}\Delta G_{Pcreatine}$=41+107,69-1089,28+237,191=$\Delta G°_{\mathbf{Pcreatine}}$=-703,4 $^{kJ}/_{mol}$

$_{Lehninger}\Delta G_{Pcreatine}$=43+107,69-1089,28+237,191=$\Delta G°_{\mathbf{Pcreatine}}$= -701,4 $^{kJ}/_{mol}$;

$$\frac{[creatine]\cdot[HPO_4^{2-}]}{[Pcreatine^{2-}]\cdot[H_2O]}$$

$\mathbf{K}_{CARLSON}$**=exp(-**$\Delta \mathbf{G}_{Carlson}$**/R/T)**=exp(41000/8,3144/298,15)=15238538,963622

=$\mathbf{K}_{Lehninge}$**=exp(-**$\Delta \mathbf{G}_{Lehninger}$**/R/T)**=exp(43000/8,3144/298,15)=34145290,2951607;

$\Delta \mathbf{G}_{Ellington}$**=-R•T•ln(K**$_{Ellington}$)=-8,3144*308***ln**(3,46*10^7)/1000=**-44,45** $^{kJ}/_{mol}$;

$$\frac{[creatine]\cdot[ATP^{3-}]}{[Pcreatine^-]\cdot[ADP^{2-}]}$$

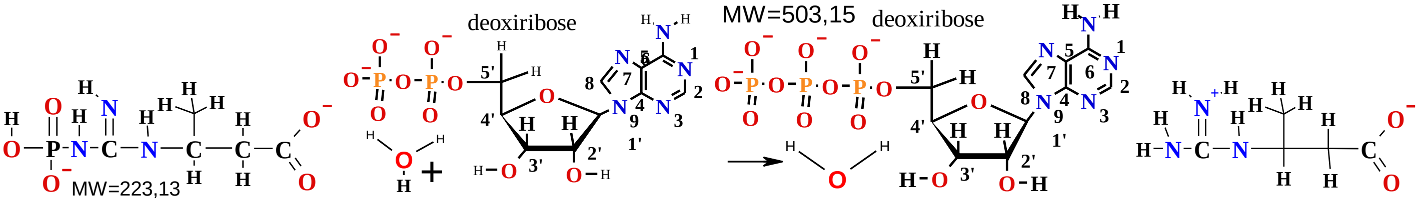
=$\mathbf{K}_{CRC}$=1/(5,78*10^(-3))=173 (310,15 K);pMg=2,47;pH=<7,199;

Pcreatine^{2-}+$\mathbf{ADP^{3-}+H_3O^+}$=>creatine+$\mathbf{ATP^{4-}+H_2O}$; pH=7,36;

$$\frac{[creatine]\cdot[ATP^{4-}]\cdot[H_2O]}{[Pcreatine^{2-}]\cdot[ADP^{3-}][H_3O^+]}$$

$\Delta \mathbf{G}_{abbLehninger}$**=-R•T•ln(K**$_a$**K**$_{bb}$)=-8,3144*298,15***ln**(154,854)/1000= -12,5 $^{kJ}/_{mol}$;

=$\mathbf{K}_{abbLehninger}$=$\mathbf{K}_a\mathbf{K}_{bb}$=34145290,295*0,000004535142=154,854;



$\mathbf{PCr^{2-}+ADP^{3-}+H_3O^+}$=>$\mathbf{Cr+ATP^{4-}+H_2O}$;pH=7,36; Pcreatine$^-$+$\mathbf{ADP^{2-}}$=>creatine+$\mathbf{ATP^{3-}}$; pH<7,199 .

$$\frac{[\text{creatine}^-]\cdot[\text{ATP}^{4-}]\cdot[\text{H}_2\text{O}]}{[\text{Pcreatine}^{2-}]\cdot[\text{ADP}^{3-}]\,[\text{H}_3\text{O}^+]}$$

$\Delta G_{abb}=\Delta G_a+\Delta G_{bb}=-43+30{,}5=$ -12,5 kJ/mol;

=$K_{abbLehninger}=K_aK_{bb}$=34145290,295*0,000004535142=154,854; at pH=7,36.

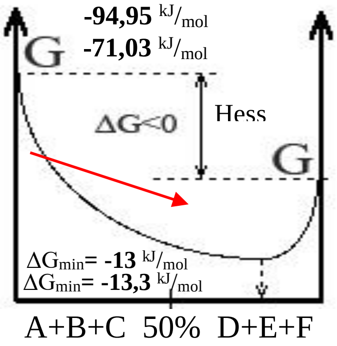
$\Delta G_{abbLehninger}=-R\bullet T\bullet\ln(K_aK_{bb})$=-8,3144*298,15*ln(154,854)/1000= -12,5 kJ/mol;

$\Delta G_{abbHess}=\Delta G°_{cHeatine}+\Delta G°_{ATP4-}+\Delta G°_{H2O}-\Delta G°_{PcHeatine2}-\Delta G°_{ADP3}-\Delta G°_{H3O}$ = -94,946 kJ/mol; exoergic CRC2010 =107,69-2292,5-237,191-(-689,08-1424,7-213,275)= -94,946 kJ/mol CRC 2010

$\Delta G_{CRCHess}=\Delta G°_{cHeatine}+\Delta G°_{ATP3-}-\Delta G°_{PcHeatine1}-\Delta G°_{ADP2}$= -71,03 kJ/mol; CRC2010;

$\Delta G_{CRC}=-R\bullet T\bullet\ln(K_{CRC})$=-8,3144*310,15*ln(173)/1000= -13,3 kJ/mol; CRC2010;

Exothermic, exoergic Pcreatin^{2-} and $\mathbf{ATP^{4-}}$ kinase Hess free energy change negative at pH=7,36 and pH<7,199 ΔG_{abb}=-94,946 kJ/mol and ΔG_{CRC}=-71,03 kJ/mol, but minimizes to $\Delta G_{min}=\Delta G_{abbLehninger}$= -12,5 kJ/mol and ΔG_{CRC}= -13,3 kJ/mol reaching equilibrium mixture $K_{abbLehninger}=K_aK_{bb}$=154,854, K_{CRC}=173 (310,15 K); Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.



reactants $\mathbf{PCr^{2-}+ADP^{3-}+H_3O^+}$

products (creatine) $Cr+ATP^{4-}+H_2O$

$\Delta G_{abbLehninger}=-R\bullet T\bullet\ln(K_{abb})$=-8,3144*310,15*ln(154,854)/1000=-13 kJ/mol;

Ellington constant in 1989 at temperature t=35° C; 308 K is $K_{Ellington}=3{,}46*10^7$;

$K_{Ellington}=\exp(-\Delta G_{Ellington}/R/T)$=exp(44454,47/8,3144/308)=3,46*10^7 ; J.exp.Biol.143,177-194,1989;

Creatine Phospho Kinase K'_{cpk} =100 to 160 (Lawson&VeecH 1979), [Pcreatine^{3-}]/[$\mathbf{ATP^{4-}}$]= 3 to 4 and [Pcreatine^{3-}]/[creatine-]= 2,5, [$\mathbf{ATP^{4-}}$]/[$\mathbf{ADP^{3-}}$]=10^2 to 10^3 . Solubility 25,51 mg/mL; 3,52 g/L;

Homeostasis free energy change $\Delta G_{Homeostasis}=\Delta G_{eq}+R\bullet T\bullet\ln K_{Homeostasis}$ is smaller as at equilibrium minimum. Hess Free energy change for pure products minus pure reactants ΔG_{Hess}= -94,95 kJ/mol minimized reaching equilibrium mixture of compounds ΔG_{abb}= -13 kJ/mol:

Homeostasis change $\Delta G_{Homeostasis}<\Delta G_{abb}$= -13 kJ/mol for first and second conditions:

1. $\Delta G_{Homeostasis}$= -6,832 kJ/mol at [creatine]=28 nM, [Pcreatine^{2-}]=28 mM,[$\mathbf{ATP^{4-}}$]=8,05 mM,[$\mathbf{ADP^{3-}}$]=0,93 mM un [$\mathbf{H_2O}$]=55,1398 M, [$\mathbf{H_3O^+}$]=10$^{-7,36}$ M;

If [creatine]/[Pcreatine^{2-}]=28*10^(-9)/28/10^(-3)=10^{-6}; than $\Delta G_{Homeostasis}$= -6,832 kJ/mol, ja [creatine]=28*10^(-9) M 26th page:

$$K_{Homeostasis}=\frac{[\text{creatine}^-]\cdot[\text{ATP}^{4-}]\cdot[\text{H}_2\text{O}]}{[\text{Pcreatine}^{2-}]\cdot[\text{ADP}^{3-}]\,[\text{H}_3\text{O}^+]}=\frac{28\bullet10^{-9}\bullet8.05\bullet10^{-5}\bullet55.1398}{28\bullet10^{-3}\bullet9{,}3\bullet10^{-3}\bullet10^{-7.36}}$$ =10,9339760517278; ln(10,934)=2,3919 .

$\Delta G_{Homeostasis}=\Delta G_{eq}+R\bullet T\bullet\ln K_{Homeostasis}$ is

=(-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 kJ/mol,

= -13000+=8,3144*310,15*2,3919=(-13000+6168)/1000= -6,832 kJ/mol,

2. $\Delta G_{Homeostasis}$=-0,3942 kJ/mol at [creatine]=280 nM, [Pcreatine^{2-}]=28 mM,[$\mathbf{ATP^{4-}}$]=8,05 mM, [$\mathbf{ADP^{3-}}$]=0,93 mM un [$\mathbf{H_2O}$]=55,1398 M, [$\mathbf{H_3O^+}$]=10$^{-7,36}$ M;

If [creatine]/[Pcreatine^{2-}]=28*10^(-8)/ 28/10^(-3)=0,001; tad $\Delta G_{Homeostasis}$= -22,67 kJ/mol, if [creatine]=28*10^(-6) M

$$K_{Homeostasis}=\frac{[\text{creatine}^-]\cdot[\text{ATP}^{4-}]\cdot[\text{H}_2\text{O}]}{[\text{Pcreatine}^{2-}]\cdot[\text{ADP}^{3-}]\,[\text{H}_3\text{O}^+]}=\frac{28\bullet10^{-8}\bullet8.05\bullet10^{-5}\bullet55.1398}{28\bullet10^{-3}\bullet9{,}3\bullet10^{-3}\bullet10^{-7.36}}$$ =109,339760517278; ln(109,34)= 4,6945 .

$\Delta G_{Homeostasis}=\Delta G_{eq}+R\bullet T\bullet\ln K_{Homeostasis}$ is

=(-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 kJ/mol,

= -13000+=8,3144*310,15*4,6945=(-13000+12105,76)/1000=-0,8943 kJ/mol,

bb) $\mathbf{ADP^{2-}+H_2PO_4^-}$=>$\mathbf{ATP^{3-}+H_2O}$; $\mathbf{ADP^{3-}+HPO_4^{2--}+H_3O^+}$=>$\mathbf{ATP^{4-}+2H_2O}$; $\Delta G_{bLehninger}$=30,5 kJ/mol;

$$\frac{[\text{H}_2\text{O}]\cdot[\text{ATP}^{4-}]}{[\text{H}_2\text{PO}_4^-]\cdot[\text{ADP}^{3-}]}$$ =K_{bbL}= $K_{bbLehninger}$[H_2O]=0,000004535142*55,3457339 =0,000251001 .

$\Delta G_{bHL}=-R\bullet T\bullet\ln(K_{bL})$=-8,3144•298,15•ln(0,000251001)=20,5512 kJ/mol;

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

$\Delta G_{bLehninger}$=30,5 kJ/mol;

THERMODYNAMICS V i **Glc 6-P^{2-}** hydrolysis to Glc + **HPO_4^{2-}** and **Glc 6-P^{2-}** to **Glc 1-P^{2-}** isomerisation

Calculate ΔH_H ΔS_H ΔG_H at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? Will be **exoergic** or **endoergic**! $\Delta G_{Lehninger}$= -13,8 $^{kJ}/_{mol}$; **$Glc6P^{2-}+H_2O$=>$Glc+HPO_4^{2-}$**;pH=7,36;ΔG_H= -38,55 $^{kJ}/_{mol}$;

$\Delta G_{Lehninger}$=13,8 $^{kJ}/_{mol}$; **$Glc+HPO_4^{2-}$ => $Glc6P^{2-}+H_2O$**; pH=7,36; ΔG_H=38,55 $^{kJ}/_{mol}$;

Substan	$\Delta H°_H$ $^{kJ}/_{mol}$	$\Delta S°_H$ $^{J}/_{mol/K}$	$\Delta G°_H$ $^{kJ}/_{mol}$
H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**
Glc	CRC10	**I**=0,25 M	-419,74
Glc	-1263,78	269,45	-919,96
Glc	**-1267,13**	**-2901,49**	**-402,05**
$H_2PO_4^-$	-1302,6	92,5	-1137,3
HPO_4^{2-}	-1292,14	-33,47	-1089,28
HPO_4^{2-}	**-1298,89**	**-810,792**	**-1057,143**
$Glc6P^{2-}$	-2260	-3291,56	-1318,92
$Glc6P^{2-}$	**-2279,314**	**-3297,196**	**-1296,262**
$Glc1P^{2-}$	-2260	-3291,56	-1311,89
$Glc1P^{2-}$	-	-	**-1289,221**
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**

$\Delta G_{Hess}=\Delta G°_{Glc}+\Delta G°_{HPO42-}-\Delta G°_{H2O}-\Delta G°_{Glc6P}$= -38,55 $^{kJ}/_{mol}$ **exoergic**

=-419,74-1089,28-(**-151,549**-1318,92)= -38,55 $^{kJ}/_{mol}$

K$_{a2Lehninger}$=EXP(13800/8,3144/298,15)=EXP(5,566899)=261,62;

K$_{a2Lehninger}$=[**Glc**]*[**HPO_4^{2-}**]/[**$Glc6P^{2-}$**]/[**H_2O**]= 261,62;

$\Delta G_{a22Lehninger}$=+13,8 $^{kJ}/_{mol}$; **$Glc+HPO_4^{2-}$=>$Glc6P^{2-}+H_2O$**; pH=7,36;

$\Delta G_{Hess}=\Delta G°_{H2O}+\Delta G°_{Glc6P}-\Delta G°_{Glc}-\Delta G°_{HPO42}$=+38,55 $^{kJ}/_{mol}$ **endoergic**

=**-151,549**-1318,92-(-419,74-1089,28)=+38,55 $^{kJ}/_{mol}$

K$_{bLehninger310}$**=exp(-$\Delta G_{bLehninger}$/R/T)**=exp(30500/8,3144/310,15)=136983,25

K$_{a22Lehninger310}$=EXP(-13800/8,3144/310,15)=0,004741

K$_{a22Lehninger}$ =EXP(-13800/8,3144/298,15)=0,003822314

K$_{a22Lehninger}$=[**$Glc6P^{2-}$**]*[**H_2O**]/[**Glc**]/[**HPO_4^{2-}**]=0,003822314;

$\Delta G_{a22Lehninger}$=+13,8 $^{kJ}/_{mol}$; **$\Delta G_{bLehninger}$**=-30,5 $^{kJ}/_{mol}$;

$Glc+ATP^{4-}+H_2O$ =>$Glc6P^{2-}+ADP^{3-}+H_3O^+$; **$\Delta G_{a22b}$**=-16,7 $^{kJ}/_{mol}$

$\Delta G_{a22b}=\Delta G_{a22}+\Delta G_{bLehninger}$=13,8 +-30,5=-16,7 $^{kJ}/_{mol}$;

$\Delta G_H=\Delta G°_{ADP3}+\Delta G°_{Glc6P}+\Delta G°_{H3O}-\Delta G°_{Glc}-\Delta G°_{ATP4}-\Delta G°_{H2O}$=**-25,2** $^{kJ}/_{mol}$

=**-1399,9**-1318,92-213,275-(**-402,05-2267,64**-237,191)= **-25,2** $^{kJ}/_{mol}$

K$_{a22b}$=EXP(16700/8,3144/298,15)=842,82;

K$_{a22b}$=**K$_{a22}$K$_b$**=0,003822314*220500,2=842,82=

$$\frac{[Glc6P^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[Glc]\cdot[H_2O]\cdot[ATP^{4-}]}$$

ΔG_{a22b}=-8,3144*298,15***ln**(842,82)/1000=-16,7 $^{kJ}/_{mol}$

310,15 K; **K**$_{a22b310}$=**K$_{a22}$K$_{bLehninger}$**=0,004741*136983,25=649,438; **K**$_{a22Lehninger310}$=0,004741;

ΔG_{eq}=-8,3144*310,15***ln**(649,438)=-16,7 $^{kJ}/_{mol}$;

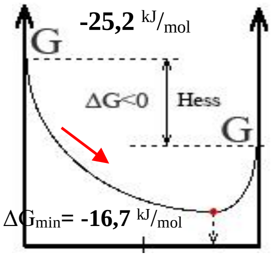
310,15 K; **K**$_{a22b310}$=**K$_{a22}$K$_{bLehninger}$**=0,004741*136983,25=649,438=

$$\frac{[Glc6P^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[Glc]\cdot[H_2O]\cdot[ATP^{4-}]}$$

Endothermic, endoergic **Glc** phosphorylation **$Glc6P^{2-}$** Hess free energy change is positive **$\Delta G_{phosphorylation}$**=38,55 but with **$ATP^{4-}$** negative**-25,2** $^{kJ}/_{mol}$, but minimizes reaching equilibrium mixture **$\Delta G_{min}=\Delta G_{eq}$=1**3,8 bet ar **$ATP^{4-}$ -16,7** $^{kJ}/_{mol}$

$$\frac{[Glc6P^{2-}]\cdot[H_2O]}{[Glc]\cdot[HPO_4^{2-}]}=\mathbf{K_a}=0{,}0382 \text{ un } \mathbf{K}_{a22b}=842{,}82=\frac{[Glc6P^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[Glc]\cdot[H_2O]\cdot[ATP^{4-}]}$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.



$Glc+ATP^{4-}+H_2O$=>$Glc1P^{2-}+ADP^{3-}+H_3O^+$; **$\Delta G_{Lehnin}$**=-9,6 $^{kJ}/_{mol}$;

$\Delta G_H=\Delta G°_{Glc1P}+\Delta G°_{ADP3}+\Delta G°_{H3O}-\Delta G°_{Glc}-\Delta G°_{ATP4}-\Delta G°_{H2O}$=**-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**$_{Lehninger}$=EXP(9600/8,3144/298,15)=48,07;

Glc+ HPO_4^{2-} =>$Glc1P^{2-}+H_2O$; $^-$;$\Delta G_{Lehninger}$=20,9 $^{kJ}/_{mol}$; $\Delta G_{Hess}=\Delta G°_{Glc1P}+\Delta G°_{H2O}-\Delta G°_{Glc}-\Delta G°_{HPO42}$= **68,25** $^{kJ}/_{mol}$;

=**-1289,221-151,549**-(-419,74-1089,28)=**68,25** $^{kJ}/_{mol}$; I=0,25 M;

$Glc1P^{2-}$=>$Glc6P^{2-}$;**$\Delta G_{Lehninger}$**=-7,02 $^{kJ}/_{mol}$; **K$_{eq}$=[$Glc6P^{2-}$]/[$Glc1P^{2-}$=**17;**ΔG_{eq}**=-8.3144***298.15*ln**(17)=-7,02 $^{kJ}/_{mol}$;

$\Delta G_{Hess}=\Delta G°_{Glc6P}+\Delta G°_{Glc1P}$=**-1296,262-(-1289,221)=-7,04** $^{kJ}/_{mol}$; ;=-1318,92-**(**-1311,89**)**=-7,03 $^{kJ}/_{mol}$;

ΔG_b=-R•T•ln(K_b)=-8,3144*298,15*ln(1,9667*10^(-6))/1000=31,4095 kJ/mol ;

Glc 1-P^{2-}=>Glc6-P^{2-};$\Delta G_{totalHess}=\Delta G°_{G1P}+\Delta G°_{G6P}$=**-20,9+13,8= -7,1** $^{kJ}/_{mol}$ **exoergic**..............$^{kJ}/_{mol}$

THERMODYNAMICS V i **Glc 1-P^{2-}** hydrolysis to Glc + **HPO_4^{2-}** and **Glc 1-P^{2-}** dephosphorilation
Calculate ΔH_H ΔS_H ΔG_H at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? Will be **exoergic** or **endoergic**!

a22 $\Delta G_{Lehninger}=+20{,}9\ ^{kJ}/_{mol}$; $\mathbf{Glc+HPO_4^{2-}+\Delta G+Q \Rightarrow Glc1P^{2-}+H_2O}$; pH=7,36; $\Delta G_{Hess}=\mathbf{36{,}1}\ ^{kJ}/_{mol}$;

a2 $\Delta G_{Lehninger}=-20{,}9\ ^{kJ}/_{mol}$; $\mathbf{Glc1P^{2-}+H_2O \Rightarrow Glc+HPO_4^{2-}+\Delta G+Q}$; pH=7,36; $\Delta G_{Hess}=\mathbf{-36{,}1}\ ^{kJ}/_{mol}$;

Substance	$\Delta H^\circ_H\ ^{kJ}/_{mol}$	$\Delta S^\circ_H\ ^{J}/_{mol/K}$	$\Delta G^\circ_H\ ^{kJ}/_{mol}$
H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**
Glc	CRC10	**I=**0,25 M	-419,74
Glc	-1263,78	269,45	-919,96
Glc	**-1267,13**	**-2901,49**	**-402,05**
$H_2PO_4^-$	-1302,6	92,5	-1137,3
HPO_4^{2-}	-1292,14	-33,47	-1089,28
HPO_4^{2-}	**-1298,89**	**-810,792**	**-1057,143**
$Glc6P^{2-}$	-2260	-3291,56	-1318,92
$Glc6P^{2-}$	**-2279,314**	**-3297,196**	**-1296,262**
$Glc1P^{2-}$	-2260	-3291,56	-1311,89
$Glc1P^{2-}$	-	-	**-1289,221**
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**

$\Delta G_{Hess}=\Delta G^\circ_{\mathbf{H2O}}+\Delta G^\circ_{\mathbf{Glc1P}}-\Delta G^\circ_{\mathbf{Glc}}-\Delta G^\circ_{\mathbf{HPO42}}=\mathbf{36{,}113}\ ^{kJ}/_{mol}$ **endoergic**

$=\mathbf{-151{,}549-1289{,}221}-(-419{,}74\mathbf{-1057{,}143})=\mathbf{36{,}113}\ ^{kJ}/_{mol}$

$\mathbf{K}_{a22Lehninger}=EXP(-20900/8{,}3144/298{,}15)=0{,}000217997$;

$\Delta G_H=\Delta G^\circ_{\mathbf{Glc}}+\Delta G^\circ_{\mathbf{HPO42}}-\Delta G^\circ_{\mathbf{H2O}}-\Delta G^\circ_{\mathbf{Glc1P}}=\mathbf{-36{,}113}\ ^{kJ}/_{mol}$ **exoergic**

$=-419{,}74\mathbf{-1057{,}143-(-151{,}549-1289{,}221)=-36{,}113}\ ^{kJ}/_{mol}$

$\mathbf{K}\ _{\mathbf{a2}Lehninger,}=EXP(20900/8{,}3144/298{,}15)=4587{,}215687$;

$\mathbf{Glc+ATP^{4-}+H_2O \Rightarrow Glc1P^{2-}+ADP^{3-}+H_3O^+}$; pH=7,36; I=0,2 M.

$\mathbf{K}_{a22b}=\mathbf{K_{a22}K_b}=0{,}000217997*220500{,}2=48{,}07$;

$\Delta\mathbf{G_{a22b}=-R\bullet T\bullet ln(K_{a22b})}=-8{,}3144*298{,}15*\mathbf{ln}(48{,}0684)=-9{,}6\ ^{kJ}/_{mol}$;

$\mathbf{Glc1P^{2-}+ADP^{3-}+H_3O^+ \Rightarrow Glc+ATP^{4-}+H_2O}$; pH=7,36; I=0,2 M.

$\mathbf{K}_{a2b}=\mathbf{K_{a2}K_b}=4587{,}215687*4{,}54*10^{\wedge(-6)}=0{,}02083$

$\Delta\mathbf{G_{a2b}=-R\bullet T\bullet ln(K_{a2b})}=-8{,}3144*298{,}15*\mathbf{ln}(0{,}02083)=9{,}6\ ^{kJ}/_{mol}$

$$\mathbf{K}_{a2b}=\mathbf{K_{a2}K_b}=0{,}02083=\frac{[Glc]\cdot[H_2O]\cdot[ATP^{4-}]}{[Glc1P^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$$

Lehningera līdzsvars ; $\mathbf{ATP^{3-}+H_2O \Leftrightarrow ADP^{2-}+H_2PO_4^-}$; $\mathbf{K}_{Lehninger}=0{,}0001739$; without pH=7,36;

$\Delta\mathbf{G}_{Lehninger}\mathbf{=-R\bullet T\bullet ln(K}_{Lehninger}\mathbf{)}=-8{,}3144*298{,}15*\mathbf{ln}(0{,}0001739)=\mathbf{21{,}46}\ ^{kJ}/_{mol}$;

$$\mathbf{K}_{Lehninger}=\mathbf{K_b}_{Lehninger}*[\mathbf{H_3O^+}]/[\mathbf{H_2O}]=220500{,}2*10^{\wedge(-7{,}36)}/55{,}3457=0{,}0001739=\frac{[H_2PO_4^-]\cdot[ADP^{3-}]}{[H_2O]\cdot[ATP^{4-}]}$$

$\Delta G_H=\Delta G^\circ_{\mathbf{ADP3}}+\Delta G^\circ_{\mathbf{H2PO4}}-\Delta G^\circ_{\mathbf{ATP4}}-\Delta G^\circ_{\mathbf{H2O}}=\mathbf{-1399{,}9-1057{,}143-(-2267{,}64}-237{,}191)=47{,}79\ ^{kJ}/_{mol}$;

b) $\mathbf{ATP^{4-}+2H_2O \Rightarrow ADP^{3-}+HPO_4^{2-}+H_3O^+}$; $\Delta\mathbf{G_b}_{Lehninger}=-30{,}5\ ^{kJ}/_{mol}$;

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

$\Delta G_H=\Delta G^\circ_{\mathbf{ADP3}}+\Delta G^\circ_{\mathbf{HPO42}}+\Delta G^\circ_{\mathbf{H3O}}-\Delta G^\circ_{\mathbf{ATP4}}-2\Delta G^\circ_{\mathbf{H2O}}=$

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

abb $\mathbf{Glc1P^{2-}+ADP^{3-}+H_3O^+ \Rightarrow Glc+ATP^{4-}+H_2O}$; $\Delta\mathbf{G_{a2b}=\Delta G_{a2}+\Delta G_b=-20{,}9}+30{,}5=\mathbf{9{,}6}\ ^{kJ}/_{mol}$;

sum $\mathbf{Glc+ATP^{4-}+H_2O \Rightarrow Glc1P^{2-}+ADP^{3-}+H_3O^+}+\Delta G\mathbf{+Q}$; $\Delta\mathbf{G_{a22b}=\Delta G_{a22}+\Delta G_b=}20{,}9+-30{,}5=-9{,}6\ ^{kJ}/_{mol}$;

$\Delta G_{Hess}=\Delta G^\circ_{\mathbf{ADP3}}+\Delta G^\circ_{\mathbf{Glc1P}}+\Delta G^\circ_{\mathbf{H3O}}-\Delta G^\circ_{\mathbf{Glc}}-\Delta G^\circ_{\mathbf{ATP4}}-\Delta G^\circ_{\mathbf{H2O}}=\mathbf{-38{,}607}\ ^{kJ}/_{mol}$;

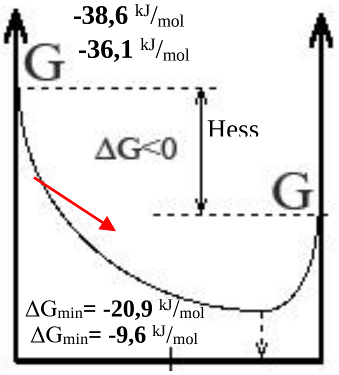
$=\mathbf{-1399{,}9-1289{,}221}-213{,}275-(-419{,}74-2292{,}5\mathbf{-151{,}549})=\mathbf{-\ 38{,}607}\ ^{kJ}/_{mol}$;

$\Delta\mathbf{G_{a22b}=-\ R\bullet T\bullet ln(K_{a22b})}=-8{,}3144*298{,}15*\mathbf{ln}(3{,}79204*10^{-8})=42{,}36\ ^{kJ}/_{mol}$.

Exothermic, exoergic **$Glc1P^{2-}$** dephosphorylation – phosphorilation Hess free energy change is negative $\Delta\mathbf{G}_{\mathbf{dephosphorylation}}=\mathbf{-36{,}113}$ and $\mathbf{-38{,}607}\ ^{kJ}/_{mol}$, but minimizes reching equilibrium $\Delta\mathbf{G_{min}=\Delta G_{a2}}_{Lehninger}=-20{,}9\ ^{kJ}/_{mol}$ and $\Delta\mathbf{G_{a22b}}=-9{,}6\ ^{kJ}/_{mol}$ mixture

$$\mathbf{K_{a2}}_{Lehninger,}=4587=\frac{[Glc]\cdot[HPO_4^{2-}]}{[Glc1P^{2-}]\cdot[H_2O]}\ \text{and}\ \mathbf{K}_{a22b}=\frac{[Glc1P^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[Glc]\cdot[H_2O]\cdot[ATP^{4-}]}=48{,}07$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta\mathbf{G}_{min}$ reaching. Free energy minimum reaching establishes equilibrium.



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

reactants **$Glc1P^{2-}$**+ H_2O

products **Glc**+ **HPO_4^{2-}**

$ADP^{2-} + H_2PO_4^- \Rightarrow ATP^{3-} + H_2O$; $\Delta G_{Lehninger} = 20{,}55\ ^{kJ}/_{mol}$; bez pH=?;

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

bb) $\mathbf{ADP^{3-}+HPO_4^{2--}+H_3O^+ \Rightarrow ATP^{4-}+2H_2O}$; $\Delta G_{bLehninger}=30{,}5\ ^{kJ}/_{mol}$; $K_{bbLehn}=$; pH=7,36;

$$\frac{[H_2O]\cdot[ATP^{3-}]}{[H_2PO_4^-]_{aqua}\cdot[ADP^{2-}]} = K_{bHL} = K_{bbLehninger}[H_2O] = 0{,}000004535142*55{,}3457339 = 0{,}000250993\ .$$

$\Delta G_{bL} = -R\bullet T\bullet \ln(K_{bL}) = -8{,}3144*298{,}15*\ln(0{,}000250993)/1000 = 20{,}5512\ ^{kJ}/_{mol}$;

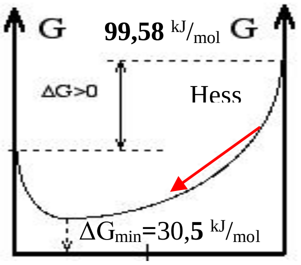
$$\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$$

$K_{bbLehningeH310} = \exp(-\Delta G_{Lehninger}/R/T) = \exp(-30500/8{,}3144/310{,}15) = 0{,}000004535142$

$= K_{bbLehningeH} = \exp(-\Delta G_{Lehninger}/R/T) = \exp(-30500/8{,}3144/298{,}15) = 0{,}000004535142$

$K_{bbLehnH} = 1/220500{,}2 = 0{,}000004535142$;

$\Delta G_{Hess} = \Delta G°_{ATP3} - 2\Delta G°_{H2O} - \Delta G°_{ADP2} - \Delta G°_{HPO42} - \Delta G°_{H3O} = \mathbf{-1399{,}9-1057{,}143}-213{,}275-(\mathbf{-2267{,}64+2*-151{,}549}) = \mathbf{99{,}58}\ ^{kJ}/_{mol}$;



A+B+C 50% 2D+E

Endothermic and endoergic **ADP**³⁻ phosphorilation Hess free energy change positive at pH 7,36 $\Delta G_{hydrolise} = \mathbf{99{,}58}\ ^{kJ}/_{mol}$, but minimizes $\Delta G_{min} = \Delta G_{bbLehningeH} = 30{,}5\ ^{kJ}/_{mol}$ reaching equilibrium mixture: $0{,}000004535142 = K_{bbLehningeH} = \dfrac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$. Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching mixture of equilibrium. Free energy change minimum reaching establishes equilibrium.

aa $\Delta G_{Lehninger}=13{,}8\ ^{kJ}/_{mol}$; $\mathbf{Glc+HPO_4^{2-}+\Delta G+Q \Rightarrow Glc6P^{2-}+H_2O}$; pH=7,36; reactants $\mathbf{HPO_4^{2-}+H_3O^++ADP^{3-}}$

$K_{aaLehninger} = EXP(-13800/8{,}3144/298{,}15) = 0{,}003822314$; product s $\mathbf{2H_2O + ATP^{4-}}$

$K_{aaLehninger} = EXP(-13800/8{,}3144/310{,}15) = 0{,}0047409841$; **T=310.15 K**

$\Delta G_{aaHess} = \Delta G°_{Glc6P} + \Delta G°_{H2O} - \Delta G°_{Glc} - \Delta G°_{HPO42} = \mathbf{-1296{,}262}+((\mathbf{-151{,}549}-237{,}191)/2)-(-419{,}74-1089{,}28) = \mathbf{18.39}\ ^{kJ}/_{mol}$

$\Delta G_{aaHess} = \Delta G°_{Glc6P} + \Delta G°_{H2O} - \Delta G°_{Glc} - \Delta G°_{HPO42} = \mathbf{-1296{,}262-151{,}549}-(-419{,}74-1089{,}28) = \mathbf{61{,}209}\ ^{kJ}/_{mol}$

$\Delta G_{aaHess} = \Delta G°_{Glc6P} + \Delta G°_{H2O} - \Delta G°_{Glc} - \Delta G°_{HPO42} = -1318{,}92-237{,}191-(-419{,}74-1089{,}28) = -47{,}09\ ^{kJ}/_{mol}$

$\Delta G_{aaHess} = \Delta G°_{Glc6P} + \Delta G°_{H2O} - \Delta G°_{Glc} - \Delta G°_{HPO42} = \mathbf{-1296{,}262-151{,}549-(-402{,}05-1057{,}143)} = \mathbf{11{,}38}\ ^{kJ}/_{mol}$

aa2 $\Delta G_{Lehninger}=-13{,}8\ ^{kJ}/_{mol}$; $\mathbf{Glc6P^{2-}+H_2O \Rightarrow Glc+HPO_4^{2-}}$; pH=7,36; $\Delta G_{aa2Hess} = \mathbf{-18.39}\ ^{kJ}/_{mol}$;

$\Delta G_{aa2Hess} = \Delta G°_{Glc} - \Delta G°_{HPO42} - \Delta G°_{Glc6P} - \Delta G°_{H2O} = -419{,}74-1089{,}28-(\mathbf{-1296{,}262}+((\mathbf{-151{,}549}-237{,}191)/2)) = \mathbf{-18.39}\ ^{kJ}/_{mol}$;

$K_{aa2Lehninger} = EXP(13800/8{,}3144/298{,}15) = 261{,}62$; $K_{a2bLehninger} = EXP(13800/8{,}3144/310{,}15) = 210{,}9$; **310,15** K;

$\mathbf{Glc+ATP^{4-}+H_2O \Rightarrow Glc6P^{2-}+ADP^{3-}+H_3O^+}$; $\Delta G_{Lehninger}=-16{,}7\ ^{kJ}/_{mol}$; $K_{aLb} = EXP(16700/8{,}3144/298{,}15) = 842{,}82$

$K_{aLb} = EXP(16700/8{,}3144/310{,}15) = 649{,}44$; $\Delta G_{aLb} = -R\bullet T\bullet \ln(K_{aLb}) = -8{,}3144*298{,}15*\ln(842{,}82) = -16.7\ ^{kJ}/_{mol}$;

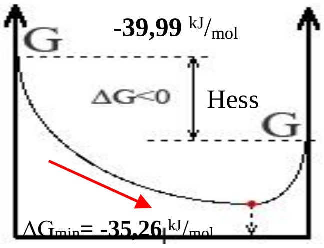
$\Delta G_{abHess} = \Delta G°_{Glc6P-} + \Delta G°_{ADP3} + \Delta G°_{H3O} - \Delta G°_{H2O} - \Delta G°_{ATP4} - \Delta G°_{Glc} = \mathbf{-25{,}2}\ ^{kJ}/_{mol}\ ^{kJ}/_{mol}$

$= \mathbf{-1399{,}9}-1318{,}92-213{,}275-(\mathbf{-402{,}05-2267{,}64}-237{,}191) = \mathbf{-25{,}2}\ ^{kJ}/_{mol}$;

$$K_{aLb} = EXP(16700/8{,}3144/298{,}15) = 842{,}82 = \frac{[Glc6P^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[Glc]\cdot[H_2O]\cdot[ATP^{4-}]}$$

$K_{a2b} = K_{aa2}K_b = 0{,}003822314*220500{,}2 = 842{,}82$; $\downarrow\Delta G_{Lehninger} = 16{,}7\ ^{kJ}/_{mol}$;

aaLbb $\mathbf{Glc6P^{2-}+ADP^{3-}+H_3O^+ \Rightarrow Glc+ATP^{4-}+H_2O}$; $K_{aLbb} = 261{,}62*0{,}000004535142 = 0{,}00118648385004$;



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

Endothermic and endoergic phosphorilation Hess free energy change positive $\Delta G_{phosphoHilation} = \mathbf{25.2}\ ^{kJ}/_{mol}$ negative, but minimized $\Delta G_{min} = \Delta G_{eq} = \mathbf{16.7}\ ^{kJ}/_{mol}$ reaching equilibrium mixture 298,15 K:

$$K_{aLbb\_298} = 261{,}62*0{,}000004535142 = 0{,}00118648385004 = \frac{[H_2O]\,[ATP^{4-}]\,[Glc]}{[Glc6P^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$$

$\Delta G_{Hess} = \Delta G°_{Glc} + \Delta G°_{ATP4} + \Delta G°_{H2O} - \Delta G°_{ADP3} - \Delta G°_{Glc6P} - \Delta G°_{H3O} = \mathbf{-25{,}2}\ ^{kJ}/_{mol}$

$= \mathbf{-402{,}05-2267{,}64}-237{,}191-(\mathbf{-1399{,}9}-1318{,}92-213{,}275) = \mathbf{25.2}\ ^{kJ}/_{mol}$;

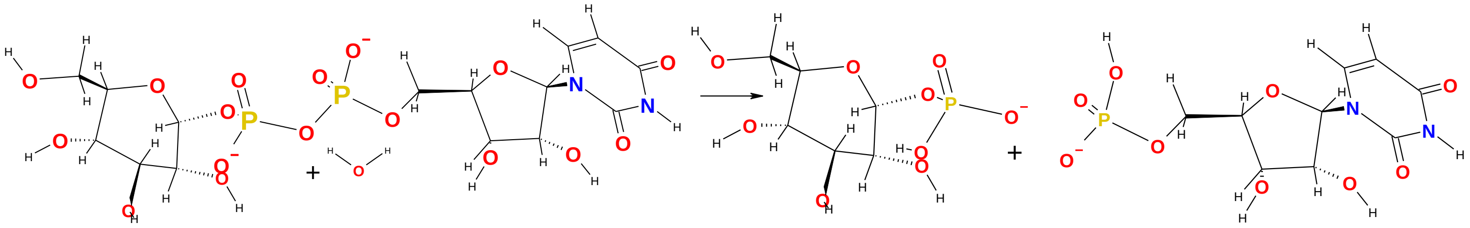
$\Delta G_{aaLbb} = -RT\ln(K_{aaLbb}) = -8{,}3144*298{,}15*\ln(0{,}00118648385004) = \mathbf{16.7}\ ^{kJ}/_{mol}$; reactants $\mathbf{Glc6P^{2-}+ADP^{3-}+H_3O^+}$

$K_{aLb\_310} = 210{,}9*0{,}0000073001623 = 0{,}00153960422907$; products $\mathbf{Glc+ATP^{4-}+H_2O}$;

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\mathbf{\Delta G}_{min}$ reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.

$\Delta G_{aaLbb310} = -RT\ln(K_{aaLbb310}) = -8{,}3144*310{,}15*\ln(0{,}00153960422907)/1000 = \mathbf{16.7}\ ^{kJ}/_{mol}$

$UDPGlc^{2-}+H_2O \Rightarrow UMP^{1-}+Glc1phosphate^{1-}$; $\Delta \mathbf{G}_{LehningeH}=-43\ ^{kJ}/_{mol}$; without pH=?



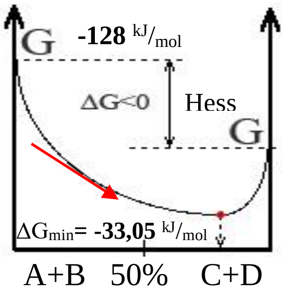
$\mathbf{K}_{Lehninger}=EXP(-\Delta G_L/R/T)=EXP(43000/8{,}3144/298{,}15)=EXP(17{,}346)=34145290=10^{-pKeq}=10^{7{,}75333}$,

$$\mathbf{K}_{Lehninger}=EXP(-\Delta G_L/R/T)=EXP(43000/8{,}3144/298{,}15)=EXP(17{,}346)=\frac{[Glc1P^{-}]\cdot[UMP^{-}]}{[UDP^{2-}Glc]\cdot[H_2O]}=34145290$$

$|\Delta \mathbf{G}_{\mathbf{a}Lehninger}=-43|\ ^{kJ}/_{mol}<|\Delta G_{Hess}=\Delta \mathbf{G}_{UMP1}+\Delta \mathbf{G}_{Glc1phosphate\mathbf{1}}-\Delta G°_{UDPGlc\mathbf{2}}-\Delta G°_{\mathbf{H2O}}=\mathbf{-128{,}642}\ ^{kJ}/_{mol}|$;

$\Delta G_H=\Delta \mathbf{G}_{LehningeH}-\Delta G°_{\mathbf{H2O}}$(BioThermodybamic 2006)$+\Delta G°_{\mathbf{H2O}}$(CRC 2010)$=-43+\mathbf{151{,}549}-237{,}191=\mathbf{-128}\ ^{kJ}/_{mol}$;

Exothermic and exoergic $UDPGlc^{2-}$ hydrolise Hess free energy change negative without pH=? $\Delta \mathbf{G}_{\mathbf{hydrolise}}=\mathbf{-128{,}642}\ ^{kJ}/_{mol}$, but minimizes reaching equilibrium mixture :$\Delta \mathbf{G}_{\mathbf{min}}=\Delta \mathbf{G}_{\mathbf{eq}}=\mathbf{-43}\ ^{kJ}/_{mol}$



$$\mathbf{K}_{Lehninger}=EXP(-\Delta G_{Lehni}/R/T)=EXP(43000/8{,}3144/298{,}15)=34145290=\frac{[Glc1P^{-}]\cdot[UMP^{-}]}{[UDP^{2-}Glc]\cdot[H_2O]}\ .$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\mathbf{\Delta G}_{min}$ reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium. Reactants $UDPGlc^{2-}+H_2O$

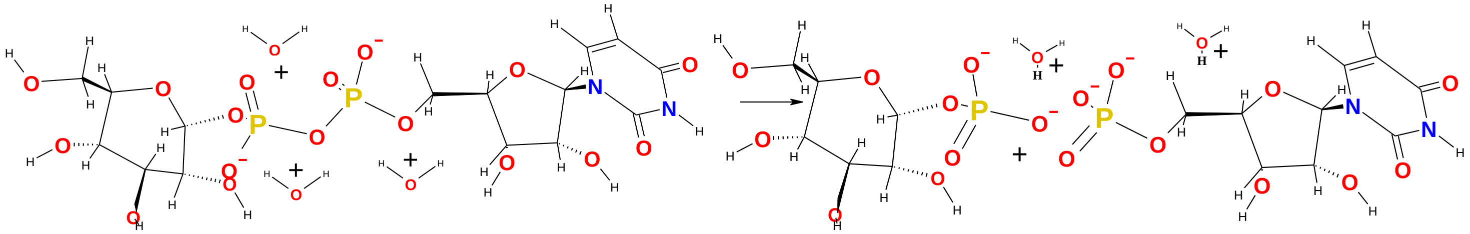
products $UMP^{1-}+Glc1phosphate^{1-}$;

$UDPGlc^{2-}+3H_2O \Rightarrow UMP^{2-}+Glc1phosphate^{2-}+2H_3O^{+}$;pH=7,36

$\Delta G_H=\Delta \mathbf{G}_{\mathbf{UMP2}}+\Delta \mathbf{G}_{Glc1phosphate\mathbf{2}}+2\Delta G°_{\mathbf{H3O}}-\Delta G°_{UDPGlc\mathbf{2}}-3\Delta G°_{\mathbf{H2O}}=\ )=\mathbf{-14{,}9}\ ^{kJ}/_{mol}$; pH=7,36

$\Delta G_H=\Delta \mathbf{G}_{LehningeH}+2\Delta G°_{\mathbf{H3O}}-3\Delta G°_{\mathbf{H2O}}=-43-2*213{,}275-(3*\mathbf{-151{,}549})=\mathbf{-14{,}9}\ ^{kJ}/_{mol}$; pH=7,36;

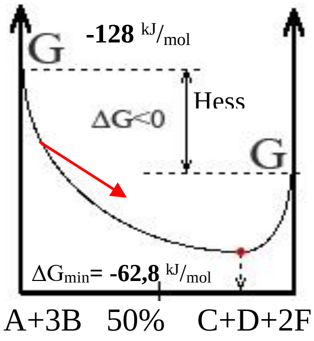
Alberty,Robert A.,Biochemical Thermodynamics: Applications of Mathematica, © 2006,Masachusetts Techn Inst.



$\mathbf{K}_a=\mathbf{K}_{Lehninger}\mathbf{*}[H_2O]^2=34145290*55{,}3457339\char`^2=104592153973{,}017=10\char`^{11.019}$;

$\Delta \mathbf{G}_{\mathbf{a}}=\mathbf{-R\bullet T\bullet ln(K_a)}=-8{,}3144*298{,}15*\mathbf{ln}(104592153973{,}017)/1000=\mathbf{-62{,}8}\ ^{kJ}/_{mol}$;

Exothermic and exoergic $UDPGlc^{2-}$ hydrolise reaction free energy change negative at pH 7,36 $\Delta \mathbf{G}_{\mathbf{hydrolise}}=\mathbf{-128}\ ^{kJ}/_{mol}$, but minimizes reaching equilibrium mixture : $\Delta \mathbf{G}_{\mathbf{min}}=\Delta \mathbf{G}_{\mathbf{eq}}=\mathbf{-62.8}\ ^{kJ}/_{mol}$



$$104592153973{,}017=\mathbf{K_a}=\frac{[Glc1P^{2-}]\cdot[UMP^{2-}]\cdot[H_3O^{+}]^2}{[UDP^{2-}Glc]\cdot[H_2O]^3}\ .$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\mathbf{\Delta G}_{min}$ reaching at equilibrium . Reactants $UDPGlc^{2-}+3H_2O$

Free energy change minimum reaching establishes equilibrium. products $UMP^{2-}+Glc1phosphate^{2-}+2H_3O^{+}$;

Exercise V j succinat**S**CoA^{4-} O_2 H_2O_2 fumarate peroxisome dehydrogenation reaction

Succinat**S**CoA^{4-} O_2 H_2O_2 fumarate dehydrogenation reaction! Will be **exoergic** or **endoergic**! CRC 2010 I=0.25 M; C_{osm}=0.305 M; **Biochemistry Thermodynamic** data, **2006** ; Reactants => products pH=7.36;

Masachusetts Techn.Institute; **Succinat**$\mathbf{SCoA^{4-}+O_{2aqua}+H_3O^+}$**=>fumarate**$^{2-}$+$\mathbf{HSCoA^{3-}}$+ $\mathbf{H_2O_{2aqua}+H_2O}+\Delta G$;

Substance	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$ kJ/mol
H_3O^+	-285.81	-3.854	-213.275
H_2O	-285.85	69.9565	-237.191
H_2O	**-286.65**	**-453.188**	**-151.549**
H_2O_{2aqua}	**-191.99**	**-481.688**	**-48.39**
H_2O_{2aqua}	-191,17	143,9	-134,03
O_{2aqua}	**-11.70**	**-94.2**	**16.4**
O_{2aqua}	-11.715	110.876	16.4
Succinat^{2-}	**-908.69**	**-1295.576**	**-522.414**
SuccinatSCoA^{4-}	-	-	**-339.2476**
HSCoA^{3-}	-	-	-7.26
HSCoA^{3-}	-	-	**-5.7716**
Fumarate^{2-}	**-776.56**	**-862.288**	**-519.4688**
UbiQuinRed	-	-	**-3849.6004**
UbiQuinOx	-		**-3853.8792**

1.$\Delta H_{Hess}=\Delta H°_{products}-\Delta H°_{reactants}$; 2. $\Delta S_{Hess}=\Delta S°_{products}-\Delta S°_{reactants}$

$\Delta G_{Hess}=\Delta H_{Hess}-T\bullet\Delta S_{Hess}=$

$\Delta G_H=\Delta G°_{fumarat}+\Delta G°_{HSCoA}+\Delta G°_{H2O2}+\Delta G°_{H2O}-$

$-\Delta G°_{O2}-\Delta G°_{SuccinatSCoA}-\Delta G°_{H3O+}$ = **-189.06** kJ/mol;

=**-519.4688-5.7716-48.39-151.549-(16.4-339.2476-**213.275)=

University Alberta = **-189.06** kJ/mol **exoergic**

$\mathbf{Succinat^{2-}+O_{2aqua}}$=>**fumarate**$^{2-}$+$\mathbf{H_2O_{2aqua}}+\Delta G$

$\Delta G_H=\Delta G°_{fumarat2-}+\Delta G°_{H2O2}-\Delta G°_{O2}-\Delta G°_{Succinat2-}$=**-61.845** kJ/mol;

=**-519.4688-48.39-(16.4-522.414)** = **-61.845** kJ/mol **exoergic**

$\Delta H_{Hess}=\Delta H°_{fumarat2-}+\Delta H°_{H2O2}-\Delta H°_{O2}-\Delta H°_{Succinat2-}$=**-48.16** kJ/mol;

=**-776.56-191.99-(-11.70-908.69)**= **-48.16** kJ/mol **exothermic**

$\Delta S_{Hess}=\Delta S°_{fumarat2-}+\Delta S°_{H2O2}-\Delta S°_{O2}-\Delta S°_{Succinat2-}$=**45.8** J/mol/K;

=**-862.288-481.688-(-94.2-1295.576)=45.8** J/mol/K **exothermic**

$\Delta G_{Hess}=\Delta H_H-T\bullet\Delta S_H$=**-48.16**-298.15*0.0458=**-61.82** kJ/mol

Spontaneous ΔG_{Hess}= **-61.82** kJ/mol. at pH=7.36 exoergic

Ox $\mathbf{O_{2aqua}+2H_3O^++2e^-=H_2O_{2aqua}+2H_2O}$; **E°** $_{OxO2}$=0.4495 V Thermodynamic University Alberta

Red $\mathbf{Succinate^{2-}+2H_2O=Fumarate^{2-}+2H_3O^++2e^-}$; **E°**$_{RedSuccinate}$=0.2512 V; Thermodynamic Lehninger 2000 ;

$\Delta G_{min}=\Delta G_{eq}=(E°_{RedSuccinate}-E°_{OxO2})*F*n$=(0.2512-0.4495)* 96485*2=(-0.1983)* 96485*2=**-38.3** kJ/mol;

peroxide, hydroxonium and anion of peroxide: G_{H2O2}=**274.5** kJ/mol; $G_{H3O+}+G_{HOO-}$=**22.44+328=350.4** kJ/mol;

$\mathbf{K_{eq}=exp(-\Delta G_{eq}/R/T)}$=exp(382565.95/8.3144/298.15)=5057721 ;

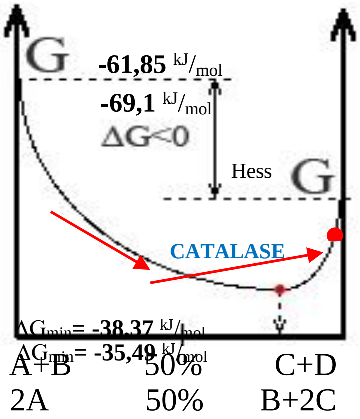
Exoergic dehydrogenation reaction favored reactants conversion to:

$\mathbf{Succinat^{2-}+O_{2aqua}}$ =>$\mathbf{fumarate^{2-}+H_2O_{2aqua}+Q+\Delta G}$;

Exoergic CATALASE erase **2H-O-O-H** peroxide $\mathbf{2H_2O_{2aq}}$=>$\mathbf{O_{2aqua}+2H_2O+Q+\Delta G}$ to $\mathbf{O_{2aqua}}$ and $\mathbf{2H_2O}$. Complex reaction sequence favors stabile unsaturated double bond product $^{\mathbf{H}}$>**C=C**<$^{\mathbf{H}}$ efficiency ● 100% as erasing molecules to

zero 0=$[\mathbf{H_2O_2}]$: $K_{eq}=5057721=\frac{[Fumarate^{2-}]\cdot[H_2O_2]\swarrow \text{CATALASE}}{[Succinate^{2-}]\cdot[O_2]}$ =5057721,

$K_{eq}=90471011.97=\frac{[UbiQuinOx]\cdot[H_2O_2]\swarrow \text{CATALASE}}{[UbiQuinRed]\cdot[O_2]}$.



Formation $\mathbf{H_{2gas}+O_{2gas}}$=>$\mathbf{H_2O_2}$; $\Delta G°_{UnivAlberta}$=-134,03 kJ/mol ; $\Delta G°_{Alberty}$=**-48,39** kJ/mol ;

$\Delta G_{Alberty}=G_{H2O2}-(G_{O2gas}+G_{H2gas})$=**274,5-(85,64+303)=-114,14** kJ/mol(-134,03 kJ/mol;)(=**-48,39** kJ/mol)

$\mathbf{UbiQuinRed^-+O_{2aqua}}$ =>$\mathbf{UbiQuinOx+H_2O_{2aqua}+\Delta G+Q}$; pH=7.36; Ubiquinol dehydrogenation with oxygene

$\Delta G_{Hess}=\Delta G°_{UbiQuinOx}+\Delta G°_{H2O2}-\Delta G°_{O2}-\Delta G°_{UbiQuinRed}$=**-3853.8792+2*-48.39-(16.4-3849.6004)**= **-69.07** kJ/mol

$\Delta G°_{Ox}$ =3668.94 kJ/mol**;**$\Delta G°_{Red}$ =3660.55 kJ/mol;CRC 2010=3668.94**+2*-48.39-(16.4**+3660.55)= **-104.79** kJ/mol;

Ox $\mathbf{O_{2aqua}+2H_3O^++2e^-=H_2O_{2aqua}+2H_2O}$; **E°** $_{OxO2}$=0.4495 V Thermodynamic University Alberta

Red $\mathbf{Ubiquinol+2H_2O=Ubiquinone+2H_3O^++2e^-}$; **E°** $_{RedH2O}$=0.2656 V Thermodynamic Lehninger 2000 ;

$\Delta G_{min}=\Delta G_{eq}=(E°_{Red}-E°_{Ox})*F*n$=(0.2656-0.4495)*96485*2=(**-1839**)* 96485*2=**-35.49** kJ/mol; Lehninger 2000

K_{eq} =EXP(-ΔG_{eq}/R/T)=EXP(**35490**/8.3144/298,15)=1650539;????

Red: $\mathbf{Ubiquinol6+2H_2O=Ubiquinone6+2H_3O^++2e^-}$; $\mathbf{E°_{Red}=E°^2_{H2O}=-0.845\ V}$; Thermodynamic CRC 2010 **E°**=-1.05 V;

$\mathbf{E°^2_{H2O}}$ **=-1.05**+0.10166+0.0591/2*log($[\mathbf{H_2O}]^2$)=(**-1.05**+0.0591/2*log(55.34573393^2))=**-0.947**+010166=-0.845 **V**

$\Delta G_{min}=\Delta G_{eq}=(E°_{Red}-E°_{Ox})*F*n$=(**-0.8453**-0.89916)*96485*2=(-1.7445)* 96485*2= **-336.6** kJ/mol;

THERMODYNAMICS Exercise V k AcetylCoA^{3-} hydrolysis

Calculate ΔH_H ΔS_H ΔG_H at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**?
AcetylCoA^{3-} and **ADP^{3-}** deacylation, phosphorilation! **Exoergic** or **endoergic** hydrolysis reactions!

a) $\Delta G_{Lehninger}$= -31,4 $^{kJ}/_{mol}$; AcetylCoA^{3-} + 2 H_2O +**ΔG+Q** => CH_3COO^- + CoA^{3-} + H_3O^+ **;** pH=7,36**;**
K$_{Lehninger}$=exp(31400/8,3144/298,15)=317017,64= **K**$_a$;
$\Delta G_H=\Delta G°_{CH3COO}+\Delta G°_{CoA2}+\Delta G°_{H3O}-\Delta G°_{Acetyl\text{-}CoA2}-2*\Delta G_{H2O}$=**-240,963-5,7716**-213,275-(**-51,8968**+2***-151,549**)=**-105.015** $^{kJ}/_{mol}$;

Substance	$\Delta H°_H$ $^{kJ}/_{mol}$	$\Delta S°_H$ $^{J}/_{mol/K}$	$\Delta G°_H$ $^{kJ}/_{mol}$
H_3O^+	-285,81	-3,854	-213,275
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**
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_3CCOOH	-484,3	159,8	-389,9
H_3CCOO^-	-486,84	82,23	-247,83
H_3CCOO^-	**-486**	**85,3**	**-240,963**

$$K_a=K_{Lehninger}=\frac{[CH_3COO^-]\cdot[HSCoA^{4-}]\cdot[H_3O^+]}{[H_2O]^2\cdot[Acetyl\text{-}CoA^{4-}]}=317017,64$$

ADP^{2-}+$H_2PO_4^-$=>ATP^{3-}+H_2O; **ΔG**$_{Lehninger}$ = 20,55 $^{kJ}/_{mol}$; pH=?

$\Delta G_{Hess}=\Delta G°_{ATP3}+\Delta G°_{H2O}-\Delta G°_{H2PO4-}-\Delta G°_{ADP2}$ =**37,85** $^{kJ}/_{mol}$

=**-2267,64-151,549-(-1399,9-1057,143)=37,85** $^{kJ}/_{mol}$

K$_{eq}$=**K**$_{Lehninger}$*[**H_2O**]= 0,000004535142*55,3= 0,000250993;
ΔG$_{eq}$=-R•T•ln(**K$_{eq}$**)=-8,3144•298,15•**ln**(0,000250993)=20,55 $^{kJ}/_{mol}$;

$$K_{bHL}=K_{bbLehninger}[H_2O]=0,000250993=\frac{[H_2O]\quad\cdot[ATP^{3-}]}{[H_2PO_4^-][ADP^{2-}]}$$

bb ADP^{3-}+HPO_4^{2-}+H_3O^+=>ATP^{4-}+2H_2O;
ΔG$_{bbLehninger}$=30,5 $^{kJ}/_{mol}$; **K**$_{bbLehn}$=0,000004535142; pH=7,36
K$_{Lehninger}$=exp(-30,5/8,3144/298,15)= 0,000004535142;
$\Delta G_H=\Delta G°_{ATP4}+2\Delta G°_{H2O}-\Delta G°_{HPO42}-\Delta G°_{ADP3}-\Delta G°_{H3O}$=**46,015** $^{kJ}/_{mol}$;
=**-2267,64**-2***151,549**-(**-1057,143-1399,9**-213,275)=**46,015**$^{kJ}/_{mol}$;

$$K_{bbLehningeH}=\exp(-\Delta G_{Lehninger}/R/T)=\exp(-30500/8,3144/298,15)=0,000004535142=\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}\ ;$$

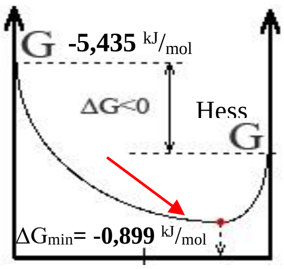
AcetylCoA^{4-}+ADP^{3-}+HPO_4^{2-}=>CH_3COO^-+CoA^{4-}+ATP^{4-};
$\Delta G_H=\Delta G°_{CH3COO}+\Delta G°_{CoA2}+\Delta G°_{ATP4}-\Delta G°_{Acetyl\text{-}CoA2}-\Delta G°_{ADP3-}-\Delta G°_{HPO42}$= **-5,4348** $^{kJ}/_{mol}$;
=**-2267,64-240,963-5,7716-(-1057,143-1399,9-51,8968)**= **-5,4348** $^{kJ}/_{mol}$;

$$K_{abb}=K_aK_{bbLehningeH}=317017,64*\ 0,000004535142=1,43772001390488=\frac{[CH_3COO^-]\cdot[HSCoA^{4-}]\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[Acetyl\text{-}CoA^{4-}]}$$

$\Delta G_{abb}=\Delta G_a+\Delta G_{bb}$=-31,409+30,51= -0,899 $^{kJ}/_{mol}$;
ΔG$_{abb}$=-R•T•ln(**K$_{abb}$**)=-8,3144*298,15***ln**(1,43772001390488)= -0,8999 $^{kJ}/_{mol}$;
Exothermic and exoergic AcetylCoA^{3-} , **ADP^{3-}** acylation, phosphorilation Hess free energy change at pH 7,36 negative **ΔG$_{esterification}$**= **-5,435** $^{kJ}/_{mol}$, but minimizes **ΔG$_{min}$**=**ΔG$_{abb}$**= **-0,899** $^{kJ}/_{mol}$ reaching equilibrium mixture:

K$_{abb}$=K$_a$K$_{bbLehningeH}$=317017,64* 0,000004535142=1,43772;

Le Chatelier principle is Prigogine attractor for Free energy change minimum **ΔG**$_{min}$ reaching at equilibrium . Free energy change minimum reaching establishes equilibrium.



Reactants

A+B+C 50% D+E+F
HPO_4^{2-}+H_3O^++ADP^{3-}
product **2H_2O +ATP^{4--}**

THERMODYNAMICS Exercise V l **Glyc31P=Glyc3P** hydrolysis

Calculate ΔH_H ΔS_H ΔG at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? Glycerate dephosphorilation **Glyc31P=Glyc3P** $^-$ with water! **Exoergic** or **endoergic**! <u>Reactants</u> **=>** <u>products</u>

Lehninger 2000 $\Delta G_{aL}=-39{,}351$ $^{kJ}/_{mol}$; c**Glycerat31P^{4-}+H_2O** =>**Glycerat3P^{3-}** + **$H_2PO_4^-$**; pH<7,199

Lehninger 2000 $\Delta G_{aLehninger}=-49{,}3$ $^{kJ}/_{mol}$; **Glycerat31P^{4-}+2H_2O=>Glycerat3P^{3-}+HPO_4^{2-}+H_3O^++ΔG+Q;** pH=7,36

Substance	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**
$H_2PO_4^-$	-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**
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

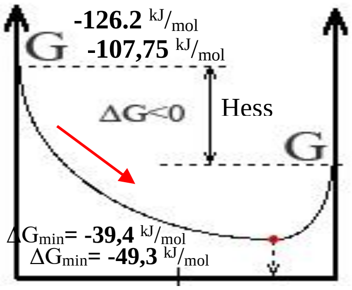
$\Delta G_{aL}=-R\bullet T\bullet\ln(K_{aL})$=-8,3144*298,15***ln**(7833705,111)= -39,351 $^{kJ}/_{mol}$

$\Delta G_{Hess}=\Delta G^\circ_{Glyc3P}+\Delta G^\circ_{H2PO4}-\Delta G^\circ_{Glyc31P}-\Delta G^\circ_{H2O}$=**-126,2** $^{kJ}/_{mol}$;

=**-1347,73**-1137,3-(-2207,3+(**-151,549**))= **-126,2** $^{kJ}/_{mo}$

$K_{aLehninger}$=exp(49300/8,3144/298,15)=433562158,5

Exoergic Glycerat31P^{4-} hydrolise Hess free energy change negative $\Delta G_{esterification}$=**-126,2** $^{kJ}/_{mol}$ and at pH 7,36 the **-107.75** $^{kJ}/_{mol}$, but minimizes to ΔG_{aL}=**-39,4** $^{kJ}/_{mol}$ and at pH=7,36 to **$\Delta G_{aLehninger}$=-49,3** $^{kJ}/_{mol}$ reaching equilibrium mixture **ΔG_{min}**:



$$\frac{[HPO_4^{2-}]\cdot[H_3O^+]\cdot[Glycerat3P^{3-}]}{[H_2O]^2\cdot[Glycerat13P^{4-}]}=433562158{,}5=K_{aLehninger}$$ **;** K_{aL}=**$K_{aLehninger}$**/[H_2O]=7833705; A+2B 50% C+D+E

$\Delta G_{Hess}=\Delta G^\circ_{H3O+}+\Delta G^\circ_{Glyc3P}+\Delta G^\circ_{HPO42-}-\Delta G^\circ_{Glyc31P}-2\Delta G^\circ_{H2O}$=**-107.75** $^{kJ}/_{mol}$; Reactants Glycerat31P^{4-}+2HO

=-213,275**-1347,73-1057,143**-(-2207,30+2***-151,549**)=**-107.75** $^{kJ}/_{mol}$. products Glycerat3P^{3-}+HPO_4^{2-}+H_3O^+

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching equilibrium .
Free energy change minimum reaching establishes equilibrium.

pH<7,199; **PyruvEnolP^{2-}+H_2O**=>$H_3CC=OCOO^-$+**$H_2PO_4^-$;**

$\Delta G_{Hess}=\Delta G^\circ_{H3CC=OCOO}+\Delta G^\circ_{H2PO4}-\Delta G^\circ_{PyruvEnolP3}-\Delta G^\circ_{H2O}$=-474,44-1137,3-(-1189,73-**155,66**)=-53,075 $^{kJ}/_{mol}$.

a PyruvEnolP^{3-} +H_2O => $H_3CC=OCOO^-$ + **HPO_4^{2-}**+ΔG+**Q;** pH=7,36 $\Delta G_{Lehninger}=-61{,}9$ $^{kJ}/_{mol}$; Lehninger 2000;

$\Delta G_H=\Delta G^\circ_{H3CC=OCOO}+\Delta G^\circ_{HPO42}-\Delta G^\circ_{PyruvEnolP3}-\Delta G^\circ_{H2O}$ =**-344,62-1057,14**-(-1189,73 **-151,549**)=**-60,481** $^{kJ}/_{mol}$.

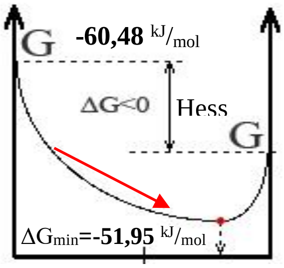
$K_{Lehninger}$=exp(-$\Delta G_{Lehninger}$/R/T)=exp(61900/8,3144/298,15)=69902464988

K_{aL}=$K_{Lehninger}$/[**H_3O^+**]=69902464988/55,3457339=1263014510

$\Delta G_a=-R\bullet T\bullet\ln(K_a)$=-8,3144*298,15*ln(1263014510)/1000= **-51,95** $^{kJ}/_{mol}$;

Exoergic **PyruvEnolP^{3-}** hydrolise Hess free energy change ΔG_{Hess} at pH 7,36 negative **-60,48** $^{kJ}/_{mol}$, but minimizes $\Delta G_{min}=\Delta G_{eq}$= **-51,95** $^{kJ}/_{mol}$ reaching

equilibrium mixture: $$\frac{[CH_3C=OCOO^-]\cdot[HPO_4^{2-}]}{[H_2O]\ \cdot[PyruvEnolP^{3-}]}=1263014510=K_a$$ **;** Le Chatelier principle is Prigogine attractor for Free energy change minimum **ΔG_{min}** reaching equilibrium . Free energy change minimum reaching establishes equilibrium.



A+B 50% C+D
Reactants **PyruvEnolP^{3-} +H_2O**
products $H_3CC=OCOO^-$ + **HPO_4^{2-}**

THERMODYNAMICS V m **Glc 6-P^{2-}**hydrolysis to Glc+**HPO$_4^{2-}$** and **Glc 6-P^{2-}**to **Glc 1-P^{2-}** isomerisation

Calculate ΔH_H ΔS_H ΔG at standard conditions 298.15 K. Reaction is **exothermic** , **athermic**, **endothermic**?
Glc 6-P^{2-}, **Glc 1-P^{2-}**dephosphorilation to Glucose! **Exoergic** or **endoergic**! Reactants => products
Lehninger 2000 $\Delta G_{Lehninger}$= -13,8 $^{kJ}/_{mol}$; **$Glc6P^{2-}+H_2O$ => $Glc+HPO_4^{2-}$+Q**+ΔG; pH=7,36; **ΔG_H**=-11,38 $^{kJ}/_{mol}$
$\Delta G_{Lehninger}$=-20,9 $^{kJ}/_{mol}$; **$Glc1P^{2-}+H_2O$** => **Glc**+**HPO_4^{2-}**+**ΔG+Q**;;pH=7,36;**ΔG_H**=-18,42 $^{kJ}/_{mol}$ **BioThermodyn 2006**

Substance	$\Delta H°_r$,$^{kJ}/_{mol}$	$\Delta S°_r$,$^{J}/_{mol/K}$	$\Delta G°_r$,$^{kJ}/_{mol}$
H_2O	-285,85	69,9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**
Glc	-1263,78	-269,45	-919,96
Glc	**-1267,13**	**-2901,49**	**-402,05**
$H_2PO_4^-$	-1302,6	92,5	-1137,3
HPO_4^{2-}	-1292,14	-33,47	-1089,28
HPO_4^{2-}	**-1298,89**	**-810,792**	**-1057,143**
$Glc6P^{2-}$	-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.$\Delta H_{Hess}=\Delta H°_{products}-\Delta H°_{reactants}$; 2.$\Delta S_{Hess}=\Delta S°_{products}-\Delta S°_{reactants}$;
3.$\Delta G_{Hess}=\Delta H_{Hess}-T\bullet\Delta S_{Hess}$;

$\Delta G_H=\Delta G°_{Glc}+\Delta G°_{HPO42-}-\Delta G°_{H2O}-\Delta G°_{Glc6P}$=-11,382 $^{kJ}/_{mol}$ **exoergic**
=-402,05-1057,143-(-151,549-1296,262)=-11,382 ......$^{kJ}/_{mol}$
$\Delta G_H=\Delta G°_{Glc}+\Delta G°_{HPO42}-\Delta G°_{H2O}-\Delta G°_{Glc1P}$=-18,423 $^{kJ}/_{mol}$ **exoergic**
=-402,05-1057,143-(-151,549-1289,221)=-18,423.........$^{kJ}/_{mol}$
1. **$\Delta H_{H6}=\Delta H°_{Glc}+\Delta H°_{HPO42-}-\Delta H°_{H2O}-\Delta H°_{Glc6P}$ =-0,056** $^{kJ}/_{mol}$ athermic
=-1267,13-1298,89-(-286,65-2279,314)= -0,056...............$^{kJ}/_{mol}$;
2. $\Delta S_{disperse}=-\Delta H_H/T$=**56**/298,15=**0,188.**...........$^{J}/_{(mol\ K)}$
2.**$\Delta S_{H6}=\Delta S°_{Glc}+\Delta S°_{HPO42}-\Delta S°_{H2O}-\Delta S°_{Glc6P}$=38,102** $^{J}/_{mol/K}$;
=-2901,49-810,792-(-453,188-3297,196)=38,102.........$^{J}/_{mol/K}$;
$\Delta G_{H6}=\Delta H_H-T*\Delta S_H$=-0,056-298,15*0,0**38102**= **-11,42** $^{kJ}/_{mol}$;
3.$\Delta S_{total}=\Delta S_H+\Delta S_{disperse}$=0,188+38,102=**38,29**......$^{J}/_{(mol\ K)}$; T•ΔS_{total}=38,29*298,15=11,42; $^{kJ}/_{mol}$ spontaneouse
$\Delta H_{H1}=\Delta H°_{Glc}+\Delta H°_{HPO42-}-\Delta H°_{H2O}-\Delta H°_{Glc1P}$ =-16,02 $^{kJ}/_{mol}$; **$\Delta S_{H1}=\Delta S°_{Glc}+\Delta S°_{HPO42}-\Delta S°_{H2O}-\Delta S°_{Glc1P}$=32,466** $^{J}/_{mol/K}$;
$\Delta G_{H1}=\Delta H_H-T*\Delta S_H$=-16,02-298,15***0,032466=-25,6997** $^{kJ}/_{mol}$;**$\Delta G_{H66}=\Delta H_{H66}-T*\Delta S_{H66}$=0,056**-298,15*-0,0**38102= 11,42** $^{kJ}/_{mol}$

$$\frac{[Glc]\cdot[HPO_4^{2-}]}{[Glc6P^{2-}]\cdot[H_2O]}$$

$\Delta G_{Lehniger6}$=-13.8; **K**$_{Lehmiger6}$=EXP(**-ΔG_H**/R/T)=EXP(13800/8,3144/298,15)=261,62;210,93
=**K_{eq6}**=4,727;3,811;298,15 K, 310,15; **K_{eq6}**=$K_{Lehmiger6}$/[**H_2O**]=261,62/55,3457339=4,727
ΔG_{eq1}= -R•T•ln(K_{eq1})=-8,3144*298,15***ln**(4,727)/1000= **-3,851** $^{kJ}/_{mol}$; **-3,45** $^{kJ}/_{mol}$
K$_{Lehmiger1}$=EXP(**-ΔG_H** /R/T)=EXP(20900/8,3144/298,15)=4587,22; 3310,4

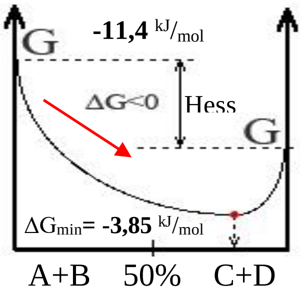
$$\frac{[Glc]\cdot[HPO_4^{2-}]}{[Glc1P^{2-}]\cdot[H_2O]}$$

=**K_{eq1}**=82,883;0, 59,813; 298,15, 310,15; **K_{eq1}**=$K_{Lehmiger1}$/[**H_2O**]= 4587,22/55,3457339=82,883
ΔG_{eq1}= -R•T•ln(K_{eq1})=-8,3144*298,15***ln**(82,883)/1000=**-10,95** $^{kJ}/_{mol}$; **-10,55** $^{kJ}/_{mol}$;

$\Delta G_{Lehniger66}$=13.8; **K**$_{Lehmiger66}$=EXP(**-ΔG_{L66}**/R/T)=EXP(-13800/8,3144/298,15)=0,003822314; 0,004740984
K_{eq66}=$K_{Lehmiger66}$*[**H_2O**]=0,003822314*55,3457339=0,21154877; 0,262393; 298,15 K , 310,15 K .
ΔG_{eq66}=-R•T•ln(K_{eq66})=-8,3144*298,15***ln**(0,21154877)/1000=**3,85** $^{kJ}/_{mol}$; **3,45** $^{kJ}/_{mol}$.

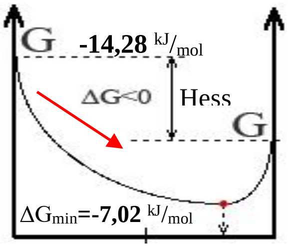
Endothermic and exoergic dephosphorilation reaction free energy **$\Delta G_{phosphorilation}$** negaitive = **-11,42** $^{kJ}/_{mol}$, but minimized to **ΔG_{min} = ΔG_{eq} = -3,851** $^{kJ}/_{mol}$ reaching equilibrium K_{eq}=**4,727 .**

Reaction Prigogine attractor is free energy change minimum **ΔG_{min} .**
Free energy minimum reaching establishes equilibrium.



Glc6P^{2-}+H_2O reactants
products Glc+HPO_4^{2-}

$Glc1P^{2-}$ <=> **$Glc6P^{2-}$** ; constant **$K_{Glc1PGlc6P}$= 17**
$\Delta G_H=\Delta G°_{Glc6P}-\Delta G°_{Glc1P}$=-1296,262-(-1289,221)=-7,042 $^{kJ}/_{mol}$ **exoergic**..............$^{kJ}/_{mol}$
$\Delta G_{total}=\Delta G°_{H66}+\Delta G°_{H1}$=11,42-25,7 = -14,28 $^{kJ}/_{mol}$ **exoergic**..............$^{kJ}/_{mol}$
K_{eq}=[Glc 6-phosphate]/[Glc 1-phosphate]=17 mM/1 mM
ΔG_{eq} = - R•T•ln(K_{eq}) = - 8,3144*298,15***ln(17)** = -7,02 $^{kJ}/_{mol}$. Endothermic and exoergic isomerisation reaction free energy change **$\Delta G_{isomerisation}$** negative ΔG_{total}=**11,42-19,63** $^{kJ}/_{mol}$ = **-8,21** $^{kJ}/_{mol}$, but minimized to **ΔG_{eq} = -7,02** $^{kJ}/_{mol}$ reaching equilibrium **ΔG_{min}** .Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching equilibrium . Free energy change minimum reaching establishes equilibrium. **$K_{aGlc1PGlc6P}$= 17** ;



Glc_1P^{2-} reactant and product Glc_6P^{2-} A 50% B

THERMODYNAMICS Exercise VI Carbonic Anhydrase protolysis equilibrium $H_2O^{/CA/}CO_2/H_3O^{+}+HCO_3^{-}$

E3 class Enzyme Carbonic anhydrase (CA) protolysis $H_2O^{/CA/}CO_2/H_3O^{+}+HCO_3^{-}$ and CO_2 reaction with $2H_2O$!

Will be **exoergic** or **endoergic**! CO_{2gas} no act H_2O just water soluble $CO_{2gas}+H_2O+\Delta G<=>CO_{2aqua}+Q$;

Substance	ΔH°_{Hess}, $^{kJ}/_{mol}$	ΔS°_{Hess}, $^{J}/_{mol/K}$	ΔG°_{Hess}, $^{kJ}/_{mol}$
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
CO_{2gas}	-393.509	213.74	-394.359

$\Delta H_H=\Delta H^\circ_{CO2aq}-\Delta H^\circ_{CO2gas}=-413.7976+393.509=-20.3\ ^{kJ}/_{mol}$

$\Delta S_{Hess}=\Delta S^\circ_{CO2aqua}-\Delta S^\circ_{CO2gas}=117.57-213.74=-96.17\ ^{J}/_{mol/K}$;

$=117.57+69.9565-(213.74+69.9565)=-96.17$....... $^{J}/_{mol/K}$

$\Delta G_H=\Delta H_H-T*\Delta S_H=-20.3+298.15*0.09617=8.385\ ^{kJ}/_{mol}$;

$\Delta G_{sp}=\Delta G^\circ_{CO2aq}-\Delta G^\circ_{CO2gas}=-385.98+394.359=8.379\ ^{kJ}/_{mol}$

$K_{sp}=EXP(-\Delta G_{sp}/R/T)=EXP(-8379/8.3144/298.15)=0.034045$

$K_{sp}=0.0341=\frac{X_{CO_2\,aqua}}{[CO_2\ gas]}=\frac{[CO_2\ aqua]}{[CO_2\ gas]\cdot[H_2O]}$ 100% mol fraction

$[CO_{2gas}]=1$; $[CO_{2aqua}]=K_{sp}[H_2O]=0.034*55.346=1.878$ M

Air 0.04% $[CO_{2gas}]=0.0004$; $[CO_{2aqua}]=K_{sp}*[CO_2\uparrow_{gas}]*[H_2O]=0.034045*0.0004*55.3457339=0.000754$ M;

Hydrolysis reaction $CO_{2aqua}+2H_2O+\Delta G+Q\ \overset{CA}{=}>\ H_3O^{+}+HCO_3^{-}$ and acid neutralisation equilibrium

$\Delta H_H=\Delta H^\circ_{H3O}+\Delta H^\circ_{HCO3}-2\Delta H^\circ_{H2O}-\Delta H^\circ_{CO2}=-285.81\mathbf{-692.4948}-(2*-285.85-413.7976)=9.7576$.........$^{kJ}/_{mol}$;

$\Delta S_{dispersed}=-\Delta H_{Hess}/T=-9.7576/298.15=-32.727$.......$^{J}/_{mol/K}$; **endothermic**........................

2. $\Delta S_{Hess}=\Delta S^\circ_{H3O}+\Delta S^\circ_{HCO3}-2\Delta S^\circ_{H2O}-\Delta S^\circ_{CO2}=-3.854+98.324-(2*69.9565+117.5704)=-163.0134$.........$^{J}/_{mol/K}$;

$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}=-32.727-163.0134=-195.169$........$^{J}/_{mol/K}$;

3. $\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=+9.7576+298.15*0.1630134=58.19$...........$^{kJ}/_{mol}$;

$T\bullet\Delta S_{total}=-195.7404^{*}298.15\ K=\mathbf{-58.19}$..........$^{kJ}/_{mol}$; bound $T\Delta Sn\leftarrow$ accumulated free energy **endoergic**..........

3. $\Delta G_{Hess}=\Delta G^\circ_{H3O}+\Delta G^\circ_{HCO3}-2\Delta G^\circ_{H2O}-\Delta G^\circ_{CO2}=-213.2746\mathbf{-544.9688}-(2*-237.191-385.98)=102\ ^{kJ}/_{mol}$;

$\Delta G_{Absolute}=G_{H3O}+G_{HCO3}-(2G_{H2O}+G_{CO2qua})=22.44+46.08-(2*0+8.379)=\mathbf{60.14}\ ^{kJ}/_{mol}$;

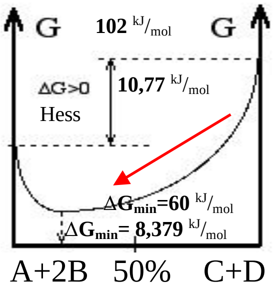
Thermodynamic unfavored $\frac{[HCO_3^-]_{aqua}\cdot[H_3O^+]}{[CO_2]_{aqua}\cdot[H_2O]^2}=K_{eqCA}=K_{HCO3}/[H_2O]^2=10\text{^}^{(-7.0512)}/55.3457339\text{^}^{2}=2.906*10^{-11}$

$\Delta G_{eqCA}=-R\bullet T\bullet\ln(K_{eqCA})=-8.3144*298.15*\ln(2.906*10\text{^}^{(-11)})=\mathbf{60}.14\ ^{kJ}/_{mol}$.

Endoergic CO_{2gas} solubility and CO_{2aq} protolysis $\Delta G_{hydratation}=10.77.\ ^{kJ}/_{mol}$ Hess free energy change positive and $\Delta G_{protolysis}$ 102 $^{kJ}/_{mol}$, but minimizes reaching mixture solubility $\Delta G_{min}=\Delta G_{sp}=8.379\ ^{kJ}/_{mol}$ and protolysis $\Delta G_{min}=\Delta G_{eq}=60\ ^{kJ}/_{mol}$:

$K_a=K_{CA}=K_{eqCA}*[H_2O]^2=\frac{[HCO_3^-]_{aqua}\cdot[H_3O^+]}{[CO_2]_{aqua}}=10^{-7.0512}$

Value $pK_a=pK_{CA}=7.0512$ is frendly to physiologic pH=7.36. Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching equilibrium . Free energy change minimum reaching establishes equilibrium.



$CO_{2aqua}+2H_2O$ products $HCO_3^{-}+H_3O^{+}$

$G_{H3O+HCO3}=G_{H3O+}+G_{HCO3-}=22.44+46.08=\Delta G_{spCO2aqua}+\Delta G_{eqCO2aqua}=8.379+60.14=68.52\ ^{kJ}/_{mol}$. [1.8,14]

In ocean with hydroxide anion irreversiblly $CO_{2aqua}+OH^{-}=>HCO_3^{-}+\Delta G(-39.7\ ^{kJ}/_{mol})+\Delta H(-48.68\ ^{kJ}/_{mol})$.

$\Delta H_{Hess}=\Delta H^\circ_{HCO3}-\Delta H^\circ_{CO2}-\Delta H^\circ_{OH}=\mathbf{-692.4948}-(-413.7976-230.015)=\mathbf{-48.68}\ ^{kJ}/_{mol}$; **exothermic**..................

$\Delta S_{dispersed}=-\Delta H_{Hess}/T=48682.2/298.15=\mathbf{163.3}\ ^{J}/_{mol/K}$; $\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}=\mathbf{163.3-601.44}=\mathbf{-438.14}\ ^{J}/_{mol/K}$;

2. $\Delta S_{Hess}=\Delta S^\circ_{HCO3}-\Delta S^\circ_{CO2}-\Delta S^\circ_{OH}=\mathbf{-494.768}-(117.5704-10.9)=\mathbf{-601.44}\ ^{J}/_{mol/K}$;

3. $\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=-48.6822-298.15*-0.\mathbf{6014384}=\mathbf{130.6}\ ^{kJ}/_{mol}$; **endoergic**..........

$T\bullet\Delta S_{total}=-0.\mathbf{43814}^{*}298.15\ K=\mathbf{-130.6}\ ^{kJ}/_{mol}$; bound $T\Delta Sn\leftarrow$ accumulated energy in products .

3. $\Delta G_{Hess}=\Delta G^\circ_{HCO3}-\Delta G^\circ_{CO2}-\Delta G^\circ_{OH}=\mathbf{-544.9688}-(-385.98-157.2)=-1.7888\ ^{kJ}/_{mol}$; pH=7.36; pOH=6.64

$\Delta G_{eqOH}=-R\bullet T\bullet\ln(K_{eqOH})=-8.3144*298.15*\ln(9180981.6)/1000=\mathbf{-39.7}\ ^{kJ}/_{mol}$; Reaction is slow at pOH=6.64

$\frac{[HCO_3^-]}{[CO_2]_{aqua}\cdot[OH^-]}$ $K_{eqOH}=K_{eqCA}/K_{H2O}=2.993*10\text{^}(^{-11})/3.26/10\text{^}^{(-18)}=9180981.6$; Reversible CA present;

$=K_{eqOH}=K_{eqCA}/K_{H2O}=9180981.6$; Ratio $K_{eqOH}[OH^-]=9180981.6*10\text{^}^{(-6.64)}=2.103=\frac{[HCO_3^-]}{[CO_2]_{aqua}}$

$\Delta G_{OH}=-R\bullet T\bullet\ln(K_{eqOH}[OH^-])=-8.3144*298.15*\ln(2.1032413768)/1000=\mathbf{-1.84}\ ^{kJ}/_{mol}$

$[HCO_3^-]=K_{eq}[OH^-]*[CO_{2aqua}]=2.103*0.00075125=0.00158$ M;

Sum is $[CO_{2aqua}]+[HCO_3^-]=0.00075125+0.00158=0.00223$ M;

$([CO_{2aqua}]+[HCO_3^-])/[CO_{2aqua\_from\_AIR}]=0.023/0.000754=30.5$ times greater with CA Carbonic Anhydrase.

Distinction of CA on Earth the bicarbonate carbon assimilation of CO_2 in aqua sphere decreases 30.5 times.

THERMODYNAMICS Exercise VII through ionic channels drive reaction $\mathbf{H_3O^+ + HCO_3^-}$ to exhale $\mathbf{CO_2}$

Air 0.04% mol fraction $[\mathbf{CO_2}\uparrow_{air}]=0.0004$ as 400 ppm parts per million of air dissolute (see 46th page,):

$$[\mathbf{CO_2}_{aqua}]=\mathbf{K}_{eq}*[\mathbf{CO_2}\uparrow_{air}]=1{,}878*0{,}0004=0{,}0007512\ \mathrm{M}.$$

In lungs $\mathbf{H^+ + HCO_3^-}$ to breath out gas $\mathbf{CO_2}$ with water $2\mathbf{H_2O}$ **exothermic**, **athermic** or **endothermic**?.Will be **exoergic** or **endoergic**! <=Reverse for photosynthesis <u>direct for oxidation</u>$\mathbf{=>H_3O^+ + HCO_3^- => CO_2}_{aqua}\mathbf{+2H_2O+Q}\ +\Delta\mathbf{G}$

Substance	$\Delta H°_{Hess}$, $^{kJ}/_{mol}$	$\Delta S°_{Hess}$, $^{J}/_{mol/K}$	$\Delta G°_{Hess}$, $^{kJ}/_{mol}$
$\mathbf{H_3O^+}$	-285,81	-3,854	-213,274599
$\mathbf{-OH^-}$	-230,015	-10,9	-157,2
$\mathbf{HCO_3^-}$	-689.93	98.324	-586,93988
$\mathbf{HCO_3^-}$	**-692,4948**	**- 494,768**	**-544,9688**
$\mathbf{H_2O}$	-285,85	69,9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{CO_2}_{aqua}$	-413,7976	117,5704	-385,98
$\mathbf{CO_2}\uparrow_{gas}$	-393,509	213,74	-394,359

$\Delta G_{Hess}=2\Delta G°_{\mathbf{H2O}}+\Delta G°_{\mathbf{CO2}}-\Delta G°_{\mathbf{H3O}}-\Delta G°_{\mathbf{HCO3}}=\mathbf{-102}\ ^{kJ}/_{mol}$

$=2*-237{,}191-385{,}98-(-213{,}2746\mathbf{-544{,}9688})=\mathbf{-102}\ ^{kJ}/_{mol};$

$\Delta H_H=2\Delta H°_{\mathbf{H2O}}+\Delta H°_{\mathbf{CO2}}-\Delta H°_{\mathbf{H3O}}-\Delta H°_{\mathbf{HCO3}}=\mathbf{-7{,}1928}\ ^{kJ}/_{mol}$

$=2*-285{,}85-413{,}7976-(-285{,}81\mathbf{-692{,}4948})=\mathbf{-7{,}1928}\ ^{kJ}/_{mol}$

$\Delta S_{dispersed}=-\Delta H_{Hess}/T=\mathbf{7{,}1928}/298{,}15=\mathbf{24{,}125}\ ^{J}/_{mol/K};$

$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}=\mathbf{756{,}1054+24{,}125=780{,}23}\ ^{J}/_{mol/K};$

$\Delta G_H=\Delta H_H-T*\Delta S_H=\mathbf{-7{,}193}-298{,}15*0{,}\mathbf{7561}=\mathbf{-232{,}6}\ ^{kJ}/_{mol};$

$\Delta S_{Hess}=2\Delta S°_{\mathbf{H2O}}+\Delta S°_{\mathbf{CO2}}-\Delta S°_{\mathbf{H3O}}-\Delta S°_{\mathbf{HCO3}}=\mathbf{756{,}1054}\ ^{J}/_{mol/K}$

$=2*69{,}9565+117{,}5704-(-3{,}854\mathbf{-494{,}768})=\mathbf{756{,}1054}\ ^{J}/_{mol/K}$

$T\bullet\Delta S_{total}=0{,}\mathbf{78023}^{*}298{,}15\ \mathrm{K}=\mathbf{232{,}63}\ ^{kJ}/_{mol}$; bound TΔSn <u>accumulate energy</u> **endoergic, non spontaneous**

CAII; RBCs, kidney, osteoclasts, eye, GI tract, lung, brain, and testis; Cytosol; Glaucoma, epilepsy, edema, altitude sickness;
$\mathbf{k_{cat}}=1{,}4\times10^{6}(\mathrm{s}^{-1})$; $\mathbf{k_{1CO2}}_{aqua}=1{,}5\times10^{8}(\mathrm{M}^{-1}\ \mathrm{s}^{-1})$; <u>**Biomed Res Int.**</u> **2015**;2015:453543. Review Article **3KS3,**
$\mathbf{v1=k_{1CO2}}_{aqua}[\mathbf{CO_2}_{aqua}]=1{,}5*10\wedge^{8}*0{,}0007512=112680\ \mathrm{s}^{-1}$; as $\mathbf{v1}=k_{cat}/K_M\mathbf{*}[E_i][S_i]$; $[E_i]=1$ M; $S_i=[\mathbf{CO_2}_{aqua}]$;

$$\text{CAII: } \mathbf{CO_2}_{aqua}+2\mathbf{H_2O}+\mathbf{\Delta G+Q=v1}\overset{CA}{\underline{\quad}}\mathbf{>H_3O^+ + HCO_3^-}\ ;\ \mathrm{pH}=7{,}36,$$

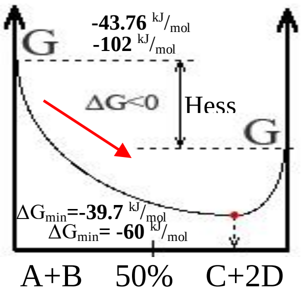
$$k_2=\mathbf{k_{1CO2}}_{aqua}\mathbf{/K}_{eqCA}=1{,}5*10\wedge^{8}/2{,}9016/10\wedge^{(-11)}=\mathbf{5.17*10\wedge^{18}}\ \mathrm{s}^{-1}=\mathbf{10\wedge^{18{,}7}\ M^{-2}}\mathrm{s}^{-1};$$

Neutralisation velocity constant $k_2=\mathbf{10\wedge^{18{,}7}\ M^{-2}}\mathrm{s}^{-1}$; $H_3O^+ + HCO_3^- => CO_2$$_{\mathbf{aqua}}\mathbf{+2}H_2O$ **;.**

$K_a=\mathbf{K_{eqCA}*[H_2O]}^2=2{,}902*10\wedge^{(-11)}\mathbf{*}(55{,}3457339)\wedge^{2}=8{,}892*10\wedge^{(-8)}=10\wedge^{(-7{,}0512)}$; $\mathbf{K_{eqCA}}=\dfrac{[\mathbf{HCO_3^-}]\cdot[\mathbf{H_3O^+}]}{[\mathbf{CO_2}]_{aqua}\cdot[\mathbf{H_2O}]^2}$

Neutralisation $\mathbf{H_3O^+ + HCO_3^- => CO_2}_{aqua}\mathbf{+2H_2O}$ velocity according bicarbonate concentration in ocean
$\mathrm{pOH}_{ocean}=5{,}9$; $\mathrm{pH}_{ocean}=8{,}1$; $\mathbf{[}HCO_3^-]=0{,}003$ M; Haack Weltmeer Atlas 1969:
$v_2=k_2\bullet\mathbf{[}H_3O^+\mathbf{][}HCO_3^-\mathbf{]=10\wedge^{18{,}7}*}10\wedge^{(-8{,}1)}*0{,}003=119432151\ \mathrm{s}^{-1};$
Extra Mitochondrial pH=5 $v_2=k_2\bullet\mathbf{[}H_3O^+\mathbf{][}HCO_3^-\mathbf{]=10\wedge^{18{,}7}*}10\wedge^{(-5)}*0{,}0154=771828339786\ \mathrm{s}^{-1};$
Neutralisation velocity constant is greater the slow hydroxide anions reaction $\mathbf{k_{1OH}}=1{,}5\times10^{2}\ \mathrm{M}^{-2}\mathrm{s}^{-1}$;
$\mathbf{HCO_3^- => CO_2}_{aqua}+\mathbf{OH^-}+\Delta G+Q$ decomposition reaction: $k_{HCO3}=1{,}5*10\wedge^{2}/9180981{,}6=0{,}000016338\ \mathrm{M}^{-1}\mathrm{s}^{-1}$;
$K_{eqOH}=k_{1OH}/k_{HCO3}=[HCO_3^-]/[CO_2{}_{aqua}]/[OH^-]=1{,}5*10^{2}\ \mathrm{M}^{-2}\mathrm{s}^{-1}/k_{HCO3}=8914110.$
$v_{HCO3}=k_{HCO3}*[HCO_3^-]=0{,}00001683*0{,}0154=0{,}000000259182\ \mathrm{s}^{-1};$
$\mathbf{CO_2}_{aqua}+\mathbf{OH^- => HCO_3^-}$: $v_{1OH}=k_{1OH}*[CO_2{}_{aqua}]*[OH^-]=1{,}5*10\wedge^{2}*0{,}0076*10\wedge^{(-6{,}63)}=0{,}000000267;\ \mathrm{s}^{-1};$
Velocity with hydroxide $k_{1OH}/\mathbf{k_{1CO2}}_{aqua}=1{,}5*10\wedge^{2}/1{,}5/10\wedge^{8}=10\wedge^{-6}$ million times slower CA.
Favored OH^- but lower at absent **CA** $\mathbf{K}_{eq}OH=\mathbf{K_{eqCA}/K}_{H2O}=2{,}993*10\wedge(^{-11})/3{,}26/10\wedge^{(-18)}=9180981{,}6=\dfrac{[\mathbf{HCO_3^-}]}{[\mathbf{CO_2}]_{aqua}\cdot[\mathbf{OH^-}]}$

$\Delta\mathbf{G}_{eq}\mathbf{OH}\mathbf{=-R\bullet T\bullet ln(K}_{eq}\mathbf{OH})=-8{,}3144*298{,}15*\mathbf{ln}(9180981{,}6)/1000=-39.7\ ^{kJ}/_{mol}$; Unfavored equilibrium.
$\Delta G_{Hess}=\Delta G°_{\mathbf{HCO3}}-\Delta G°_{\mathbf{O\ H}}-\Delta G°_{\mathbf{CO2}}=-586{,}93988-(-157{,}2-385{,}98)=-43.76\ ^{kJ}/_{mol};$
$\mathbf{K_{eq}}\mathbf{O}H=\mathbf{K_{eqCA}/K}_{H2O}=2{,}993*10\wedge(^{-11})/3{,}26/10\wedge^{(-18)}=9180981{,}6$; $\mathbf{K}_{eq}\mathbf{HCO3}=1/\mathbf{K}_{eq}\mathbf{OH}=1/9180981{,}6=0.0000001089;$
Neutralisation is faster 34463449218 times over carbonic anhydrase CA driven velocity $\mathbf{k_{1CO2}}_{aqua}=1{,}5*10^{8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$;
$1/\mathbf{K}_{eqCA}=k_2/\mathbf{k_{1CO2}}_{aqua}=\mathbf{10\wedge^{18{,}7}}/1{,}5/10\wedge^{8}=33412482242$; $\mathbf{K}_{eqCA}=\mathbf{k_{1CO2}}_{aqua}/k_2=1{,}5*10\wedge^{8}/\mathbf{10\wedge^{18{,}7}}=2{,}993*10\wedge^{(-11)}\mathbf{;}$
Exothermic and exoergic neutralization $\mathbf{H_3O^+ + HCO_3^- <=> CO_2}_{aqua}+2\mathbf{H_2O}$ Hess free energy negaitive



$\Delta G_{neutralisation}$ -102 $^{kJ}/_{mol}$, -43.76 $^{kJ}/_{mol}$ $CO_2{}_{\mathbf{aqua}}\mathbf{+}OH^-$ => HCO_3^-, but $\Delta G_{min}=\Delta G_{eq}=-60\ ^{kJ}/_{mol}$
minimized -39.67 $^{kJ}/_{mol}$., reaching $\mathbf{K}_{eq}\mathbf{HCO3}=1/\mathbf{K}_{eq}\mathbf{OH}=1/9180981{,}6=0.0000001089$
equilibrium mixture $\mathbf{K}_{eq}\mathbf{O}H=\mathbf{K_{eqCA}/K}_{H2O}=9180981{,}6.$

Le Chatelier principle is Prigogine attractor free energy change minimum reaching ΔG_{min} at mixture. Free energy minimum reaching establishes equilibrium.
$\Delta\mathbf{G}_{1/eq}\mathbf{OH}\mathbf{=-R\bullet T\bullet ln(1/K}_{eq}\mathbf{OH})=-8{,}3144*298{,}15*\mathbf{ln}(34463449218)/1000=-60\ ^{kJ}/_{mol}$;
$\mathbf{CO_2}_{aqua}+\mathbf{OH^-}$; $\mathbf{H_3O^+ + HCO_3^-}$ reactants products $CO_2{}_{\mathbf{aqua}}\mathbf{+2}H_2O\mathbf{;}$
Protolysis of water pH=pOH=7 $G_{H3O++OH-}=G_{H3O+}+G_{OH}=22.44+77.36=99.8\ ^{kJ}/_{mol}$

CA $\mathbf{G}_{\mathbf{H3O+HCO3}}=\mathbf{G}_{\mathbf{H3O+}}+\mathbf{G}_{\mathbf{HCO3-}}=22.44+46.08=\Delta\mathbf{G}_{spCO2aqua}+\Delta\mathbf{G}_{eqCO2aqua}=8.379+60.14=68.52\ ^{kJ}/_{mol}$. [1,8,14]

THERMODYNAMICS Exercise VIII Glycine+glycine→ glycylglycine dipeptide synthesis

Calculate ΔH_H ΔS_H ΔG_H at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? For peptide synthesis polycondensation Enzyme ribosome governed reaction with amino acids glycine Gly (G) using the data table! Mention whether the reaction will be **exoergic** or **endoergic**! Glycine+glycine→ glycylglycine dipeptide synthesis; $\mathbf{Q}+\Delta G+\mathbf{Gly}_{aq}+\mathbf{Gly}_{\mathbf{aq}}\xrightarrow{\text{Ribosome}}\mathbf{GlyGly}_{aqua}+\mathbf{H_2O}$

1. $\Delta H_{Hess}=\Delta H^\circ_{\mathbf{GlyGly}}+\Delta H^\circ_{\mathbf{H_2O}}-2\,\Delta H^\circ_{\mathbf{Gly}}$=-790,99-285,85-(2*-554,56)=-1033.53 +1028.72= -32,28 $^{kJ}/_{mol}$ **exothermic**.

2. $\Delta S_{dispersed}=-\Delta H_H/T$=4,81/298.1516.13 $^{J}/_{mol/K}$;

$\Delta S_{Hess}=\Delta S^\circ_{\mathbf{Gly\text{-}Gly}}+\Delta S^\circ_{\mathbf{H_2O}}-2\,\Delta S^\circ_{\mathbf{Gly}}$ =111+69,9565-(2*158,45)=180,957-316,9 = -135,9435 $^{J}/_{mol/K}$**;**

3.$\Delta S_{total}=\Delta S_r+\Delta S_{dispersed}$=-135,9435+16.13 = -119,81 $^{J}/_{mol/K}$;

$\Delta G_H=\Delta H_H-T^*\Delta S_H$=-4.81-298.15*-0.1359435 = - 4,81+41,128= 35,72 $^{kJ}/_{mol}$; **endoergic** non **spontaneous**

$T\bullet\Delta S_{total}$= -119,81 $^{J}/_{K/mol}$•298,15 K=**-35,72** $^{kJ}/_{mol}$;bound accumulate energy in peptide product

Glycine carboxylic acid C**OO**H protolysis constant: $K_{eq}=K_{COOH}/[\mathbf{H_2O}]$=1/12416,5=10^(-4,094)=

$H_3N^+\text{-}CH_2\text{-}COOH+\mathbf{H_2O}\Rightarrow H_3N^+\text{-}CH_2\text{-}COO^-+\mathbf{H_3O^+}$; pK_{COOH}=2,351 ΔH_H =4,0 $^{kJ}/_{mol}$; ΔS_H= -139 $^{J}/_{K/mol}$

$\Delta H_H=\Delta H^\circ_{H3N+CH2COO}+\Delta H^\circ_{\mathbf{H3O}}-\Delta H^\circ_{H3N+CH2COOH}-\Delta H^\circ_{\mathbf{H2O}}$=4 $^{kJ}/_{mol}$; $K_a=K_{COOH}$=1/224,39=10^(-2,351)=

$\Delta H^\circ_{H3N+CH2COO}=4+\Delta H^\circ_{\mathbf{H2O}}-\Delta H^\circ_{\mathbf{H3O}}+\Delta H^\circ_{H3N+CH2COOH}$=4**-286,65**+285,81**-525,06**=**-521,9** $^{kJ}/_{mol}$;

$\Delta S^\circ_{H3N+CH2COO}=-139+\Delta S^\circ_{\mathbf{H2O}}-\Delta S^\circ_{\mathbf{H3O}}+\Delta S^\circ_{H3N+CH2COOH}$=-139**-453,188**+3,854**-1204,952**=**-1793,3** $^{J}/_{K/mol}$;

$\Delta G_H=\Delta H_H-T^*\Delta S_H$=4-298,15***-0,139**=45,44 $^{kJ}/_{mol}$;**endoergic**

$$K_{COOH}=10^{-2,351}=\frac{[H^+]\cdot[H_3N^+CH_2COO^-]Gly}{[H_3N^+CH_2COOH]}\;;\;K_{eq}=K_{COOH}/[\mathbf{H_2O}]=10^{-2,351}/55,33=10^{-4,094}=\frac{[H_3O^+]\cdot[H_3N^+CH_2COO^-]Gly}{[H_2O]\cdot[H_3N^+CH_2COOH]}$$

$\Delta\mathbf{G_{eq}=-R\bullet T\bullet ln(K_{eq})}$=-8,3144•298,15•**ln**(10$^{-4,094}$)=23,37 $^{kJ}/_{mol}$, $K_{eq}=K_{H3N+}/[\mathbf{H_2O}]$=1/108902871=10^(-9,78)=

$H_3N^+\text{-}CH_2\text{-}COO^-+\mathbf{H_2O}\Leftarrow H_2N\text{-}CH_2\text{-}COO^-+\mathbf{H_3O^+}$; pK_{H3N+}=9,780; ΔH_{Hess}<=44,2 $^{kJ}/_{mol}$; ΔS_{Hess}<= -57 $^{J}/_{K/mol}$

$\Delta H_{Hess}=\Delta H^\circ_{H2NCH2COO}+\Delta H^\circ_{\mathbf{H3O}}-\Delta H^\circ_{H3N+CH2COO}-\Delta H^\circ_{\mathbf{H2O}}$=44,2 $^{kJ}/_{mol}$; $K_a=K_{H3N+}$=1/6025595861=10^(-9,78)=

$\Delta H^\circ_{H3N+CH2COO}=-44,2+\Delta H^\circ_{H2NCH2COO}+\Delta H^\circ_{\mathbf{H2O}}-\Delta H^\circ_{\mathbf{H3O}}$=-44,2**-525,06-286,65**+285,81= **-570,1** $^{kJ}/_{mol}$;

$\Delta S^\circ_{H3N+CH2COO}=--57+\Delta S^\circ_{H2NCH2COO}+\Delta S^\circ_{\mathbf{H2O}}-\Delta S^\circ_{\mathbf{H3O}}$=-57,137**-1204,952-453,188**+3,854=**-1597,3** $^{J}/_{K/mol}$;

$\Delta G_H=\Delta H_H-T^*\Delta S_H$=44,2-298,15***0,057**=27,2 $^{kJ}/_{mol}$; **endooergic**

$$K_{COOH}=10^{-9,78}=\frac{[H^+]\cdot[H_2NCH_2COO^-]}{\cdot[H_3^+NCH_2COO^-]Gly}\;;\;K_{eq}=K_{H3N+}/[\mathbf{H_2O}]=10^{-9,78}/55,33=10^{-11,523}=\frac{[H_3O^+]\cdot[H_2NCH_2COO^-]}{[H_2O]\cdot[H_3^+NCH_2COO^-]Gly}$$

$\Delta\mathbf{G_{eq}=-R\bullet T\bullet ln(K_{eq})}$=-8,3144•298,15•**ln**(10$^{-11,523}$)=-65,773+23,37 = **-42,403** $^{kJ}/_{mol}$,

Glycylglycine carboxylic acid C**OO**H protolysis constant: pK_{COOH}=3,14;ΔH_{Hess}=0,11 $^{kJ}/_{mol}$; ΔS_{Hess}=-128 $^{J}/_{K/mol}$

$H_3N^+CH_2(O{=}C)NHCH_2COOH+\mathbf{H_2O}\Rightarrow H_3N^+CH_2(O{=}C)NHCH_2COO^-+\mathbf{H_3O^+}$;

$\Delta H_{Hess}=\Delta H^\circ_{H3N_{glygly}COO}+\Delta H^\circ_{\mathbf{H3O}}-\Delta H^\circ_{H3N_{glygly}COOH}-\Delta H^\circ_{\mathbf{H2O}}$=0,11 $^{kJ}/_{mol}$;

$\Delta H^\circ_{H3N_{glygly}COO}=0,11+\Delta H^\circ_{\mathbf{H2O}}-\Delta H^\circ_{\mathbf{H3O}}+\Delta H^\circ_{H3N_{glygly}COOH}$=0,11**-286,65**+285,81**-737,55**= **-738,3** $^{kJ}/_{mol}$;

$\Delta S^\circ_{H3N_{glygly}COO}=-128+\Delta S^\circ_{\mathbf{H2O}}-\Delta S^\circ_{\mathbf{H3O}}+\Delta S^\circ_{H3N_{glygly}COOH}$=-128**-453,188**+3,854**-1877,952**=**-2455,3** $^{J}/_{K/mol}$;

$\Delta G_H=\Delta H_H-T^*\Delta S_H$=**0,11**-298,15***-0,128**=38,27 $^{kJ}/_{mol}$; **endooergic**; $K_a=K_{COOH}$=1/1380,4=10^(-3,14);

$$K_{COOH}=10^{-3,14}=\frac{[H^+]\cdot[H_3N^+GlyGlyCOO^-]Gly}{[H_3N^+GlyGly\,COOH]}\;;\;K_{eq}=K_{COOH}/[\mathbf{H_2O}]=10^{-3,14}/55,33=10^{-4,883}=\frac{[H_3O^+]\cdot[H_3N^+GlyGlyCOO^-]Gly}{[H_2O]\cdot[H_3N^+GlyGly\,COOH]}$$

$\Delta\mathbf{G_{eq}=-R\bullet T\bullet ln(K_{eq})}$=-8,3144*298,15***ln**(10^(-4,8831))=27,873 $^{kJ}/_{mol}$, $K_{eq}=K_{COOH}/[\mathbf{H_2O}]$=1/76383,6=10$^{-4,883}$;

Glycilglycine amonium group H_3N^+ deprotonation constant: pK_{H3N}=8,265; ΔH_{Hess}=43,4 $^{kJ}/_{mol}$; ΔS_{Hess}=-16 $^{J}/_{K/mol}$;

$H_3N^+CH_2(O{=}C)NHCH_2COO^-+\mathbf{H_2O}\Leftarrow H_2NCH_2(O{=}C)NH\text{-}CH_2\text{-}COO^-+\mathbf{H_3O^+}$;

$\Delta H_{Hess}=\Delta H^\circ_{H2N_{glygly}COO}+\Delta H^\circ_{\mathbf{H3O}}-\Delta H^\circ_{H3N_{glygly}COO}-\Delta H^\circ_{\mathbf{H2O}}$=43,4 $^{kJ}/_{mol}$;

$\Delta H^\circ_{H3N_{glygly}COO}=-(43,4-\Delta H^\circ_{H2N_{glygly}COO}+\Delta H^\circ_{\mathbf{H2O}}-\Delta H^\circ_{\mathbf{H3O}})$=-(43,4+**737,55-286,65**+285,81)= **-780,11** $^{kJ}/_{mol}$;

$\Delta S^\circ_{H3N_{glygly}COO}=-(-16-\Delta S^\circ_{H2N_{glygly}COO}+\Delta S^\circ_{\mathbf{H2O}}-\Delta S^\circ_{\mathbf{H3O}})$=-(-16+**1877,952-453,188**+3,854)=**-1412,6** $^{J}/_{K/mol}$;

$\Delta G_H=\Delta H_H-T^*\Delta S_H$=**43,4**-298,15***-0,016=48,17** $^{kJ}/_{mol}$; **endoergic**

$K_{eq}=K_{H3N+}/[\mathbf{H_2O}]$=1/10232929923=10^(-10,01)=; $K_a=K_{H3N+}$=1/184077200=10^(-8,265)=

$$K_{H3N+}=10^{-8,265}=\frac{[H^+]\cdot[H_2N\,GlyGly\,COO^-]}{[H_3N^+GlyGlyCOO^-]Gly}\;;\;K_{eq}=K_{H3N+}/[\mathbf{H_2O}]=10^{-8,265}/55,33=10^{-10,01}=\frac{[H_3O^+]\cdot[H_2N\,GlyGly\,COO^-]}{[H_2O]\cdot[H_3N^+GlyGlyCOO^-]Gly}$$

$\Delta\mathbf{G_{eq}=-R\bullet T\bullet ln(K_{eq})}$=-8,3144•298,15•**ln**(10$^{-10,01}$)=-57,137+27,873= **-29,262** $^{kJ}/_{mol}$,

Substance	ΔH°_H $^{kJ}/_{mol}$	ΔS°_H $^{J}/_{mol/K}$	ΔG°_H $^{kJ}/_{mol}$	**I=0,1 M**	I=0.2 M	Protolysis increases ΔG°_H $^{kJ}/_{mol}$
$\mathbf{Gly}_{aqua}$	-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_3NCH_2COO-	**-521,9**	**-1793,3**	23,37	$pK_a<2,351$	-	23,37
H_3NCH_2COO-	**-570,1**	**-1597,3**	-65,773	$pK_a>9,78$	-	-65,773
Average Sum	**-546**	**-1695,3**	**-42,403**	pH 7,36	-	**-42,403**
$H_3NglyglyCOO-$	**-738,3**	**-2455,3**	27,873	$pK_a<3,14$	-	27,873
$H_3NglyglyCOO-$	**-780,11**	**-1412,6**	-57,137	$pK_a>8,265$	-	-57,137
Average Sum	**-759,205**	**-1933,95**	**-29,262**	pH 7,36	-	**-29,262**
H_3O^+	-285,81	-3,854	-213,275	-	-	-
H_2O	-285,85	69,9565	-237,191	-	-	-
H_2O	**-286,65**	**-453,188**	**-151,549**	-	-	-Peptide synthesis:

$\Delta H_H=\Delta H°_{GlyGly}+\Delta H°_{H2O}-2\Delta H°_{Gly}$=**-737,55-286,65**-(2***-525,06**)=**25,92** kJ/mol=**-759,205-286,65**-(2***-546**)=**46,145** kJ/mol;

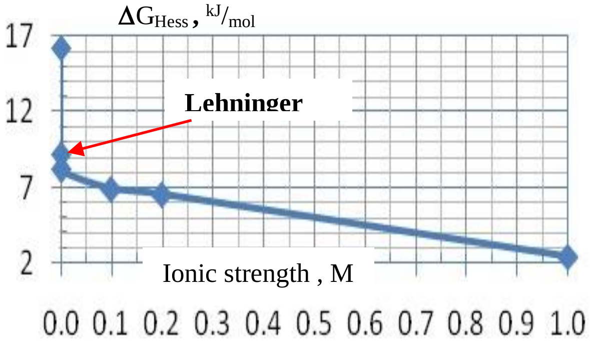
$\Delta S_H=\Delta S°_{GlyGly}+\Delta S°_{H2O}-2\Delta S°_{Gly}$=**-1877,952-453,188**-(2***-1204,952**)=**78,764** J/mol/K;=**-1933,95-453,188**-(2***-1695,3**)=**1003,5** J/mol/K;

$\Delta S_{disperse}=-\Delta H_H/T$=**-25,92**/298,15= **-86,94** J/(mol K) ; $\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}$=**-86,94+78,764=-8,176** J/(mol K);

$\Delta G_H=\Delta H_H-T*\Delta S_H$=**25,92**-298,15***0,078764**= **2,4365** kJ/mol; **endoergic;=46,145**-298,15***0,10035=16,226** kJ/mol;

$K_{Lehninger}$=exp(-9200/8,3144/298,15)=1/40,9=0,02445;**ab) $Gly_{aq}+Gly_{aq}$=> $Gly\text{-}Gly_{aq}+H_2O$**; $\Delta G_{abLehninger}$= 9,2 kJ/mol;

Chem. Phys. CRC, 2010, 1148;**BioThermodynamic**,Alberty,2006.



$Gly_{aq}+Gly_{aq}$=>$GlyGly_{aqua}+H_2O$;$\Delta G_H=\Delta G°_{GlyGly}+\Delta G°_{H2O}-2\Delta G°_{Gly}$=

=**16,2**; Lehninger = **9,2**; **8,16**; **6,94**; **6,54**; **2,43** kJ/mol

ΔG_{Hess}**=46,145-298,15*0,10035**=**16,2265** kJ/mol protolīze;I=0 M

ΔG_{Heq}=-200,55**-151,549**-(2*-180,13)= **8,161** kJ/mol endoergic;I=0 M

ΔG_{Heq}=**-195,65-151,549**-(2***-177,07**)=**6,941** kJ/mol endoergic;I=0,1 M

ΔG_{Heq}=-194,07**-151,549**-(2*-176,08)=**6,541** kJ/mol endoergic;I=0,2 M

ΔG_{Heq}=**-177,6324-151,549**-(2***-165,8056**)=**2,4298** kJ/mol; I=1 M;

Hydrolysis: $\Delta G_H=2\Delta G°_{Gly}-\Delta G°_{GlyGly}-\Delta G°_{H2O}$=**-2,44** kJ/mol; I=1 M**; K_{prot}**=exp(2429,8/8,3144/298,15)=**2,665**;

Hydrolysis: **$Gly\text{-}Gly_{aqua}+H_2O$=>$Gly_{aqua}+Gly_{aqua}$**; $\Delta G_{Lehninger}$= -9,2 kJ/mol; I=0 M;

$$\frac{[H_3N^+CH_2COO^-]Gly^2}{[H_2O]\cdot[H_3N^+GlyGlyCOO^-]Gly}$$

$K_{Lehninger}$=**exp(-$\Delta G_{Lehninger}$/R/T)**=exp(-9200/8,3144/298,15)= 0,02445 synthesis .

=$K_{Lehninger}$=**exp(-$\Delta G_{Lehninger}$/R/T)**=exp(9200/8,3144/298,15)=40,91= hydrolise .

$K_{0,2M}$=**exp(-$\Delta G_{0,2M}$/R/T)**=exp(6541/8,3144/298,15)=13,994;pH=7,36; **$\Delta G_{0,2M}$=**-8,3144*298,15***ln**(14)=**-6,54** kJ/mol

Exothermic and exoergic hydrolysis Hess free energy change negative

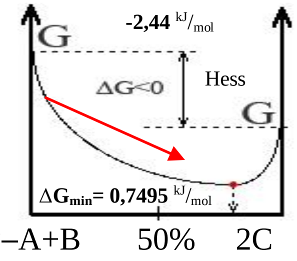
$\Delta G_{hydrolysis}$ = **-16,23** kJ/mol , but minimized reaching equilibrium mixture at ionic strength

I=0,2 M **ΔG_{min}= $\Delta G_{0,2M}$=-6,54** kJ/mol; **$K_{0,2M}$=13,994**.

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

reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.

Reactants **$Gly\text{-}Gly_{aqua}+H_2O$=>$Gly_{aqua}+Gly_{aqua}$** products



$\Delta G_{bLehninger}=-R\bullet T\bullet\ln(K_{bLehninger})=-8{,}3144*298{,}15*\ln(220500{,}2)/1000=-30{,}5\ ^{kJ}/_{mol}$;
$K_{eq}=K_{bLehninger}=\exp(-\Delta G_{bLehninger}/R/T)=\exp(30500/8{,}3144/298{,}15)=\exp(12{,}304)=220500{,}2=\dfrac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_2O]^2\cdot[ATP^{4-}]}$
$\Delta G_{Lehninger}=-R\bullet T\bullet\ln(K_{Lehninger})=-8{,}3144*298{,}15*\ln(0{,}0001739)/1000=\mathbf{21{,}46}\ ^{kJ}/_{mol}$.

pH<7,199.$ATP^{3-}+H_2O\Rightarrow ADP^{2-}+H_2PO_4^-$; $K_{Lehninger}=K_{bLehninger}*[H_3O^+]/[H_2O]=0{,}0001739=\dfrac{[H_2PO_4^-]\cdot[ADP^{2-}]}{[H_2O]\cdot[ATP^{3-}]}$;

$\Delta G_H=\Delta G°_{ADP3}+\Delta G°_{HPO42}-\Delta G°_{ATP4}-\Delta G°_{H2O}=\mathbf{-1399{,}9-1057{,}143}-(\mathbf{-2267{,}64}-237{,}191)=\mathbf{47{,}79}\ ^{kJ}/_{mol}$;

b) $ATP^{4-}+2H_2O\Rightarrow ADP^{3-}+HPO_4^{2-}+H_3O^+$; $\Delta G_{bLehninger}=-30{,}5\ ^{kJ}/_{mol}$; $K_{bLehninger}=K_{Lehninger}[H_2O]/[H_3O^+]=220500{,}2$;

$\Delta G_H=\Delta G°_{ADP3}+\Delta G°_{HPO42}+\Delta G°_{H3O}-\Delta G°_{ATP4}-2\Delta G°_{H2O}=\mathbf{-1399{,}9-1057{,}143}-213{,}275-(\mathbf{-2267{,}64+2*-151{,}549})=\mathbf{-99{,}58}\ ^{kJ}/_{mol}$;

a) $Gly_{aq}+Gly_{aq}\Rightarrow Gly\text{-}Gly_{aq}+H_2O$; $\Delta G_{0,2M}=\mathbf{6{,}54}\ ^{kJ}/_{mol}$; $K_{0,2M}=\exp(\mathbf{-6541}/8{,}3144/298{,}15)=\mathbf{0{,}07146}$.

$K_{0,2Mhydrolyse}=1/K_{0,2M}=1/\mathbf{0{,}07146}=13{,}994$;

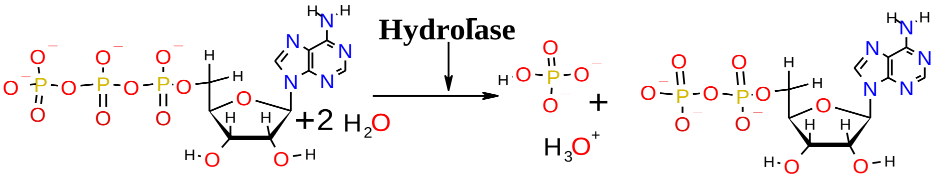
ab)$Gly_{aq}+Gly_{aq}+ATP^{4-}+H_2O\Rightarrow GlyGly_{aq}+ADP^{3-}+HPO_4^{2-}+H_3O^+$;$\Delta G_{ab}=\Delta G_{0,2M}+\Delta G_{bLehninger}=\mathbf{6{,}54}-30{,}5=-23{,}96\ ^{kJ}/_{mol}$;

$\Delta G_H=\Delta G°_{Gly\text{-}Gly}+\Delta G°_{ADP3}+\Delta G°_{HPO42}+\Delta G°_{H3O}-2\Delta G°_{Gly}-\Delta G°_{ATP4}-\Delta G°_{H2O}=$
$=\mathbf{-177{,}632-1399{,}9-1057{,}143}-213{,}275-(2*\mathbf{-165{,}806-2267{,}64-151{,}549})=\mathbf{-97{,}15}\ ^{kJ}/_{mol}$;

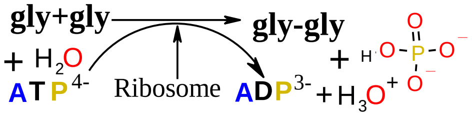
Substance $\Delta H°_H\ ^{kJ}/_{mol}$ $\Delta S°_H\ ^{J}/_{mol/K}$ $\Delta G°_H$, $^{kJ}/_{mol}$; $=\mathbf{-177{,}632-1399{,}9-1057{,}143}-213{,}275-(2*\mathbf{-165{,}806-2267{,}64-151{,}549})=\mathbf{-97{,}15}\ ^{kJ}/_{mol}$;

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) $ATP^{4-}+2H_2O\Rightarrow ADP^{3-}+HPO_4^{2-}+H_3O^+$; $\Delta G_{bLehninger}=-30{,}5\ ^{kJ}/_{mol}$;
$K_{bLehninger}=220500{,}2$; pH=7,36;



a) $Gly_{aq}+Gly_{aq}\Rightarrow Gly\text{-}Gly_{aq}+H_2O$; $\Delta G_{0,2M}=\mathbf{6{,}54}\ ^{kJ}/_{mol}$;



ab)$Gly_{aq}+Gly_{aq}+ATP^{4-}+H_2O\Rightarrow GlyGly_{aq}+ADP^{3-}+HPO_4^{2-}+H_3O^+$;
$\Delta G_{ab}=\Delta G_{0,2M}+\Delta G_{bLehninger}=\mathbf{6{,}54}-30{,}5=-23{,}96\ ^{kJ}/_{mol}$;
Peptide bond synthesis in Ribosomes.

$K_{eq}=K_{0,2M}K_b=\mathbf{0{,}07146}*220500{,}2=[GlyGly]*[ADP^{3-}]*[HPO_4^{2-}]*[H_3O^+]/[Gly]^2/[ATP^{4-}]/[H_2O]=15756{,}9$.

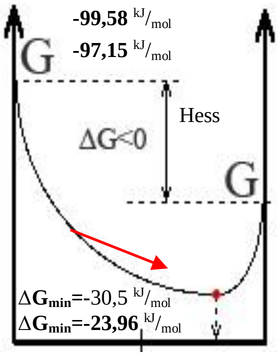
$$K_{eq\_a0,2Mb}=K_{0,2M}K_b=\frac{[H_3N^+GlyGlyCOO^-]Gly\cdot[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_3N^+CH_2COO^-]Gly^2\cdot[H_2O]\cdot[ATP^{4-}]}=\mathbf{15756{,}944}\ .$$

$\Delta G_{eqLehninger}=-R\bullet T\bullet\ln(K_{eqLehninger})=-8{,}3144*298{,}15*\ln(15756{,}944)/1000=\mathbf{-23{,}959}\ ^{kJ}/_{mol}$.

$K_{eqLehninger}=K_{Lehninger}[H_2O]/[H_3O^+]=0{,}000012428*55{,}3457/10^{\wedge(-7,36)}=\mathbf{15756{,}944}$.

Lehninger exoergic ATP^{4-} hydrolise **GlyGly** synthesis in Ribosome Hess free energy change at pH=7,36 negative $\Delta G_{hydrolise}=\mathbf{-99{,}58}\ ^{kJ}/_{mol}$, $\mathbf{-97{,}15}\ ^{kJ}/_{mol}$, but is minimized $\Delta G_{min}=\Delta G_{eq}=-30{,}5\ ^{kJ}/_{mol}$ and = $\mathbf{-23{,}96}\ ^{kJ}/_{mol}$ reaching equilibrium mixture to $K_{bLehninger}=220500{,}2$ and $K_{eq\_a0,2Mb}=\mathbf{15757.}$ Le Chatelier principle is Prigogine attractor for

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



Free energy change minimum reaching establishes equilibrium.

reactants A+2B+C 50% D+E+F+G
$ATP^{4-}+Gly_{aq}+Gly_{aq}+H_2O$
products $GlyGly_{aq}+ADP^{3-}+HPO_4^{2-}+H_3O^+$;

THERMODYNAMICS Exercise VIII a Maltose hydrolise to **Glc**$^{-}$+**Glc**

Calculate ΔH_H ΔS_H ΔG_H at standard conditions 298.15 K. Reaction **exothermic** , **athermic**, **endothermic**? For the **Lactose**$^{-}$hydrolise to Glucose and Galactose! Will be **exoergic** or **endoergic**!

Lehninger 2000 $\Delta G_{Lehninger}$=-15,9 $^{kJ}/_{mol}$;Lactose+**H_2O**<=>Glc+Gal;pH=7,36; **ΔG_H**= **-20,3** $^{kJ}/_{mol}$;

Maltose^{-}hydrolise to Glucose! Will be **exoergic** or **endoergic**!

Lehninger 2000 $\Delta G_{Lehninger}$=-15,5 $^{kJ}/_{mol}$;Maltose+**H_2O**<=>Glc+Glc;pH=7,36; **$\Delta G_{ALBERTY}$**= **19,9** $^{kJ}/_{mol}$;

BioThermodyn 2006 pH=7,36; reactants => products pH=7,199; pH=7,36 ; I=0,25 M

Substance	$\Delta H°_H$ $^{kJ}/_{mol}$	$\Delta S°_H$ $^{J}/_{mol/K}$	$\Delta G°_H$ $^{kJ}/_{mol}$
H_2O	-285,85	69,9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**
Gal	**-1260,14**	**-2901,428**	**-395,080**
Glc	-1263,78	269,45	-919,96
Glc	**-1267,13**	**-2901,49**	**-402,05**
Maltose	**-2247,12**	**-5415,032**	**-632,6312**
Lactose	**-2242,14**	**-5423,03**	**-625,27**

BioThermodyn06

$\Delta G_{ALBERTY}=\Delta G°_{Glc}+\Delta G°_{Gal}-\Delta G°_{Lactoze}-\Delta G°_{H2O}$=**-402,05**2**-395,08-(-625,27-151,549)**= **-20,3** $^{kJ}/_{mol}$ **exoergic**;

$\Delta G_{ALBERTY}=2\Delta G°_{Glc}-\Delta G°_{Maltose}-\Delta G°_{H2O}$ =2***-402,05-(-632,6312-151,549)**= **-19,92** $^{kJ}/_{mol}$ **exoergic**;

1. $\Delta H_H=2\Delta H°_{Glc}-\Delta H°_{MaltoHe}-\Delta H°_{H2O}$=2***-1267,13-(-2247,12-151,549)**= **-135,591** $^{kJ}/_{mol}$ **exothermic** ;

2. $\Delta S_{disperse}$= $\Delta H_H/T$=**-135,591**/298,15= **454,774442** $^{J}/_{(mol\ K)}$;

2. $\Delta S_H=2\Delta S°_{Glc}-\Delta S°_{Maltose}-\Delta S°_{H2O}$ =2***-2901,49-(-5415,032-453,188)**= **65,24** $^{J}/_{mol/K}$;

3.$\Delta S_{total}=\Delta S_H+\Delta S_{disperse}$=**454,774442+65,24**= **520,0144442** $^{J}/_{(mol\ K)}$;

$\Delta G_H=\Delta H_H-T^*\Delta S_H$=**-135,591**-298,15*0,**06524**=**-155,0423** $^{kJ}/_{mol}$ **exoergic** ;

3. T•ΔS_{total}=**520,0144442***298,15=**155,0423** $^{kJ}/_{mol}$ TΔS_{total} <u>bound energy dispersed</u> **spontaneous**.

K$_{Lehninger}$=**exp(-ΔG**$_{Lehninger}$**/R/T**)=exp(15500/8,3144/298,15)=519,4=$10^{2,7155}$

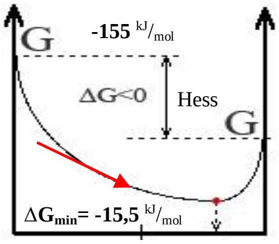
$$K_{eq}=\mathbf{K}_{Lehninge}=519,4=\frac{[Glc]\cdot[Glc]}{[Maltose]\cdot[H_2O]}$$

Prigogine attractor minimum $\Delta G_{min}=\Delta G_{eq}$=**-19,9** $^{kJ}/_{mol}$; $\Delta G_{Lehninger}$=-15,5 $^{kJ}/_{mol}$; **ΔG_{Hess}**= **-155** $^{kJ}/_{mol}$;
Endothermic and exoergic hydrolysis Hess free energy change negative

$\Delta G_{hydrolysis}$ = **-155** $^{kJ}/_{mol}$, but Prigogine attractor favored equilibrium constant

free energy change minimum $\longrightarrow$ **ΔG_{min}= ΔG_{eq} = -15,5** $^{kJ}/_{mol}$;

$$\text{at reaching equilibrium } K_{eq}=\frac{[Glc]\cdot[Glc]}{[Maltose]\cdot[H_2O]}=\mathbf{519,4;}$$



Reactants and products
Glc+Glc .

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.

THERMODYNAMICS Exercise VIII b Lactose hydrolise to **Glc**$^-$+**Gal** reaction BioThermodyn 2006 pH=7,36 Calculate ΔH_H ΔS_H ΔG_H at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? For the **Lactose**$^-$hydrolise reaction with water to Glucose and Galactose! Will be **exoergic** or **endoergic**!

Lehninger 2000 $\Delta G_{Lehninger}$= -15,9 $^{kJ}/_{mol}$; Lactose + H_2O <=> Glc + Gal; pH=7,36; ΔG_{Hess}= **-20,3** $^{kJ}/_{mol}$; I=0,25 M

BioThermodyn 2006 pH=7,36 reactants <=> products ;

Substance	$\Delta H°_H$ $^{kJ}/_{mol}$	$\Delta S°_H$ $^{J}/_{mol/K}$	$\Delta G°_H$ $^{kJ}/_{mol}$	
H_2O	-285,85	69,9565	-237,191	
H_2O	**-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**
Lactose	**-2242,14**	**-5423,03**	**-625,27**	

$\Delta G_{Hess}=\Delta G°_{Glc}+\Delta G°_{Gla}-\Delta G°_{Laktoze}-\Delta G°_{H2O}$=**-402,05-395,08-(-625,27-151,549)= -20,311** $^{kJ}/_{mol}$ **eksoerģiska**

1. $\Delta H_H=2\Delta H°_{Glc}-\Delta H°_{MaltoHe}-\Delta H°_{H2O}$=2*-**1267,13-(-2247,12-151,549)= -135,591** $^{kJ}/_{mol}$ **exothermic** ;
2. $\Delta S_{disperse}$= $\Delta H_H/T$=**-135,591**/298,15= **454,774442** $^{J}/_{(mol\ K)}$;
2. $\Delta S_H=2\Delta S°_{Glc}-\Delta S°_{Maltose}-\Delta S°_{H2O}$ =2*-**2901,49-(-5415,032-453,188)= 65,24** $^{J}/_{mol/K}$;
3.$\Delta S_{total}=\Delta S_H+\Delta S_{disperse}$=**454,774442+65,24= 520,0144442** $^{J}/_{(mol\ K)}$;

$\Delta G_H=\Delta H_H-T*\Delta S_H$=**-135,591**-298,15*0,**06524=-155,0423** $^{kJ}/_{mol}$ **exoergic** ;

3. T•ΔS_{total}=**520,0144442***298,15=**155,0423** $^{kJ}/_{mol}$ $T\Delta S_{total}$ bound energy dispersed **spontaneous**.

$K_{Leninger}=\exp(-\Delta G_{Leninger}/R/T)$=exp(20300/8,3144/298,15)=3601

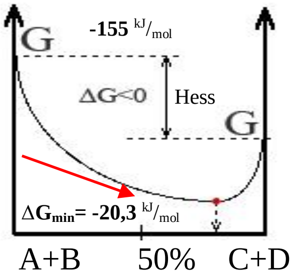
$$K_{eq}=K_{Leninge}=3601=\frac{[Glc]\cdot[Gal]}{[Laktoze]\cdot[H_2O]}$$

Prigogine attractor minimum $\Delta G_{min}=\Delta G_{eq}$=-15.9 $^{kJ}/_{mol}$; $\Delta G_{Lehninger}$=-15,9 $^{kJ}/_{mol}$; ΔG_{Hess}= **-20,311** $^{kJ}/_{mol}$;

Prigogine attractor favored equilibrium constant by Hess law solution.

Endothermic and exoergic hydrolysis Hess free energy change negative $\Delta G_{HessHydrolysis}$= **-155** $^{kJ}/_{mol}$, but Prigogine attractor favored equilibrium constant free energy change minimum $\longrightarrow$ $\Delta G_{min}=\Delta G_{eq}$ = **-20,3** $^{kJ}/_{mol}$

reaching equilibrium $K_{eq}=\frac{[Glc]\cdot[Gal]}{[Lactose]\cdot[H_2O]}$ =3601. Le Chatelier principle is reaching Prigogine attractor - Free energy change minimum ΔG_{min} in mixture. Free energy change minimum reaching establishes equilibrium.



Lactose+H_2O Glc+Gal_reactants & products.

THERMODYNAMICS Exercise IX bicarbonate neutralisation for CO_2 gas evaporation

Along concentration gradients through proton H^+ channels $[H_3O^+]_{right}/[H_3O^+]_{left}$ and through bicarbonate HCO_3^- channels $[HCO_3^-]_{right}/[HCO_3^-]_{left}$ evaporation in lungs of water and CO_2 gas.

Substance	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
H_3O^+	-285,81	-3,854	-213,275
HCO_3^-	-689,93	98,324	-586,94
HCO_3^-	**-692,4948**	**-494,768**	**-544,9688**
H_2O	-285,85	69,9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**
$H_2O\uparrow_{gas}$	-241,8352	188,7402	-228,6
$CO_2\uparrow_{gas}$	-393,509	213,74	-394,359
CO_{2aq}	-413,798	117,5704	-385,98

$Q+H_3O^++HCO_3^- \xRightarrow{\text{channals } H^+;\ HCO_3^-} H_2O+H_2O_{gas}+CO_{2gas}+\Delta G$

$\Delta H_H=\Delta H^\circ_{H_2O}+\Delta H^\circ_{H_2Ogas}+\Delta H^\circ_{CO_2gas}-\Delta H^\circ_{H_3O}-\Delta H^\circ_{HCO_3}=54{,}546$ kJ/mol;

$=-285{,}85-241{,}8352-393{,}509-(-285{,}81-689{,}93)=54{,}546$ kJ/mol **endoth**

$\Delta G_H=\Delta G^\circ_{H_2O}+\Delta G^\circ_{H_2Ogas}+\Delta G^\circ_{CO_2gas}-\Delta G^\circ_{H_3O}-\Delta G^\circ_{HCO_3}=-59{,}935$ kJ/mol

$=-237{,}191-228{,}6-394{,}359-(-213{,}275-586{,}94)=-59{,}935$ kJ/mol **exoergic**

$\Delta S_{dispersed}=-\Delta H_H/T=-54{,}546/298{,}15=-182{,}948$ J/mol/K;

$\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=-182{,}948+377{,}966=195{,}016$ J/mol/K

$\Delta G_H=\Delta H_H-T*\Delta S_H=54{,}546-298{,}15*0{,}377966=-58{,}144$ kJ/mol; **exoergic**

$\Delta S_{Hess}=\Delta S^\circ_{H_2O}+\Delta S^\circ_{H_2O}\uparrow_{gas}+\Delta S^\circ_{CO_2}\uparrow_{gas}-\Delta S^\circ_{H_3O}-\Delta S^\circ_{HCO_3}=377{,}966$ J/mol/K

$=69{,}956+188{,}74+213{,}74-(-3{,}854+98{,}324)=353{,}652-94.47=+377{,}966$ J/mol/K;

$T\bullet\Delta S_{total=}195{,}016$ J/K/mol$\bullet 298{,}15$ K=**+58.144**.....................kJ/mol;

bound TΔSn← <u>dispersed-lost energy $\Delta G_{reverseHess}$ ←</u>.Q= -54.546 kJ/mol **spontaneous** $\Delta G_{Hess}=-58{,}14$ kJ/mol.

channels H^+ : $\Delta G_H=RT\ln([H_3O^+]_{right}/[H_3O^+]_{left})$

channels HCO_3^-: $\Delta G_{HCO_3}=RT\ln([HCO_3^-]_{right}/[HCO_3^-]_{left})$

$\Delta S_H=-R\ln(10^{-5{,}5}/0{,}02754)=75{,}42909$ J/mol/K...............

$\Delta S_{HCO_3}=-R\ln(0{,}0154/0{,}0338919)=6{,}55847$............. J/mol/K

$\Delta S_H=377{,}966+75{,}42909+6{,}55847=459{,}954$ J/mol/K..........

$\Delta G_H=RT\ln(10^{-5{,}5}/0{,}02754)=-22{,}48918$ kJ/mol.......

$\Delta G_{HCO_3}=RT\ln(0{,}0154/0{,}0338919)=-1{,}9554$kJ/mol..........

$\Delta G_H=\Delta H_H-T*\Delta S_H=+54{,}546-298{,}15*0{,}459954=-82{,}589$..............kJ/mol; **exoergic**............

$T\bullet\Delta S_{Htotal=}277{,}004$ J/K/mol$\bullet 298{,}15$ K$=-58{,}144-22{,}48918-1{,}9554=$ **+82.589** kJ/mol...

bound TΔSn← <u>dispersed-lost energy ΔGreverse$_{Hess}$ ←</u>.Q= -54.546 kJ/mol.**spontaneous** $\Delta G_{Hess}=-82{,}589$ kJ/mol...

THERMODYNAMICS Exercise X. $HCO_3^-+H_3O^+$ products apparent carbonic acid $H_2O+H_2CO_3$

Calculate ΔH_H ΔS_H ΔG_H at standard conditions 298.15 K. Reaction is **exothermic** , **athermic**, **endothermic**? For transfer bicarbonate and proton through channels on membrane ***lung*** epithelia cell surface $H_2O+H_2CO_3$ using the data table! Will be **exoergic** or **anenergic** or **endoergic**! $H_3O^++HCO_3^-\overset{\text{Membrane}}{\longleftrightarrow}H_2O+H_2CO_3+\Delta G+Q$.

Substance	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
H_3O^+	-285,81	-3,854	-213,275
HCO_3^-	-689,93	98,324	-586,94
HCO_3^-	**-692,4948**	**-494,768**	**-544,9688**
H_2CO_3	-699,65	187,00	-755,47
H_2O	-285,85	69,9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**
$H_2O\uparrow_{gas}$	-241,8352	188,7402	-228,6
$CO_2\uparrow_{gas}$	-393,509	213,74	-394,359
CO_{2aq}	-413,798	117,5704	-385,98

$\Delta H_{Hess}=\Sigma\Delta H^\circ_{products}-\Sigma\Delta H^\circ_{reactants}$; $\Delta S_{Hess}=\Sigma\Delta S^\circ_{products}-\Sigma\Delta S^\circ_{reactants}$

$\Delta G_{Hess}=\Delta H_{Hess}-T\bullet\Delta S_{Hess}$

$H_{Hess}=\Delta H^\circ_{H_2O}+\Delta H^\circ_{H_2CO_3}-\Delta H^\circ_{H_3O}-\Delta H^\circ_{HCO_3}=\mathbf{-7{,}9952}$ kJ/mol;

$=-285{,}85-699{,}65-(-285{,}81-689{,}93)=-9.76$ kJ/mol **exothermic**....

$=\mathbf{-286{,}65}-699{,}65-(-285{,}81\mathbf{-692{,}4948})=\mathbf{-7{,}9952}$ kJ/mol

$\Delta G_{Hess}=\Delta G^\circ_{H_2O}+\Delta G^\circ_{H_2CO_3}-\Delta G^\circ_{H_3O}-\Delta G^\circ_{HCO_3}=\mathbf{-148{,}8}$ kJ/mol

$=-237{,}191-755{,}47-(-213{,}275-586{,}94)=-192{,}4$ kJ/mol **exoergic**

$=\mathbf{-151{,}549}-755{,}47-(-213{,}275\mathbf{-544{,}9688})=\mathbf{-148{,}8}$ kJ/mol **exoergic**

$\Delta S_{Hess}=\Delta S^\circ_{H_2O}+\Delta S^\circ_{H_2CO_3}-\Delta S^\circ_{H_3O}-\Delta S^\circ_{HCO_3}=\mathbf{232{,}4}$ J/mol/K;

$=69{,}956+187-(-3{,}854+98{,}324)=162{,}486$ J/mol/K;

$\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=\mathbf{26{,}816+232{,}4=259{,}216}$ J/mol/K; $=\mathbf{-453{,}188}+187-(-3{,}854\mathbf{-494{,}768})=\mathbf{232{,}4}$ J/mol/K;

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=\mathbf{-7{,}9952}-298{,}15*0{,}\mathbf{2324=-77{,}3}$ kJ/mol ; **exoergic**.

$T\bullet\Delta S_{total}=\mathbf{0{,}259216}$ J/K/mol$\bullet 298{,}15$ K=**+77,3** kJ/mol ; $\Delta S_{dispersed}=-\Delta H_H/T=\mathbf{7{,}9952}/298{,}15=\mathbf{26{,}82}$ J/mol/K;

bound TΔSn← <u>dispersed-lost energy into products and surrounding</u>

THERMODYNAMICS Exercise XIII, XIV. O_2↑gas respiration through membrane aquaporins to form $O_{2aqua-Blood}$

AIR O_2↑gas assimilation reaction for human body respiration through membrane aquaporins to form concentration. **endoergic** $\Delta G+O_2\uparrow_{gas\ AIR}+H_2O\xrightarrow{Aquporin}O_{2aqua-Blood}+Q$; $O_{2aqua}+Q\Rightarrow O_{2gas}+H_2O+\Delta G$ **exoergic**

Substance	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$ kJ/mol
O2aqua	**-11.70**	**-94,2**	**16,40**
O2aqua	-11.715	110,876	16,4
O_2↑gas	0,0	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**

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

Alberty [8];$\Delta G_{HAlberty}=G_{O2aqua}-G_{O2gas}-G_{H2O}$ =**330-303-0=27** kJ/mol;

$\Delta H_H=\Delta H°_{O2aqua}-\Delta H°_{O2gas}-\Delta H°_{H2O}=$**-11.7**-0+**286,65=274,95** kJ/mol;

$\Delta S_{dispersed}=-\Delta H_{Hess}/T=$**-274,95**/298.15=**-922,2** J/mol/K ;

$\Delta S_{Hess}=\Delta S°_{O2aq}-\Delta S°_{O2gas}-\Delta S°_{H2O}=$**-164,2** J/mol/K

=110,876-205,152-69,9565=-**164,2** J/mol/K

$\Delta G_H=\Delta H_H-T*\Delta S_H=$**274,95**-298,15*-0,**1642=323,9** kJ/mol **endoergic**;

$\Delta S_{total}=\Delta S_H+\Delta S_{izkliede}$=-164,2 **-922,2**= -1086,4 J/mol/K ;

$T\bullet\Delta S_{kopējā}$=-1,0864 kJ/K/mol•298,15K= **-323,9** kJ/mol; bound TΔSn← accumulate energy non-**spontaneous**

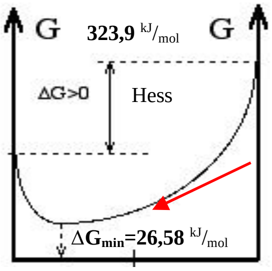
ELSEVIER, Rotating Electrode Method and Oxygen reduction Electrocatalysts, 2014, p.1-31,

1. WeiXingaMinYinbQingLvbYangHubChangpengLiubJiujunZhangc. As pure 1atm mol fraction is $[O_{2gas}]$ =1 .

Solubility product $K_{sp}=\dfrac{[O_{2\ aqua}]}{[O_{2\ gas}]\cdot[H_2O]}$ $=K_{O2}/[H_2O]=1.22*10^{-3}/55.3=2.205*10^{-5}$ and ratio $\dfrac{[O_{2\ aqua}]}{[O_{2\ gas}]}$ $=K_{O2}$ as value $1.22*10^{-3}$ M/1 ELSEVIER distribution between gas and water solubility from Air 20.95% $[O_{2Air}]=0.2095$ is concentration $[O_{2aqua}]=1.22*10^{-3}*0.2095=2.556*10^{-4}$ M;. $[O_{2aqua}]/0.2095=1.22*10^{-3}$ M; Solubility free energy change $\Delta G_{sp}=-R\bullet T\bullet\ln(K_{sp})=-8.3144*298.15*\ln(2.205*10^{-5})=-8.3144*298.15*6.414=$**26.58** kJ/mol;

Hess law **is** exothermic and endoergic oxygen water solubility free energy change positive $\Delta G_{solubility}$=**323,9** kJ/mol ,

but minimized at equilibrium $K_{sp}=\dfrac{[O_{2\ aqua}]}{[O_{2\ gas}]\cdot[H_2O]}$ $=2.205*10^{-5}=10^{-4.66}$ free energy change value $\Delta G_{min}=\Delta G_{eq}$=**26.58** kJ/mol . Le Chatelier principle is Prigogine attractor for free energy change minimum ΔG_{min} reaching the equilibrium.



A+B 50% C+D

reactants $O_2\uparrow_{gas}+H_2O$

product O_{2aqua}.

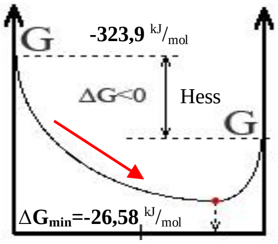
Evapration $K_{eq}=\dfrac{[O_{2\ gas}]\cdot[H_2O]}{[O_{2\ aqua}]}$ $=[H_2O]/K_{O2}$=55,3457339/1,22/10^(-3)=45365,4;

Hess endothermic and exoergic oxygen O_{2gas} evaporation free energy change is negative ΔG_{Hess}=**-323,9** kJ/mol , but minimized by evaporation equilibrium state

$\Delta G_{min}=\Delta G_{eq}=-R\bullet T\bullet\ln(K_{eq})$=-8,3144*298,15*ln(45365,35566)=**-26,58** kJ/mol

reaching the equilibrium state K_{eq}=45365,4 - the Prigogine attractor for non equilibrium states. Free energy change minimum reaching establishes equilibrium. Solubility from air **$[O_{2aqua}]$**$=9.77\cdot10^{-5}$ M if osmolar, ionic force C_{osm}=0.305 M, **I**=0.25 M, oxygen air 20.95% concentration at physiologic condition, but zero osmolar and ionic force concentration C_{osm}=0 and **I**=0 M like pure distilled water $[O_{2aqua}]=2.556*10^{-4}$ M.

Physiologic $K_{O2Asins}=[O_{2aqua}]/[O_{2gas}]=9.768\cdot10^{-5}/0.2095=4.663*10^{-4}=10^{-3.3314}=10^{pK}$ is equilibrium constant. Arterial $[O_{2aqua}]=6\cdot10^{-5}$ M and venous $[O_{2aqua}]=0.486\cdot10^{-5}$ M concentrations are isooxia conditions for Human blood $[O_{2aqua}]$ concentrations .



A+B 50% C+D

reactant O_{2aqua}

products $O_2\uparrow_{gas}+H_2O$

Avaporation $\Delta H_H=\Delta H°_{O2gas}+\Delta H°_{H2O}-\Delta H°_{O2aqua}$=**-286,65+0-11,7=-274,95** kJ/mol is

exothermic exoergic $\Delta G_H=\Delta H_H-T*\Delta S_H$=**11.7**-298.15***0.399352=-77.55** kJ/mol.

Alberty [8] free energy for hydrogen gas $G°_{H2gas}$=**85.64** kJ/mol lets appreciate oxygen Free energy for gas and aqua G_{O2gas}=**303.1** kJ/mol and G_{O2aqua}=**329.68** kJ/mol ,

Photosynthesis restore global atmospheric attractor $[O_{2gas\_AIR}]$=0.2095 mol fraction of oxygen.
At equilibrium water concentration $[O_{2aqua}]=[O_{2gas\_AIR}]*[H_2O]/K_{sp}$=0.2095*55.3/45365=0.0002556 M maintains atmospheric oxygen $[O_{2gas\_AIR}]$=0.2095 mol fraction. Photosynthesis $[O_{2aqua\_photosynthesis}]>[O_{2aqua}]$=0.0002556 M activate concentration in water over equilibrium: and oxygen evaporates. Photosynthesis slow down reaching equilibrium concentration $[O_{2aqua}]$=0.0002556 M, what reaches Prigogine attractor free energy change minimum in global photosynthesis to maintain oxygen $[O_{2gas\_AIR}]$=0.2095 mol fraction in atmosphere .

Alberty and CRC Thermodynamic data. [8,1] Exel $\mathbf{2H_2O_2 \Rightarrow O_{2aqua} + 2H_2O + Q + \Delta G}$;

Substance	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$ kJ/mol
$\mathbf{C_{gr}}$	0	5.74	0
G_{CO2gr}	G_{gr}	-	**91.26**
$\mathbf{CO}\uparrow_{gas}$	-110.525	197.674	-137.2
$\mathbf{CO_2}\uparrow_{gas}$	**-393.5**	**2.9**	**-394.36**
$\mathbf{CO_{2aq}}$	-413.8	117.5704	-385.98
$\mathbf{HCO_3^-}$	**-692.495**	**-494.768**	**-544.9688**
$\mathbf{H_{2aq}}$	**-5.02**	**-363.92**	**103.24**
$\mathbf{H_{2gas}}$	**-0.82**	**-283.82**	**85.64**
$\mathbf{H_{2gas}}$	0	130.68	0
$\mathbf{H_{atomic}}$	218.0	114.7	203.3
$\mathbf{OH^-}$	-230.00	-10.539	-157.2
$\mathbf{O_2}\uparrow_{gas}$	0	205.152	0
$\mathbf{O_{2aqua}}$	-11.715	110.876	16.4
$\mathbf{O_{2aqua}}$	**-11.7**	**-94.2**	**16.4**
$\mathbf{H_2O_{2aqua}}$	**-191.99**	**-481.688**	**-48.39**
$\mathbf{H_2O_{2(aq)}}$	-191.17	143.9	-134.03
$\mathbf{H_2O}$	-285.85	69.9565	-237.191
$\mathbf{H_2O}$	**-286.65**	**-453.188**	**-151.549**
$\mathbf{H_2O}\uparrow_{gas}$	-241.8352	188.74024	-228.6
$\mathbf{CH_{4aq}}$	**-90.69**	**-763.476**	**136.95**
$\mathbf{CH_{4gas}}$	**-76.46**	**-648.44**	**120.56**
$\mathbf{CH_{4gas}}$	-74.6	186.3	-50.5

$\Delta G_{eqStandard} = (E°_{Red} - E°_{Ox})*F*n = (0.89916 - 2.08366)*96485*2 = -228.6$ kJ/mol

$\Delta G_{eqStandard} = G_{O2\ aqua} + G_{O2sp} + 2*G_{H2O BioChemistry} - 2*G_{H2O2} = \mathbf{-228.6}$ kJ/mol;

carbon (graphite) $G_{gr} = \mathbf{91.26}$ kJ/mol;

$= \mathbf{303.1} + \mathbf{26.58} + 2*\mathbf{85.65} - (2*G_{H2O2}) = \mathbf{-228.6}$ kJ/mol; **Alberty**

$G_{H2O2} = (G_{O2aqua} + G_{O2sp} + 2G_{H2O\_Biochemistry} - \Delta G_{eqStandard})/2 = \mathbf{364.79}$ kJ/mol

364.79 kJ/mol $= \mathbf{729.58}/2 = (\mathbf{303.1} + 26.58 + 2*\mathbf{85.65} + \mathbf{228.6})/2 = \Delta G_{H2O2}$;

$G_{CgrCH4gas} = G_{CO2gr} = -G_{Hess\_CO2gas} - G_{O2gas} = \mathbf{394.36} - \underline{303.1} = \mathbf{91.26}$ kJ/mol ;

$G°_{H2aq} = \underline{\mathbf{103.24}}$ kJ/mol; **Alberty** R.A. Biochem. Thermodynamic's, 2006.

$G°_{H2gas} = \underline{\mathbf{85.64}}$ kJ/mol; **Alberty** R.A. Biochem. Thermodynamic's, 2006

$G_{O2gas} = 303.1$ kJ/mol; $\mathbf{H_{2gas}} + 1/2\mathbf{O_{2gas}} \Rightarrow \mathbf{H_2O}$; $G°_{H2O} = -237.19$ kJ/mol;

$2\mathbf{H_{2gas}} + \mathbf{O_{2aqua}} \Rightarrow 2\mathbf{H_2O} \Leftrightarrow \mathbf{H_3O^+} + \mathbf{OH^-}$;

$\Delta G_{eqH2gas+O2gas} = (2G_{H2O} - 2G°_{H2gas} - G_{O2gas})/2 = -474.38/2 = -237.19$ kJ/mol ;

$\Delta G°_{H2OHess} = 2*0 - 2*\mathbf{85.64} - 303.1 = -474.38/2 = -237.19$ kJ/mol;

$G_{O2gas} = (-\Delta G°_{H2OHess} - G°_{H2gas})*2 = (237.19 - \underline{\mathbf{85.64}})*2 = \underline{303.1}$ kJ/mol;

Oxygen aqua $G_{O2aqua} = G_{O2gas} + G_{O2sp} = 303.1 + 26.58 = 329.68$ kJ/mol ;

$G_{O2sp} = -\mathbf{R \bullet T \bullet \ln(K_{sp})} = 26.58$ kJ/mo ; $\mathbf{K_{sp}} = 2.205*10^{-5}$; 3rd page;[14]

$\Delta G_{HessH2O} = G°_{H2O} - (-_{Hess}G°_{H2} - _{Hess}G°_{O2gas}/2) = -237.19 - (0+0) = -237.19$ kJ/mol

BioChemic background zero $G_{CO2gasO2} = G_{H2O} = 0$ kJ/mol;

$2G_{OH-} - G_{H2aq} - G_{O2aqua} = 2G_{OH-} - \mathbf{103.24} - 329.68 =$

$\mathbf{H_{2aq}} + \mathbf{O_{2aq}} + 2e^- <=> 2\mathbf{OH^-}$; $E°_{H2aqO2aq=2OH-} =$??? Volts

BioTherm2006 Alberty R.A. $G_{H2O\_Biochemistry} = \mathbf{85{,}65}$ kJ/mol

BioTherm2006 Alberty R.A. Biochem. Thermodynamic's 463, 2006

$_{Hess}G_{O2gas} = 0$; $_{Hess}G°_{H2} = 0$; $_{Hess}G°_{gr} = 0$; $_{Hess}G°_{N2gas} = 0$; $_{Hess}G°_{Srombic} = 0$;

Red $H_2O_2 + 2H_2O = O_{2aqua} + 2H_3O^+ + 2e^-$; absolūtā $E°_{H2O2aqRed} = 0{,}4495$ V Alberta University classic $\mathbf{E°}_{H2O2} = 0{,}7975$ V;

$E_{Red} = E°_{H2O2} + 0{,}0591/2 \bullet \lg([O_{2aqua}]*[H_3O^+]^2/[H_2O_2]/[H_2O]^2) = 0{,}4495 + 0{,}0591/2*\lg(6*10^{\wedge(-5)}*10^{\wedge(-7{,}36*2)}/1/55{,}3^{\wedge 2}) = 0{,}23643$ V

Oks $H_2O_2 + 2H_3O^+ + 2e = 4H_2O$; $E°_{H2O2aqOx} = 1{,}6855$ V [18]; $[H_2O_2] = 1$ M; $[O_{2aqua}] = 6*10^{-5}$ M, $[H_3O^+] = 10^{-7{,}36}$ M, $[H_2O] = 55{,}3$ M

$E_{Ox} = E°_{H2O2Ox} + 0{,}0591/2 \bullet \log([H_2O]^4/[H_2O_2]/[H_3O^+]^2) = 2{,}08366 + 0{,}0591/2*\log(55{,}3^{\wedge}4/10^{\wedge}(-7{,}36*2)*1) = 1{,}443$ V;

$\Delta G_{eqStandart} = (E_{Red} - E_{oOx})*\mathbf{F}*\mathbf{n} = (0{,}4495 - 1{,}6855)*96485*2 = (-1{,}236)*96485*2 = \mathbf{-238{,}51}$ kJ/mol

$\Delta G_{Alberty} = \mathbf{-238{,}51}$ kJ/mol; $\underline{G_{Standarta\mathbf{H2O2}} = G_{\mathbf{O2}aqua} + 2*G_{\mathbf{H2O}} + \Delta G_{Alberty} = (\mathbf{330+2*0+238{,}51})/2 = \mathbf{568{,}5}/2 = \mathbf{284{,}25}\ \text{kJ/mol}}$;

$\Delta \mathbf{G}_{\mathbf{eq}BioChem} = (E_{Red} - E_{oOx})*\mathbf{F}*\mathbf{n} = (-0{,}2132 - 1{,}0455)*96485*2 = (-1{,}2066)*96485*2 = \mathbf{-242{,}9}$...... kJ/mol ;

$2*G_{H2O2} = G_{O2Biochem\_arteriaj} + 2*G_{H2OBioChemistry} + \Delta G_{Alberty} \underline{\mathbf{= 330 + 2*0 + 238{,}51} = 2*\mathbf{284{,}5} = \mathbf{568{,}5}}$ kJ/mol;;

Solubility $\mathbf{H_{2gas}} + \mathbf{H_2O} \Rightarrow \mathbf{H_{2aq}}$ $\Delta G_{H2spAlberty} = G_{H2aq} - G_{H2gas} - G_{H2O\ Biochem} = \mathbf{103{,}24 - 85{,}64 - 85{,}6 = -68{,}05}$ kJ/mol **Alberty**:

$[\mathbf{H_{2aq}}]/[\mathbf{H_{2gas}}]/[\mathbf{H_2O}] = K_{sp} = \text{EXP}(-\Delta \mathbf{G}_{H2spAlberty}/R/T) = \text{EXP}(\mathbf{68050}/8{,}3144/298{,}15) = 10^{\wedge 11{,}9}$. [8] **Alberty**

Solubility spontaneouse $[\mathbf{H_{2aq}}] = K_{sp}*[\mathbf{H_2O}] = 10^{\wedge 11{,}9}*55{,}3 = 10^{\wedge 13{,}6}$ M, if $\mathbf{H_{2gas}}$ mol fraction is one $[\mathbf{H_{2gas}}] = 1$ pure gas.

Proton reduction at hydroxonium capture electron from crystal lattice $\underline{(Pt)} + e^-$. Hess free energy change $H_3O^+ + \underline{(Pt)} + e^- \Leftrightarrow \underline{(Pt)H} + H_2O$ is $\Delta \mathbf{G}_{Hess(Pt)H} = G_{H3O+} + G_{\underline{(Pt)}} + G_{\underline{e-}} - (G_{H2O} + G_{H(Pt)}) = 22{,}44 + \mathbf{28{,}525} + 0 - (0 + 41{,}2) = \underline{9{,}765}$ kJ/mol.

$\Delta \mathbf{G}_{\mathbf{eq}(Pt)H} = E°_H \bullet F \bullet 1 = 0.10166*96485/1000 = 9.81$ kJ/mol give equilibrium free energy change minimum of metallic hydrogen $\underline{(Pt)H}$ oxidation on zero scale $G_{\underline{(Pt)}} + G_{\underline{e-}} = G_{H2O} = G_{CO2gas} = 0$ kJ/mol of indifferent $\underline{(Pt),}$ $+e^-$, water and $\mathbf{CO_{2gas}}$.

Hydrogen electrode thermodynamic standard potential $E°_H = 0.10166$ V is over classic zero $E°_{Hclassic} = 0$ Volts.

Red: $\mathbf{H_{2aq}} + 2\underline{(Pt)} \Leftrightarrow 2\underline{(Pt)H} + H_2O$; $\Delta \mathbf{G}_{Hess\_šķ(Pt)H} = 2G_{H(Pt)} + G_{H2O} - (G_{H2aq} + 2G_{\underline{(Pt)}}) = 2*\mathbf{51{,}05} + 0 - (\mathbf{103{,}24} + 2*\mathbf{38{,}375}) = -\underline{77{,}89}$ kJ/mol.

$E°_{H3O+} = -77{,}89*1000/96485/2 = -0{,}4036$ V; $\mathbf{H_{2aq}} + 2\underline{(Pt)} \Leftrightarrow 2\underline{(Pt)H} + H_2O$; $2\mathbf{H_3O^+} + 2e^- \Leftrightarrow \mathbf{H_{2aq}} + 2H_2O$;

$K_{šķ(Pt)H} = [\mathbf{H_2O}]*[\underline{(Pt)H}]^2/[\mathbf{H_{2aq}}]/[\underline{(Pt)}]^2 = \text{EXP}(-\Delta \mathbf{G}_{(Pt)H}/R/T) = \text{EXP}(\mathbf{77890}/8{,}3144/298{,}15 = 10^{13{,}65}$. [8]

Ox: $2\mathbf{H_3O^+} + 2e^- + H_2O \Leftrightarrow \mathbf{H_{2aq}} + 2H_2O$; $\Delta \mathbf{G}_{Hess\_H3O+} = 2G_{H3O+} + 2G_{\underline{e-}} - (G_{H2aq} + G_{H2O}) = -\underline{58{,}12}$ kJ/mol; $E°_{H3O+} = -58{,}36*1000/96485/2 = -0{,}302$ V

$\Delta E°_{eqH3O+} = -0{,}4036 - (-0{,}302) = 0{,}40366$ V; $\Delta \mathbf{G}_{eqH3O+} = \Delta E°_{H3O+} \bullet F \bullet 2 = 0{,}40366*96485*2 = 77{,}89$ kJ/mol; Metal hydrogen insoluble $2\underline{(Pt)H} + \mathbf{H_2O} \Leftrightarrow \mathbf{H_{2aq}} + 2\underline{(Pt)}$; $K_{šķ(Pt)H} = [\mathbf{H_{2aq}}]/[\underline{(Pt)}]^2\ [\mathbf{H_2O}]*[\underline{(Pt)H}]^2 = \text{EXP}(-\Delta \mathbf{G}_{(Pt)H}/R/T) = \text{EXP}(\mathbf{-77890}/8{,}3144/298{,}15 = 10^{\wedge(-13{,}65)}$:

$\Delta \mathbf{G}_{sp(Pt)H} = E°_{sp(Pt)H} \bullet F \bullet 2 = -0.109*96485*2/1000 = -21.0$ kJ/mol; $E°_{sp(Pt)H} = -21.03*1000/2/96485 = -0.109$ V; The mol fraction of Metallic hydrogen is one $[\underline{(Pt)H}] = 1$ and $[\underline{(Pt)H}]^2 = 1$. The metallic hydrogen (Pt)H $[\mathbf{H_{2aq}}] = K_{sp}*[\mathbf{H_2O}] = 10^{\wedge 11{,}9}*55{,}3 = 10^{\wedge 13{,}6}$ M created concentration and gas $[\mathbf{H_{2aq}}] = K_{sp}*[\mathbf{H_2O}] = 10^{\wedge 11{,}9}*55{,}3 = 10^{\wedge 13{,}6}$ M hydrogen solubility, if $\mathbf{H_{2gas}}$ mol fraction is one $[\mathbf{H_{2gas}}] = 1$ pure gas. 0,000771899 M in water, than minimal is $[\mathbf{H_{2gas}}] = 0{,}000771899$ M$/10^{\wedge 13{,}6}$ M$= 10^{\wedge(-16{,}7)}$ mol fraction for gas

THERMODYNAMICS Exercise XV. vitamin B3 $H_3O^+_{in}$ to $H_3O^+_{out}$ inter membrane space

For vitamin B3 reduced form NADH and oxidized form $NADP^+$ translocate hydrogen ions as protons through membrane from inner $H_3O^+_{in}$ to out side mitochondria $H_3O^+_{out}$ inter membrane space

$NADP^+ + NADH + H_3O^+_{in} + Q(weak) \xrightarrow{\text{Membrane}} NADPH + NAD^+ + H_3O^+_{out} + \Delta G(weak)$;

Substance	$\Delta H°_H$, kJ/mol	$\Delta S°_H$, J/mol/K	$\Delta G°_H$ kJ/mol
$H_3O^+_{in\_out}$	-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**

Proton translocating transhydrogenase (EC1.6.1.1) ENZYME
found in bacteria and animal mitochondria
that couples the transfer of reducing equivalents between
NAD(H) and NADP(H) to the translocation of protons across the membrane

$\Delta H_{Hess}=\Delta H°_{NADPH}+\Delta H°_{NAD}-\Delta H°_{NADP}-\Delta H°_{NADH}=4,4$ kJ/mol;

$=-1036,66-1007,48-(-1007,48-1036,66)=$ 0.0 kJ/mol **endothermic** **neutral**

$=-1040,78-10,3-(-1014,07-41,41)=4,4$ kJ/mol

$S_{dispersed}=-\Delta H_{Hess}/T=-4,4/298,15=-14,76$ J/mol/K;

......Proofing membrane channel penetrating athermic-neutral process $\Delta H_{Hess}=0.0$ kJ/mol in friction less manner.

......No heat dispersion through membrane channel

$\Delta S_H=\Delta S°_{NADPH}+\Delta S°_{NAD}-\Delta S°_{NADP}-\Delta S°_{NADH}=-4465,708-3766,008-(-4166,096-4081,784)=16,164$ J/mol/K;

$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}=16,164-14,76=1,404$ J/mol/K;

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=4,4-298,15*0,016164=-0,4193$ kJ/mol; **weak exoergic**.

$\Delta G_{Hess}=\Delta G°_{NADPH}+\Delta G°_{NAD}-\Delta G°_{NADP}-\Delta G°_{NADH}=290,6776+1112,534-(228,052+1175,5732)=-0,4136$ kJ/mol;

$T\bullet\Delta S_{total}=0,001404$ J/K/mol$\bullet$298,15 K$=0,419$ kJ/mol; bound lost energy for proton gradient H^+ **spontaneous weak exoergic**

Ox $NADP^+ + H^-(H^+ + 2e^-) = NADPH$; absolute $E°_{NADP}=-0,4135$ **V;**

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

$NADP^+ + NADH + H_3O^+_{in} + Q(weak) \xrightarrow{\text{Membrane}} NADPH + NAD^+ + H_3O^+_{out} + \Delta G(weak)$;

$\Delta E°=E°_{NADH}-E°_{NADH}=-0,4095-(-0,4135)=0,004$ V, **n** is **2**;

$\Delta G_{eq}=\Delta E°\bullet F\bullet n=0,004\ V\bullet 2\ mol\bullet 96485\ C/mol=(-0,4095-(-0,4135))*2*96485=-R\bullet T\bullet ln(K_{eq})=0,77188$ kJ/mol

$EXP(-\Delta G_{eq}Aerobic/R/T)=EXP(-771,88/8,3144/298,15)=0,7324=K_{eq}Aerobic$;

$$K_{eq}\text{Aerobic}=\frac{[NAD^+]\cdot[NADPH]\cdot[H_3O^+]}{[NADH]\,[NADP^+]\,[H_3O^+]}=e^{-\frac{\Delta G_{eqAerobic}}{R\bullet T}}=e^{-\frac{771,88}{8.314\bullet 298.15}}=0,7324;$$

Mitochondria channels

H^+ : $\Delta G_H=RTln([H_3O^+]_{right}/[H_3O^+]_{left})$ generate gradient quasi equilibrium $K_{eq}=10^{\wedge(-5,5)}/10^{\wedge(-7,36)}=72,44$

$\Delta S_{eq}=8,3144*ln(10^{\wedge(-5,5)}/10^{\wedge(-7,36)})=35,609$ J/mol/K;

$\Delta G_{eq}=8,3144*298,15*ln(10^{\wedge(-5,5)}/10^{\wedge(-7,36)})=10,617$ kJ/mol;

$\Delta S_{Hess\_sum}=16,164+75,42909=459,954$ J/mol/K;

$Q+H_3O^+ + HCO_3^- \xrightarrow{\text{channaels } H_2O,\ H^+;\ HCO_3^-} H_2O + H_2O\uparrow_{gas} + CO_2\uparrow_{gas} + \Delta G.\text{exhale } H_2O\uparrow_{gas} + CO_2\uparrow_{gas}$;

$\Delta S_{Hess}=\Delta S°_{H2O}+\Delta S°_{H2Ogas}+\Delta S°_{CO2gas}-\Delta S°_{H3O}-\Delta S°_{HCO3}=69,956+188,74+213,74-(-3,854+98,324)=377,966$ J/mol/K;

channels HCO_3^-: $\Delta G_{HCO3}=RTln([HCO_3^-]_{right}/[HCO_3^-]_{left})$

$\Delta S_{HCO3}=8,1344*ln(0,0154/0,0338919)=-6,55847$ J/mol/K

$\Delta G_{HCO3}=8,3144*298,15*ln(0,0154/0,0338919)=-1,9554$ kJ/mol;

$\Delta S_{Hess\_sum}=377,966+35,609-\underline{6,55847}=407$ J/mol/K;

$\Delta S_{Hess\_sum}=377,966+35,609+\underline{6,55847}=420,1$ J/mol/K;

$=0,0591/2*log([H_2O])=0,0591/2*log(55,34573393)=$ **0,051508** V

$=0,0591/2*log([H_2O]^2)=0,0591/2*log(55,34573393^{\wedge 2})=$ **0,1030** V

THERMODYNAMICS Exercise XVI. NAD**H**+**H_3O^+** +**O_{2aqua}** $\xleftrightarrow{\text{FMN(B2vitamin)}}$ NAD^++ **H_2O** + **H_2O_{2aqua}+Q**

For vitamin B3 reduced form NADH or NADPH flavin B2 vitamin FMN enzyme using oxygen **O_{2aqua}** as electron acceptor for the oxidation of NADH with the production of hydrogen peroxide! CRC Handbook of Chemistry and Physics 90th Edition CD-ROM Version 2010; eactants => products

Substance	$\Delta H°_{Hess}$, $^{kJ}/_{mol}$	$\Delta S°_{Hess}$, $^{J}/_{mol/K}$	$\Delta G°_H$ $^{kJ}/_{mol}$
O_{2aq}	**-11,70**	**-94,2**	**16,40**
O_{2aqua}	-11,715	110,876	16,4
NAD**H***(aq)*	-1036,66	-140,5	-
NAD**H***(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**
NAD^+*(aq)*	-1007,48	-183	-
NAD^+*(aq)*	**-1010,3**	**-3766,008**	**1112,534**
$H_2O_{2\,l}$	-237,129	69,91	-237,129
H_2O_{2aqua}	-191,17	143,9	-134,03
H_2O_{2aqua}	**-191,99**	**-481,688**	**-48,39**

H_3O^++O_{2aqua}+NADH$\xrightarrow{\text{FMN(B2vitamin)}}$=>**$H_2O_{2aqua}$+$H_2O$**+$NAD^+$**+Q**

BioChemistry Thermodynamic 2006 Massachusetts Techn.Inst.

$\Delta H_H=\Delta H°_{H2O2}+\Delta H°_{H2O}+\Delta H°_{NAD}-\Delta H°_{H3O}-\Delta H°_{O2}-\Delta H°_{NADH}=$**-150** $^{kJ}/_{mol}$

$\Delta H_H=$**-191,99-286,65-1010,3**-(-285,81**-11,70-1041,41**)=**-150** $^{kJ}/_{mol}$;

=-191,17-285,85-1007,48-(-285,81-11,715-1036,66)=150,315 $^{kJ}/_{mol}$;

$\Delta S_H=\Delta S°_{H2O2}+\Delta S°_{H2O}+\Delta S°_{NAD}-\Delta S°_{H3O}-\Delta S°_{O2}-\Delta S°_{NADH}=$**-521,05** $^{J}/_{mol/K}$

=**-481,688-453,188-3766,008**-(-3,854**-94,2-4081,784**)=**-521,05** $^{J}/_{mol/K}$;

=143,9+69,9565-183-(-3,854+110,876-140,5)=64,3345 $^{J}/_{mol/K}$;

$\Delta G_H=\Delta H_H-T*\Delta S_H=$**-150,02**-298,15*-**0,52105**=**5,33** $^{kJ}/_{mol}$; **endoergic**

$\Delta G_H=\Delta H_H-T*\Delta S_H$=-150,315-298,15*0,064335=-169,5 $^{kJ}/_{mol}$; **exoergic**

$\Delta G_{Hess}=\Delta G°_{H2O2}+\Delta G°_{H2O}+\Delta G°_{NAD}-\Delta G°_{H3O}-\Delta G°_{O2}-\Delta G°_{NADH}=$

ΔG_{Hess}=-134,03+(-237,191**-151,549**)/2+**1112,534**-(-213,275+**16,4**+**1175,5732**)= **-194,56** $^{kJ}/_{mol}$;;

$\Delta S_{dispersed}=-\Delta H_{Hess}/T$=**150**/298,15= **503,1** $^{J}/_{mol/K}$; $\Delta S_{dispersed}=-\Delta H_{Hess}/T$=150,315/298,15= 504,1 $^{J}/_{mol/K}$;

$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}$=**-521,1+503,1=-18** $^{J}/_{mol/K}$; $\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}$=64,3345+504,1=568,44 $^{J}/_{mol/K}$;

T•ΔS_{total}=0,5684345 $^{J}/K/_{mol}$•298,15 K=+169.5 $^{kJ}/_{mol}$; bound TΔSn⟵dispersed-lost energy and is **spontaneous**

Ox O_{2aqua}+H_3O^++H^-(H^++2e^-)=H_2O_{2aqua}+H_2O ; **$E°_{H2O2}$**=0.4495 V Alberta University NADH and NADPH oxidase.

Red **NAD^+ + H^-(H^++2e^-) =NADH** ; **$E°^2$**=-0,4095 **V;** David Harris

H_3O^++O_{2aqua}+NADH$\xrightarrow{\text{FMN(B2vitamin)}}$=>**$H_2O_{2aqua}$+$H_2O$**+$NAD^+$**+Q+ΔG**

Free energy of activate homeostasis products referring to water and **CO_{2gas}** zero $G_{H2O}=G_{CO2gas}=0$ $^{kJ}/_{mol}$ are peroxide, hydroxonium and anion of peroxide: G_{H2O2}=284,25 $^{kJ}/_{mol}$; $G_{H3O+}+G_{HOO-}$=22.44+**337,8**=360.24 $^{kJ}/_{mol}$;

$\Delta E°=E°^2- E_{H2O}°^1$=-0,4095-0.4495= **-0,859 V**, **n** is **2**;

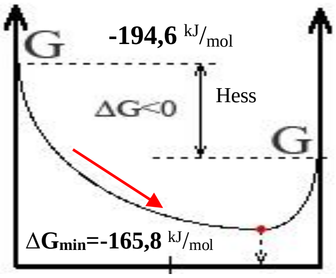
$\Delta G_{eq}=(E°^2-E_{H2O}°^1)$•F•n=-0,859*2*96485$^C/_{mol}$=(-0,4095-0.4495)***2*96485$^C/_{mol}$=-R•T•ln(K_{eq})=-165,8** $^{kJ}/_{mol}$;

K_{eq}Aerobic=EXP(-Δ**G_{eq}**Aerobi/R/T)=EXP(**165761**/8,3144/298,15)=**1,097*10^^{29}**;

$$K_{eq}\text{Aerobic}=\frac{[NAD^+]\cdot[H_2O_2]_{aqua}\cdot[H_2O]}{[NADH]\cdot[O_2]_{aqua}\cdot[H_3O^+]}=e^{-\frac{\Delta G_{eqAerobi}C}{R\bullet T}}=e^{-\frac{-165761}{8.314\bullet 298.15}}=\mathbf{1{,}097*10^{29}};$$

Prigogine attractor favored equilibrium by Hess law solution **is** exothermic and exoergic oxidation of NADH free energy change is negative Δ**G_{Hess}** = **-194,56** $^{kJ}/_{mol}$, but minimized constant free energy change value Δ**G_{min}= ΔG_{eq}** = **-165,8** $^{kJ}/_{mol}$ reaching equilibrium **K_{eq}**Aerobic=**1,097*10^^{29}** ;

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching. Free energy change minimum reaching establishes equilibrium.



reactants _ H_3O^++O_{2aqua}+NADH A+B+C 50% D+E+F
and products_ H_2O_{2aqua}+H_2O+**NAD^+;**

THERMODYNAMICS Exercise XVII Peroxide $\mathbf{2H_2O_{2(aq)}}$ conversion to $\mathbf{O_2}_{\text{aqua}}$ + $\mathbf{2H_2O+Q}$

High rate protolysis Peroxide anions $\mathbf{H^++HOO^-><^-OOH+H^+}$ collision activation energy is very high **Ea**=79000 $^{J}/_{mol}$ versus collision $\mathbf{HOO^-=>Fe^{3+}}$ activation energy **Ea**=29 $^{J}/_{mol}$ of Catalase is low. Conversion to $\mathbf{O_{2aqua}+2H_2O+Q}$,

reactants $\mathbf{2H_2O_{2(aq)}}$<=>$\mathbf{O_{2aqua}+2H_2O+Q}+\Delta G_H$ products ;

$\Delta G_{Hess}=\Delta G°_{O2}+2\Delta G°_{H2O}-2\Delta G°_{H2O2}=16{,}40+2*(-237{,}191)-(2*-134{,}03)=\mathbf{-189{,}9}$......... $^{kJ}/_{moll}$ **eksoerģiski**

$\Delta G_{AlbertyHomeostasis}=G_{O2Biochem\_arteriaj}+2*G_{H2O BioChemistry}-2*G_{H2O2}=\mathbf{88{,}04+2*85{,}64-2*\underline{284{,}25}=-309{,}18}$ $^{kJ}/_{mol}$;; **Alberty**

Substance	$\Delta H°_H$ $^{kJ}/_{mol}$	$\Delta S°_H$ $^{J}/_{mol/K}$	$\Delta G°_H$ $^{kJ}/_{mol}$
$\mathbf{H_3O^+}$	-285,81	-3,854	-213,275
$\mathbf{O_{2aqua}}$	-11.715	110,876	16,4
$\mathbf{O_{2aqua}}$	**-11.70**	**-94,2**	**16,40**
$\mathbf{H_2O}$	-285,85	69,9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{H_2O_2}$ *(aq)*	**-191,99**	**-481,688**	**-48,39**
$\mathbf{H_2O_{2(aq)}}$	-191,17	143,9	-134,03
$\mathbf{H_2O_2}$ *l*	-237,129	69,91	-237,129

Mischenko 1972, Himia, Leningrad [26]

$\Delta H_{Hess}=2\Delta H°_{H2O}+\Delta H°_{O2}-2\Delta H°_{H2O2}=\mathbf{-202{,}66}$.........$^{kJ}/_{mol}$ **exothermic**

$=\mathbf{-11{,}7}-2*\mathbf{286{,}65}-(2*\mathbf{-191{,}17})=\mathbf{-202{,}66}$ $^{kJ}/_{mol}$

CRC 2010; 2.$\Delta S_{dispersed}=-\Delta H_H/T=-(\mathbf{-202{,}66})/298{,}15=\mathbf{679{,}725}$ $^{J}/_{mol/K}$

BiochemThermodynamic 2006 Masachusets Technology institute

University Alberta 1997. $\Delta S_{Hess}=2\Delta S°_{H2O}+\Delta S°_{O2}-2\Delta S°_{H2O2}=$

$=110.876+2*69{,}9565-(2*\mathbf{-481{,}688})=\mathbf{1214}$ $^{J}/_{mol/K}$

3. $\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}=1214+\mathbf{679{,}725=1893{,}7}$.......... $^{J}/_{mol/K}$

4. $\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=\mathbf{-202{,}66}-298{,}15*1{,}214165=\mathbf{-564{,}66}$..... $^{kJ}/_{mol}$ **exoergic**..........

$T\bullet\Delta S_{total}=1{,}893725*298{,}15=\mathbf{+564{,}6}$.......... $^{kJ}/_{mol}$; bound TΔSn← <u>dispersed energy ΔG_{Hess}</u>.

Red: $H_2O_2+2H_2O=O_2+2H_3O^++2e^-$; $\mathbf{E°_{Red}=E°}_{H2O2}=0.4495$ V Alberta University classic E_o =0,694 V;

Ox: $H_2O_2+2H_3O^++2e=4H_2O$; $\mathbf{E°_{Ox}}=1{,}6855$ V Suhotina classic E_o =1,776 V

$\mathbf{2H_2O_{2(aq)}}$ => $\mathbf{O_{2aqua}+2H_2O+Q}+\ \mathbf{\Delta G}$;

Half reactions RedOx Nernst's equations for biochemistry environment form balance of electrons 2 e^-:

$[H_2O_2]=1$; $10^{\wedge(-10)}$ M Biochemistry concentrations $[O_{2aqua}]=6*10^{-5}$ M, $[H_3O^+]=10^{-7{,}36}$ M, $[H_2O]=55{,}3$ M.

Red: $E_{oH2O2}=E°_{H2O2}+0.0591/2\bullet\lg(O_{2aqua}]*[H_3O^+]^2/[H_2O_2]/[H_2O]^2)_{=0.4495+0.0591/2*\lg(6*10^{\wedge(-5)}*10^{\wedge(-7.36*2)}/1/55.3^{\wedge 2})=}-0.213$ V

Ox: $E_{oOx}=E°_{H2O2Ox}+0.0591/2\bullet\log([H_2O_2]*[H_3O^+]^2/[H_2O]^4)=1{,}6855+0.0591/2*\lg(1*10^{\wedge(-7.36*2)}/55.3^{\wedge 4})=1{,}0445$ V

Homeostāze: $\Delta\mathbf{G_{eq}}_{BioChem}=(E_{Red}-E_{oOx})*\mathbf{F*n}=(-0.2132-1{,}0445)*96485*2=(-1{,}258)*96485*2=\mathbf{-242{,}7}$ $^{kJ}/_{mol}$;

<u>$\Delta G_{AlbertyStandart}=G_{O2Biochem\_arteriaj}+2*G_{H2O BioChemistry}-2*G_{H2O2}=\mathbf{78{,}08+2*85{,}64-2*284{,}25=-238{,}5}$ $^{kJ}/_{mol}$</u>; **Alberty**

<u>$2G_{H2O2}=G_{O2aqua}+2*G_{H2O}+\Delta G_{AlbertyStandart}=\mathbf{330+2*0+218{,}9}=2*\mathbf{284{,}25}=$</u>$\mathbf{548{,}9}$ $^{kJ}/_{mol}$;;

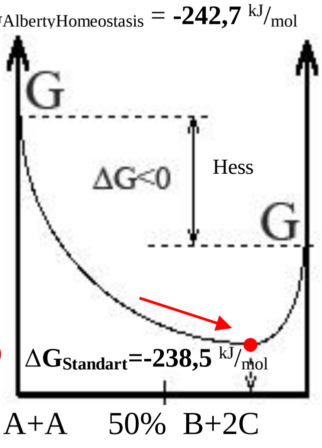
Free energy of activate homeostasis products referring to water and $\mathbf{CO_2}_{gas}$ zero $G_{H2O}=G_{CO2gas}=0$ $^{kJ}/_{mol}$ are peroxide, hydroxonium and anion of peroxide: $G_{H2O2}=\mathbf{\underline{284{,}25}}$ $^{kJ}/_{mol}$; $G_{H3O+}+G_{HOO-}=22.44+\mathbf{\underline{337{,}8}}=360{,}24$ $^{kJ}/_{mol}$

$\Delta G_{eqStandart}=(E_{Red}-E_{oOx})*\mathbf{F*n}=(0{,}4495-1{,}6855)*96485*2=(-1{,}24)*96485*2=\mathbf{-238{,}5}$ $^{kJ}/_{mol}$;

$$\mathbf{K_{eq}}_{Standart}=\frac{[O_2]_{aqua}\cdot[H_2O]^2}{[H_2O_2]^2_{aqua}}=\mathbf{K_{H2O2}=exp(-\Delta G_{eq}/R/T)}=\exp(238510/8.3144/298.15)=10^{41{,}75}........$$

Exothermic and exoergic $\mathbf{H_2O_2}$ (aq) dismutation Hess free energy change $\Delta\mathbf{G}_{AlbertyHomeostasis}$ are negative **-242,7** $^{kJ}/_{mol}$, but minimized $\Delta\mathbf{G_{eq}}_{BioChem}$ at **-238,5** $^{kJ}/_{mol}$ reaching equilibrium mixture constant $\mathbf{K_{eq}}_{BioChem}\mathbf{=}10^{41}$ Le Chatelier principle is Prigogine attractor free energy change minimum ΔG_{min} at equilibrium state. High rate protolysis attractors pH=7,36, air oxygen 20,95% stay at equilibrium state, while homeostasis irreversibly continues, as is non equilibrium state. Prigogine attractor Nobel Prize Chemistry 1977th. CATALASE erase peroxide molecules $\mathbf{H_2O_2}$ promoted 100% ω=6, ω=3 effency for fatty acids C20:4 elongation synthesis in peroxisomes. CATALASE reactivity is irreversible homeostasis indispensible Brawnian molecular engine for evolution and survival.

reactants $2\mathbf{H_2O_{2(aq)}}$ produkti_$\mathbf{O_{2aqua}+2H_2O}$



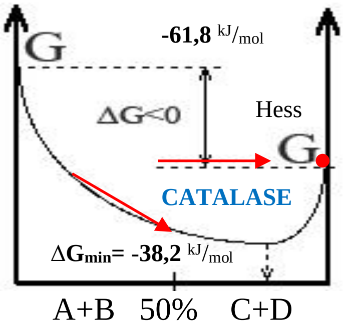
THERMODYNAMICS Exercise VII a succinat**SCoA^{4-}** **O_2** **H_2O_2** fumarate dehydrogenation reaction

Succinat**SCoA^{4-}** **O_2** **H_2O_2** fumarate dehydrogenation reaction! Will **exoergic** or **endoergic**! I=0,25 M;
Biochemistry thermodynamic data **2006**; **Succinat^{2-}+O_{2aqua}=>fumarate^{2-}+H_2O_{2aqua}**+ΔG ; pH=7,36
Red: **Succinate^{2-}+2H_2O=Fumarate^{2-}+2H_3O^+ +2e$^-$; E° $_{Red}$**=0.2512 V Lehninger 2000; Univ.Alberta 1997;
Ox: **O_{2aqua}+2H_3O^++2e$^-$=H_2O_{2aqua}+2H_2O; E° $_{Ox}$**=0,4495 V; ΔE=(**E° $_{Red}$-E° $_{Ox}$**)=(0,2512-0,4495)=-0,1983 V;
ΔG_{min}=ΔG_{eq}=(**E°$_{RedSuccinate}$-E°$_{OxO2}$**)***F*n**=(0,2512-0,4495)*96485*2=(-0,1983)* 96485*2=**-38,3** $^{kJ}/_{mol}$;
K_{eq}=**exp(-ΔG_{eq}/R/T)**=exp(**38270**/8,3144/298,15)=5065991 **labvēlīgs** līdzsvars.
ΔG_{Hess}=ΔG°$_{H2O2}$+ΔG°$_{fumarat}$-ΔG°$_{O2}$-ΔG°$_{Succinat}$=**-48,39-519,4688-(16,4-522,414)** = **-61,845** $^{kJ}/_{mol}$;

Substance	ΔH°$_{Hess}$, $^{kJ}/_{mol}$	ΔS°$_{Hess}$, $^{J}/_{mol/K}$	ΔG°$_{Hess}$, $^{kJ}/_{mol}$
H_3O^+	-285,81	-3,854	-213,275
H_2O	**-286,65**	**-453,188**	**-151,549**
H_2O_2 *aq*	**-191,99**	**-481,688**	**-48,39**
O_2*aqua*	**-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**

ΔG_H=ΔH_H–T*ΔS_H=-48,16-298,15***0,0458**= **-61,815**.$^{kJ}/_{mol}$ **exoergic**

Exothermic and exoergic fatty acid C20:4 ethyl groups **-CH_2-CH_2-** dehydrogenation to cis bonds **^{H}>C=C<^{H}** in peroxisomes Hess law free energy change **ΔG**$_{Hess}$ is negative **-61,8** $^{kJ}/_{mol}$, but reachied minimum at equilibrium mixture **ΔG_{min}=ΔG_{eq}=-48,12** $^{kJ}/_{mol}$



reactants **Succinat^{2-}+O_2**$_{aqua}$ products **fumarate^{2-}+H_2O_2**

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

$$\text{at equilibrium mixture : } K_{eq}=\frac{[\text{Fumarate}^{2-}]\cdot[H_2O_2]\swarrow \text{CATALASE}}{[\text{Succinate}^{2-}]\cdot[O_2]}=5065991.$$

Irreversibility in sequence of complex enzymatic reactions order providing CATALASE reactivity which peroxide consumed to zero [**H_2O_2**]=0 $^{mol}/_{liter}$ and process velocity limits only dehydrogenase enzyme. CATALASE in complex reaction sequence providing stabile unsaturated essential ω=6 and ω =3 fatty acid efficiency ● 100% in peroxysomal products because of erasing peroxide molecules **H_2O_2** .

Ubiquinol oxidation – dehydrogenation efficiency ● 100% providing CATALASE reactivity.

Ubiquinol + **O_2**$_{aqua}$ => **Ubiquinone** + **H_2O_2**$_{aqua}$ **+ΔG+Q;**
ΔG_{Hess}=ΔG°$_{UbiQuinOx}$+ΔG°$_{H2O2}$-ΔG°$_{O2}$-ΔG°$_{UbiQuinRed}$=**-3853,8792-48,39-(16,4-3849,6004)**= **-69,07** $^{kJ}/_{mol}$
Ox: **O_{2aqua} +2H_3O^++2e$^-$=H_2O_{2aqua} +2H_2O; E° $_{Ox}$**=0,4495 V University Alberta
Red: **Ubiquinol+2H_2O = Ubiquinone+2H_3O^+ +2e$^-$; E° $_{Red}$**=0,2656 V Lehninger 2000 ;
ΔG_{min}=ΔG_{eq}=(**E°$_{Red}$-E°$_{Ox}$**)***F*n**=(0,2656-0,4495)*96485*2=(-0,1839)* 96485*2= **-35,49** $^{kJ}/_{mol}$;
K_{eq}=**exp(-ΔG_{eq}/R/T)**=exp(**35490**/8,3144/298,15)=90471395= 1650539 **labvēlīgs** līdzsvars .

????

Red: **Ubiquinol6+2H_2O=Ubiquinone6+2H_3O^++2e**; absolūtais potenciāls **E°$_{Red}$=-1,2435 V**; **E°**$_{klasika}$=-1,05 V CRC 2012 ;
ΔG_{min}=ΔG_{eq}=(**E°$_{Red}$-E°$_{Ox}$**)***F*n**=(**-1,2435**-0,4495)*96485*2=(-1,693)* 96485*2= **-336,6** $^{kJ}/_{mol}$;
K_{eq}=**exp(-ΔG_{eq}/R/T)**=exp(**336628**/8,3144/298,15)=90471395=10$^{\wedge 58,975}$ **spontaneous**.

THERMODYNAMICS Exercise XVII b Malate to Fumarate conversion dehydratation H_2O BioThermod2006

Malate to fumarate conversion dehyratation H_2O at temperatures 298,15 K, using the data table! Mention whether the reaction will be **exoergic** or **endoergic**! $Malate^{2-}+Q+\Delta G \Rightarrow Fumarate^{2-}+H_2O$; 2000 $\Delta G_{Lehninger}= 3{,}1\ ^{kJ}/_{mol}$; _

Substance	$\Delta H°_H,\ ^{kJ}/_{mol}$	$\Delta S°_H,\ ^{J}/_{mol/K}$	$\Delta G°_H,\ ^{kJ}/_{mol}$
H_3O^+	-285,81	-3,854	-213,275
H_2O	**-286,65**	**-453,188**	**-151,549**
H_2O	-285,85	69,9565	-237,191
O_{2aqua}	**-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. $\Delta H_{Hess}=\Delta H°_{products}-\Delta H°_{reactants}$

2. $\Delta S_{Hess}=\Delta S°_{products}-\Delta S°_{reactants}$; 3. $\Delta G_H=\Delta H_H - T\bullet\Delta S_H$;

$\Delta H_{Hess}=\Delta H°_{H2O}+\Delta H°_{Fumarate}-\Delta H°_{Malate}=16{,}586\ ^{kJ}/_{mol}$; **endothermic**

$=-286{,}65-776{,}56-(-1079{,}796)= 16{,}586\ ^{kJ}/_{mol}$

BioTherm06; $\Delta S_{dispersed}=-\Delta H_{Hess}/T=-16{,}586/298{,}15= -55{,}63\ ^{J}/_{mol/K}$

BioThermod06; $\Delta S_H=\Delta S°_{H2O}+\Delta S°_{Fumarate}-\Delta S°_{Malate}=43{,}5\ ^{J}/_{mol/K}$

$=-453{,}188-862{,}288-(-1358{,}976)=43{,}5\ ^{J}/_{mol/K}$

$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}=-55{,}63+43{,}5= -12{,}3\ ^{J}/_{mol/K}$

$\Delta G_H=\Delta H_H-T*\Delta S_H=16{,}586-298{,}15*0{,}0435=3{,}6165\ ^{kJ}/_{mol}$;

$\Delta G_H=\Delta G°_{H2O}+\Delta G°_{fumarat} -\Delta G°_{Malate}=3{,}606\ ^{kJ}/_{mol}$

$3{,}606\ ^{kJ}/_{mol} =-151{,}549-519{,}4688-(-674{,}624)$

$T\bullet\Delta S_{total} =-0{,}01214*298{,}15 = -3{,}6195\ ^{kJ}/_{mol}$ bound to products

$T\Delta Sn$ <u>accumulate energy</u>

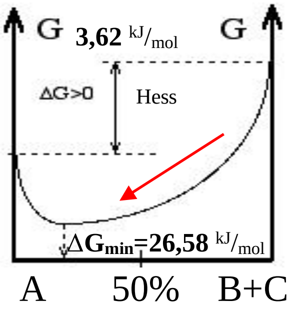
$$\frac{[Fumarat^{2-}]\cdot[H_2O]}{[Malat^{2-}]}=K_{eq}=K_{Lehninge}=\exp(-\Delta G_{eq}/R/T)=\exp(-3100/8{,}3144/298{,}15)=0{,}28635=10^{-0{,}543}$$ **unfavored**

Hess dehydratation products minus reactants unfavored free energy change $\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=3{,}62\ ^{kJ}/_{mol}$.

Endothermic and endoergic dehydratation reaction free energy change ΔG_{Hess} positive $3{,}62\ ^{kJ}/_{mol}$, but at equilibrium reach minimum $\Delta G_{min}=\Delta G_{eq}= 3{,}1\ ^{kJ}/_{mol}$ as Prigogine attractor constant in mixture ratio is

$$K_{eq}=\frac{[Fumarat^{2-}]\cdot[H_2O]}{[Malat^{2-}]}=0{,}28635$$. Le Chatelier principle is

Prigogine attractor free energy minimum ΔG_{min} reacing at equilibrium mixture. Free energy minimum reaching establishes equilibrium.



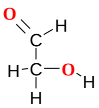
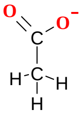
Malate^{2-} reactant
with **Fumarate**$^{2-}$+H_2O

$=0{,}0591/2*\log([H_2O])=0{,}0591/2*\log(55{,}34573393)=0{,}051508$ V
$=0{,}0591/2*\log([H_2O]^2)=0{,}0591/2*\log(55{,}34573393\text{^}2)= 0{,}1030$ V

THERMODYNAMICS Exercise XVIII Glycolaldehyde $H_2C(OH)CHO$ conversion to $H_3CCOO^- + H_3O^+ + Q$

Glycolaldehyde $H_2C(OH)CHO$ conversion to acetate $H_3CC{=}OO^- + H_3O^+ + Q$ (25 C) 298.15 K, using the data table!
Mention whether the reaction will be **exoergic** or **endoergic**! <u>Reactants</u> Glyoxal => <u>products</u> acetate + $H_3O^+ + Q$

Substance	$\Delta H°_H$, $^{kJ}/_{mol}$	$\Delta S°_H$, $^{J}/_{mol/K}$	$\Delta G°_H$, $^{kJ}/_{mol}$
$H_2C(OH)CHO$	-212	272,5	-313,83
H_2O	**-286,65**	**-453,188**	**-151,549**
$H_2O_{(aq)}$	-285.85	69,9565	-237,191
$H_3O^+_{(aq)}$	-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**

Glycolaldehyde  $+H_2O=>$  $+H_3O^+ + \Delta G + Q$

$H_2C(OH)CHO + H_2O => H_3CCOO^- + H_3O^+ + Q + \Delta G$

$\Delta H_{Hess} = \Delta H°_{H3CCOO-} + \Delta H°_{H3O} - \Delta H°_{H2O} + \Delta H°_{H2C(OH)CHO} = {}^{kJ}/_{mol}$

$= -485{,}64 - 285{,}81 - (-212 - 285{,}85) = -273{,}32 -$ $^{kJ}/_{mol}$ **exothermic**

$= \mathbf{-486} - 285{,}81 - (-212 \mathbf{-286{,}65}) = \mathbf{-273{,}16} -$ $^{kJ}/_{mol}$ **exothermic**

$\Delta S_{dispersed} = -\Delta H_H/T = \mathbf{273{,}16}/298{,}15 = \mathbf{916{,}2}$ $^{J}/_{K/mol}$

$\Delta G_H = \Delta G°_{CH3COO} + \Delta G°_{H3O} - \Delta G°_{H2O} - \Delta G°_{H2C(OH)CHO} = -31{,}624$ $^{kJ}/_{mol}$

$\Delta G_{Hess} = 369{,}37 - 213{,}275 - (-237{,}191 - 313{,}83) = -31{,}624$ $^{kJ}/_{mol}$;

$\Delta S_{Hess} = \Delta S°_{CH3COO} + \Delta S°_{H3O} - \Delta S°_{H2O} - \Delta S°_{H2C(OH)CHO} = 87{,}58 - 3{,}854 - (69{,}9565 + 272{,}5) = -258{,}73$ $^{J}/_{mol/K}$ **;**

$\Delta S_{total} = \Delta S_{Hess} + \Delta S_{dispersed} = 918{,}966 - 261{,}014 = 660{,}236$ $^{J}/_{mol/K}$;

$\Delta G_H = \Delta H_H - T*\Delta S_H = \mathbf{-273{,}16} - 298{,}15*-0{,}25873 = -196$ $^{kJ}/_{mol}$ **exoergic**

$T \bullet \Delta S_{total} = 660{,}236^* 298{,}15\ K = \mathbf{+196}$ $^{kJ}/_{mol}$;

bound $T\Delta S n \leftarrow$ <u>dispersed-lost energy $\Delta G_{reversereaction}$</u>$\leftarrow Q = 273{,}96$ $^{kJ}/_{mol}$.......**spontaneous** $\Delta G_{Hess} = -196{,}14$ $^{kJ}/_{mol}$...

Formation in space. UV-irradiation of methanol ices containing CO yielded organic compounds such as glycolaldehyde and methyl formate, the more abundant isomer of glycolaldehyde.

Ethylene Glycol and 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 and dust near the center of the Milky Way galaxy,[16] in a star-forming region 26000 light-years from EartH [17] and around a protostellar binary star, *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 and 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 and be released. The molecule will emit radio waves that can be detected and analyzed. The Atacama Large Millimeter/submilliter 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 and 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 and from purone catabolism. It can form by action of ketolase on fructose 1, 6-bisphosphate in an alternate glycolysis pathway. This compound is transferred by thiamin pyrophosphate during the pentose phosphate shunt. InTissue neurons; Mitochondria;

Solar-type protostar with ALMA. Glycolaldehyde (HCOCH2OH) is the simplest sugar and 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 star, through Atacama Large Millimeter Array (ALMA) observations of the Class 0 protostellar binary IRAS 16293-2422 at 220 GHz (6 transitions) and 690 GHz (7 transitions). Glycolaldehyde co-exists with its isomer, methyl formate (HCOOCH3), 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 and emission at the systemic velocity offset from this by about 0.2" (25 AU). We discuss the constraints on the chemical formation of glycolaldehyde and other organic species - in particular, in the context of laboratory experiments of photochemistry of methanol-containing ices. The relative abundances appear to be consistent with UV photochemistry of a CH3OH-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.

THERMODYNAMICS Exercise XIX Glycolic acid $H_2COH\text{-}COOH$ conversion to $H_3C\text{-}COOH$ **+Q**

Glycolic acid Formation 61st page $2C+2{*}H_{2gas}+1{,}5O_{2gas} \Rightarrow H_2COHCOOH$; $\Delta G_{H2COHCOOH}=\mathbf{-403{,}2968}\ {}^{kJ}/_{mol}$ [8];

$\Delta G_{H2COHCOOH}=G_{H2COHCOOH}-(\mathbf{2G_{Cgraph}}+2G_{H2gas}+\mathbf{1{,}5{*}}G_{O2gas})=\mathbf{-403{,}2968}\ {}^{kJ}/_{mol}$;

$G_{H2COHCOOH}=\mathbf{-403{,}2968}+(\mathbf{2{*}91{,}26}+2{*}\mathbf{85{,}6}+\mathbf{1{,}5{*}303})=\mathbf{404{,}9232}\ {}^{kJ}/_{mol}$;

Glycolic acid $H_2COHCOOH+\mathbf{H_2O} \Leftrightarrow H_2COHCOO^-+H_3O^+$; $pK_{a1}=3{,}83$; Wikipedia

$K_{eq}=[H_2COHCOO^-]{*}[H_3O^+]/[H_2COHCOOH]/[\mathbf{H_2O}]=K_a/[\mathbf{H_2O}]=10^{\wedge(-3{,}83)}/55{,}3=2{,}675{*}10^{\wedge(-6)}=10^{\wedge(-5{,}573)}$;

$\Delta G_{\mathbf{eq}OHCCOOH}=-R{\bullet}T{\bullet}\ln(K_{\mathbf{aeq}})=-8{,}3144{*}298{,}15{*}\ln(10^{\wedge(-5{,}573)})/1000=\mathbf{31{,}81}\ {}^{kJ}/_{mol}$.

$\Delta G_{\mathbf{eq}OHCCOOH}=G_{OHCCOO}+G_{H3O+}-(G_{OHCCOOH}+G_{H2O})=G_{OHCCOO}+\mathbf{22{,}44}-(\mathbf{404{,}9232}+\mathbf{0})=\mathbf{31{,}81}\ {}^{kJ}/_{mol}$;

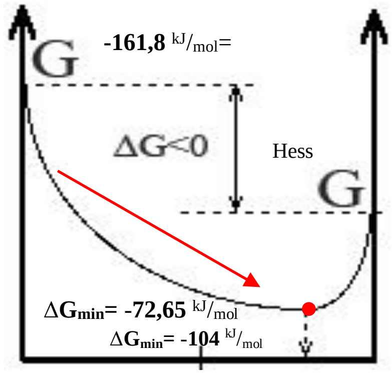
$G_{OHCCOO}=\Delta G_{\mathbf{eq}OHCCOOH}-G_{H3O+}+(G_{OHCCOOH}+G_{H2O})=\mathbf{31{,}81-22{,}44}+(\mathbf{404{,}9232}+\mathbf{0})=\mathbf{414{,}3}\ {}^{kJ}/_{mol}$;

Substance Glyoxylate	$\Delta H°_{Hess}$ $^{kJ}/_{mol}$	$\Delta S°_{Hess}$ $^{J}/_{mol/K}$	$\Delta G°_{Hess}$ $^{kJ}/_{mol}$
$OHCCOO^-$	-	-	**-426,588**
$H_2COHCOO^-$	-	-	**-403,2968**
$H_2COHCOOH$	- 651	318,6	-
$NADH_{(aq)}$	-1036,66	-140,5	-
$NADH_{(aq)}$	**-1041,41**	**-4081,784**	**1175,5732**
$\mathbf{H_3O^+}_{(aq)}$	-285.81	-3,854	-213,2746
$NAD^+_{(aq)}$	-1007,48	-183	-
$NAD^+_{(aq)}$	**-1010,3**	**-3766,008**	**1112,534**
$\mathbf{H_3CCOOH}$	-484,09	159,83	-531,743
$\mathbf{H_3CCOO^-}$	-486,84	82,23	-247,83
$\mathbf{H_3CCOO^-}$	**-486**	**85,3**	**-240,963**
$\mathbf{H_2O}$	-285,85	69,9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**

$H_2COHCOOH+H_2O \Leftrightarrow H_2COHCOO+H_3O^+$;pKa=3,83

$G_{OHCCOO}=\Delta G_{\mathbf{eq}OHCCOOH}-G_{H3O+}+(G_{OHCCOOH}+G_{H2O})=\mathbf{414{,}3}\ {}^{kJ}/_{mol}$;

Exothermic, exoergic reduction Hess free energy change negative **-161,8** $^{kJ}/_{mol}$ or **-129,6** $^{kJ}/_{mol}$, but minimized $\mathbf{\Delta G_{min}=\Delta G_{eq}=-85}\ {}^{kJ}/_{mol}$ or **-104** $^{kJ}/_{mol}$ reaching Prigogine attractor free energy change $G_{H3CCOOH}=\mathbf{-415{,}8}\ {}^{kJ}/_{mol}$; $G_{H3CCOO}=\mathbf{430{,}46}\ {}^{kJ}/_{mol}$; minimum ΔG_{min} at equilibrium mixture.



A+B+C 50% D+2E+F

Acetic acid Formation 61st page $2C+2\mathbf{H_{2gas}}+\mathbf{O_2}_{gas} \Rightarrow H3CCOOH$; $\Delta G_{OHCCOOH}=\mathbf{-240{,}963}\ {}^{kJ}/_{mol}$ [8];

$\Delta G_{H3CCOOH}=G_{H3CCOOH}-(\mathbf{2G_{Cgraph}}+2G_{H2gas}+\mathbf{1{*}}G_{O2gas})=\mathbf{-240{,}963}\ {}^{kJ}/_{mol}$;

$G_{H3CCOOH}=\mathbf{-240{,}963}+(\mathbf{2{*}91{,}26}+2{*}\mathbf{85{,}6}+\mathbf{1{*}303})=\mathbf{415{,}8}\ {}^{kJ}/_{mol}$;

Acetic acid $H3CCOOH+\mathbf{H_2O} \Leftrightarrow OHCCOO^-+H_3O^+$; $pK_{a1}=4{,}76$; Wikipedia

$K_{eq}=[H3CCOO^-]{*}[H_3O^+]/[H3CCOOH]/[\mathbf{H_2O}]=K_a/[\mathbf{H_2O}]=10^{\wedge(-4{,}76)}/55{,}3=3{,}1425{*}10^{\wedge(-7)}=10^{\wedge(-6{,}5)}$;

$\Delta G_{\mathbf{eq}H3CCOO}=-R{\bullet}T{\bullet}\ln(K_{\mathbf{aeq}})=-8{,}3144{*}298{,}15{*}\ln(10^{\wedge(-6{,}5)})/1000=\mathbf{37{,}1}\ {}^{kJ}/_{mol}$.

$\Delta G_{\mathbf{eq}OHCCOOH}=G_{OHCCOO}+G_{H3O+}-(G_{OHCCOOH}+G_{H2O})=G_{OHCCOO}+\mathbf{22{,}44}-(\mathbf{296{,}032}+\mathbf{0})=\mathbf{37{,}1}\ {}^{kJ}/_{mol}$;

$G_{OHCCOO}=\Delta G_{\mathbf{eq}OHCCOOH}-G_{H3O+}+(G_{OHCCOOH}+G_{H2O})=\mathbf{37{,}1-22{,}44}+(\mathbf{415{,}8}+\mathbf{0})=\mathbf{430{,}46}\ {}^{kJ}/_{mol}$;

Oks: $H_2COHCOO^-+\mathbf{H^-(H^++2e^-)+H_3O^+} \Rightarrow \mathbf{H_3CCOO^-}+\mathbf{2H_2O}$; $\mathbf{E°_{Ox}}{}_{H2COHCOO}=-0{,}033$ V absolute; [23]

$\mathbf{\Delta G_{eq}}=\mathbf{E°_{Ox}}{}_{H2COHCOO}{*}\mathbf{F}{*}\mathbf{n}=(0{,}033){*}96485{*}2==\mathbf{6{,}368}\ {}^{kJ}/_{mol}$;

$\mathbf{\Delta G_{eq}}=G_{H3CCOO}+2G_{H2O}-(G_{OHCCOO}+G_{H3O+}+G_{H-})=\mathbf{430{,}46}+2{*}\mathbf{0}-(\mathbf{414{,}3}+\mathbf{22{,}44})=\mathbf{-6{,}28}\ {}^{kJ}/_{mol}$;

$\mathbf{\Delta G_{eq}}=G_{H3CCOO}+2G_{H2O}-(G_{OHCCOO}+G_{H3O+}+G_{H-})=\mathbf{430{,}46}+2{*}\mathbf{85{,}6}-(\mathbf{414{,}3}+\mathbf{22{,}44})=\mathbf{164{,}92}\ {}^{kJ}/_{mol}$;

$G_{H-}=G_{H3CCOO}+2G_{H2O}-(G_{OHCCOO}+G_{H3O+}+\mathbf{\Delta G_{eq}})=\mathbf{430{,}46}+2{*}\mathbf{0}-(\mathbf{414{,}3}+\mathbf{22{,}44}+\mathbf{6{,}368})=\mathbf{-12{,}648}\ {}^{kJ}/_{mol}$;

$G_{H-}=G_{H3CCOO}+2G_{H2O}-(G_{OHCCOO}+G_{H3O+}+\mathbf{\Delta G_{eq}})=\mathbf{430{,}46}+2{*}\mathbf{85{,}6}-(\mathbf{414{,}3}+\mathbf{22{,}44}+\mathbf{6{,}368})=\mathbf{158{,}55}\ {}^{kJ}/_{mol}$;

Glycolate $H_2COHCOO^-$+ NADH + $\mathbf{H_3O^+}$ => acetate $\mathbf{H_3CCOO^-}+2\mathbf{H_2O}$ + NAD^+

$\Delta G_{Hess}=\Delta G°_{\mathbf{CH3COO}}+\mathbf{\Delta G°_{NAD+}}+\mathbf{2\Delta G°_{H2O}}-\Delta G°_{H2COHCOO}-\mathbf{\Delta G°_{NADH}}-\mathbf{\Delta G°_{H3O}}=\mathbf{-161{,}8}\ {}^{kJ}/_{mol}$;

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

$\mathbf{\Delta G_{eq}}=(\mathbf{E°_{Red}}-\mathbf{E°_{Ox}}{}_{H2COHCOO}){*}\mathbf{F}{*}\mathbf{n}=(-0{,}4095--0{,}033){*}96485{*}2=(-0{,}38){*}96485{*}2=\mathbf{-72{,}65}\ {}^{kJ}/_{mol}$;

Red: $\mathbf{NADH = NAD^+ + H^-(H^++2e^-)}$; $\mathbf{E°_{Red}}=-0{,}4095$ V David Harris absolute

Glyoxylate Oks: $OHCCOO^-+\mathbf{H^-(H^++2e^-)+H_3O^+} \Rightarrow$ Glycolate $H_2COHCOO^-+\mathbf{H_2O}$; $\mathbf{E°_{Ox}}=0{,}1305$ V absolute

Glyoxylate $OHCCOO^-+NADH+H_3O^+ \Rightarrow H_2COHCOO^-+NAD^++H_2O$ Glycolate

$\mathbf{\Delta G_{eq}}=(\mathbf{E°_{Red}}-E_{oH2O}){*}\mathbf{F}{*}\mathbf{n}=(-0{,}4095-0{,}1305){*}96485{*}2=(-0{,}54){*}96485{*}2=\mathbf{-104{,}2}\ {}^{kJ}/_{mol}$;

$\Delta G_{Hess}=\Delta G°_{H2COHCOOH}+\mathbf{\Delta G°_{NAD+}}+\mathbf{\Delta G°_{H2O}}-\Delta G°_{H2COHCOO}-\mathbf{\Delta G°_{NADH}}-\mathbf{\Delta G°_{H3O}}=\mathbf{-63{,}66}\ {}^{kJ}/_{mol}$;

$=\mathbf{-403{,}2968}+\mathbf{1112{,}534}-\mathbf{151{,}549}-(\mathbf{-426{,}588}+\mathbf{1175{,}5732}-213{,}2746)=\mathbf{21{,}98}\ {}^{kJ}/_{mol}$ **;**

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

$=\mathbf{-403{,}2968}+\mathbf{1112{,}534}+0-(\mathbf{-426{,}588}+\mathbf{1175{,}5732}+\mathbf{22{,}44})=\mathbf{-62{,}2}\ {}^{kJ}/_{mol}$ **exoergic**..............;

v

THERMODYNAMICS Exercise XX Pyruvate $H_3CC{=}OCOO^-$ decarboxylation $H_3CCHO + HCO_3^-$

Pyruvate $H_3CC{=}OCOO^-$ conversion to acetaldehyde $H_3CCHO + HCO_3^-$ (25 C) 298.15 K, using the data table!

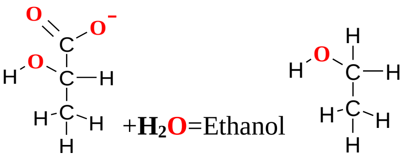
Reactants Pyruvic acid+**Q** => products acetaldehyde bicarbonate + H_3O^+

Substance	ΔH°$_H$ $^{kJ}/_{mol}$	ΔS°$_H$ $^{J}/_{mol/K}$	ΔG°$_H$ $^{kJ}/_{mol}$
$H_3CCH(OH)COO^-$	**-688,29**	**-1290,852**	**-303,4256**
$H_3CCH(OH)COO^-$	-686,2	-557,71	-313.70
$H_3CCH_2OH_{aq}$	**-290,77**	**-1227,764**	**75,2864**
$H_3CCH_2OH_l$	-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**

$H_3CC{=}OCOO^- + H_2O \Rightarrow H_3CCHO + HCO_3^- + \Delta G + Q$

BioThermodynamics06;

CRC 2010;



Lactate +H_2O=Ethanol +HCO_3^- +ΔG +**Q**

exothermic............

$\Delta G_{Hess}=\Delta G°_{H3CCH2OH}+\Delta G°_{HCO3}-\Delta G°_{H2O}-\Delta G°_{H3CCH2OHCOO-}=75{,}2864-544{,}9688-(-151{,}549-303{,}4256)=-14{,}71$ $^{kJ}/_{mol}$

$\Delta H_{Hess}=\Delta H°_{H3CCH2OH}+\Delta H°_{HCO3}-\Delta H°_{H2O}-\Delta H°_{H3CCH2OHCOO-}=-290{,}77-692{,}4948-(-286{,}65-688{,}29)=-8{,}325$ $^{kJ}/_{mol}$

$\Delta S_{dispersed}=-\Delta H_{Hess}/T=8{,}325/298{,}15=27{,}9$ $^{J}/_{K/mol}$;

BioThermodynam06 $\Delta S_{Hess}=\Delta S°_{H3CCH2OH}+\Delta S°_{HCO3-}-\Delta S°_{H2O}-\Delta S°_{H3CCH2OHCOO-}=$ **21,51** $^{J}/_{mol/K}$;

$=-1227{,}764-494{,}768-(-453{,}188-1290{,}852)=21{,}51$ $^{J}/_{mol/K}$....

$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}=21{,}51+27{,}9=49{,}41$ $^{J}/_{mol/K}$;

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=-8{,}325-298{,}15*0{,}02151=-14{,}738$ $^{kJ}/_{mol}$ **exoergic......**

$T\bullet\Delta S_{total}=0{,}04941*298{,}15\ K=14{,}73$ $^{kJ}/_{mol}$; bound TΔSn ;dispersed-lost energy **spontaneous**

Red **lactate**$^-$**+**H_2O<=>**pyruvate**$^-$**+**$H_3O^+ + H^-$($H^+ + 2e^-$) ; absolute potential $E°_{H3CHC(OH)COO}=-0{,}0159$ V;

Ox **NAD**$^+$**+H**$^-$**(2e**$^-$**)=NADH** ; **E°**^{1}**=-0,4095 V;** OksRed **NAD**$^+$+**lactate**$^-$**+**H_2O**=NADH+ pyruvate**$^-$**+**H_3O^+;

Balanced **n=2=m** with **2e**$^-$ electrons ΔE° **NAD**$^+$ **accept** electrons from **lactate**:

$$\Delta G_{eq}Aerobic=\Delta E°\bullet F\bullet n=(E°_{Red}-E°_{Ox})*F*n=(-0{,}0159—0{,}4095)*96485*2=(0{,}3936)*F*n=75{,}95\ ^{kJ}/_{mol}$$

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

$$K_{eq}Aerobic=\frac{[NADH]\cdot[pyruvate^-]\cdot[H_3O^+]}{[NAD^+]\cdot[lactate^-]\cdot[H_2O]}=e^{-\frac{\Delta G_{eqAerobic}}{R\bullet T}}=e^{-\frac{75955}{8.314\bullet 298.15}}=10^{-13{,}3};$$

$\Delta G_{Hess}=\Delta G°_{NADH}+\Delta G°_{H3CC=OCOO}+\Delta G°_{H3O}-\Delta G°_{NAD+}-\Delta G°_{H3CCH2OHCOO}-\Delta G°_{H2O}=45{,}764$ $^{kJ}/_{mol}$

$\Delta G_{Hess}=1175{,}5732-344{,}6168-213{,}275-(1112{,}534-303{,}4256-237{,}191)=45{,}764$ $^{kJ}/_{mol}$

$\Delta H_{Hess}=\Delta H°_{NADH}+\Delta H°_{H3CC=OCOO}+\Delta H°_{H3O}-\Delta H°_{NAD+}-\Delta H°_{H3CCH2OHCOO}-\Delta H°_{H2O}=60{,}18$ $^{kJ}/_{mol}$

$\Delta H_{Hess}=-1041{,}41-597{,}04-285{,}81-(-1010{,}3-1290{,}852-285{,}85)=60{,}18$ $^{kJ}/_{mol}$

$\Delta S_{Hess}=\Delta S°_{NADH}+\Delta S°_{H3CC=OCOO}+\Delta S°_{H3O}-\Delta S°_{NAD+}-\Delta S°_{H3CCH2OHCOO}-\Delta S°_{H2O}=-547{,}9605$ $^{kJ}/_{mol}$

$\Delta S_{Hess}=-4081{,}784-846{,}664-3{,}854-(-3766{,}008-688{,}29+69{,}9565)=-547{,}9605$ $^{kJ}/_{mol}$

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=45{,}764-298{,}15*-0{,}5479605=209{,}14$....... $^{kJ}/_{mol}$ **endoergic**.............

Aerobic endoergic **lactate** oxidation Hesa free energy change positive $\Delta G_{Hess}=209{,}14$........ $^{kJ}/_{mol}$ inverse **pyruvate** anaerobic reduction negative $\Delta G_{Hess}=-209{,}14$........ $^{kJ}/_{mol}$, bet minimized inverse aerobic oxidation $\Delta G_{min}=\Delta G_{eq}Aerobic=76$...... $^{kJ}/_{mol}$ and $\Delta G_{min}=\Delta G_{eq}Anaerobic=-76$....... $^{kJ}/_{mol}$ reduction reaching equilibrium mixture constant $4{,}9336\bullet 10^{-14}=K_{eq}Aerobic$ value.

Prigogine attractor is free energy change absolute minimum ΔG_{min} reaching equilibrium.

$\Delta G_{min}=76$....... $^{kJ}/_{mol}$$=|\Delta G_{eq}|<|\Delta G_{Hess}|=209$........ $^{kJ}/_{mol}$.

Homeostasis maintain O_{2aqua} NADH oxidase with aerobic ration $[NADH]/[NAD^+]=10^{-6}$ favored lactate dehydrogenase eficiency $\Delta G_{aerobi}=75{,}955+RTln(1/10^6*1/1*10^{-7{,}36}/55{,}3)=75{,}955-86{,}2=-10{,}245$ $^{kJ}/_{mol}$.

THERMODYNAMICS Exercise XXI Lactate $\mathbf{H_3CCH(OH)COO^-}_{aq}$ decarboxylation $\mathbf{H_3CCH_2OH+HCO_3^-}$

Lactate $\mathbf{H_3CC{=}OCOO^-}$ conversion to ethanol $\mathbf{H_3CCHO}$ $\mathbf{+HCO_3^-}$ (25 C) 298.15 K, using the data table!

Reactants Lactate**+Q** => products ethanol bicarbonate

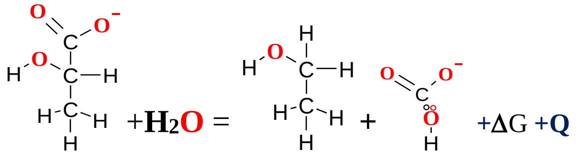
Substance	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$ kJ/mol
$\mathbf{H_3CCH(OH)COO^-}$	**-688,29**	**-1290,852**	**-303,4256**
$\mathbf{H_3CCH(OH)COO^-}$	-686,2	-557,71	-313.70
$\mathbf{H_3CCH_2OH_{aq}}$	**-290,77**	**-1227,764**	**75,2864**
$\mathbf{H_3CCH_2OH_l}$	-277,6	160,7	62.96
$\mathbf{H_2O}$	-285,85	69,9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$\mathbf{HCO_3^-}$	-689,93	98,324	-586,94
$\mathbf{HCO_3^-}$	**-692,4948**	**-494,768**	**-544,9688**

$\mathbf{H_3CCH(OH)COO^- + H_2O \Rightarrow H_3CCH_2OH_l + HCO_3 + Q} + \Delta G$

BioThermodynam06; $\Delta H_{Hess} = \Sigma\Delta H°_{products} - \Sigma\Delta H°_{reactants}$

CRC2010

$\Delta S_{Hess} = \Sigma\Delta S°_{products} - \Sigma\Delta S°_{reactants}$; $\Delta G_{Hess} = \Delta H_{Hess} - T\bullet\Delta S_{Hess}$



Lactate Ethanol **exothermic............**

$\Delta G_{Hess} = \Delta G°_{H3CCH2OH} + \Delta G°_{\mathbf{HCO3}} - \Delta G°_{\mathbf{H2O}} - \Delta G°_{H3CCH2OHCOO-} = \mathbf{75{,}2864 - 544{,}9688 - (-151{,}549 - 303{,}4256) = -14{,}71}$ kJ/mol

$\Delta H_{Hess} = \Delta H°_{H3CCH2OH} + \Delta H°_{\mathbf{HCO3}} - \Delta H°_{\mathbf{H2O}} - \Delta H°_{H3CCH2OHCOO-} = \mathbf{-290{,}77 - 692{,}4948 - (-286{,}65 - 688{,}29) = -8{,}325}$ kJ/mol

$\Delta S_{dispersed} = -\Delta H_{Hess}/T = \mathbf{8{,}325}/298{,}15 = \mathbf{27{,}9}$ J/K/mol;

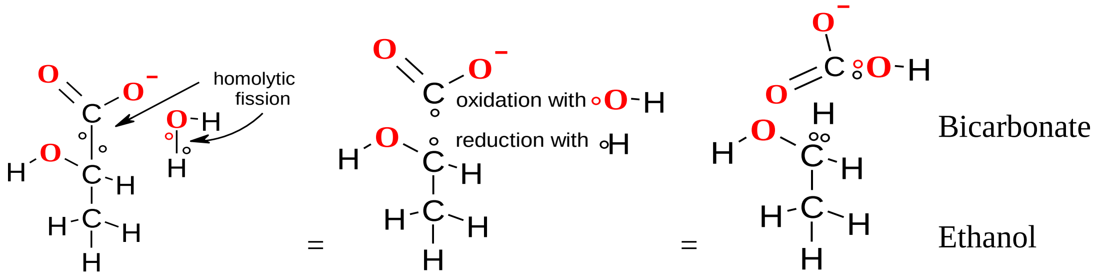
BioThermodynam06 $\Delta S_{Hess} = \Delta S°_{H3CCH2OH} + \Delta S°_{\mathbf{HCO3-}} - \Delta S°_{\mathbf{H2O}} - \Delta S°_{H3CCH2OHCOO-} =$ **21,51** J/mol/K;

$= \mathbf{-1227{,}764 - 494{,}768 - (-453{,}188 - 1290{,}852) = 21{,}51}$ J/mol/K**....**

$\Delta S_{total} = \Delta S_{Hess} + \Delta S_{dispersed} = \mathbf{21{,}51 + 27{,}9 = 49{,}41}$ J/mol/K;

$\Delta G_{Hess} = \Delta H_{Hess} - T^*\Delta S_{Hess} = \mathbf{-8{,}325} - 298{,}15^*0\mathbf{{,}02151 = -14{,}738}$ kJ/mol **exoergic**......

$T\bullet\Delta S_{total} = \mathbf{0{,}04941}^*298{,}15\ K = \mathbf{14{,}73}$ kJ/mol; bound TΔSn ;dispersed-lost energy **spontaneous**



Homolytic fission is chemical bond dissociation of a molecular bond by a process where each of the fragments (an atom or molecule) retains one of the original covalent bonded pair of electrons.

Decarboxiation with carboxilate molecule and water molecule homolitic fission carboxilate oxidises with **HO●** radical about bicarbonate ion $\mathbf{HCO_3^-}$ and carboxilate second fragment of molecule reducing with hydrogen radical **H●** (Ethanol).

THERMODYNAMICS Exercise XXII alanine $H_3CCHNH_3^+COO^-$ deamination pyruvate $H_3CC{=}OCOO^-$

Physiologic conditions pH=7,36 T=310,15 K (37° C)

Alanine deamination to pyruvic acid and pyruvate $H_3CC{=}OCOO^{--}$ (37 C) 310.15 K, using the data table!

<u>Reactants</u> Alanine $++O_{2aqua}+H_2O$ => <u>products</u> pyruvate + $2NH_4^+ + \Delta G + Q$

Substance	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$ kJ/mol
$H_3CC{=}OCOOH_{(aq)}$	-607,82	179,91	-
$H_3CC{=}OCOO^-$	-603,7	-433,54	-
$H_3CC{=}OCOO^-$	**-597,04**	**-846,664**	**-344,6168**
$H_3CCHNH_3^+COO^-$	-554,80	-616,47	-
NH_4^+ (aq)	-132,5	113,4	-79,3
NH_{3gas}	-45,94	192,77	-16,4
NH_{3aq}	**-132,5608**	**-739,2922**	**91,1056**
H_2O	-285,85	69,9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**
$H_3O^+_{(aq)}$	-285,81	-3,854	-213,27
O_{2aqua}	-11,715	110,876	16,4
O_{2aqua}	**-11.7**	**-94,2**	**16,4**

CRC10 1. $\Delta H_{Hess} = \Sigma\Delta H°_{products} - \Sigma\Delta H°_{reactants}$

Weak acid $NH_4^+{}_{(aq)} + H_2O + \Delta G + Q \Rightarrow H_3O^+ + NH_{3(aq)}$

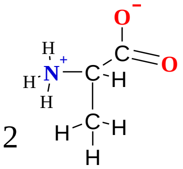
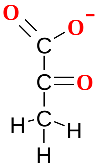
BioThermodynamics 2006; MassachusettsTinstitute

$pKa=9,245$; $\Delta G_H = -RTln(10^{-pKa}) = 52,77$ kJ/mol

$\Delta G_{eq} = -8,3144*298,15*ln(10^{-9,245}) = 52,77$ kJ/mol

$\Delta G_{Hess} = \Delta G°_{NH3} + \Delta G°_{H3O} - \Delta G°_{NH4} - \Delta G°_{H2O} = 151,5$ kJ/mol

$= \mathbf{91,1056} - 213,27 - (-79,3 + (\mathbf{-151,549} - 237,19)/2) = 151,5$ kJ/mol

D-Alanine 2  $+O_{2aqua}+H_2O$ =>Pyruvate 2  $+2NH_4^+ + \Delta G + Q$;

Alkaline solution $2H_3CCHNH_3^+COO^-{}_{(aq)} + O_{2aqua} + 2\ H_2O + Q \Rightarrow 2H_3CC{=}OCOO^-{}_{(aq)} + 2\ NH_{3(aq)} + H_3O^+ + \Delta G$

pH=7,36 BioChemic manner $2H_3CCHNH_3^+COO^- + O_{2aqua} + H_2O \Rightarrow 2H_3CC{=}OCOO^- + 2NH_4^+ + \Delta G + Q$

1. $\Delta H_{Hess} = 2\Delta H°_{H3CC=OCOO-} + 2\Delta H°_{NH4} - 2\Delta H°_{alanine} - \Delta H°_{O2} - \Delta H°_{H2O} = -51,13$ kJ/mol **exothermic**........................

$= 2*\mathbf{-597,04} + 2*-132,5 - (2*-554,8 \mathbf{-11,7-286,65}) =$ -51,135 exothermic.......................

2. $\Delta S_{dispersed} = -\Delta H_{Hess}/T = 51,135/298,15 = 171,51$ J/K/mol;

2. $\Delta S_{Hess} = 2\Delta S°_{H3CC=OCOO-} + 2\Delta S°_{NH4} - 2\Delta S°_{alanine} - \Delta S°_{O2} - \Delta S°_{H2O} = 313,8$ J/mol/K;

$= 2*\mathbf{-846,664} + 2*113,4 - (2*-616,47 \mathbf{-94,2-453,188}) = 313,8$.......... J/mol

3. $\Delta S_{total} = \Delta S_{Hess} + \Delta S_{dispersed} = 313,8 + 171,51 = 485,31$ J/mol/K

4. $\Delta G_{Hess} = \Delta H_{Hess} - T*\Delta S_{Hess} = -51,13 - 298,15*0,3138 = -144,7$ kJ/mol **exoergic**...

$T \bullet \Delta S_{total} = 485,31$ J/K/mol$\bullet 298,15$ K= **144,7.** kJ/mol;bound TΔSn <u>dispersed energy ΔG</u>$_{reversereaction}$ **spontaneous** ΔG_{Hess}

THERMODYNAMICS Exercise XXIII succinate $^{-}OOCCH_2CH_2COO^{-}$ malate $^{-}OOCHCOHCH_2COO^{-}$

Physiologic conditions pH=7,36 T=310,15 K (37° C)

Succinate $^{-}OOCCH_2CH_2COO^{-}$ to malate $^{-}OOCHCOHCH_2COO^{-}$ (37 C) 310.15 K, using the data table!

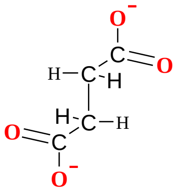
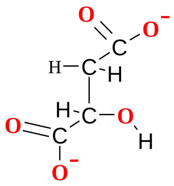
Reactants succinate + O_{2aqua} => products malate ionic force **I**=0 .

Substance	$\Delta H°$,$^{kJ}/_{mol}$	$\Delta S°$,$^{J}/_{mol/K}$	ΔG_h,$^{kJ}/_{mol}$	ΔH_h,$^{kJ}/_{mol}$	ΔS_h,$^{J}/_{mol/K}$	pK
$HOOCCH_2CH_2COO^{-}_{(aq)}$	-	-	24.02	3.36	-69.29	pK2=
$^{-}OOCCH_2CH_2COO^{-}_{(aq)}$	-908,7	-1,268	32.18	0.16	-107.40	pK1=
$^{-}OOCHCOHCH_2COO^{-}_{(aq)}$	-1079,8	-1,3314	30.02	0.16	-100.15	pK1=
O_{2aqua}	-11,715	110,876	-	-	-	-

1.$\Delta H_h=2\Delta H°_{-OOCHCOHCH2COO-}-2\Delta H°_{-OOCCH2CH2COO-}-_{\Delta}H°_{O2}$=..$^{kJ}/_{mol}$....

=2*-1079,8-2*-908,7-(-11,715)= -2159,6+1829,115= -330,485 **exothermic**...$^{........kJ}/_{mol}$.....

2.$\Delta S_{dispersed}$= -ΔH_h/T=330,485/310,15= 1065,565..............$^{J}/_{K/mol}$

succinate 2  + O_{2aqua} => malate 2  +ΔG +**Q**

2 $^{-}OOCCH_2CH_2COO^{-}_{(aq)}$ + O_{2aqua} => 2 $^{-}OOCHCOHCH_2COO^{-}_{(aq)}$ +ΔG +**Q**

2. $\Delta S_H=2\Delta S°_{-OOCHCOHCH2COO-}-2\Delta S°_{-OOCCH2CH2COO-}-_{\Delta}S°_{O2}$ =..$^{J}/_{mol/K}$....

....................=2*-1,3314-2*-1,268110,876=-2,6628-108,34= -111,0..$^{J}/_{mol/K}$....

3. $\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}$ =1065,565-111 = 954,565 .... $^{J}/_{mol/K}$

4. $\Delta G_H=\Delta H_H-T^{*}\Delta S_H$ = -330,485-310,15*0,111= -296,06...**exoegic**.$^{kJ}/_{mol}$......

T•ΔS_{total}=954,565 $^{J}/K/_{mol}$•310,15 K= **296,06**...$^{kJ}/_{mol}$.....

bound TΔSn← dispersed energy $\Delta G_{reversereaction}$ Q=330,485 $^{kJ}/_{mol}$ **spontaneous** ΔG_{Hess} = -296 $^{kJ}/_{mol}$...

$pK_{eq}=-\log(K_{eq})=-\ln(10)*(-\Delta G_{eq}/R/T)=-\ln(10)*(296,06*1000/8,3144/310,15)=-\ln(10)*79,9081=$ -4,38088.....

$K_{eq}=EXP(-\Delta G_{eq}/R/T)=10^{-pKeq}=10^{4,38088}=2,4*10^{4}$ temperature 310,15 K (37° C)

CRC Substance	$\Delta H°$,$^{kJ}/_{mol}$	$\Delta S°$,$^{J}/_{mol/K}$	ΔG_H,$^{kJ}/_{mol}$	ΔH_H,$^{kJ}/_{mol}$	ΔC_H,$^{J}/_{mol/K}$	pK	pK
$HOOCCH_2CH_2COO^{-}_{(aq)}$	-	-	-	3.0	-121	4,207	pK1=
$^{-}OOCCH_2CH_2COO^{-}_{(aq)}$	-	-	-	-0,5	-217	5,636	pK2=
$^{-}OOCHCOHCH_2COO^{-}_{(aq)}$	-	-	-	-3,6	-31	6,27	pK2=
$HOOCHCOHCH_2COO^{-}_{(aq)}$	-	-	-	1,1	-21	1,92	pK1=

THERMODYNAMICS Exercise XXIV xanthine $C_5H_4N_4O_2$ ureate $C_5H_4N_4O_3^-{}_{(s)}$
Physiologic conditions pH=7,36 T=310,15 K (37° C)

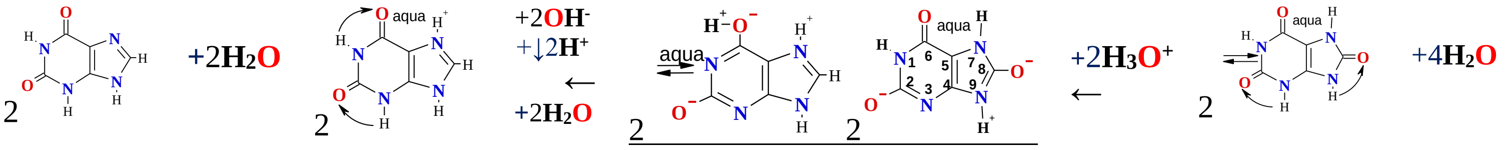
Xanthine $^-$ $C_5H_4N_4O_{2(s)}$ to ureate $^-$ $C_5H_4N_4O_3^-{}_{(s)}{}^-$ (37 C) 310.15 K, using the data table!
Reactants xanthine +O_{2aqua}=> products ureate ionic force **I**=0,25 .
pK$_a$ Alberty, Robert A.Q 2006.

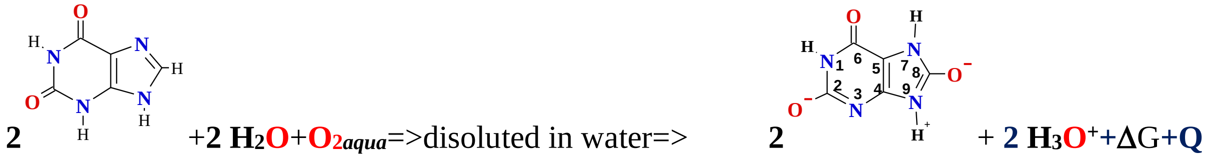
CRC 2010 *Substance*	$\Delta H°$, kJ/mol	$\Delta S°$, J/mol/K	ΔG_H, kJ/mol	ΔH_H, kJ/mol	ΔC_H, J/mol/K	pK	pK
Uric acid $C_5H_5N_4O_3^+{}_{(aq)}$	-	-	-193,84	3.0	-121	pK2=	4,207
ureate $C_5H_4N_4O_{3(aq)}$	-	-	-	-0,5	-217	pK1=	5,636
ureate $C_5H_3N_4O_3^-{}_{(s)}$	-618,80	173,20	-204,41	-	-	pK0=	11,3
xanthine $C_5H_5N_4O_2^+{}_{(aq)}$				1,1	-21	pK2=	1,92
xanthine $C_5H_4N_4O_{2(s)}$	-379,60	161,10	*-429,565*	-3,6	-31	pK1=	6,27
xanthine $C_5H_3N_4O_2^-{}_{(aq)}$	-	-	-	-	-	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	-	-	-	-

1.$\Delta H_H=2\Delta H°_{C5H3N4O3-}+ 2\Delta H°_{H3O} - 2\Delta H°_{H2O} -2\Delta H°_{C5H4N4O2}-\Delta H°_{O2}$=-466,605 **exothermic**........................kJ/mol....
=2*-618,80+2*-285,81-(-11,715+2*-285,85-2*379,6)=-1809,22+1342,615= -466,605..........................kJ/mol;

2.$\Delta S_{dispersed}=-\Delta H_H/T$=466,605/310,15=1504,449..J/K/mol

Xanthine protonation and protolysis (dissociation)





Reactants **2** $C_5H_4N_4O_{2(aqua)}$ +**2** H_2O + O_{2aqua} => **2** $C_5H_3N_4O_3^-{}_{(s)}$ **+2** H_3O^++ΔG **+Q** produkti
Xanthine$_{aqua}$ Ureate$_{aqua}$

2. $\Delta S_H=2\Delta S°_{C5H3N4O3-}+ 2\Delta S°_{H3O} - 2\Delta S°_{H2O} -2\Delta S°_{C5H4N4O2}-\Delta S°_{O2}$=..J/mol/K...
......=2*173,2+2*-3,854110,876-2*69,96-2*161,1=338,692-572,996= -234,304...J/mol/K;

3. $\Delta S_{total}= \Delta S_H+ \Delta S_{dispersed}$ =1504,449-234,304= 1270,145...J/mol/K;

4. $\Delta G_H = \Delta H_H - T^*\Delta S_H$ = -466,605-310,15*-0,234304= -393,936...**exoergic**.kJ/mol;

$T\bullet\Delta S_{total}$=1270,145 J/K/mol•310,15 K= **393,94**...kJ/mol;

bound TΔSn← dispersed energy Q=466,605 kJ/mol **spontaneous** ΔG_{Hess} = -393,936 kJ/mol...

pK$_{eq}$=-log(K$_{eq}$)=-ln(10)*(-ΔG$_{eq}$/R/T)=-ln(10)*(466,605*1000/8,3144/310,15)= -ln(10)*180,945= -5,19819............
K$_{eq}$ =EXP(-ΔG$_{eq}$/R/T)= $10^{-pKeq}=10^{5,19819}=1{,}58*10^5$ temperature 310,15 K (37° C)

5.$\Delta G_H=2\Delta G°_{C5H3N4O3-}+2\Delta G°_{H3O}-2\Delta G°_{H2O}-2\Delta G°_{C5H4N4O2}-\Delta G°_{O2}$=-1215,38 **exothermic**................................kJ/mol;
=2*-204,41+2*-213,275-(16,4+2*-237,191-2*-429,565)=-835,37-401,148= -1236,52.................................kJ/mol;

1.Alberty,Robert A.Q 2006,p463,John Wiley & Sons, Biochemical Thermodynamics Applications of Mathematica
2. David R. Lide, CRC Handbook of Chemistry and Physics, 2010, ©, p.2760

THERMODYNAMICS Exercise XXV CH_3CH_2-O-OCCH_3 hydrolysis to CH_3CH_2OH+HOOCCH_3

CH_3CH_2-O-OCCH_3+H_2O=>CH_3CH_2OH+$^-$O-OCCH_3;$\Delta G_{Lehninger}$=-19,6 $^{kJ}/_{mol}$

$\Delta G_{Hess}=\Delta G°_{CH3CH2OH}+\Delta G°_{CH3COO}-\Delta G°_{CH3CH2-O-OCCH3}-\Delta G_{H2O}$=**75,2864-241,663-(4,9176-151,549)=-19,745** $^{kJ}/_{mol}$;

$$K_{Lehninger}=\exp(19600/8,3144/298,15)=\frac{[CH_3COO^-\}\,[CH_3CH_2OH]}{[H_2O]\cdot[CH_3CH_2OOCCH_3]}=2715,172$$

I=0,25 M, **BioTherm06**, pH=7,36, $\Delta G_{Hess}=\Delta G°_{CH3CH2OH}+\Delta G°_{CH3COO}+\Delta G°_{H3O+}-\Delta G°_{CH3CH2-O-OCCH3}-2{*}\Delta G_{H2O}$= 89,8$^{kJ}/_{mol}$;

$\Delta H°,^{kJ}/_{mol}$	$\Delta H°,^{J}/_{mol/K}$	$\Delta S_H,^{kJ}/_{mol}$	$\Delta G°,^{kJ}/_{mol}$
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**
$C_2H_4OOCCH_3$	**-485,3**	**-1644,15**	**4,9176**
$C_2H_4OOCCH_3$	-	-	-11,52
CH_3CH_2OH	-	-	62.96
CH_3CH_2OH	-277,6	160,7	-174,8
CH_3CH_2OH	**-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**

=**75,2864-241,663**-213,275-(**4,9176**+2*****-237,191)=89,8 $^{kJ}/_{mol}$; pH=7,36

CH_3CH_2-O-OCCH_3+2H_2O=>CH_3CH_2-OH+$^-$O-OCCH_3+H_3O^+;

$\Delta H_H=\Delta H°_{CH3CH2OH}+\Delta H°_{CH3COO}+\Delta H°_{H3O}-\Delta H°_{CH3CH2OOCCH3}-2{*}\Delta H_{H2O}$=**-6,42**$^{kJ}/_{mol}$

=**-290,77-486,836**-285,81-(**-485,3+**2*****-285,85)=**-6,42** $^{kJ}/_{mol}$

$\Delta S_H=\Delta S°_{CH3CH2OH}+\Delta S°_{CH3COO}+\Delta S°_{H3O+}-\Delta S°_{CH3CH2-O-OCCH3}-2{*}\Delta S_{H2O}$=**-540,4** $^{J}/_{mol/K}$

=**-1227,76-813,043**-3,854-(**-1644,15+**2*****69,9565)=**-540,4** $^{J}/_{mol/K}$

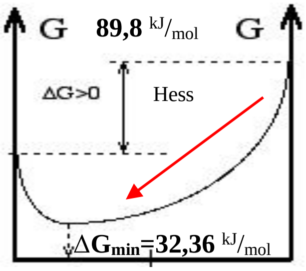
$\Delta G_H=\Delta H_H-T{*}\Delta S_H$=**-6,42**-298,15*-0,**5404=154,7**.$^{kJ}/_{mol}$ **endoergic**;

$$K_{eqLehninger}=K_{Lehninger}[H_3O^+]/[H_2O]=2715,172/55,34573{*}10^{\wedge(-7,36)}=\frac{[CH_3COO^-]\cdot[CH_3CH_2OH]\cdot[H_3O^+]}{[H_2O]^2\cdot[CH_3CH_2OOCCH_3]}=10^{\wedge(-5,67)}$$ At pH=7,36

ΔG_{eq}=-R•T•ln(K_{eq})=-R•T•ln($10^{\wedge(-5,67)}$)=-8,3144*298,15* **ln**($10^{\wedge(-5,67)}$)=32,36 $^{kJ}/_{mol}$;

Endoergic exothermic CH_3CH_2-O-OCCH_3 hydrolizeHess free energy change positive **$\Delta G_{hydrolise}$**=89,8 $^{kJ}/_{mol}$, but minimizes Δ**G_{min}**=Δ**G_{eq}**= 32,36 $^{kJ}/_{mol}$ reaching

equilibrium mixture **K_{eq}**=$10^{\wedge(-5,67)}$= $\frac{[CH_3COO^-]\cdot[CH_3CH_2OH]\cdot[H_3O^+]}{[H_2O]^2\cdot[CH_3CH_2OOCCH_3]}$.



A+2B 50% C+D+E

CH_3CH_2-O-OCCH_3+2**H_2O** reactants $^-$

products **H_3O^+** **CH_3CH_2OH+$^-$OOCCH_3**

Le Chatelier principle is

Prigogine attractor free energy change minimum **ΔG**$_{min}$ reacing at equilibrium mixture.

Free energy change minimum reaching establishes equilibrium.

THERMODYNAMICS Exercise XXVI. Osmolar concentration gradient $11=\Delta C_{osm}$ in green plants Calculate ΔH_H, ΔS_H, ΔG_H and the amount of heat **exothermic**, **athermic** or **endothermic** reaction at standard conditions 298.15 K. **PRC** Photo Synthetic Reaction Center ENZYME complex drive green plants products $\mathbf{C_6H_{12}O_6}$ and oxygen $6O_{2aqua}$. by photon **E=h•v** absorption Aquaporin substrates oxygen $\mathbf{6O_2}$ and water $\mathbf{6H_2O}$ increase **osmotic** pressure to outside cell 11 times as concentration in cell decreases from initial times $12=C_{osm}=6+6$ to one glucose $\mathbf{C_6H_{12}O_6}$ molecule $C_{osm}=1$. So total flow out of plant organisms through aquaporins increases 11 times:

$$\mathbf{6HCO_3^- + 6H_3O^+ + Q} \overset{PRC+hv}{=\!\!>} \mathbf{C_6H_{12}O_6 + 6O_{2aqua} + 6H_2O}$$

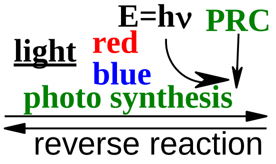
against **osmolar** concentration gradient 12/1. Oxygen $\mathbf{6O_2}$ and water $\mathbf{6H_2O}$ pushed out

out of cell $6H_2O+6O_{2aqua} \overset{\mathbf{Aquaporins}}{<\!=} 6O_{2aqua}+6H_2O$ inside cell

through Aquaporins in the **athermic** $\Delta H_{channel}= 0\ ^{kJ}/_{mol}$ manners (as no heat waste) and used energy gained from **PRC** Photo Synthetic Reaction Center ENZYME complexes $\Delta G_{PCR}=3040{,}1\ ^{kJ}/_{mol}$ (Exercise III) via absorbtion red and blue Photon energy **E=h•v** and through heat supply **Q**: p.4th

Bicarbonate + hydrogen ions + heat supply

$\mathbf{6HCO_3^- + 6H_3O^+ + Q} + \Delta G_{Hess}$



glucose + **oxygen** water

$\mathbf{C_6H_{12}O_6 + 6\ O_2 + 6H_2O}$

Mention whether the reaction will be **exoergic** or **endoergic**! Universal gas constant $R=8{,}3144\ ^{J}/_{mol/K}$;

$\Delta G_{channel}=\mathbf{-RTln}(C_{osm}[\mathbf{6O_{2aqua}+6H_2O}]_{left}/C_{osm}[\mathbf{6O_{2aqua}+6H_2O}]_{righ})=-12\mathbf{RTln}(12/1)= -36.96\ ^{kJ}/_{mol}$..........

Substance	before	after
O_{2aqua}	$[O_2]=6•10^{-5}$ M	$[O_2]=6•10^{-5}$ M
H_2O	55,3457 M	55,3457 M

$\Delta G_{O_2}=\mathbf{-RTln}([O_2]_{right}/[O_2]_{left})= \mathbf{-RTln}(K_{equilibrium})= -6.1599$ ....

....= $-8{,}3144*298{,}15*\mathbf{ln}(12/1)= -8{,}3144*298{,}15*-2.4849= -6.1599.\ ^{kJ}/_{mol}$

For $\mathbf{6O_{2}}_{aqua}$ $\Delta G_{6O_2}= -6.1599*6= -36.9596$ ....$^{kJ}/_{mol}$

$\Delta G_{6H_2O}=-6\mathbf{RTln}([H_2O]_{right}/[H_2O]_{left})=6*8{,}3144*310{,}15*\mathbf{ln}(1/12)= -36.9596$..$^{kJ}/_{mol}$...

For **6** $\mathbf{H_2O}$ $\Delta G_{6H_2O} = -6.1599*6= -36.9596$ ....$^{kJ}/_{mol}$

.**exoergic**......

......

$\Delta S_{6O_2}=-6\mathbf{Rln}([O_2]_{right}/[O_2]_{left})=-8{,}3144*\mathbf{ln}(1/12)=20{,}66*6=123.96$...$^{J}/_{mol/K}$;

$\Delta S_{6H_2O}=-6\mathbf{Rln}([H_2O]_{right}/[H_2O]_{left})= -8{,}3144*\mathbf{ln}(1/12)=123.96$..$^{J}/_{mol/K}$;

......

$\Delta H_{channel}=.0$........ $^{kJ}/_{mol}$..no heat waste...

......

$T•\Delta S_{6O2}= -0{,}12396•298{,}15=\mathbf{36.9596}$................kJ/mol used energy of **PRC** bound $T\Delta Sn=3040{,}1\ ^{kJ}/_{mol}$ out off $\mathbf{O_2}$...

$T•\Delta S_{6H2O} = -0{,}12396•298{,}15=\mathbf{36.9596}$.............kJ/mol used energy of **PRC** bound $T\Delta Sn=3040{,}1\ ^{kJ}/_{mol}$ out off $\mathbf{H_2O}$

......

For $\mathbf{6O_{2}}_{aqua}+\mathbf{6H_2O}$ $T•\Delta S_{6H2O+6O2}=\mathbf{36.9596+36.9596=73.919}$............kJ/mol of **PRC** bound $T\Delta Sn=3040{,}1\ ^{kJ}/_{mol}$

athermic $\Delta H°_{Hess}$ =+0 kJ/mol; Q= -0 kJ/mol ...**spontaneous** $\Delta G°_{Hess}$ = **-73.919** kJ/mol ....

The **Photosynthesis** dilutes of osmolar concentration by $\mathbf{6O_{2}}_{aqua}+\mathbf{6H_2O}$ consuming bicarbonate end hydrogen ions $\mathbf{6HCO_3^- + 6H_3O^+}$ drive spontaneous flow of $\mathbf{6O_{2}}_{aqua}+\mathbf{6H_2O}$ through aquaporins out of **PRC** cells against membrane concentration gradient 12/1 with standard free energy $\Delta G_{6H2O+6O2}=$ **-73.919** kJ/mol per one glucose mol $\mathbf{C_6H_{12}O_6}$!

THERMODYNAMICS IV Vitamin B3 the **RetinolCH_2-OH** oxidation to **RetinalCH=O** aerobic Vitamin B3 for anaerobic ethanal reduction to ethanol product with alcohol dehydrogenase using the data table!

RetnolCH_2-OH+NAD^++**H_2O**+**ΔG+Q**=>**RetinalCH=O**+NAD**H**+**H_3O^+**

Substance	ΔH°_H $^{kJ}/_{mol}$	ΔS°_H $^{J}/_{mol/K}$	ΔG°_H $^{kJ}/_{mol}$
RetinalCH=O			**1141,45**
RetinalCH=O	**-**	**-**	**1198,9852**
Retinol**CH_2OH**			**1195,07**
Retinol**CH_2OH**	-	-	**1256,7164**
NAD**H**	**-41,41**	**-4465,708**	**1175,5732**
NAD**H**	-1036,66	-140,50	1120,09
H_3O^+	-285.81	-3.854	-213,275
NAD^+	**-10,30**	**-3766,008**	**1112,534**
NAD^+	-1007,48	-183	1059,11
H_2O	-285.85	69.9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**

I=0 M; I=0,1 M

1118,78;1135,91;

Thermodynamic **$E^{\circ 2}_{Retinol}$=0,2415+0,10166=0,34316 V**;

1170,78;1189,14;

Absolute **$E^{\circ 2}_{Retinol}$=0,34316**-0,3982=-0,05504 **V**;

Biochemistry Thermodynamic 2006, Alberty Masachusetts

CRC Handbook of Chemistry un Physics 2010 90th David R. Lide

Red RetnolOH +2H_2O=RetinalCH=O+2H_3O^++H^-(2e^-) ;

$E^{\circ 2}_{H2O}$ =0,190+0,0591/2*log([**H_2O**]^2)=**0,2415 V**;

Ox NAD$^+$+H^-(2e^-)=NADH ; **$E^{\circ 1}$**=-0,4095 **V;**

Standard potential **E° voltos** David Harris; KortlyShucha data

$\Delta G_{Hess}=\Delta G^\circ_{\mathbf{RetinalCHO}}+\Delta H^\circ_{\mathbf{NADH}}+\Delta G^\circ_{\mathbf{H3O}}-\Delta G^\circ_{\mathbf{RetinnnolOH}}-\Delta H^\circ_{\mathbf{NAD+}}-\Delta H^\circ_{\mathbf{H2O}}=$

ΔG_{Hess}=**1198,9852+1175,5732-151,549-(1256,7164**+1059,11-237,191)=144,4 $^{kJ}/_{mol}$ endoergic;

Summary **Red** - **Ox**: **RetnolCH_2-OH**+NAD^++**H_2O**+**ΔG+Q**=>**RetinalCH=O**+NAD**H**+**H_3O^+;**

By convention balanced **n = 2 = m** number of electrons **2e^-**ΔE° is expressed as **$E^{\circ 2}_{H2O}$** of the electron **donor** minus **$E^{\circ 1}$** of the electron **acceptor**. Because **NAD$^+$** is **accepting** electrons from **ethanol** in our example

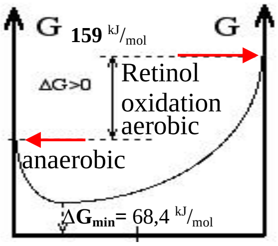
Absolute **$E^{\circ 2}_{Retinol}$=0,34316**-0,3982=-0,05504 **V**

$\Delta E^\circ=E^{\circ 2}_{H2O}-E^{\circ 1}$=-0,05504–(-0,4095)=**0,3545 V**, **n** is **2**;

$\Delta G_{eq Aerobic}=\Delta E^\circ\bullet F\bullet n=(-0,05504-(-0,4095))*2*96485=(0,3545)*2*96485=-R\bullet T\bullet \ln(K_{eq})= 68,4$ $^{kJ}/_{mol}$

$$K_{eq Aerobic}=\frac{[NADH]\cdot[Retinal\,CHO]\cdot[H_3O^+]}{[NAD^+]\cdot[Retinol\,OH]\cdot[H_2O]}=e^{-\frac{\Delta G_{eqAerobic}}{R\bullet T}}=e^{-\frac{68408}{8.314\bullet 298.15}}=1{,}036\bullet 10^{-12}=10^{-11{,}985}$$; Homeostasis joined

O_2aqua NADH oxidase with alcochol dehydrogenase ratio [**NADH**]/[**NAD$^+$**]=10^{-6} favored $\Delta G_{aerobic}$**=68,4**+ **R•T•ln**(1/10^6*1/1*$10^{-7,36}$/55,3)=**68,4**-86,2= -17,8.......$^{kJ}/_{mol}$ negative. Aerobic endothermic and endoergic Retinol**OH** oxidation Hess law free energy change positive **ΔG_{Hess}**= 144,4........$^{kJ}/_{mol}$ inverse to **Retinal=O** anaerobic reduction negative **ΔG_{Hess}**= -144,4........$^{kJ}/_{mol}$, but minimized inverse in aerobic oxidation **ΔG_{min}**=**ΔG_{eq}**Aerobic=68,4......$^{kJ}/_{mol}$ and anaerobic **ΔG_{min}**=**ΔG**eqAnaerobic= -68,4.......$^{kJ}/_{mol}$ reduction reaching equilibrium mixture constants **$10^{-11,985}$=K_{eq}**Aerobic Retinol**OH** oxidation and **Retinal=O** reduction anaerobic **$10^{11,985}$=K_{eq}**Anaerobic.



A+B+C50%D+E+F

NAD^++H_3CCH_2OH+ H_2O

NADH+H_3CCHO+H_3O^+

Prigogine attractor is free energy change absolute minimum at Equilibrium

ΔG_{min}=68,4.......$^{kJ}/_{mol}$= | **ΔG_{eq}** | < | **ΔG_{Hess}** | **=144,4**........$^{kJ}/_{mol}$.

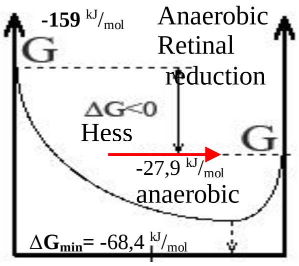
Anaerobic **ΔG_{eq}=ΔE°•F•n**=-0.3545 V•2 mol•96485 $^{C}/_{mol}$= -68,4........$^{kJ}/_{mol}$ favored.

Insufficient low **O_2**aqua concentration hypoxia to anaerobic alcohol oxidation unfavored but ethanal reduction to ethanol favored ratio [**RetinolOH**]/[**Retinal=O**]=1/10 **homeostasis** reduction with NADH reductase enzyme as negative free energy change

$\Delta G_{anaerobic}$= -27,86........$^{kJ}/_{mol}$

Anaeirobic homeostasis ratio [**NAD$^+$**]/[**NADH**]=1/10 over [**NADH**] favore reduction:

$$\Delta G_{anaerobic}=-68{,}4+8{,}3144*298{,}15*\ln\left(\frac{1}{10}\,\frac{1}{10}\,\frac{55.333}{10^{-7.36}}\right)=-27{,}86\ ^{kJ}/_{mol}$$;



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

NADH+H_3CCHO+H_3O^+

NAD^++H_3CCH_2OH+ H_2O

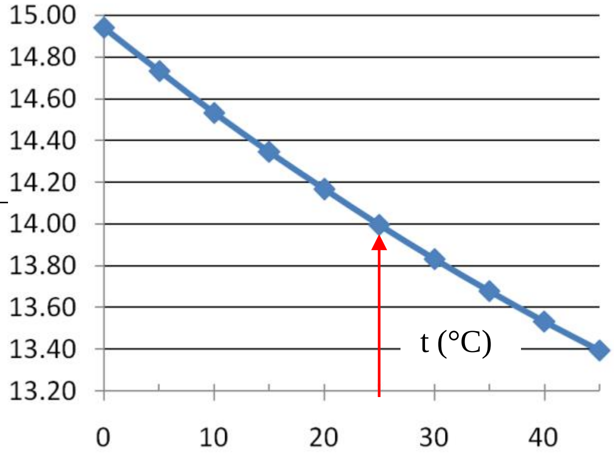
$$K_{eqAnaerobic}=\frac{[NAD^+]\cdot[Retinol\,OH]\cdot[H_2O]}{[NADH]\cdot[Retinal\,CHO]\cdot[H_3O^+]}$$; **K_{eq}** Weak Aerobic=$\frac{[NADH]\cdot[Retinal\,CHO]\cdot[H_3O^+]}{[NAD^+]\cdot[Retinol\,OH]\cdot[H_2O]}$;[**NADH**]/[**NAD$^+$**]=770/1;

$\Delta G_{aerobic}$=68,4+8,3144*298,15*ln(770/1*1/1*55,3457/$10^{-7,36}$)=0,028 $^{kJ}/_{mol}$.

Table 1.6 Ion product of water at different temperatures. (According to B. E. Conway)

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



$$K_{eq1}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=3.26\bullet 10^{-18};$$

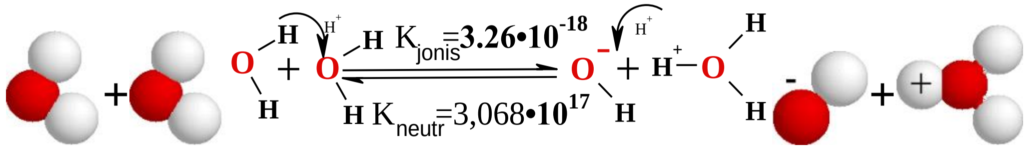
$=10^{\wedge(-13,9965)}/55,34573^{\wedge 2}=3,291*10^{\wedge(-18)}$;

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

endoergic..................

Equilibrium reached by free energy minimum at compounds mixture ratio in expression: Thermodynamic unfavored:

Alberty [8] free energy for hydrogen gas $G°_{H2gas}=85.64$ kJ/mol lets appreciate oxygen free energy for gas and aqua $G_{O2gas}=303.1$ kJ/mol; $G_{O2aqua}=329.68$ kJ/mol , relative to homeostasis products zero $G_{H2O}=G_{CO2gas}=0$ kJ/mol and for $G_{H3O++OH-}=G_{H3O+}+G_{OH-}=22.44+77.36=G_{H3O+}+G_{OH-}-G_{2H2O}=-R\bullet T\bullet\ln(K_{H3O++OH-})+2*0=99.8$ kJ/mol hydroxonium and hydroxide ions. [1,8,14]

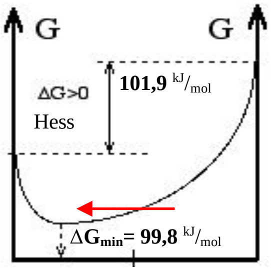


$$K_{eq1}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=\mathbf{3,26\bullet 10^{-18}}$$

$$\Delta \mathbf{G_{eq1}} = -\mathbf{R\bullet T\bullet \ln}(K_{eq1})= -\mathbf{R\bullet T\bullet \ln}\left(\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}\right) = 99,8 \text{ kJ/mol},$$

Endothermic and endoergic water protolysis reaction Hess free energy change $\Delta \mathbf{G_{Hess}}=\Delta \mathbf{G_{protolyse}}=101,9$ kJ/mol positive, but minimizes reached equilibrium

$$\mathbf{K_{eq1}}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=\mathbf{3.26\bullet 10^{-18}} \text{; up to } \Delta \mathbf{G_{min}} = \Delta \mathbf{G_{eq}} = 99,8 \text{ kJ/mol}$$



A+B 50% C+D

$\mathbf{H_2O+H_2O}$ reactants

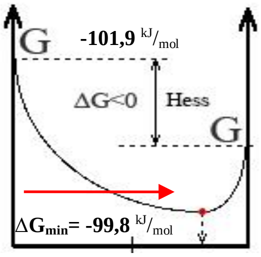
products $\mathbf{H_3O^++OH^-}$

Free energy change $\Delta \mathbf{G}_{Hess}$ for pure compounds by absolute value in Hess law is greater. Reaching equilibrium mixture of compounds free energy change minimizes: $\mathbf{99,8}$ **kJ/mol** $=|\Delta \mathbf{G_{eq}}|<|\Delta \mathbf{G_{Hess}}|=\mathbf{101,9}$ **kJ/mol**

All reactions trend to Prigogine attractor minimum of free energy change $\Delta \mathbf{G_{min}} = \Delta \mathbf{G_{eq}}$ at equilibrium mixture with active mass law inverse reactions constants:

$$3.26\bullet 10^{-18}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=K_{eq1}=\frac{1}{K_{eq2}}=\frac{1}{\frac{[H_2O]\cdot[H_2O]}{[OH^-]\cdot[H_3O^+]}}=\frac{1}{3,068*10^{17}}\,.$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum ΔG_{min} reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.



C+D 50% A+B

$\mathbf{H_3O^++OH^-}$ reactants

products $\mathbf{H_2O+H_2O}$.

Water factorial constant and concentration square K_w water constant.

$K_{eq1}*[\mathbf{H_2O}]^2=3.26\bullet 10^{-18}*55,33^2=10^{-14}=K_w$,

one calculates water ions factorial constant $K_w = [\mathbf{H_3O^+}][\mathbf{OH^-}]=10^{-14}$,

In 1977 declared Ilya Prigogine attractors create order in apparent chaos of universe.

It claims that our Universe was created in perfect order and show that each process trends to Prigogine attractor – energy change minimum in mixture of dissipated structures.

Glucose (Glc) $C_6H_{12}O_6$, biochemical water **$6H_2O$** and oxygen **$6O_{2aqua}$** energy $\Delta G_{Lehninger}= +2840\ ^{kJ}/_{mol}$ by oxidation generate concentrations gradients of **$6HCO_3^-$** and **$6H_3O^+$** ions:

$$C_6H_{12}O_6+6O_{2aqua}+6H_2O=>6H_3O^++6HCO_3;\ \Delta G_{Lehninger}= -2840\ ^{kJ}/_{mol} .$$

Generated **$6HCO_3^-$+$6H_3O^+$** ions drive $6O_{2aqua}+6H_2O$ through membranes aquaporins channels for osmosis against the concentration gradients but transporting ions **$6HCO_3^-$+$6H_3O^+$** down the gradients through membrane bicarbonate and proton channels .

Glc Formation 6^{th} page $C+6H_{2gas}+3O_{2gas}=>C_6H_{12}O_6$; $\Delta G^{\circ}_{Alberty}=\mathbf{-402{,}05}\ ^{kJ}/_{mol}$; $\Delta G^{\circ}_{HessCRC}=-919\ ^{kJ}/_{mol}$;

$$\Delta G^{\circ}_{Alberty}=G_{C6H12O6}-(6G_{Cgraph}+6*G_{H2gas}+3*G_{O2gas})=-402{,}05\ ^{kJ}/_{mol} ;$$

$$\Delta G^{\circ}_{Alberty}+(6G_{Cgraph}+6*G_{H2gas}+3*G_{O2gas})=-402{,}05+(6*91{,}26+6*85{,}6+3*303)=G_{C6H12O6}=1568\ ^{kJ}/_{mol} ;$$

$$\Delta G^{\circ}_{HessCRC}+(6G_{Cgraph}+6*G_{H2gas}+3*G_{O2gas})=-919+(6*91{,}26+6*85{,}6+3*303)=G_{C6H12O6}=1051\ ^{kJ}/_{mol} ;$$

Glucose free energy by Alberty $G_{C6H12O6}=\mathbf{1568}\ ^{kJ}/_{mol}$ and Alberty - Lehninger $G_{C6H12O6}=2268.8\ ^{kJ}/_{mol}$. [8,6]
Free energy at quasi equilibrium calculates one using Lehninger data [6] for oxidation -2840 $^{kJ}/_{mol}$ and

$$C_6H_{12}O_6+6O_{2aqua}+6H_2O=>6H_3O^++6HCO_3;\ \Delta G_{Lehninger}= -2840\ ^{kJ}/_{mol} .$$

$$\underline{-2840}=-G_{C6H12O6}-6*G_{O2Homeostasis\_arterial}-6*G_{H2O\_Biochem}+(6*G_{H3O+}+6*G_{HCO3-})$$

$$G_{C6H12O6}=\underline{2840}-6*G_{O2Homeostasis\_arterial}-6*G_{H2O\_Biochem}+(6*G_{H3O+}+6*G_{HCO3-})=2268.8\ ^{kJ}/_{mol}.$$

Free energy of glucose $G_{C6H12O6}=\underline{2840}-6*\mathbf{78.08}-6*\mathbf{85.64}+6*(\mathbf{22.44}+\mathbf{46.08})=2268.8\ ^{kJ}/_{mol}$,
Free energy of glucose__$G_{C6H12O6}=\underline{2840}-6*\mathbf{330}-6*\mathbf{0}+6*(\mathbf{22.44}+\mathbf{46.08})=\mathbf{1271}\ ^{kJ}/_{mol}$,
Free energy of glucose_$G_{C6H12O6}$ $=2840-6*\mathbf{330}-6*\mathbf{85{,}64}+6*(\mathbf{22{,}44}+\mathbf{46{,}08})=\mathbf{757}\ ^{kJ}/_{mol}$,
Free energy of glucose $G_{C6H12O6}=\underline{2840}-6*\mathbf{78.08}-6*0+6*(\mathbf{22.44}+\mathbf{46.08})\underline{=2782.6}\ ^{kJ}/_{mol}$.
Glucose free energy by Alberty $G_{C6H12O6}=\mathbf{1568}\ ^{kJ}/_{mol}$ and Alberty - Lehninger $G_{C6H12O6}=2268.8\ ^{kJ}/_{mol}$. [8,6]

Oxygen absolute Standard potential $E^{\circ}_{O2}=1.0868$ V create arterial absolute potential 0.4349 Volts at homeostasis attractors $[H_3O^+]=10^{\wedge(-7{,}36)}$ M, $[HCO_3^-]=\mathbf{0{,}0154}$ M, $[C_6H_{12}O_6]= 5*10^{\wedge(-3)}$ M and $[H_2O]=55{,}3$ M:
It's relative include in Alberty data formed scale with hydrogen absolute standard potential $E^{\circ}_{H(Pt)}=\mathbf{-0.2965}$ V.
Note: Classic potential scale is assumed for hydrogen classic reference zero $E^{\circ}_{H(Pt)classic}=\mathbf{0}$ V.

Nernst's half reaction: $6H_2O<=>O_{2aqua}+4H_3O^++4e^-$; $E^{\circ}_{O2}=1.0868$ V; $\Delta G_{eqO2}=E^{\circ}_{O2aq}\bullet F\bullet n_{\underline{e-}}=\mathbf{419{,}3}\ ^{kJ}/_{mol}$.

$$\Delta G_{O2aqAlberty}=G_{O2aq}+4G_{H3O+}-6G_{H2O}=\mathbf{330}-4*\mathbf{22{,}44}-6*\mathbf{0}=\mathbf{419{,}76}\ ^{kJ}/_{mol}\ \Delta G_{eqO2}=1{,}0865*96485*4=\mathbf{419{,}3}\ ^{kJ}/_{mol}:$$

$$E_{O2}=E^{\circ}_{O2}+{}^{0.0591}/_{4}\bullet\log([O_{2aqua}]\bullet[H_3O^+]^4/_{[H2O]^6})=1.0868+{}^{0.0591}/_{4}*\log(6*10^{-5}*10^{\wedge(-7.36*4)}/_{55.346^{\wedge 6}})=0.4349\text{ Volts} .$$

Oxygen homeostasis energy change $\Delta G_{eqHomeostasisO2}=E^{\circ}_{O2}\bullet F\bullet 1\bullet 4=0{,}4346*96485*4=\mathbf{167{,}7}\ ^{kJ}/_{mol}$
as reductant with six oxygen molecules half reactions produce Lehninger energy change $\Delta G_{Lehninger}=-2840\ ^{kJ}/_{mol}$.
Potentials difference is $\Delta E=\Delta G_{eq}/F/n=(E^{\circ}_{C6H12O6}-E^{\circ}_{O2})=-2840000/96485/24=-1.2264$ V.
Absolute Standard potential for glucose from Lehninger data is: $E^{\circ}_{C6H12O6}=\Delta E+E_{O2}=-1{,}226+1{,}0868=-0{,}1392$ V :
Nernst's half reaction $C_6H_{12}O_6+42H_2O<=>30H_3O^++6HCO_3^-+24\ e^-$ has potential $E^{\circ}_{C6H12O6}=-0{,}1392$ V :
$\Delta G_{AlbertyAbsoluteC6H12O6}=E^{\circ}_{C6H12O6}\bullet F\bullet 1\bullet 24=\mathbf{-0{,}}1392*96485*24=\mathbf{-322}\ ^{kJ}/_{mol}$ calculated is exoergic free energy change: $\Delta G_{AlbertyC6H12O6}=30*G_{H3O+}+6*G_{HCO3-}\ (G_{C6H12O6}+6*G_{O2Homeostasis\_arterial}+42*G_{H2O\_Biochem})=\mathbf{-\ 1086{,}8}\ ^{kJ}/_{mol}$
negative $\Delta G_{AlbertyHessC6H12O6}=30*\mathbf{22{,}44}+6*\mathbf{46{,}08}-(\mathbf{1568}+6*\mathbf{78{,}08}+42*\mathbf{0})=\mathbf{-1086{,}8}\ ^{kJ}/_{mol}$.

Homeostasis potential **is** $E_{C6H12O6}=E^{\circ}_{C6H12O6}+{}^{0.0591}/_{24}\bullet\log([HCO_3^-]^6\bullet[H_3O^+]^{30}/_{[C6H12O6]}/_{[H2O]^{42}})=$
$=-0{,}1392+{}^{0{,}0591}/_{24}*\log(\mathbf{0{,}0154}^{\wedge\mathbf{6}}*10^{\wedge(-7{,}36*30)}/5/10^{\wedge(-3)}/_{55{,}346^{\wedge 42}})=\mathbf{-0{,}8843}$ Volts and free energy change of homeostasis is exoergic, negative $\Delta G_{HomeostasisC6H12O6}=E^{\circ}_{C6H12O6}\bullet F\bullet 1\bullet 24=\mathbf{-0{,}88427}*96485*24=\mathbf{-2047{,}65}\ ^{kJ}/_{mol}$.
$\Delta G_{Lehninger}= \Delta E\bullet F\bullet n=(E^{\circ}_{C6H12O6}-E^{\circ}_{O2})\bullet F\bullet n=(-0{,}1392-1{,}0868)\bullet F\bullet n=-1{,}226*96485*24=\mathbf{-2840}\ ^{kJ}/_{mol}$.

$$\Delta G_{Homeostasis}= \Delta E\bullet F\bullet n=(E^{\circ}_{C6H12O6}-E^{\circ}_{O2})\bullet F\bullet n=(\mathbf{-0{,}88427}-0{,}4349)\bullet F\bullet n=-1{,}31917*96485*24=\mathbf{-3054{,}7}\ ^{kJ}/_{mol}.$$

Glucose Nernst's half reaction $\Delta G_{eqC6H12O6}=E^{\circ}_{C6H12O6}\bullet F\bullet 1\bullet 24=-0{,}1392*96485*24/1000=\mathbf{-322{,}34}\ ^{kJ}/_{mol}$
on Alberty data Hess calculated $\Delta G_{AlbertyC6H12O6}=30*\mathbf{22{,}44}+6*\mathbf{46{,}08}-(\mathbf{1271}+6*\mathbf{78.1}+42*\mathbf{0})=\mathbf{-789{,}9}\ ^{kJ}/_{mol}$ and
Biochemistry conditions Hes s value $\Delta G_{HessC6H12O6}=30*\mathbf{22{,}44}+6*\mathbf{46{,}08}-(2268{,}8+6*\mathbf{78.1}+42*\mathbf{0})=\mathbf{-1787{,}7}\ ^{kJ}/_{mol}$.
The oxygen reduction: $6*(O_{2aqua}+4H_3O^++4e^-\Leftrightarrow 6H_2O;)$ standard potential $E^{\circ}_{O2}=\mathbf{1.0868}$ Volts and Glucose Homeostasis constant with values $[H_3O^+]=10^{-7{,}36}$ M, $[HCO_3^-]=\mathbf{0{,}0154}$ M, $/[C_6H_{12}O_6]=5*10^{-3}$ M , water $[H_2O]=55{,}3$ M and $\Delta G_{Lehninger}=2840\ ^{kJ}/_{mol}$ is greater about one $K_{eqHomeostasis}=10^{\wedge 498}{}_t$:

$$K_{eqHomeostasis}=\frac{[HCO_3^-]^6[H_3O^+]^6}{[C_6H_{12}O_6].[O_2]^6[H_2O]^6}=EXP(-\Delta G_{eqHomeostasis}/R/T)=EXP(\mathbf{2840000}/8{,}3144/298{,}15=10^{\wedge 498}:$$

Quasi state equilibrium drived irreversibly as engine of photosynthesis accumulates free energy in products:

$$6H_3O^++6HCO_3=\text{Photosynthesis}=>C_6H_{12}O_6+6O_{2aqua}+6H_2O;\ \Delta G_{Lehninger}= 2840\ ^{kJ}/_{mol} .$$

Using Hess law 2840 $^{kJ}/_{mol}=G_{C6H12O6}+6*G_{O2Homeostasis\_arterial}+6*G_{H2O\_Biochem}-(6*G_{H3O+}+6*G_{HCO3-})$.
Free energy content of one mol glucose is Hess law calculates referring Alberty [8,15] data**.**

THERMODYNAMICS V h **Pyruvate** Nernsta laktāts $H_3CHC(OH)COO^-$.

$H_3CHC(OH)COO^- + \mathbf{H_2O} \Rightarrow H_3CC{=}OCOO^- + \mathbf{H_3O^+} + \mathbf{H^-(H^+ + 2e^-)}$; $\mathbf{E^\circ}_{H3CHC(OH)COO} = -0,0159$ V;

$\Delta \mathbf{G}_{\mathbf{eq}H3CHC(OH)COO} = \mathbf{E^\circ}_{\mathbf{eq}H3CHC(OH)COO} \bullet F \bullet 2 = \mathbf{-0,}0159 * 96485 * 2 = \mathbf{-3,068}$ kJ/mol;

$\Delta \mathbf{G}_{\mathbf{HessCH3CH2OH}} = \mathbf{G}_{H3CC=OCOO} + G_{H3O+} + G_{H-} - (\mathbf{G}_{H3CHC(OH)COO} + G_{\mathbf{H2O}}) = \mathbf{534,2} + \mathbf{22,44} + G_{H-} - (\mathbf{668,8} + 0) = \mathbf{-3,068}$ kJ/mol.

$\Delta \mathbf{G}_{\mathbf{HessCH3CH2OH}} = \mathbf{G}_{H3CC=OCOO} + G_{H3O+} + G_{H-} - (\mathbf{G}_{H3CHC(OH)COO} + G_{\mathbf{H2O}\_Biochem}) = \mathbf{534,2} + \mathbf{22,44} + G_{H-} - (\mathbf{668,8} + \mathbf{85,64}) = \mathbf{-3,068}$ kJ/mol.

$\Delta \mathbf{G}_{\mathbf{HessCH3CH2OH}} - \mathbf{G}_{H3CC=OCOO} - G_{H3O+} + (\mathbf{G}_{H3CHC(OH)COO} + G_{\mathbf{H2O}}) = G_{H-} = \mathbf{-3,068-534,2-22,44+(668,8}+0\mathbf{)=109,092}$ kJ/mol.

$\Delta \mathbf{G}_{\mathbf{HessCH3CH2OH}} - \mathbf{G}_{H3CC=OCOO} - G_{H3O+} + (\mathbf{G}_{H3CHC(OH)COO} + G_{\mathbf{H2O}\_Biochem}) = G_{H-} = \mathbf{-3,068-534,2-22,44+(668,8+85,64)=194,7}$ kJ/mol.

I=0,25 M, **BioTherm06**, pH=7,36, $\Delta G_H = G^\circ_{H3CC=OCOO-} + G^\circ_{\mathbf{H3O}+} + G_{H-} - G_{H3CHC(OH)COO-} - G_{\mathbf{H2O}} =$ kJ/mol;

Viela	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H , kJ/mol ;
PyruvEnolP^{3-}	-1400	-1100	-1189,73
$H_3CC{=}OCOO^-$	-597,4	-850	-350,78
$H_3CC{=}OCOO^-$	-603,7	-433,54	-474,44
$H_3CC{=}OCOO^-$	**-597,04**	**-846,66**	**-344,62**
$\mathbf{H_3O^+}$	-285,81	-3,854	-213,275
$\mathbf{H_2O}$	-285,85	69,9565	-237,191
$\mathbf{H_2O}$	**-286,65**	**-453,188**	**-151,549**
$H_3CHC(OH)COO^-$	**-688,29**	**-1290,9**	**-303,4**
$H_3CHC(OH)COOH$			

$G_{\mathbf{H2O}} = \mathbf{0}$ kJ/mol; $G_{H-} = \mathbf{-3,068-534,2-22,44+(668,8}+0\mathbf{)=109,092}$ kJ/mol

$G_{\mathbf{H2O}\_Biochem} = \mathbf{85,64}$ kJ/mol; $G_H = \mathbf{-3,068-534,2-22,44+(668,8}+\mathbf{85,64)=194,7}$ kJ/mol

$G_{H3CHC(OH)COO} = \mathbf{534,2}$ kJ/mol;

$G_{H3CHC(OH)COO} = \mathbf{668,8}$ kJ/mol;

$G_{H3CHC(OH)COOH+} = 3G_{C\mathbf{O2}gas} + 3G_{H2O} - (3G_{\mathbf{O2}gas}) = \mathbf{2271}$ kJ/mol;

$\mathbf{pK_a} = 3,86$; $\Delta H_c^\circ = 1361,9$ kJ/mol; $G_{H3CHC(OH)COOH} = \mathbf{2271}$ kJ/mol; $H_3CHC(OH)COOH + 3\mathbf{O_2}_{gas} = 3C\mathbf{O_2}_{gas} + 3\mathbf{H_2O}$;

$\mathbf{\Delta} H_c^\circ = 3G_{C\mathbf{O2}gas} + 3G_{H2O} - (G_{H3CHC(OH)COOH} + 3G_{\mathbf{O2}gas}) = 3*\mathbf{0} + 3*\mathbf{0} - (G_{H3CHC(OH)COOH} + 3\mathbf{*303}) = 1361,9$ kJ/mol;

$G_{H3CHC(OH)COOH+} = 3G_{C\mathbf{O2}gas} + 3G_{H2O} - (3G_{\mathbf{O2}gas}) = 3*\mathbf{0} + 3*\mathbf{0} - (+3\mathbf{*303}) - 1361,9 = G_{H3CHC(OH)COOH} = \mathbf{2271}$ kJ/mol;

Lactic acid Formation 71st page $3\mathbf{C} + 3\mathbf{H_{2gas}} + 1,5\mathbf{O_2}_{gas} \Rightarrow H_3CHC(OH)COOH$; $G_{H3CHC(OH)COOH} = \mathbf{-303,4}$ kJ/mol [8];

$\mathbf{\Delta} G_{H3CHC(OH)COOH} = G_{H3CHC(OH)COOH} - (\mathbf{3G}_{\mathbf{C}graph} + \mathbf{3*}G_{\mathbf{H2}gas} + \mathbf{1,5*}G_{O2gas}) = \mathbf{-303,4}$ kJ/mol;

$G_{H3CHC(OH)COOH} = \mathbf{-303,4} + (\mathbf{3*91,26+3*85,6+1,5*303}) = \mathbf{681,7}$ kJ/mol;

Lactic acid $H_3CHC(OH)COOH + \mathbf{H_2O} \Leftrightarrow H_3CHC(OH)COO^- + H_3O^+$; $pK_{a1} = 3,86$;

$K_{eq} = [H_3CHC(OH)COO^-] * [H_3O^+] / [H_3CHC(OH)COOH] / [\mathbf{H_2O}] = K_a / [\mathbf{H_2O}] = 10^{(-3,86)}/55,3 = 2,5*10^{(-6)} = 10^{(-5,603)}$;

$\Delta G_{\mathbf{eq}H3CHC(OH)COOH} = -R \bullet T \bullet \ln(K_{\mathbf{aeq}}) = -8,3144*298,15*\ln(10^{(-5,603)})/1000 = \mathbf{31,98}$ kJ/mol .

$\mathbf{\Delta} G_{H3CHC(OH)COO} = G_{H3CHC(OH)COO} + 2G_{H3O+} - (G_{\mathbf{LacticAc}} + 2G_{H2O}) = G_{\mathbf{Succinat}} + \mathbf{2*22,44-(681,7+2*0)} = \mathbf{31,98}$ kJ/mol;

$G_{H3CHC(OH)COO} = \mathbf{\Delta} G_{H3CHC(OH)COO} - 2G_{H3O+} + (G_{\mathbf{LacticAc}} + 2G_{H2O}) = \mathbf{31,98-2*22,44+(681,7+2*0)=668,8}$ kJ/mol;

Pyruvic acid$^-$ Formation 71st page $3\mathbf{C} + 2\mathbf{H_{2gas}} + 1,5\mathbf{O_2}_{gas} \Rightarrow H_3CC{=}OCOOH$; $\mathbf{\Delta} G_{\mathbf{Succinat}} = \mathbf{-344,62}$ kJ/mol [8];

$\mathbf{\Delta} G_{\mathbf{Fumarat}} = G_{\mathbf{Fumarat}} - (\mathbf{3G}_{\mathbf{C}graph} + 2G_{\mathbf{H2}gas} + \mathbf{1,5*}G_{O2gas}) = \mathbf{-344,62}$ kJ/mol;

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

Pyruvic acid $H_3CC{=}OCOOH + \mathbf{H_2O} \Leftrightarrow H_3CHC(OH)COO^- + H_3O^+$; $pK_{a1} = 2,5$;

$K_{eq} = [H_3CHC(OH)COO^-] * [H_3O^+] / [H_3CC{=}OCOOH] / [\mathbf{H_2O}] = K_a / [\mathbf{H_2O}] = 10^{(-2,5)}/55,3 = 2,5*10^{(-6)} = 10^{(-4,243)}$;

$\Delta G_{\mathbf{eq}H3CC=OCOOH} = -R \bullet T \bullet \ln(K_{\mathbf{aeq}}) = -8,3144*298,15*\ln(10^{(-4,243)})/1000 = \mathbf{24,22}$ kJ/mol .

$\mathbf{\Delta} G_{H3CHC(OH)COO} = G_{H3CHC(OH)COO} + 2G_{H3O+} - (G_{\mathbf{LacticAc}} + 2G_{H2O}) = G_{\mathbf{Succinat}} + \mathbf{2*22,44-(554,86+2*0)=24,22}$ kJ/mol;

$G_{H3CHC(OH)COO} = \mathbf{\Delta} G_{H3CHC(OH)COO} - 2G_{H3O+} + (G_{\mathbf{LacticAc}} + 2G_{H2O}) = \mathbf{24,22-2*22,44+(554,86+2*0)=534,2}$ kJ/mol;

NADPH = NADP$^+$ + H$^-$(H$^+$+2e$^-$); $\mathbf{E^\circ}_{\mathbf{NADH}} = -0,41135$ V; absolute Lehninger; [6]$^-$

H_2O_2 veidošanās 41st page $H_{2gas}+O_{2gas}=>H_2O_2$; $\Delta G°_{UnivAlberta}=-134,03$ kJ/mol ; $\Delta G°_{Alberty}=\mathbf{-48,39}$ kJ/mol ;

$\Delta G_{Alberty}=G_{H2O2}-(G_{O2gas}+G_{H2gas})=\underline{274,5-(85,64+303)}=\mathbf{-114,14}$ kJ/mol(-134,03 kJ/mol;)(=**-48,39** kJ/mol)

Viela	$\Delta H°_H$ kJ/mol	$\Delta S°_H$ J/mol/K	$\Delta G°_H$ kJ/mol
H_2O_{2aqua}	**-191,99**	**-481,688**	**-48,39**
H_2O_{2aqua}	-191,17	143,9	-134,03
Succinat^{2-}	**-908,69**	**-1295,576**	**-522,414**
Fumarate^{2-}	**-776,56**	**-862,288**	**-519,4688**

Alberty nulles $G_{H2O}=\mathbf{0}$ kJ/mol; atskaitē bāzēti $\underline{G_{H2O2}=274,5}$ kJ/mo
University Alberta
$G_{Succinat}=\mathbf{650,8}$ kJ/mol;$G_{SuccinatFor}=-522,4+(4*91,26+2*85,6+2*303)=\mathbf{619,8}$ kJ/mol
$G_{Fumarat}=\mathbf{554,75}$ kJ/mol;$G_{FumaricFor}=-519,5+(4*91,26+85,6+2*303)=\mathbf{537,1}$ kJ/mol

Succinat^{2-} Formation 41st page $4C+2H_{2gas}+2O_{2gas}=>(CH_2)_2(CO_2^-)(CO_2^-)$; $\Delta G_{Succinat}=\mathbf{-522,4}$ kJ/mol Alberty;
$\Delta G_{SuccinatFor}=G_{SuccinatFor}-(4G_{Cgraph}+2*G_{H2gas}+2*G_{O2gas})=\mathbf{-522,4}$ kJ/mol;
$G_{SuccinatFor}=-522,4+(4*91,26+2*85,6+2*303)=\mathbf{619,8}$ kJ/mol;

Fumarate^{2-} Formation 41st page $4C+H_{2gas}+2O_{2gas}=>(CH)_2(CO_2^-)(CO_2^-)$; $\Delta G_{Fumarat}=\mathbf{-519,5}$ kJ/mol Alberty;
$\Delta G_{Fumarat}=G_{FumaratFor}-(4G_{Cgraph}+G_{H2gas}+2*G_{O2gas})=\mathbf{-519,5}$ kJ/mol;
$G_{FumaratFor}=-519,5+(4*91,26+85,6+2*303)=\mathbf{537,1}$ kJ/mol; ;

Succinic acid $(CH_2)_2(CO_2H)_2+H_2O<=>(CH_2)_2(CO_2H)(CO_2)^-+H_3O^+$; $pK_{a1}=4,2$;
$K_{a1eq}=[(CH_2)_2(CO_2H)(CO_2)^-]*[H_3O^+]/[(CH_2)_2(CO_2H)_2]/[H_2O]=K_{a1}/[H_2O]=10\wedge^{(-4,2)}/55,3=1,14*10\wedge^{(-6)}=10\wedge^{(-5,94)}$;
Succinat^{2-} $(CH_2)_2(CO_2H)(CO_2)^-+H_2O<=>(CH_2)_2(CO_2^-)(CO_2^-)+H_3O^+$; $pK_{a2}=5,6$;
$K_{a2eq}=[(CH_2)_2(CO_2^-)(CO_2^-)]*[H_3O^+]/[(CH_2)_2(CO_2H)(CO_2)^-]/[H_2O]=K_{a2}/[H_2O]=10\wedge^{(-5,6)}/55,3=4,54*10\wedge^{(-8)}=10\wedge^{(-7,34)}$;
$(CH_2)_2(CO_2H)_2+2H_2O<=>(CH_2)_2(CO_2^-)(CO_2^-)+2H_3O^+$; $K_{aeq}=K_{a1eq}*K_{a2eq}=1,14*10\wedge^{(-6)}*4,54*10\wedge^{(-8)}=10\wedge^{(-13,3)}$;
$\Delta G_{eqSuccinat}=-R\bullet T\bullet\ln(K_{aeq})=-8,3144*298,15*\ln(10\wedge^{(-13,3)})/1000=\mathbf{75,9}$ kJ/mol .
$\Delta G_{Succinat}=G_{Succinat}+2G_{H3O+}-(G_{SuccinicAc}+2G_{H2O})=G_{Succinat}+2*22,44-(619,8+2*0)=\mathbf{75,9}$ kJ/mol;
$G_{Succinat}=\Delta G_{Succinat}-2G_{H3O+}+(G_{SuccinicAc}+2G_{H2O})=75,9-2*22,44+(619,8+2*0)=\mathbf{650,8}$ kJ/mol;

Fumaric acid $(CH)_2(CO_2H)_2+H_2O<=>(CH)_2(CO_2H)(CO_2)^-+H_3O^+$; $pk_{a1}=3,03$;
$K_{a1eq}=[(CH)_2(CO_2H)(CO_2)^-]*[H_3O^+]/[(CH)_2(CO_2H)_2]/[H_2O]=K_{a1}/[H_2O]=10\wedge^{(-3,03)}/55,3=1,69*10\wedge^{(-5)}=10\wedge^{(-4,77)}$;
Fumarate^{2-} $<=>(CH)_2(CO_2H)(CO_2)^-+H_2O<=>(CH)_2(CO_2^-)(CO_2^-)+H_3O^+$; $pK_{a2}=4,44$;
$K_{a2eq}=[(CH)_2(CO_2^-)(CO_2^-)]*[H_3O^+]/[(CH)_2(CO_2H)(CO_2)^-]/[H_2O]=K_{a2}/[H_2O]=10\wedge^{(-4,44)}/55,3=6,57*10\wedge^{(-7)}=10\wedge^{(-6,18)}$;
$(CH)_2(CO_2H)_2+2H_2O<=>(CH)_2(CO_2^-)(CO_2^-)+2H_3O^+$; $K_{aeq}=K_{a1eq}*K_{a2eq}=1,69*10\wedge^{(-5)}*6,57*10\wedge^{(-7)}=10\wedge^{(-10,955)}$;
$\Delta G_{eqFumarat}=-R\bullet T\bullet\ln(K_{aeq})=-8,3144*298,15*\ln(10\wedge^{(-10,955)})/1000=\mathbf{62,53}$ kJ/mol .
$\Delta G_{Fumarat}=G_{Fumarat}+2G_{H3O+}-(G_{FumaricAc}+2G_{H2O})=G_{Fumarat}+2*22,44-(537,1+2*0)=\mathbf{62,53}$ kJ/mol;
$G_{Fumarat}=\Delta G_{Fumarat}-2G_{H3O+}+(G_{FumaricAc}+2G_{H2O})=62,53-2*22,44+(537,1+2*0)=\mathbf{554,75}$ kJ/mol;

Ox $O_{2aqua}+2H_3O^++2e^-=H_2O_{2aqua}+2H_2O$; $E°_{OxO2\_H2O2}=-0,4495$ V absolute University Alberta ;
$\underline{\Delta G_{AlbertyOxO2\_H2O2}=G_{H2O2}+2*G_{H2O}-(G_{O2aqua}+2*G_{H3O+})=274,5+2*0-(330+2*22,44)=-100,4}$ kJ/mol ;
$\Delta G_{eqAlbertyAbsoluteOxO2\_H2O2}=E°_{eqOxO2\_H2O2}\bullet F\bullet 1\bullet 2=\mathbf{-0},4495*96485*2=\mathbf{-86,7}$ kJ/mol;

Nernst's half Red **Succinate^{2-}+2H$_2$O = Fumarate^{2-}+2H$_3$O$^+$ +2e$^-$** ; $E°_{RedSuccinate}=0,2512$ V; absolute potential ;
Alberty $\Delta G_{eqSuccinat\_Fumarat}=G_{Fumarat}+2G_{H3O+}-(G_{Succinat}+2G_{H2O})=\mathbf{554,75}+2*\mathbf{22,44}-(\mathbf{650,8}+2*0)=\mathbf{-51,2}$ kJ/mol;
$\Delta G_{eqAlbertyNernstRedSuccinatFumarat}=E°_{eqNernstHalfSuccinat\_Fumarat}\bullet F\bullet 1\bullet 2=\mathbf{0},2512*96485*2=\mathbf{48,47}$ kJ/mol;
Standard equilibrium state attractor for non equilibrium states

Succinat^{2-}+O$_{2aqua}$=>fumarate^{2-}+H$_2$O$_{2aqua}$+Q+ΔG; $\Delta G_{min}=\Delta G_{eqSuccinat\_H2O2}=\mathbf{-38,3}$ kJ/mol;
Alberty $\underline{\text{Hess }\Delta G_{Succinat\_H2O2}=G_{Fumarat}+G_{H2O2}-(G_{Succinat}+G_{O2aqua})=554,75+274,5-(650,8+330)=-151,55}$ kJ/mol;
$\Delta G_{min}=\Delta G_{eq}=(E°_{RedSuccinate}-E°_{OxO2})*F*n=(0,2512-0,4495)*96485*2=(-0,1983)*96485*2=\mathbf{-38,3}$ kJ/mol;

Nernst's half Red **Succinate^{2-}+2H$_2$O = Fumarate^{2-}+2H$_3$O$^+$ +2e$^-$** ; $E°_{RedSuccinate}=0,2512$ V; absolute potential ;
$\Delta G_{eqSuccinat\_Fumarat}=G_{FumaratFor}+2G_{H3O+}-(G_{SuccinatFor}+2G_{H2O})=\mathbf{537,1}+2*\mathbf{22,44}-(\mathbf{619,8}+2*0)=\mathbf{-37,82}$ kJ/mol;
$\Delta G_{eqSuccinat\_Fumarat}=G_{FumaratFor}+2G_{H3O+}-(G_{SuccinatFor}+2G_{H2O})=\mathbf{537,1}+2*\mathbf{22,44}-(\mathbf{619,8}+2*85,64)=\mathbf{-209,1}$ kJ/mol;
$\Delta G_{eqAlbertyNernstRedSuccinatFumarat}=E°_{eqNernstHalfSuccinat\_Fumarat}\bullet F\bullet 1\bullet 2=\mathbf{0},2512*96485*2=\mathbf{48,47}$ kJ/mol;
Standard equilibrium state attractor for non equilibrium states

Succinat^{2-}+O$_{2aqua}$=>fumarate^{2-}+H$_2$O$_{2aqua}$+Q+ΔG; $\Delta G_{min}=\Delta G_{eqSuccinat\_H2O2}=\mathbf{-38,3}$ kJ/mol;
Alberty Hess $\underline{\Delta G_{Succinat\_H2O2}=G_{Fumarat}+G_{H2O2}-(G_{Succinat}+G_{O2aqua})=537,1+274,5-(619,8+330)=-151,55}$ kJ/mol;
$\Delta G_{min}=\Delta G_{eq}=(E°_{RedSuccinate}-E°_{OxO2})*F*n=(0,2512-0,4495)*96485*2=(-0,1983)*96485*2=\mathbf{-38,3}$ kJ/mol;

CH_3CH_2OH ethanol formation from elements:

$2C+3H_{2gas}+1/2O_{2gas}\Rightarrow CH_3CH_2OH$; $\Delta G^\circ_{Alberty}=75{,}2864$ kJ/mol ; $\Delta G^\circ_{HessCRC}=-181$ kJ/mol ;

$\Delta G^\circ_{Alberty}=G_{CH3CH2OH}-(2G_{Cgraph}+3*G_{H2gas}+1/2*G_{O2gas})=75{,}2864$ kJ/mol ;

$\Delta G^\circ_{CRC}=G_{CH3CH2OH}-(2G_{Cgraph}+3*G_{H2gas}+1/2*G_{O2gas})=-181$ kJ/mol ;

$\Delta G^\circ_{Alberty}+(2G_{Cgraph}+3*G_{H2gas}+1/2*G_{O2gas})=75{,}2864+(2*91{,}26+3*85{,}6+1/2*303)=G_{CH3CH2OH}=666{,}106$ kJ/mol ;

$\Delta G^\circ_{CRC}+(2G_{Cgraph}+3*G_{H2gas}+1/2*G_{O2gas})=-181+(2*91{,}26+3*85{,}6+1/2*303)=G_{CH3CH2OH}=409{,}82$ kJ/mol ;

CH_3CHO acetaldehyde formation from elements: $2C+2H_{2gas}+1/2O_{2gas}\Rightarrow CH_3CHO$;

$\Delta G^\circ_{Alberty}=G_{CH3CHO}-(2G_{Cgraph}+2*G_{H2gas}+1/2*G_{O2gas})=32{,}282$ kJ/mol ;

$\Delta G^\circ_{CRC}=G_{CH3CHO}-(2G_{Cgraph}+2*G_{H2gas}+1/2*G_{O2gas})=24{,}06$ kJ/mol ;

$\Delta G^\circ_{Alberty}+(2G_{Cgraph}+2*G_{H2gas}+1/2*G_{O2gas})=32{,}282+(2*91{,}26+2*85{,}6+1/2*303)=G_{CH3CHO}=537{,}5$ kJ/mol ;

$\Delta G^\circ_{CRC}+(2G_{Cgraph}+2*G_{H2gas}+1/2*G_{O2gas})=24{,}06+(2*91{,}26+2*85{,}6+1/2*303)=G_{CH3CHO}=529{,}28$ kJ/mol ;

$CH_3CH_2OH+H_2O=CH_3CHO+H_3O^++H^-(H^++2e^-)$; absolute potential $E^\circ_{CH3CH2OH}=-0{,}055$ V; Kortly, Shucha; [19]

$\Delta G_{eqCH3CH2OH}=E^\circ_{eqNernsCH3CH2OH}\bullet F\bullet 2=-0{,}055*96485*2=-10{,}6$ kJ/mol;

$\Delta G_{HessCH3CH2OH}=G_{CH3CHO}+G_{H3O+}+G_{H-}-(G_{CH3CH2OH}+G_{H2O})=537{,}5+22{,}44+G_{H-}-(409{,}82+0)=-10{,}6$ kJ/mol.

$\Delta G_{HessCH3CH2OH}=G_{CH3CHO}+G_{H3O+}+G_{H-}-(G_{CH3CH2OH}+G_{H2O\_Biochem})=537{,}5+22{,}44+G_{H-}-(409{,}82+85{,}64)=-10{,}6$ kJ/mol.

$\Delta G_{HessCH3CH2OH}-G_{CH3CHO}-G_{H3O+}+(G_{CH3CH2OH}+G_{H2O})=G_{H-}=-10{,}6-537{,}5-22{,}44+(409{,}82+0)=-160{,}7$ kJ/mol.

$\Delta G_{HessCH3CH2OH}-G_{CH3CHO}-G_{H3O+}+(G_{CH3CH2OH}+G_{H2O\_Biochem})=G_{H-}=-10{,}6-537{,}5-22{,}44+(409{,}82+85{,}64)=-75{,}08$ kJ/mol.

Substance	ΔH°_H kJ/mol	ΔS°_H J/mol/K	ΔG°_H kJ/mol
$H_3C\text{-}CH{=}O$	-212,23	-281,84	24,06
$H_3C\text{-}CH{=}O$	**-213,88**	**-825,64**	**32,2824**
NAD**H**	**-41,41**	**-4465,708**	**1175,5732**
NAD**H**	-1036,66	-140,50	1120,09
H_3O^+	-285.81	-3.854	-213,275
NAD^+	**-10,30**	**-3766,008**	**1112,534**
NAD^+	-1007,48	-183	1059,11
H_3CCH_2OH	**-290,77**	**-1227,764**	**75,2864**
$H_3CCH_2OH_{aq}$	-288,3	-357,7394	-181,64
H_2O	-285.85	69.9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**

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$G_{CH3CHO}=529{,}28$ kJ/mol ;

$G_{CH3CHO}=537{,}5$ kJ/mol ;

BioThermodynam06;

BioThermodynamic,2006,Massachusetts Tecnology Institute,Alberty

Alberty $G_{CH3CH2OH}=666{,}106$ kJ/mol ;

CRC $G_{CH3CH2OH}=409{,}82$ kJ/mol ;

$G_{H2O}=0$ kJ/mol; $G_{H-}=-10{,}6-537{,}5-22{,}44+(409{,}82+0)=-160{,}7$ kJ/mol.

$G_{H2O\_Biochem}=85{,}64$ kJ/mol. $G_{H-}=-10{,}6-537{,}5-22{,}44+(409{,}82+85{,}64)=-75{,}08$ kJ/mol

$NADH = NAD^+ + H^-(H^++2e^-)$; $E^\circ_{NADH}=-0{,}4095$ V; absolute David Harris; [22]

NAD^++~~$H^-(H^++2e^-)$~~$+CH_3CH_2OH+H_2O=NADH+CH_3CHO+H_3O^++$~~$H^-(H^++2e^-)$~~;

$NAD^++CH_3CH_2OH+H_2O=NADH+CH_3CHO+H_3O^+$;

$\Delta G_{min}=\Delta G_{eq}=(E^\circ_{eqNernsCH3CH2OH}-E^\circ_{NAD+})*F*n=(-0{,}055+0{,}4095)*96485*2=(0{,}4562)*96485*2=68{,}408$ kJ/mol;

$\Delta G_{HessAlbertyCH3CH2OH}=G_{NADH}+G_{H3O+}+G_{CH3CHO}-(G_{NAD+}+G_{CH3CH2OH}+G_{H2O})=\underline{68{,}02}$ kJ/mol.

$=1112{,}534+22{,}44+537{,}5-(1175{,}5+666{,}106+0)=-169{,}1$ kJ/mol.

$=1112{,}534+22{,}44+32{,}282-(1175{,}5+75{,}2864+0)=-83{,}53$ kJ/mol.

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

$=1112{,}534+22{,}44+32{,}282-(1175{,}5+75{,}2864+85{,}64)=-169{,}2$ kJ/mol.

$H_3CHC(OH)COO^-+\mathbf{H_2O}=>H_3CC{=}OCOO^-+\mathbf{H_3O^+}+\mathbf{H^-(H^++2e^-)}$; $\mathbf{E°}_{\mathrm{H3CHC(OH)COO}}=-0{,}0159$ V;

$\Delta\mathbf{G}_{\mathbf{eq}\mathrm{H3CHC(OH)COO}}=\mathbf{E°}_{\mathbf{eq}\mathrm{H3CHC(OH)COO}}\bullet F\bullet 2=\mathbf{-0,}0159*96485*2=\mathbf{-3{,}068}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;

$\Delta\mathbf{G}_{\mathbf{HessCH3CH2OH}}=\mathbf{G}_{\mathrm{H3CC=OCOO}}+G_{\mathrm{H3O+}}+G_{\mathrm{H-}}\mathbf{-(G}_{\mathrm{H3CHC(OH)COO}}+G_{\mathbf{H2O}}\mathbf{)=534{,}2+22{,}44}+G_{\mathrm{H-}}\mathbf{-(668{,}8}+0\mathbf{)=-3{,}068}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$.

$\Delta\mathbf{G}_{\mathbf{HessCH3CH2OH}}=\mathbf{G}_{\mathrm{H3CC=OCOO}}+G_{\mathrm{H3O+}}+G_{\mathrm{H-}}\mathbf{-(G}_{\mathrm{H3CHC(OH)COO}}+G_{\mathbf{H2O}\mathrm{\_Biochem}}\mathbf{)=534{,}2+22{,}44}+G_{\mathrm{H-}}\mathbf{-(668{,}8}+\mathbf{85{,}64)=-3{,}068}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$.

$\Delta\mathbf{G}_{\mathbf{HessCH3CH2OH}}\mathbf{-G}_{\mathrm{H3CC=OCOO}}-G_{\mathrm{H3O+}}+\mathbf{(G}_{\mathrm{H3CHC(OH)COO}}+G_{\mathbf{H2O}}\mathbf{)}=G_{\mathrm{H-}}=\mathbf{-3{,}068-534{,}2-22{,}44+(668{,}8}+0\mathbf{)=109{,}092}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$.

$\Delta\mathbf{G}_{\mathbf{HessCH3CH2OH}}\mathbf{-G}_{\mathrm{H3CC=OCOO}}-G_{\mathrm{H3O+}}+\mathbf{(G}_{\mathrm{H3CHC(OH)COO}}+G_{\mathbf{H2O}\mathrm{\_Biochem}}\mathbf{)}=G_{\mathrm{H-}}=\mathbf{-3{,}068-534{,}2-22{,}44+(668{,}8}+\mathbf{85{,}64)=194{,}7}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$.

I=0,25 M, **BioTherm06**, pH=7,36, $\Delta G_{\mathrm{H}}=G°_{\mathrm{H3CC=OCOO-}}+G°_{\mathbf{H3O+}}+G_{\mathrm{H-}}-G_{\mathrm{H3CHC(OH)COO-}}-G_{\mathbf{H2O}}=$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;

Viela	$\Delta H°_{\mathrm{H}}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$	$\Delta S°_{\mathrm{H}}$ ${}^{\mathrm{J}}/_{\mathrm{mol/K}}$	$\Delta G°_{\mathrm{H}}$, ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;
PyruvEnolP^{3-}	-1400	-1100	-1189,73
$H_3CC{=}OCOO^-$	-597,4	-850	-350,78
$H_3CC{=}OCOO^-$	-603,7	-433,54	-474,44
$H_3CC{=}OCOO^-$	**-597,04**	**-846,66**	**-344,62**
H_3O^+	-285,81	-3,854	-213,275
H_2O	-285,85	69,9565	-237,191
H_2O	**-286,65**	**-453,188**	**-151,549**
$H_3CHC(OH)COO^-$	**-688,29**	**-1290,9**	**-303,4**

$G_{\mathbf{H2O}}=\mathbf{0}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$; $G_{\mathrm{H-}}=\mathbf{-3{,}068-534{,}2-22{,}44+(668{,}8}+0\mathbf{)=109{,}092}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$

$G_{\mathbf{H2O}\mathrm{\_Biochem}}=\mathbf{85{,}64}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;$G_{\mathrm{H}}=\mathbf{-3{,}068-534{,}2-22{,}44+(668{,}8+85{,}64)=194{,}7}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$

$G_{\mathrm{H3CHC(OH)COO}}=\mathbf{534{,}2}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$; p$K_a$=2,5;

$G_{\mathrm{H3CHC(OH)COO}}=\mathbf{668{,}8}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$; p$K_a$=3,86;

pK_a=3,86; $\Delta H_c°$=1361,9 ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$; $G_{\mathrm{H3CHC(OH)COOH}}=\mathbf{2271}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;$H_3CHC(OH)COOH+3\mathbf{O_2}_{\mathrm{gas}}=3C\mathbf{O_2}_{\mathrm{gas}}+3\mathbf{H_2O}$;

$\Delta H_c°=3G_{\mathrm{C}\mathbf{O2}\mathrm{gas}}+3G_{\mathrm{H2O}}-(G_{\mathrm{H3CHC(OH)COOH}}+3G_{\mathbf{O2}\mathrm{gas}})=3*\mathbf{0}+3*\mathbf{0}-(G_{\mathrm{H3CHC(OH)COOH}}+3\mathbf{*303})=$ 1361,9 ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;

$G_{\mathrm{H3CHC(OH)COOH}}+=3G_{\mathrm{C}\mathbf{O2}\mathrm{gas}}+3G_{\mathrm{H2O}}-(\ 3G_{\mathbf{O2}\mathrm{gas}})=3*\mathbf{0}+3*\mathbf{0}-(+3\mathbf{*303})$ $-1361{,}9=G_{\mathrm{H3CHC(OH)COOH}}=\mathbf{2271}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;

Lactic acid Formation 71st page $3\mathbf{C}+3\mathbf{H_2}_{\mathbf{gas}}+1{,}5\mathbf{O_2}_{\mathrm{gas}}=>H_3CHC(OH)COOH$; $G_{\mathrm{H3CHC(OH)COOH}}=\mathbf{-303{,}4}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$ [8];

$\Delta G_{\mathrm{H3CHC(OH)COOH}}=G_{\mathrm{H3CHC(OH)COOH}}\mathbf{-(3G}_{\mathbf{C}\mathrm{graph}}\mathbf{+3*}G_{\mathbf{H2}\mathrm{gas}}\mathbf{+1{,}5*}G_{\mathrm{O2gas}})=\mathbf{-303{,}4}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;

$G_{\mathrm{H3CHC(OH)COOH}}=\mathbf{-303{,}4+(3*91{,}26+3*85{,}6+1{,}5*303)=681{,}7}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;

Lactic acid $H_3CHC(OH)COOH+\mathbf{H_2O}<=>H_3CHC(OH)COO^-+H_3O^+$; p$K_a$=3,86;

$K_{\mathrm{eq}}=[H_3CHC(OH)COO^-]*[H_3O^+]/[\ H_3CHC(OH)COOH]/[\mathbf{H_2O}]=K_a/[\mathbf{H_2O}]=10$^(-3,86)/55,3=2,5*10^(-6)=10^(-5,603);

$\Delta G_{\mathbf{eq}\mathrm{H3CHC(OH)COOH}}=-R\bullet T\bullet\ln(K_{\mathbf{aeq}})=-8{,}3144*298{,}15*\ln(10$^(-5,603))/1000=**31,98** ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$.

$\Delta G_{\mathrm{H3CHC(OH)COO}}=G_{\mathrm{H3CHC(OH)COO}}+2G_{\mathrm{H3O+}}-(G_{\mathbf{LacticAc}}+2G_{\mathrm{H2O}})=G_{\mathbf{Succinat}}\mathbf{+2*22{,}44-(681{,}7+2*0)=31{,}98}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;

$G_{\mathrm{H3CHC(OH)COO}}=\Delta G_{\mathrm{H3CHC(OH)COO}}-2G_{\mathrm{H3O+}}+(G_{\mathbf{LacticAc}}+2G_{\mathrm{H2O}})=\mathbf{31{,}98-2*22{,}44+(681{,}7+2*0)=668{,}8}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;

Pyruvic acid$^-$ Formation 71st page $3\mathbf{C}+2\mathbf{H_2}_{\mathbf{gas}}+1{,}5\mathbf{O_2}_{\mathrm{gas}}=>H_3CC{=}OCOOH$; $\Delta G_{\mathbf{Succinat}}=\mathbf{-344{,}62}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$ Alberty;

$\Delta G_{\mathbf{Fumarat}}=G_{\mathbf{Fumarat}}\mathbf{-(3G}_{\mathbf{C}\mathrm{graph}}+2G_{\mathbf{H2}\mathrm{gas}}\mathbf{+1{,}5*}G_{\mathrm{O2gas}})=\mathbf{-344{,}62}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;

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

Pyruvic acid $H_3CC{=}OCOOH+\mathbf{H_2O}<=>H_3CHC(OH)COO^-+H_3O^+$; p$K_a$=2,5;

$K_{\mathrm{eq}}=[H_3CHC(OH)COO^-]*[H_3O^+]/[H_3CC{=}OCOOH]/[\mathbf{H_2O}]=K_a/[\mathbf{H_2O}]=10$^(-2,5)/55,3=2,5*10^(-6)=10^(-4,243);

$\Delta G_{\mathbf{eq}\mathrm{H3CC=OCOOH}}=-R\bullet T\bullet\ln(K_{\mathbf{aeq}})=-8{,}3144*298{,}15*\ln(10$^(-4,243))/1000=**24,22** ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$.

$\Delta G_{\mathrm{H3CHC(OH)COO}}=G_{\mathrm{H3CHC(OH)COO}}+2G_{\mathrm{H3O+}}-(G_{\mathbf{LacticAc}}+2G_{\mathrm{H2O}})=G_{\mathbf{Succinat}}\mathbf{+2*22{,}44-(554{,}86+2*0)=24{,}22}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;

$G_{\mathrm{H3CHC(OH)COO}}=\Delta G_{\mathrm{H3CHC(OH)COO}}-2G_{\mathrm{H3O+}}+(G_{\mathbf{LacticAc}}+2G_{\mathrm{H2O}})=\mathbf{24{,}22-2*22{,}44+(554{,}86+2*0)=534{,}2}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$;

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

Red lactate$^-$+H$_2$O<=>pyruvate$^-$+H$_3$O$^+$+H$^-$(H$^+$+2e$^-$) ; absolute potential **E°**$_{\mathrm{H3CHC(OH)COO}}$=-0,0159 V;

Ox NAD$^+$+H$^-$(2e$^-$)=NADH ; **E°^{1}=-0,4095 V;** OksRed **NAD$^+$**+**lactate$^-$+H$_2$O=NADH+ pyruvate$^-$+H$_3$O$^+$**;

Balanced **n=2=m** with **2e$^-$** electrons ΔE° **NAD$^+$ accept** electrons from **lactate**:

$\Delta\mathbf{G}_{\mathbf{eq}\mathrm{Aerobic}}\mathbf{=\Delta E°\bullet F\bullet n=(E°_{Red}-E°_{Ox})*F*n=}(-0{,}0159—\mathbf{0{,}4095})*96485\mathbf{*2=}(0{,}3936)\mathbf{*2=75{,}95}$ ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$

$\mathbf{K}_{\mathbf{eq}\mathrm{Aerobic}}=\mathrm{EXP}(-\Delta\mathbf{G}_{\mathbf{eq}\mathrm{Aerobic}}/R/T)=\mathrm{EXP}(-75950/8{,}3144/298{,}15)=10^{-13{,}3}$;

$$\mathbf{K}_{\mathbf{eq}\mathrm{Aerobic}}=\frac{[\mathrm{NADH}]\cdot[\mathrm{pyruvate}^-]\cdot[\mathrm{H_3O^+}]}{[\mathrm{NAD^+}]\cdot[\mathrm{lactate}^-]\cdot[\mathrm{H_2O}]}=e^{-\frac{\Delta G_{\mathrm{eqAerobic}}}{R\bullet T}}=\mathbf{e}^{-\frac{759500}{8.314\bullet 298.15}}=\mathbf{10^{-13{,}3}};$$

$\Delta G_{\mathrm{Hess}}=\Delta H_{\mathrm{Hess}}-T*\Delta S_{\mathrm{Hess}}=\mathbf{45{,}764}-298{,}15*\mathbf{-0{,}5479605=209{,}14}$....... ${}^{\mathrm{kJ}}/_{\mathrm{mol}}$ **endoergic**; formation 62nd page