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$\Delta H_H$ $\Delta S_H$ $\Delta G_H$ 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•v** absorption in photosynthetic reaction center PRC+**h•v** for production **$6O_{2aqua}$** and **$C_6H_{12}O_6$** using the data table!

Mention whether the reactio6n will be **exoergic** or **endoergic**! Reactants => products 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* | $\Delta H^\circ_H\ {}^{kJ}/_{mol}$ | $\Delta S^\circ_H\ {}^{J}/_{mol/K}$ | $\Delta G^\circ_H\ {}^{kJ}/_{mol}$ |
|---|---|---|---|
| $C_6H_{12}O_{6aq}$ | -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** |

$\Delta G_H=\Delta G^\circ_{C6H12O6}+6\Delta G^\circ_{O2}+6\Delta G^\circ_{H2O}-6\Delta G^\circ_{H3O}-6\Delta G^\circ_{HCO3}=3336.5\ {}^{kJ}/_{mol}$

$=-402,05+6*16,4+6*-151,549-(6*-544,9688+6*-213,274599)=3336.5\ {}^{kJ}/_{mol}$

**Biothermodynamic 2006**; data recalculate for pH=7.36. [8]

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

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

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

$=-2901,49+6*-94,2+6*-453,188-(6*-494,768+6*-3,854)=-3194.\ 1\ {}^{J}/_{mol/K}$

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

CRC102. $\Delta S_{dispersed}=-\Delta H_{Hess}/T=-2812,6/298,15=9433.5\ {}^{J}/_{mol/K}$;

$\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=3194,1+9433,5=12627.6\ {}^{J}/_{mol/K}$;

$T\bullet\Delta S_{total}=-12,6276*298,15=-3764.9\ {}^{kJ}/_{mo}$ accumulate energy .

$\Delta G_{Hess}=3764.92\ {}^{kJ}/_{mol} > \Delta G_{Lehninger}=2840\ {}^{kJ}/_{mol}$;

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.

$6CO_{2gas}\uparrow+12H_2O\Rightarrow 6CO_{2aqua}+12H_2O\Rightarrow 6H_3O^++6HCO_3\Rightarrow C_6H_{12}O_6+6O_{2aqua}+6H_2O\Rightarrow C_6H_{12}O_6+6O_{2\ gas}\uparrow+6H_2O$

$\Delta G_H=\Delta G^\circ_{C6H12O6}+6\Delta G^\circ_{O2}+6\Delta G^\circ_{H2O}-6\Delta G^\circ_{CO2aqua}-12\Delta G^\circ_{H2O}=2921.5\ {}^{kJ}/_{mol}$;

$=-402,05+6*16,4+6*-151,549-(6*-385,98+12*-151,549)=2921.5\ {}^{kJ}/_{mol}$;

$\Delta G_H=\Delta G^\circ_{C6H12O6}+6\Delta G^\circ_{O2}+6\Delta G^\circ_{H2O}-6\Delta G^\circ_{CO2gas}-12\Delta G^\circ_{H2O}=2971.8\ {}^{kJ}/_{mol}$;

$=-402,05+6*16,4+6*-151,549-(6*-394,359+12*-151,549)=2971.8\ {}^{kJ}/_{mol}$;

$\Delta G_H=\Delta G^\circ_{C6H12O6}-6\Delta G^\circ_{O2\ gas}-6\Delta G^\circ_{H2O}-6\Delta G^\circ_{CO2gas}+12\Delta G^\circ_{H2O}=2873.4\ {}^{kJ}/_{mol}$;

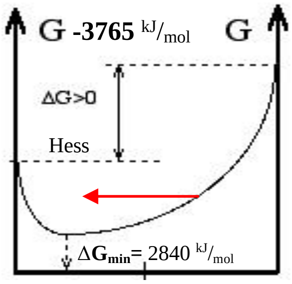
$=-402,05+6*0+6*-151,549-(6*-394,359+12*-151,549)=2873.4$; $\Delta G_{BioChem}=2873.4\ {}^{kJ}/_{mol}$;

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

$\Delta G_{Hess}=3764.92\ {}^{kJ}/_{mol} > \Delta G_{Lehninger}=2840\ {}^{kJ}/_{mol}$;

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

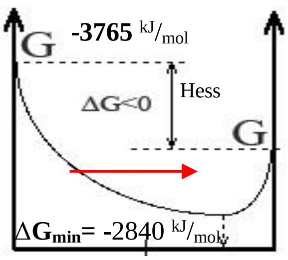
Exothermic and endoergic photosynthesis Hess free energy change positive for gas gas $6O_2$ , $6CO_2$ $\Delta G_{photosynthesis}=2873\ {}^{kJ}/_{mol}$ so $\Delta G_{photosynthesis}=2971.8\ {}^{kJ}/_{mol}$ more positive for aqua $6O_{2aqua}$ and $\Delta G_{photosynthesis}=2921.5\ {}^{kJ}/_{mol}$ for both aqua $6O_{2aqua}$ , $6CO_{2aqua}$ , CA Carbonic Anhydrase driven $\Delta G_{photosynthesis}=3336,5\ {}^{kJ}/_{mol}$ $6O_{2aqua}$ , $6H_3O^+$ , **$6HCO_3^-$**, 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 $C_6H_{12}O_6+6O_{2aqua}+6H_2O$



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

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

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



Homeostasis Quasi Equilibrium is Prigogine attractor free energy change minimum $\Delta G_{min}$. 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 $\Delta H_H$ $\Delta S_H$ $\Delta G_H$ 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* | $\Delta H^\circ_H$ $^{kJ}/_{mol}$ | $\Delta S^\circ_H$ $^{J}/_{mol/K}$ |
|---|---|---|
| $O_2\uparrow_{gas}$ | 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\. $\Delta H_H=\Delta H^\circ_{C6H12O}+6\Delta H^\circ_{O2}-6\Delta H^\circ_{H2O}-6\Delta H^\circ_{CO2}=$.............$^{kJ}/_{mol}$
................$= -1263,78-6*0-(6*-285,85+6*-393,509)= -1263,78+4076,154= +2812.37$ $^{kJ}/_{mol}$ **endothermic**....
2\. $\Delta S_{dispersed}= -\Delta H_H/T = -2812,37/298.15= -9432.59$ $^{J}/_{mol/K}$ .
$\Delta S_H=\Delta S^\circ_{C6H12O}+6\Delta S^\circ_{O2}-6\Delta S^\circ_{H2O}-6\Delta S^\circ_{CO2}=269,45+6*205,04-(6*69,9565+6*213,74)= -202.489$ $^{J}/_{mol/K}$ .
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\. $\Delta H_H=6\Delta H^\circ_{H2O}+6\Delta H^\circ_{CO2}-\Delta H^\circ_{C6H12O}-6\Delta H^\circ_{O2}= 6*-285,85+6*-393,509-(-1263,78-6*0)= -2812.37$ $^{kJ}/_{mol}$
2\. $\Delta S_{dispersed}= -\Delta H_H/T = --2812,37/298.15= +9432.59$ $^{J}/_{mol/K}$ . **exothermic** .
$\Delta S_H=6\Delta S^\circ_{H2O}+6\Delta S^\circ_{CO2}-\Delta S^\circ_{C6H12O}-6\Delta S^\circ_{O2}=6*69,9565+6*213,74-(269,45+6*205,04)=+202.489$ $^{J}/_{mol/K}$ .
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 $G_{O2Biochem}=78.08$ $^{kJ}/_{mol}$.

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

Solubility $O_{2gas\ AIR}+H_2O+\Delta G\xRightarrow{Aquaporins}O_{2aqua-Blood}+Q$ constant:
$=K_{sp}=2.205*10^{-5}$. $G_{O2aqua}=-R\bullet T\bullet\ln(K_{sp})=-8.3144*298.15*\ln(2.205*10^{-5})=26.58$ $^{kJ}/_{mol}$.

$O_{2aqua}+4H_3O^++4e^-=5H_2O$ ; $-E^\circ=$**-1,0868** V inverse absolute standard potential.
$E=E^\circ+{}^{0,0591}/_4\bullet lg([O_{2aqua}]\bullet[H_3O^+]^4/_{[H2O]^6})=1,0868+{}^{0,0591}/_4*\log(6*10^{\wedge(-5)}*10^{\wedge(-7,36*4)}/_{55,346^{\wedge5}})=0,46068$ Volts .
$\Delta E_{H2O}=-E^\circ+E_o=-1,0868+0,46068=-0,62612$ 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 :
$K_{spCO2aqua}=[CO_{2aqua}]/[CO_{2gas}]/[H_2O]=EXP(-\Delta G_{sp}/R/T)=EXP(-8379/8,3144/298,15)=0.034045$.
$\Delta G_{spCO2aqua}=-R\bullet T\bullet\ln(K_{spCO2aqua})=-8.3144*298.15*\ln(0.034045)/1000=8.379$ $^{kJ}/_{mol}$ .

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

$CO_{2aqua}+2H_2O+\Delta G+Q=v1\overset{CA}{>}H_3O^++HCO_3^-$ velocity constant $k_{1CO2aqua}=1.5\times10^8\ M^{-1}s^{-1}$. [9]
$=K_{eqCAHCO3aqua}=K_{a\_CO2aqua}/[H_2O]^2=10^{-7.0512}/55.3^2=2.906*10^{-11}$. Equilibrium constant.
$\Delta G_{eqCO2aqua}=-R\bullet T\bullet\ln(K_{eqCO2aqua})=-8,3144*298,15*\ln(2,906*10^{\wedge(-11)})/1000=60.14$ $^{kJ}/_{mol}$ .
$G_{H3O+}+G_{HCO3-}=22.44+46.08=G_{H3O+HCO3-}=\Delta G_{spCO2aqua}+\Delta G_{eqCO2aqua}=8.379+60.14=68.52$ $^{kJ}/_{mol}$ .
Water protolysis increases free energy content from zero $G_{2H2O}=0$ $^{kJ}/_{mol}$ to $G_{H3O+OH}=99.8$ $^{kJ}/_{mol}$ .

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

$H_2O+H_2O<=>H_3O^++OH^-$;
$= K_{H3O++OH-}=[H_3O^+]*[OH^-]/[H_2O]^2=3.26\bullet10^{-18}$;
$\Delta G_{H3O++OH-}=-R\bullet T\bullet\ln(K_{H3O++OH-})=-8,3144*298,15*\ln(3,26\bullet10^{\wedge(-18)})/1000=99.8$ $^{kJ}/_{mol}$ .

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

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

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

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{\text{Power Staition}}6CO_2\uparrow_{gas}+\Delta G+Q$1. $\Delta H_H=6\Delta H^\circ_{CO2}-6\Delta H^\circ_{Cgr}+6\Delta H^\circ_{O2}=$.............. **exothermic** $^{kJ}/_{mol}$

| *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 | 0 |
| $C_{gas}$ | 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 $T\Delta Sn\leftarrow$ <u>lost free energy</u>; $G^\circ_{Cgr}=-671,3$ $^{kJ}/_{mol}$;

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

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

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

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

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

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

$G^\circ_{CH4gas}=-50,5+(-671,3+2*\underline{237,19/2})=-484.61$ $^{kJ}/_{mol}$;

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

| *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 $T\Delta Sn\leftarrow$ <u>lost free energy</u>

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

$6\ CO\uparrow_{gas}+6\ H_{2gas}+6\ O_2\uparrow_{gas}\xrightarrow{\text{generator-gas}}6CO_2\uparrow_{gas}+6\ H_2O\uparrow_{gas}+\Delta G+Q$ **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 $T\Delta Sn\leftarrow$ <u>dispersed-lost energy;</u> 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 $C_{16}H_{32liq}+24O_2\uparrow_{gas}\xrightarrow{\text{burm}}16CO_{2gas}+16H_2O+\Delta G+Q$

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 $T\Delta Sn\leftarrow$ <u>lost free energy</u>

$C_{16}H_{32liq}$ $^{kJ}/_{mol}$/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

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

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

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

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

| *Substance* | $\Delta H^\circ_H$ $^{kJ}/_{mol}$ | $\Delta S^\circ_H$ $^{J}/_{mol/K}$ | $\Delta G^\circ_H$ $^{kJ}/_{mol}$ |
|---|---|---|---|
| $CO_2\uparrow_{gas}$ | -393.509 | 213,74 | -394,359 |
| $H_2O$ | -285,85 | 69,9565 | -237,191 |
| $CO_{2aqua}$ | -413,7976 | 117,5704 | -385,98 |

$CO_2\uparrow_{gas}+H_2O+\Delta G \xrightarrow{\text{Stomata Cell Membranes}} CO_{2aqua}+Q$

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

$\Delta G_{sp}=\Delta G^\circ_{CO2aqua}-\Delta G^\circ_{CO2gas}-\Delta G^\circ_{H2O}=8.379\ ^{kJ}/_{mol}$

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

$G_{šķCO2}=\Delta G^\circ_{CO2aq}-\Delta G^\circ_{CO2gas}-\Delta G^\circ_{H2O}=-385{,}98+394{,}359+237{,}191=245{,}57\ ^{kJ}/_{mol}$;

$\Delta H_H=\Delta H^\circ_{CO2aq}-\Delta H^\circ_{CO2gas}-\Delta H^\circ_{H2O}=-413{,}7976-(-393{,}509-285{,}85)=$ -20.2886.......$^{kJ}/_{mol}$ **exothermic**...........

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

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

$\Delta S_H=\Delta S^\circ_{CO2aqua}-\Delta S^\circ_{CO2gas}=117{,}57+69{,}9565-(213{,}74+69{,}9565)=-96.17$...........$^{J}/_{mol/K}$

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

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

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

$\Delta G_{hydratationHess}=\Delta H_{hydratationHess}-T*\Delta S_{hydratationHess}=-17{,}9-298.15*-96{,}17=+10.77$......... $^{kJ}/_{mol}$...**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 $T\Delta Sn\leftarrow$ <u>accumulate energy $\Delta G_{reversereaction}$</u> **not spontaneous** $\Delta G_{Hess}=8.3845\ ^{kJ}/_{mol}$ . Mol fraction $X^{CO_2}{}_{aqua}$:

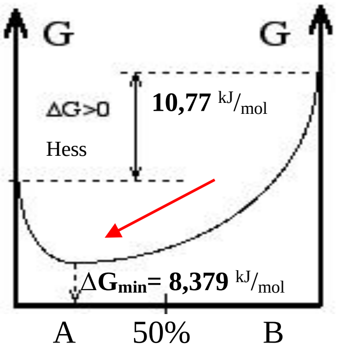
solubility $K_{sp}=\dfrac{X^{CO_2}{}_{aqua}}{[CO_2\ gas]}=\dfrac{[CO_2\ aqua]}{[CO_2\ gas]\cdot[H_2O]}$ $=EXP(-\Delta G_{sp}/R/T)=EXP(-8379/8{,}3144/298{,}15)=0.034045=1/29.375$;

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

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

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

Equilibrium reaching is Prigogine attractor free energy change minimum $\Delta G_{min}$ .
Air 0.04% mol fraction $[CO_2\uparrow_{air}]=0.0004$ as 400 ppm units per milion air molecules, disolutes in water $[CO_{2aqua}]$ as molarity $[CO_{2aqua}]= 0.00075125$ M;
$[CO_{2aqua}]=K_{sp}*[CO_2\uparrow_{air}]*[H_2O]=0{,}034045*0{,}0004*55{,}346=0.00075125$........M ;



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

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

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

$\dfrac{[HCO_3^-]_{aqua}\cdot[H_3O^+]}{[CO_2]_{aqua}\cdot[H_2O]^2}=K_{eqCAHCO3aqua}=K_{a\_CO2aqua}/[H_2O]^2=10^{-7.0512}/55.3^2=2.906*10^{-11}$. CA equilibrium constant accumulate energy: $\Delta G_{eqCO2aqua}=-R\bullet T\bullet \ln(K_{eqCO2aqua})=-8{,}3144*298{,}15*\ln(2{,}906*10\text{^}(^{-11}))/1000=60.14\ ^{kJ}/_{mol}$ .

$G_{H3O+HCO3}=G_{H3O+}+G_{HCO3-}=22.44+46.08=\Delta G_{spCO2aqua}+\Delta G_{eqCO2aqua}=8.379+60.14=68.52\ ^{kJ}/_{mol}$ . [1,8,14]

$K_{CO2aqua}=[CO_{2aqua}+HCO_3^-]/[CO_2\uparrow_{air}]=0{,}023/0{,}00075125=30.6$ 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 $\mathbf{6HCO_3^- + 6H_3O^+}$ photosynthesis to $\mathbf{6O_2}$ and $\mathbf{C_6H_{12}O_6}$

Calculate $\Delta H_H$ $\Delta S_H$ $\Delta G_H$. 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 |
|---|---|---|---|
| $\mathbf{C_6H_{12}O_{6aq}}$ | -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** |
| $\mathbf{H_2O}$ | -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** |

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

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; $\Delta S_{total} = \Delta S_H + \Delta S_{dispersed} = \mathbf{-3194{,}1 - 9433{,}51 = -12627.6}$ J/mol/K;

$T•\Delta S_{total} = \mathbf{-12627{,}6}*298{,}15K = \mathbf{-3764.9}$ 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

$\Delta G_H = \Delta H_H - T*\Delta S_H = \mathbf{-2812{,}6} - 298{,}15*\mathbf{-3{,}1941} = \mathbf{-3765}$ 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;

$T•\Delta S_{total} = \mathbf{12627{,}6}*298{,}15K = \mathbf{3764.9}$ 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 $\mathbf{6CO}\uparrow + \mathbf{6H_{2gas}}$ is home heating, street lightning fuel of 19th as 20th century beginning in Riga city.

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

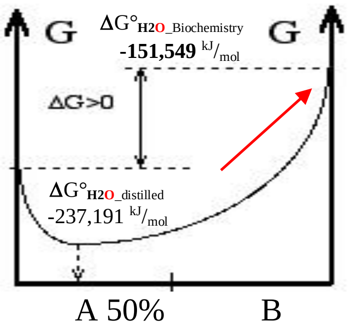
$\Delta G_H = \Delta H_H - T*\Delta S_H = -3148{,}89-298{,}15*-0{,}785399= -3148{,}89+234{,}16= -2914.72$.................. kJ/mol **exoergic**....

$T•\Delta S_{total} = 9776*298{,}15 = \mathbf{+2914.7}$................................................. 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 $C_6H_{12}O_6$ oxidation by $6O_{2aqua}$ to $6HCO_3^-$ $+6H_3O^+$

Calculate $\Delta H_H$ $\Delta S_H$ $\Delta G_H$. Reaction is **exothermic** , **athermic**, **endothermic**? Glucose $C_6H_{12}O_6$ oxidation by $6O_{2aqua}$ to $6HCO_3^-$ $+6H_3O^+$ at standard conditions 298.15 K using the data table! Mention whether the reaction will be **exoergic** or **endoergic**! $C_6H_{12}O_6+6O_2 \Rightarrow 6CO_2+6H_2O+\Delta G+Q$; $\Delta G_{Lehninger}=-2840$ 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 | -213,274599 |
| $CO_2\uparrow_{gas}$ | -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** |

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

$\Delta G_H=6\Delta G°_{H3O}+6\Delta G°_{HCO3}-\Delta G°_{C6H12O6}-6\Delta G°_{O2}-6\Delta G°_{H2O}=$ 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**

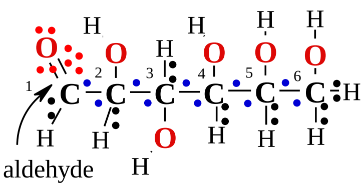
Alb$\Delta G_H=\Delta H_H-T*\Delta S_H=-2805,27-298,15*-0,787625=-2570.4$ kJ/mol

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



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

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

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

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

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

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

$[H_3O^+]=10^{-7,36}$ M, $[O_{2aq}]=6*10^{-5}$M; $E_{O2}=E°+{}^{0,0591}/_4\bullet\log([O_{2aqua}]\bullet[H_3O^+]^4/[H_2O]^5)=$

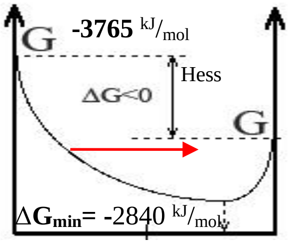
$=$**0,1392**$+{}^{0,0591}/_{24}*\log(6*10^{\wedge(-5)}*10^{\wedge(-7,36*4)}/55,3^{\wedge 5})=$**0,03485** V

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

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

$|\Delta G_{Heas}=$**-3764.92** kJ/mol $| > |$ $\Delta G_{Lehninger}=-2840$ kJ/mol $|$;

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



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

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

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

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

Calculate $\Delta H_H$ $\Delta S_H$ $\Delta G_H$ at standard conditions 298.15 K. Reaction is **exothermic** , **athermic**, **endothermic**?
Beta oxidation in mitochondria, peroxysomes of palmitic acid with $O_{2aqua}$ standard conditions (25°C) 298.15 K, using data on table! Will reaction **exoergic** or **endoergic**! Reactants =>products bicarbonate +hydronium ions

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

biooxidation 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. $\Delta G_H=\Delta H_H-T\bullet\Delta S_H$

| *Substance* | $\Delta H°_H\ ^{kJ}/_{mol}$ | $\Delta S°_H\ ^{J}/_{mol/K}$ | $\Delta G°_H\ ^{kJ}/_{mol}$ |
|---|---|---|---|
| $C_{16}H_{32}O_2$ | - | - | **1067,2384** |
| $C_{16}H_{32}O_{2s}$ | -891,5 | 452,4 | - |
| $C_{16}H_{32}O_{2liq}$ | -838,1 | - | 1003,54 |
| $O_{2aqua}$ | -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 | -213,2746 |
| $CO_2\uparrow_{gas}$ | -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** |

2.$\Delta S_{dispersed}=-\Delta H_H/T=9930,7/298,15=3337.7\ ^{J}/_{mol/K}$;**33224.5**
$\Delta S_{total}= \Delta S_H+ \Delta S_{dispersed}=33307,7-2610,33= 30697.47\ ^{J}/_{mol/K}$;
$\Delta S_{total}= \Delta S_H+ \Delta S_{dispersed}=$**33224,5+987,26=34211.76** $^{J}/_{mol/K}$;
$\Delta G_H=\Delta H_H- T*\Delta S_H=-9930,7-298,15* -2,61933= -9152.5\ ^{kJ}/_{mol}$;
$\Delta G_H=\Delta H_H- T*\Delta S_H=$**-9905,9**-298,15***0,987256**= **-10200.2** $^{kJ}/_{mol}$;
$T\bullet\Delta S_{total}=30,69747^*298,15=9152.5\ ^{kJ}/_{mol}$ lost free energy
$T\bullet\Delta S_{total}=$**34,21173**$^*$298,15=**10200.2** $^{kJ}/_{mol}$ lost free energy
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***-544,9688**+16*-213,2746-(16***-151,549**+23***16,4**+**1067,2384**)=**-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***-151,549**+23***16,4**+**1067,2384**)=**-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***-151,549**+23***16,4**+**1067,2384**)=**-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***-692,4948**+16*-285,81-(16***-286,65**+23***-11,7**-891.5)= **-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***-494,768**+16*-3,854-(16***-453,188**+23***-94,2**+452,4)= **987,256** $^{J}/_{mol/K}$;

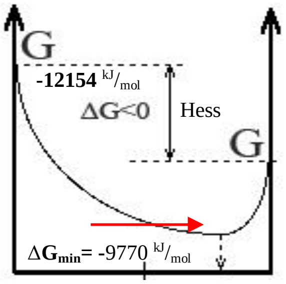
$$\Delta G_{eq}=-R\bullet T\bullet \ln(K_{eq})=-8,3144\bullet 298,15\bullet \ln(10^{1711,6428})=-9770\ ^{kJ}/_{mol}$$

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

$O_{2aqua}$ > for gas $CO_{2gas}\uparrow$ $\Delta G_{oxidation}$=**-12154** $^{kJ}/_{mol}$ and

$\Delta G_{oxidation}$=**-12020** $^{kJ}/_{mol}$ for both aqua $O_{2aqua}$ and $CO_{2aqua}$, but minimizes

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



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

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

A+23B 50%
16C+16D
products 16C+16D
$16CO_2+16H_2O$

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

Free energy minimum reaching establishes equilibrium mixture.

THERMODYNAMICS IV Vitamin B3 ethanol **$H_3C$-$CH_2$-OH** oxidation to ethanal **$H_3C$-CH=O** aerobic Calculate $\Delta H_H$ $\Delta S_H$ $\Delta G_H$ 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**! **$H_3C$-$CH_2$-OH**+$NAD^+$**+$H_2O$**+**ΔG+Q** => **$H_3C$-CH=O**+NAD**H+$H_3O^+$**

| *Substance* | $\Delta H°_H$ $^{kJ}/_{mol}$ | $\Delta S°_H$ $^{J}/_{mol/K}$ | $\Delta G°_H$ $^{kJ}/_{mol}$ |
|---|---|---|---|
| **$H_3C$-CH=O** | -212,23 | -281,84 | 24,06 |
| **$H_3C$-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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$\Delta H_{Hess}=\Delta H°_{H3O}+\Delta H°_{CH3CHO}+\Delta H°_{NADH}-\Delta H°_{CH3CH2OH}-\Delta H°_{H2O}-\Delta H°_{NAD+}=$
$=\mathbf{-213,88}-1036,66-285,81-(-288,3-1007,48-285.85)=45,28$ $^{kJ}/_{mol}$

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

$\Delta S_{Hess}=\Delta S°_{H3O}+\Delta S°_{CH3CHO}+\Delta S°_{NADH}-\Delta S°_{CH3CH2OH}-\Delta S°_{H2O}-\Delta S°_{NAD+}=$
$=\mathbf{-825,64}-140,50-3,854-(-357,7394-183+69,9565)=-499,211$ $^{J}/_{mol/K}$

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

$\Delta G_{Hess}=\Delta G°_{H3O}+\Delta G°_{CH3CHO}+\Delta G°_{NADH}-\Delta G°_{CH3CH2OH}-\Delta G°_{H2O}-\Delta G°_{NAD+}=$

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

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

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

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

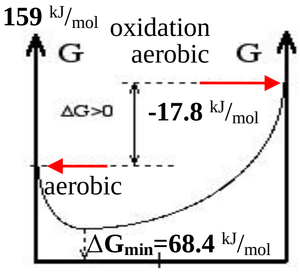
sum **$NAD^+$+$CH_3$-$CH_2$-OH+$H_2O$=>NADH+$CH_3$-HC=O+$H_3O^+$**;

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

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

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

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



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

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

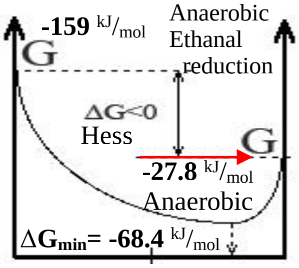
**$H_3C$-CH=O**+NAD**H+$H_3O^+$** =>**$H_3C$-$CH_2$-OH**+$NAD^+$**+$H_2O$**+**ΔG+Q**;

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

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

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

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



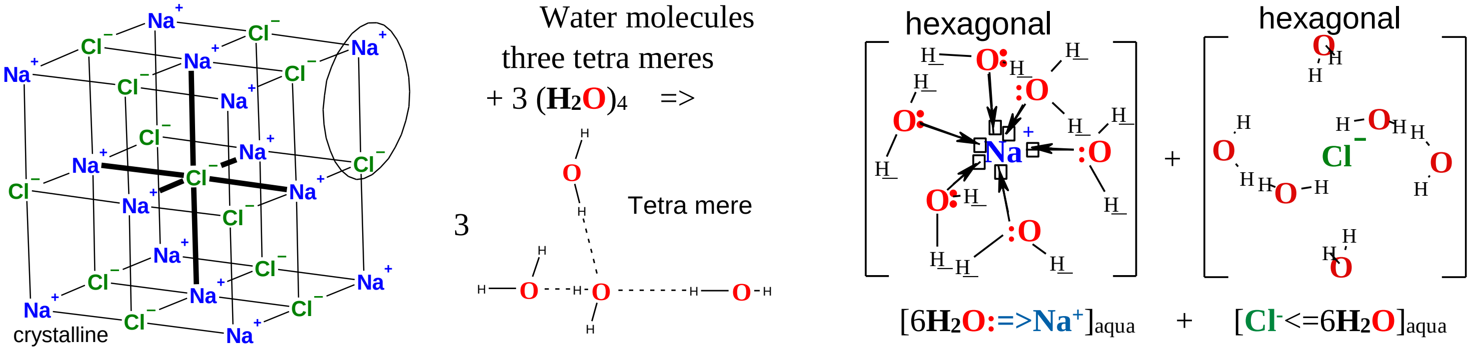
D+E+F 50% A+B+C
$NADH+H_3CCHO+H_3O^+$
$NAD^++H_3CCH_2OH+H_2O$

$$K_{AnaerobicRed}=10^{12}=\frac{[NAD^+]\cdot[CH_3CH_2OH]\cdot[H_2O]}{[NADH]\cdot[CH_3CHO]\cdot[H_3O^+]};\ K_{AerobicOx}=10^{-12}=\frac{[NADH]\cdot[CH_3CHO]\cdot[H_3O^+]}{[NAD^+]\cdot[CH_3CH_2OH]\cdot[H_2O]}$$ ; favored oxidation

$[NADH]/[NAD^+]=1/7700$; $\Delta G_{AerobicRed}=68,4+8,3144*298,15*ln(1/7700*1/10*10^{-7,36}/55,3457)/1000=-1\mathbf{1.5}$ $^{kJ}/_{mol}$.

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

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



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

1. $Na^+Cl^- => Na^+ + Cl^-$ ; energy $\Delta G_{Na+Cl-}$ = 700 $^{kJ}/_{mol}$ ; Ionu crystalline destruction.
2. $3(H_2O)_4 => 12H_2O$ ; energy $3*\Delta G_{(H2O)4} = 3*90 = 270$ $^{kJ}/_{mol}$ ; Tetra mer destruction.
3. $Na^+ + 6H_2O => [6(H_2O{:}\rightarrow\square)\text{-}Na^+]$ energy $6*\Delta G_{[H2O:=>Na+]} = 6*-400 = -2400$ $^{kJ}/_{mol}$ ; Coordination hexagonal.
4. $Cl^- + 6H_2O => [Cl^-\text{-}(....6H_2O)]$ energy $6*\Delta G_{[Cl--(....H2O)]} = 6*-30 = -180$ $^{kJ}/_{mol}$ ; Six hydrogen bons creation.

$\Delta G_{reaction} = \Delta G_{Na+Cl-} + 3*\Delta G_{(H2O)4} + 6*\Delta G_{[H2O:=>Na+]} + 6*\Delta G_{[Cl--(....H2O)]} = 700+270-2400-180 = -1610$ $^{kJ}/_{mol}$ ;

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

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

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

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

1. $\Delta H_H = \Delta H°_{Na} + \Delta H°_{Cl} - \Delta H°_{NaCl}$ =..........$^{kJ}/_{mol}$. **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.........$^{J}/_{(mol\ K)}$

$\Delta S_H = \Delta S°_{Na} + \Delta S°_{Cl} - \Delta S°_{NaCl}$=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•298,15=**9.15** .......$^{kJ}/_{mol}$ bound free energy
Non dissociated salt neutral molecules form in two ways:

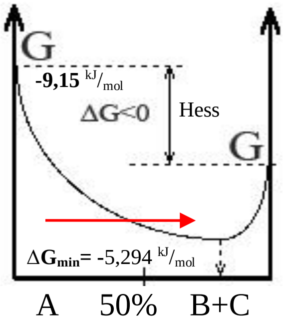
1. **Electrostatic** atraction ions *Debye - Hückels'* physiology 0,9% solution forms osmolar $C_{osm}$=0,305 M concentration with sodium chloride ions and salt neutral molecules : $NaCl \rightleftarrows Na^+ + Cl^-$ in litre 1000 mL .
$C_{osm} = [Na^+]+[Cl^-]+[NaCl] = i*C_M$=0,305 M. $m_{NaCl}/m_{šķ}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

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

Endothermic and exoergic solubility Hess free energy change $\Delta G_{Hess}$= -9,15 $^{kJ}/_{mol}$ is negative, but minimized $\Delta G_{min} = \Delta G_{0,9\%}$= -5,294 $^{kJ}/_{mol}$ in physiologic 0,9 % mixture reached equilibrium

$K_{0,9\%} = K_{0,9\%} = [Na^+_{aq}]*[Cl^-_{aq}]/[NaCl_{aq}]$= 8,46 or solubility product

$\Delta G_{sp}$= -6,25 $^{kJ}/_{mol}$ reached $K_{sp} = K_{eq}$=12,44. Le Chatelier principle is Prigogine attractor free energy change minimum $\Delta G_{sp}$ for crystalline sodium chloride $Na^+Cl^-$ **solubility** product. At free energy minimum $\Delta G_{min}$ reaching establishes equilibrium.



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

Note: 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.

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

Crystalline $\mathbf{Na^+OH^-}$ 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 |
| $\mathbf{H_2O}$ | -285.85 | 69,9565 | -237,191 |
| $\mathbf{H_2O}$ | **-286,65** | **-453,188** | **-151,549** |
| $\mathbf{H_3O^+}$ | -285,81 | -3,854 | -213,275 |
| $\mathbf{Na+_{aqua}}$ | -240,10 | 59,00 | -261,9 |
| $\mathbf{OH^-}$ | -230.00 | -10,539 | -157,2 |

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

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

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

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

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

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

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

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

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

Non dissociated hydroxide neutral molecules not forming:

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

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

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

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

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

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

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

<u>Solubility</u> 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 $\mathbf{Na^+}$ ions, but $\mathbf{OH^-}$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:$\Delta G_{eq}=\Delta G_{sp}=-8,3144\bullet298,15\bullet\ln(0,\mathbf{2025})=\mathbf{3,959}\ ^{kJ}/_{mol}$.

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

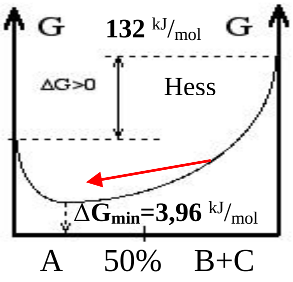
1. Ions lattice destruction: $\mathbf{NaOH=>Na^++OH^-}$ energy: $\Delta G_{NaOH}=887\ ^{kJ}/_{mol}$ .
2. Tetra mer destruction: $(\mathbf{H_2O})_4=>4\mathbf{H_2O}$ energy $\Delta G_{(H2O)4}=90\ ^{kJ}/_{mol}$. w%=50 %

3.a Two $\mathbf{H_2O}$ 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: <u>Strong electrolytes</u> are soluble with negative $\Delta\mathbf{G<0}$ and greater one $\mathbf{K_{eq}>>1}$ ;

<u>Weak electrolytes</u> with positive $\Delta\mathbf{G}_{eq}\mathbf{>0}$ and $0<\mathbf{K_{eq}<1}$ **endoergic** are <u>water insoluble</u> .

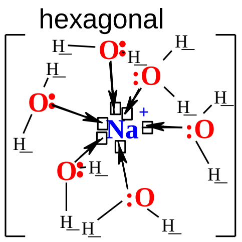


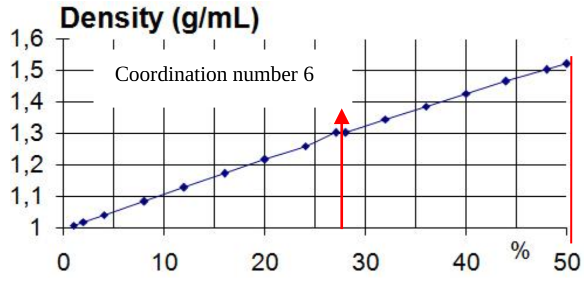
$\mathbf{Na^+OH^{-}}_{Cryst}=>$products $\mathbf{Na^++OH^-}$

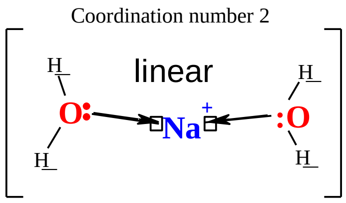
At 0% < w% < 27 % $\mathbf{NaOH}_{Cryst}$ solution density 1,301 $^{g}/_{mL}$ $2\mathbf{Na^+OH^-}+3(\mathbf{H_2O})_4=>2[6\mathbf{H_2O:=>Na^+}]_{aqua}+2\mathbf{OH^-}$;

3.b Six $\mathbf{H_2O}$ 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

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

CRC 2010 Reaction is **exothermic** , **athermic**, **endothermic**,**exoergic**, **endoergic**! ?$\mathbf{HCl}_{gas}\Rightarrow\mathbf{HCl}_{aqua}+\Delta G+\mathbf{Q}$;

| *Substance* | $\Delta H^\circ_H$ $^{kJ}/_{mol}$ | $\Delta S^\circ_H$ $^{J}/_{mol/K}$ | $\Delta G^\circ_H$ $^{kJ}/_{mol}$ |
|---|---|---|---|
| **$Na^+Cl^-$** | -411,12 | 72,00 | - |
| **$Na^+$**$_{aqua}$ | -240,10 | 59,00 | - |
| **$Cl^-$**$_{aqua}$ | -167,08 | 56,50 | - |
| **$H_2O_{aq}$** | -285,85 | 69,956 | -237,191 |
| **$H_2O$** | **-286,65** | **-453,188** | **-151,549** |
| **$H_3O^+$** | -285,81 | -3,854 | -213,275 |
| **$HCl_{gas}$** | -92,31 | 186,902 | -95,3 |
| **$HCl_{aqua}$** | -167,2 | 56,5 | -131,2 |

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

1\. $\Delta H_{Hess}= \Sigma\Delta H^\circ_{products}- \Sigma\Delta H^\circ_{Reactants}$; **exoergic**..................

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

2\. $\Delta S_{Hess}= \Sigma\Delta S^\circ_{products}- \Sigma\Delta S^\circ_{Reactants}$; **exothermiska**...................

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

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

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

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

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

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

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

$\Delta H_{Hess}=\Delta H^\circ_{\mathbf{H_3O}}+\Delta H^\circ_{\mathbf{Cl}-}-\Delta H^\circ_{\mathbf{HCl}aq}-\Delta H^\circ_{\mathbf{H_2O}}= -285{,}81-167{,}08-(-167{,}2-285{,}85)=0{,}16$.......$^{kJ}/_{mol}$; **athermic**..............

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

$\Delta S_{Hess}=\Delta S^\circ_{\mathbf{H_3O}} + \Delta S^\circ_{\mathbf{Cl}-}-\Delta S^\circ_{\mathbf{HCl}} -\Delta S^\circ_{\mathbf{H_2O}}=-3{,}854+56{,}60-(69{,}96+56{,}5)= 52{,}64-126{,}46=-73{,}714$........$^{J}/_{mol/K}$

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

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

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

$m_{\mathbf{H_2O}}=1180-436{,}6=743{,}4$ g; $n_{\mathbf{H_2O}}=743{,}4/18=41{,}3$ $^{mol}/_{L}$, First solution:

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

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

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

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

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

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 $\boldsymbol{\alpha}$**=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 $^{mol}/_{L}$;

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

$$\frac{[H_3O^+]\cdot[Cl^-]_{aqua}}{[HCl]_{aqua}\cdot[H_2O]}=\mathbf{K_{eq}}=(0{,}25235*0{,}25235)/( 41{,}04765*11{,}725664)=0{,}000132306=10^{-3{,}878};$$

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

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

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

$$\frac{[H_3O^+]\cdot[Cl^-]_{aqua}}{[HCl]_{aqua}\cdot[H_2O]}=\mathbf{K_{eq}}=(0{,}04728863*0{,}04728863)/(55{,}23*0{,}05271137)=0{,}000768129= \mathbf{K_{dis1}};\ \mathbf{C_M} = 0{,}1 \text{ M}$$

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

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

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

0,04728863 M =$[\mathbf{H_3O^+}]=10^{-pH}=10^{-1{,}325}$; 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 , $\boldsymbol{\alpha}$**%=** 4,7%; $\boldsymbol{\alpha}_{0,01}$=0,008343/0,01=0,8343, $\boldsymbol{\alpha}$**%=**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;

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

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

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

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;

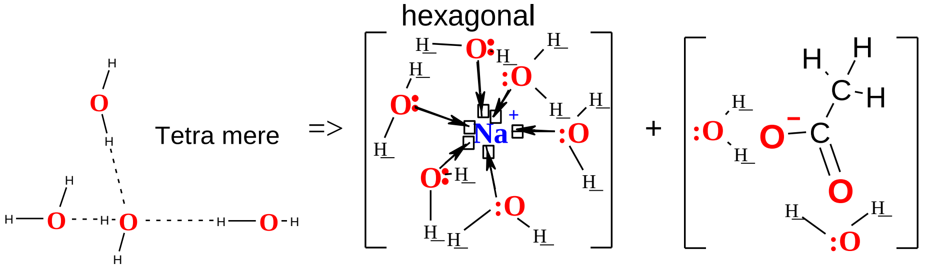
Complete dissociation in ideal solution coordinate 6 $\mathbf{H_2O}$ , 2 $\mathbf{H_2O}$ sodium ions and acetate ions crystalline $\mathbf{CH_3COONa_s} \rightleftarrows \mathbf{Na^+ + CH_3COO^-}$ solie, poore compound mol fraction is one $[\mathbf{CH_3COONa}]_{solid}$ = 1 and solubility product constant: $\mathbf{K_{sp}= K_{eq}} =[\mathbf{Na^+}]*[\mathbf{CH_3COO^-}]$=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:

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

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

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



+ **Q** + ΔG;

| Substance | $\Delta H°_{Hess}$, $^{kJ}/_{mol}$ | $\Delta S°_{Hess}$, $^J/_{mol/K}$ | $\Delta G°_{Hess}$, $^{kJ}/_{mol}$ |
|---|---|---|---|
| $\mathbf{Na^+}_{aqua}$ | -240.1 | 59 | - |
| $\mathbf{CH_3COO^-}_{aq}$ | -486 | 85.3 | -247.83 |
| $\mathbf{CH_3COO^-}_{aq}$ | **-486.836** | **-822.3** | **-241.663** |
| $\mathbf{CH_3COONa_s}$ | -708.8 | 123.0- | -607.7- |

CRC 2010 reactant => products

$\mathbf{CH_3COONa_s => Na^+_{aqua}+CH_3COO^-_{aqua}} + \mathbf{Q} + \Delta G;$

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...........$^J/_{mol/K}$;

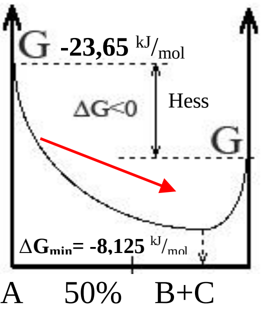
1. $\mathbf{\Delta H_{Hess}=\Delta H°_{H3CCOO-}+\Delta H°_{Na}-\Delta H°_{H3CCOO\,Na}}$=-486-240.1-(-708.8)= -17.3 $^{kJ}/_{mol}$ **eksotermiska**..................

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

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

Free energy change minimum reaching establishes equilibrium



reactant crystalline $\mathbf{CH_3COONa_s}$_

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

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 $m_{\mathbf{H2O}}=m_{šķ}-m_{NH4Cl}$ = 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 :

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

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

| *Substance* | $\Delta H°_{Hess}$,$^{kJ}/_{mol}$ | $\Delta S°_{Hess}$,$^{J}/_{mol/K}$ | $\Delta G°_{Hess}$,$^{kJ}/_{mo}$ |
|---|---|---|---|
| $\mathbf{Cl}$-$_{aqua}$ | -167.2 | 56.50 | - |
| $\mathbf{NH_4}^+_{(aq)}$ | -132.5 | 113.4 | - |
| $\mathbf{NH_4Cl}_{(s)}$ | -314.4 | 94.6- | -202.97 |

reactants $\mathbf{NH_4Cl}_{(s)}$ +**Q** **=>** $\mathbf{NH_4}^+$**+** $\mathbf{Cl}^-_{aqua}$ +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. $\Delta G_{Hess}= \Delta H_{Hess}-T•\Delta S_{Hess}$

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**.............................

$T•\Delta S_{total}$=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 ..........$^{mol}/_{L}$ ,

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

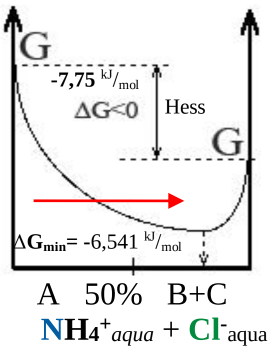
$\mathbf{\Delta G_{eq}=-R•T•ln(K_{eq})}$=-8.3144•298.15•**ln**(13.9935)= -6. 541 ..........$^{kJ}/_{mol}$, Endothermic and exoergic $\mathbf{NH_4Cl}_{(s)}$ dissociation Hess free energiy change $\Delta\mathbf{G_{dis}}_{Hess}$=-7.75 ..........$^{kJ}/_{mol}$ negative, but minimized reaching $\Delta\mathbf{G_{min}}=\Delta\mathbf{G_{eq}}$= -6. 541.........$^{kJ}/_{mol}$ equilibrium mixture

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

Prigogine attractor for Free energy change minimum $\Delta G_{min}$ reaching at equilibrium.

reactant non dissociated amonium chloride $\mathbf{NH_4Cl}_{aqua}$_

and products



Free energy change minimum reaching establishes equilibrium

THERMODYNAMICS Exercise V.b acetic acid **$CH_3COOH$** in protolytic reaction

Calculate $\Delta H_H$, $\Delta S_H$, $\Delta G_H$ at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? For the **$CH_3COOH$** protolytic reaction with water! Will be **exoergic** or **endoergic**!

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

Reactants => products

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

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

1. $\Delta H_H=\Delta H^\circ_{H3CCOO-} + \Delta H^\circ_{H3O} - \Delta H^\circ_{H2O} - \Delta H^\circ_{H3CCOOH}$ =-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. $\Delta S_H=\Delta S^\circ_{H3CCOO-} +\Delta S^\circ_{H3O}-\Delta S^\circ_{H2O}-\Delta S^\circ_{H3CCOOH}$ =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..................................................................... $^{J}/_{(mol\ K)}$....

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

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

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

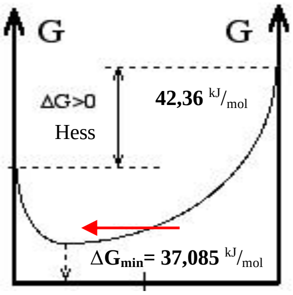
Equilibrium reached by free energy minimum at compounds mixture ratio in expression:

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

$\mathbf{\Delta G_{eq} = -R\bullet T\bullet ln(K_{eq})}$= - 8,3144•298,15•**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_**$CH_3COOH+H_2O$**

**$H_3O^++CH_3COO^{-}$**

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 **$[H_2O]$= 55,3 M**

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ 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 $\mathbf{H_2O}$ Water ionization and neutralization inverse attractors of reaction

Calculate $\Delta H_{Hess}$, $\Delta S_{Hess}$, $\Delta G_{Hess}$ at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? For the water $\mathbf{H_2O}$ protolytic reaction with water! Will be **exoergic** or **endoergic**!

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

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

$\Delta G_{Hess}=\Delta G°_{OH}+\Delta G°_{\mathbf{H3O}}\mathbf{-2}\Delta G°_{\mathbf{H2O}}=103.907\ ^{kJ}/_{mol}$;

$=-157{,}2-213{,}275-2*-237{,}191=103.907\ ^{kJ}/_{mol}$;

$\Delta H_{Hess}=\Delta H°_{OH}+\Delta H°_{\mathbf{H3O}}\mathbf{-2}\Delta H°_{\mathbf{H2O}}=55{,}89\ ^{kJ}/_{mol}$; **endothermic**.

$=-285{,}81-230-(2*(-285{,}85))=-515.81+571{,}7=55{,}89\ ^{kJ}/_{mol}$;

$\Delta S_{disperse}=-\Delta H_{Hess}/T=-55{,}89/298{,}15=-187{,}456\ ^{J}/_{(mol\ K)}$;

$\Delta S_{Hess}=\Delta S°_{OH}+\Delta S°_{\mathbf{H3O}}\mathbf{-2}\Delta S°_{\mathbf{H2O}}=-3{,}854-10{,}539-2*69{,}956=14.393-139.912=-154.305\ ^{J}/_{mol/K}$;

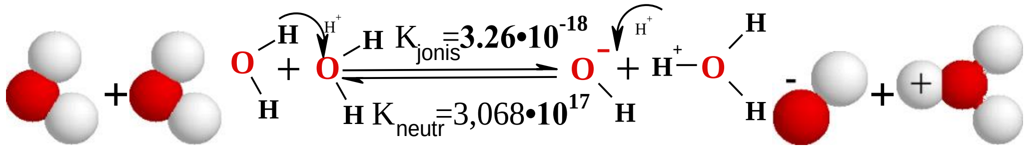
$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{disperse}=-187{,}456-154{,}305=-341{,}761\ ^{J}/_{(mol\ K)}$;

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=55{,}89+298{,}15*0{,}154305=101{,}8967\ ^{kJ}/_{mol}$; **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**

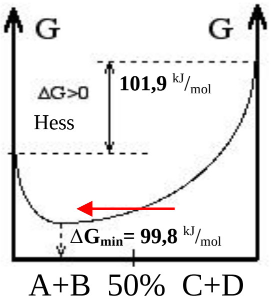
Equilibrium reached by free energy minimum at compounds mixture ratio in expression:

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



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

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



$\mathbf{H_2O+H_2O}$ reactants products $\mathbf{H_3O^+ + OH^-}$

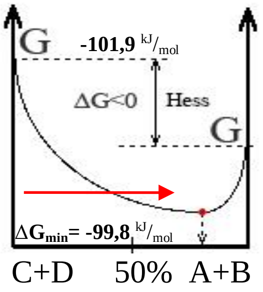
Endothermic and endoergic water protolysis reaction Hess free energy change $\Delta\mathbf{G_{Hess}}=\Delta\mathbf{G_{protolyse}}=101{,}9\ ^{kJ}/_{mol}$ positive, but minimizes reached equilibrium

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

Free energy change $\Delta G_{Hess}$ 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:

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



$\mathbf{H_3O^+ + OH^-}$ reactants products $\mathbf{H_2O+H_2O}$.

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.

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 $K_w=[\mathbf{H_3O^+}][\mathbf{OH^-}]=10^{-14}$ , 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.

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

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

## THERMODYNAMICS Exercise V.d solubility $\mathbf{NH_3}_{gas}$, $\mathbf{NH_4^+}$ in protolytic reaction and protonation of $\mathbf{NH_3}_{aqua}$

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 $NH_4^+ + H_2O \Rightarrow NH_{3\,(aq)} + H_3O^+$ ;

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

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

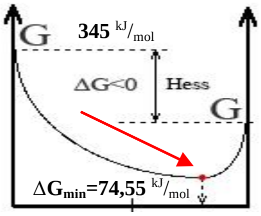
$G_{Hydration}+G_{NH3gas}+\Delta G_{H2O}=G_{NH3aq}=107,5+165,7+0=273,2$ kJ/mol;

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

$\Delta S_{Hydration}=\Delta S^\circ_{NH3aqua}-\Delta S^\circ_{NH3gas}-\Delta S^\circ_{H2O}=-739,2922-192,77-69,9565=-1002$ 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;

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



A 50% B

reactants $NH_{3gas}+H_2O$

un produkt $NH_{3aq}$

Ammonia $NH_{3aq}$ protonation:

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

$\Delta H_{Hess}=\Delta H^\circ_{NH4+}+\Delta H^\circ_{OH}-\Delta H^\circ_{NH3}-\Delta H^\circ_{H2O}=55.8$ 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* | $\Delta H^\circ_H$ 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** |
| $NH_4^+$ | -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; $\Delta S_{Hess}=\Delta S^\circ_{NH4+}+\Delta S^\circ_{OH}-\Delta S^\circ_{NH3}-\Delta S^\circ_{H2O}=771.8$ 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**; $\Delta G_{Hess}=\Delta G^\circ_{NH4+}+\Delta G^\circ_{OH}-\Delta G^\circ_{NH3}-\Delta G^\circ_{H2O}=-90.415$ 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.$\Delta H_H=\Delta H^\circ_{NH3}+\Delta H^\circ_{H3O}-\Delta H^\circ_{NH4+}-\Delta H^\circ_{H2O}=-132.5-285.81-(-132.5608-286.65)=0.901$.........kJ/mol **athermic**......

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

2. $\Delta S_{Hess}=\Delta S^\circ_{NH3}+\Delta S^\circ_{H3O}-\Delta S^\circ_{NH4+}-\Delta S^\circ_{H2O}=-739.2922-3.854-(113.4-453.188)=-403.4$..........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 ;

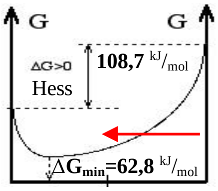
$$K_{eq2}=\frac{[OH^-]\cdot[NH_4^+]}{[NH_3]_{aqua}\cdot[H_2O]}=10^{15,84};\ K_{eq3}=\frac{[NH_3]_{aqua}\cdot[H_3O^+]}{[NH_4^+]\cdot[H_2O]}=[H_2O]\cdot K_{H2O}/K_{NH4OH}=[H_2O]\frac{3.26\cdot10^{-18}}{1,78\cdot10^{-5}}=1,014\cdot10^{-11};$$

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

$\Delta G_{eq3}=-R\bullet T\bullet\ln(K_{eq3})=-8.3144\bullet298.15\bullet\ln(1.014\cdot10^{-11})=62.75$ 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 enerģgy 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 $K_{eq2}=10^{15.84}$;



A+B 50% C+D

reactants – $NH_4^+ + H_2O$

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

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 $\Delta H_H$ $\Delta S_H$ $\Delta G_H$ 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 **Na$H_2PO_4$** $2H_2O$ solubility 94,9 $^{g}/_{100g}$ $H_2O$, density 1,32 $^{g}/_{mL}$, **$Na_2HPO_{4s}$** 11,8 $^{g}/_{100g}$ $H_2O$, density 1,1 $^{g}/_{mL}$, CRC 2010 ; **BioThermodynamic2006** $\mathbf{H_2PO_4^- + H_2O} + \Delta G + \mathbf{Q} \Rightarrow \mathbf{HPO_4^{2-} + H_3O^+}$ 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.$\Delta G_{Hess}=\Delta H_{Hess}-T\bullet\Delta S_{Hess}$

=**-1057,143**-213,275-(-1137,3**-151,549**)= **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 $^{kJ}/_{mol}$; =**4,55**-298,15***-0,454**=**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: $\dfrac{[HPO_4^{2-}]\cdot[H_3O^+]}{[H_2PO_4^-]\cdot[H_2O]}$ =$\mathbf{K_{eq2}}$= $\mathbf{K}_{a2}/[\mathbf{H_2O}]=10^{-7,199}/55,3457339=1,144*10^{-9}$; $pK_{a2}$=7,199

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

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

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

$\mathbf{HPO_4^{2-} + H_2O \Rightarrow PO_4^{3-} + H_3O^+}$=$\mathbf{K_{eq3}}$= $\mathbf{K}_{HPO42-}/[\mathbf{H_2O}]$= 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•298,15•**ln**(8,07*10$^{-15}$)=80,44 $^{kJ}/_{mol}$,

$\mathbf{H_3PO_4 + H_2O \Rightarrow H_2PO_4^- + H_3O^+}$; $\mathbf{K_{eq1}}$= $\mathbf{K}_{H3PO4}/[\mathbf{H_2O}]$= 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•298,15•**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

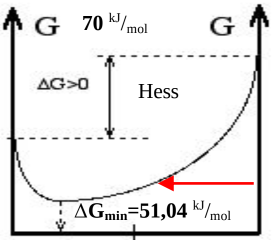
$\mathbf{HPO_4^{2-} + H_2O \Rightarrow PO_4^{3-} + H_3O^+}$; $\mathbf{H_2PO_4^- + H_2O \Rightarrow HPO_4^{2-} + H_3O^+}$;

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

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

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

$\dfrac{[PO_4^{3-}]\cdot[H_3O^+]}{[HPO_4^{2-}]\cdot[H_2O]}$ = $\mathbf{K_{eq3}}$= $\mathbf{K}_{HPO42-}/[\mathbf{H_2O}]$= 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 $\mathbf{ATP^{4-}}$ adenosine triphosphate hydrolysis reaction

Calculate $\Delta H_r$, $\Delta S_r$, $\Delta G$ at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? For the $\mathbf{ATP^{4-}}$ adenosine triphosphate hydrolysis reaction with water! Will be **exoergic** or **endoergic**!

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

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

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

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

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

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

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

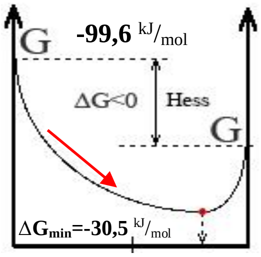
$\mathbf{K_{bLehninger}=exp(-\Delta G_{bLehninger}/R/T)}=\exp(30500/8{,}3144/298{,}15)=\exp(12{,}304)=220500{,}2=\dfrac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_2O]^2[ATP^{4-}]}$

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

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

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

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



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

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

A+2B 50% C+D+E

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

| | | | |
|---|---|---|---|
| $\mathbf{H_3O^+}$ | -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** |

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

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

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

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

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

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

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

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

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

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

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

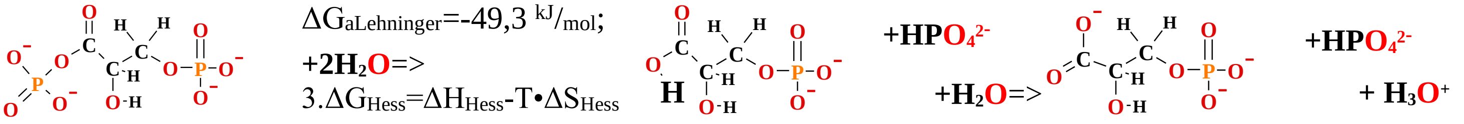
$\Delta G_H=\Delta G°_{\mathbf{ATP4}}-2\Delta G°_{\mathbf{H2O}}-\Delta G°_{\mathbf{ADP3}}-\Delta G°_{\mathbf{HPO42}}-\Delta G°_{\mathbf{H3O}}=$

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

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

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

Calculate $\Delta H_H$ $\Delta S_H$ $\Delta G_H$ 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$^+$**) $\Delta H°_{Hess}=-285,81\ ^{kJ}/_{mol}$; $\Delta G_{Hess}=\Delta G°_{H3O+}+\Delta G°_{Glyc3P}+\Delta G°_{HPO42-}-\Delta G°_{Glyc31P}-2\Delta G°_{H2O}=\mathbf{-107.75}\ ^{kJ}/_{mol}$;

*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$_3$O$^+$** | -285,81 | -3,854 | -213,275 |
| **H$_2$O** | -285,85 | 69,9565 | -237,191 |
| **H$_2$O** | **-286,65** | **-453,188** | **-151,549** |
| **H$_2$PO$_4^-$** | -1296,3 | 90,4 | -1130,2 |
| **H$_2$PO$_4^-$** | -1302,6 | 92,5 | -1137,3 |
| **HPO$_4^{2-}$** | -1292,14 | -33,47 | -1089,28 |
| **HPO$_4^{2-}$** | **-1298,89** | **-810,792** | **-1057,143** |
| 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**; $=-213,275\mathbf{-1347,73-1057,143}-(-2207,30+2*\mathbf{-151,549})=\mathbf{-107.75}\ ^{kJ}/_{mol}$;

CRC10 **Glyc3P$^{2-}$+H$_2$O =>Glycerol+HPO$_4^{2-}$+$\Delta$G+Q;** $\mathbf{\Delta G}_{Lehninger}=-9,2\ ^{kJ}/_{mol}$;

CRC10 $\Delta G_{Hess}=\Delta G°_{Glycerol}+\Delta G°_{HPO42-}-\Delta G°_{Glyc3P}-\Delta G°_{H2O}=\mathbf{-46,43}\ ^{kJ}/_{mol}$

CRC10$=-171,35-1089,28-(\mathbf{-1062,65}+(\mathbf{-151,549}))=\mathbf{-46,43}\ ^{kJ}/_{mol}$;

$K_{aLehninger}=\exp(9200/8,3144/298,15)=40,906$

Glycerol1P$^-$+ADP$^{2-}$(+H$_2$O)=>Glycerol+ATP$^{3-}$; $\mathbf{\Delta G}_{Lehninger}=11.35\ ^{kJ}/_{mol}$;

$K_{aL}=K_{Lehninger}*[H_2O]=0,000185513*55,3457339=0,0102673531329907$

$\Delta G_H=\Delta G°_{Glyc}+\Delta G°_{ATP3}-\Delta G°_{Glyc3P}-\Delta G°_{ADP2}=\mathbf{40}\ ^{kJ}/_{mol}$;

$=-171,35\mathbf{-2267,64-(-1062,65-1399,9)}=\mathbf{39,998}\ ^{kJ}/_{mol}$;

abb)Glycerol1P$^{2-}$+ADP$^{3-}$+H$_3$O$^+$=>Glycerol+ATP$^{4-}$+H$_2$O; $\mathbf{\Delta G}_{Lehninger}=21.3\ ^{kJ}/_{mol}$

$K_{abb}=K_aK_{bb}=40,906*0,000004535142=0,000185515$

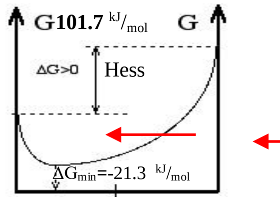
$K_{abb}=\exp(-21300/8,3144/298,15)=0,000185513$;

$\Delta G_H=\Delta G°_{Glyc}+\Delta G°_{ATP4}+\Delta G°_{H2O}-\Delta G°_{Glyc3P}-\Delta G°_{ADP3}-\Delta G°_{H3O}=\mathbf{101.724}\ ^{kJ}/_{mol}$;

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

$\Delta G_{abb}=\Delta G_a+\Delta G_{bb}=-9,2+30,5=21.3\ ^{kJ}/_{mol}$;

Exoergic transfer **HPO$_4^{2-}$** from Glycerol1P$^{2-}$to ATP$^{4-}$ positive $\mathbf{\Delta G}_{\mathbf{transfer}}=\mathbf{101.}7\ ^{kJ}/_{mol}$, but minimizes reaching $\mathbf{\Delta G}_{abb}=\Delta G_a+\Delta G_{bb}=21.3\ ^{kJ}/_{mol}$ equilibrium mixture $K_{abb}=K_aK_{bb}=40,906*0,000004535142=0,000185513$. $\mathbf{\Delta G}_{aL}=-8,3144*298,15*\mathbf{ln}(0,010267353)=11,35\ ^{kJ}/_{mol}$



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$^+$

$$\frac{[Glycerol]\cdot[HPO_4^{2-}]\cdot[ATP^{4-}]}{[H_2O]\cdot[Glycerol1P^{2-}]\cdot[ADP^{3-}]}=\mathbf{K}_{\mathbf{eqL}}=$$

$K_{abb}=K_aK_{bb}=0,000185513$ Products Glycerol+ATP$^{4--}$+H$_2$O;;

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

$\Delta G_{Hess}=\Delta G°_{Glyc3P}+\Delta G°_{H2PO4-}-\Delta G°_{Glyc31P}-\Delta G°_{H2O}=\mathbf{-1347,73}-1137,3-(-2207,3+(-237,191))=\mathbf{-40.54}\ ^{kJ}/_{mol}$ ;

$\mathbf{\Delta G}_{\mathbf{eaL}}=\mathbf{-R\bullet T\bullet ln}(K_{aL})=-8,3144\bullet 298,15\bullet\mathbf{ln}(7833705)=-39,35\ ^{kJ}/_{mol}$ ;

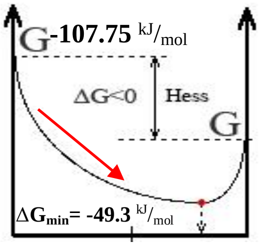
$$K_{aL}=K_{Lehninger}/[H_2O]=433562158,5/55,3457339=7833705=\frac{[Glycerat3P^{3-}]\cdot[H_2PO_4^-]}{[H_2O]\cdot[Glycerat13P^{4-}]}$$

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

**Glycerat31P$^{4-}$+ 2H$_2$O => Glycerat3P$^{3-}$+ HPO$_4^{2-}$+ H$_3$O$^+$**; pH=7,36; $\Delta G_{Lehninger}=-49,3\ ^{kJ}/_{mol}$,;
$\mathbf{K}_{\mathbf{a}Lehninger}=\mathbf{=exp(-\Delta G}_{Lehninger}\mathbf{/R/T)}=\exp(49300/8,3144/298,15)=433562158,5$;
Equilibrium favored pH=7,36. Exothermic and exoergic **1,3-bis-phospho-glycerate** hydrolize reaction free energy change negative $\mathbf{\Delta G}_{\mathbf{hydrolise}}=\mathbf{-107.75}\ ^{kJ}/_{mol}$ , but minimizes $\mathbf{\Delta G}_{\mathbf{eq}}=-49.3\ ^{kJ}/_{mol}$

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

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

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

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

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

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

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

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

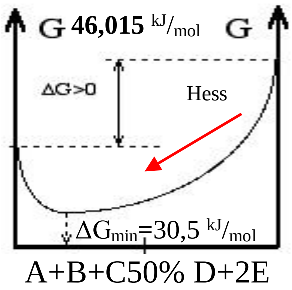
$\Delta G_H=\Delta G°_{ATP4}+2\Delta G°_{H2O}-\Delta G°_{HPO42}-\Delta G°_{ADP3}-\Delta G°_{H3O}=\mathbf{46,015}\ ^{kJ}/_{mol}$;

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

**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 $\mathbf{\Delta G_{Hess}=46.015}\ ^{kJ}/_{mol}$ , but minimizes $\Delta \mathbf{G_{min}}=\Delta \mathbf{G_{eq}}=30.5\ ^{kJ}/_{mol}$ reaching

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



$\mathbf{HPO_4^{3-}+ADP^{3-}+2H_3O^{+}}$
products $\mathbf{HPO_4^{2-}+ATP^{4-}}$

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

Free energy change minimum reaching establishes equilibrium.

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

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

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

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

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

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

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

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

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

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

$\mathbf{Glycerat31P^{4-}+H_2O=>Glycerat3P^{3-}+H_2PO_4;}$ pH<7,199; $G_{aLehninger}=-39,4\ ^{kJ}/_{mol}$; $\dfrac{[Glycerat3P^{3-}].[H_2PO_4^{-}]}{[H_2O]\cdot\ [Glycerat13P^{4-}]}$

$\mathbf{K_{a}}_{Lehninger}=\mathbf{K}_{Lehninger}/\mathbf{[H_2O]}=433562158,5/55,3457339=7833705,111=$

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

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

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

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

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

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

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

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

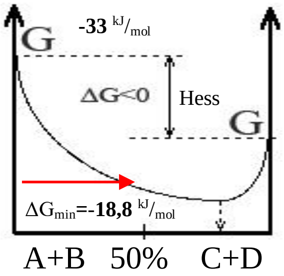
$\mathbf{K_a K_{bb}=K_{abb}}=433562158,5*0,000004535142=1966.266=\dfrac{[Glycerat3P^{3-}]\cdot[ATP^{4-}]}{[Glycerat13P^{4-}]\cdot[ADP^{3-}]}$

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

$\Delta \mathbf{G_{min}}=\Delta \mathbf{G_{eq}}=\ \mathbf{-18,8}\ ^{kJ}/_{mol}$ reaching equilibrium mixture :

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

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



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** $^{kJ}/_{mol}$;

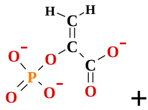
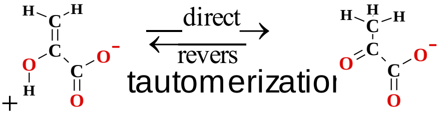
=**-597,04-1298,89**-(-1400-**286,65**)= **-209** $^{kJ}/_{mol}$; **exothermic**

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

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

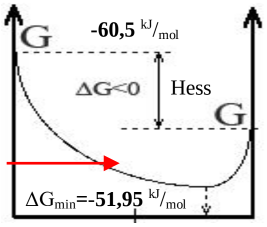
$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}$=**-209**-298,15*-0,104264=**-177,9** $^{kJ}/_{mol}$;

**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 $^{kJ}/_{mol}$ ;

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



Exothermic and exoergic **PyruvEnolP$^{3-}$** hydrolize reaction Hess free energy change negative at pH=7,36 **$\Delta G_{hydrolise}$=-190.3** $^{kJ}/_{mol}$ , but minimizes **$\Delta G_{min}$=$\Delta G_a$**= -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 **$\Delta G_{min}$** .

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$^{4-}$+$H_2O$; **$\Delta G_{abb}$=$\Delta G_a$+$\Delta G_{bb}$**=-61,9+30,5= -31,4 $^{kJ}/_{mol}$**;**

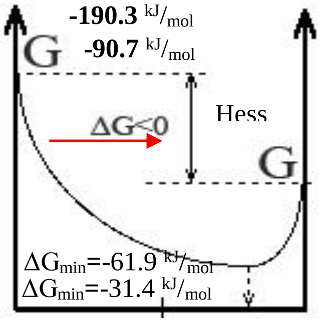
$\Delta G_{Hess}=\Delta G°_{ATP4-}+\Delta G°_{H2O}+\Delta G°_{H3CC=OCOO}-\Delta G°_{PyruvEnolP3-}-\Delta G°_{ADP3}-\Delta G°_{H3O-}$=**-90.724** $^{kJ}/_{mol}$;

=**-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** $^{kJ}/_{mol}$;

**$\Delta G_{abb}$=-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 **$\Delta G_{hydrolise}$= -190.3** $^{kJ}/_{mol}$ and **-90.724** $^{kJ}/_{mol}$, but minimizes **$\Delta G_{min}$**=**$\Delta G_{abb}$**= **-**61.9 $^{kJ}/_{mol}$ and -31,4 $^{kJ}/_{mol}$ reaching equilibrium mixture :

69902464988= $\frac{[CH_3C=OCOO^-]\cdot[HPO_4^{2-}]}{[H_2O]\cdot[PyruvEnolP^{3-}]}$ =**K$_a$**; **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 **$\Delta G_{min}$.**

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$^{4-}$+$H_2O$** _

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

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

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

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

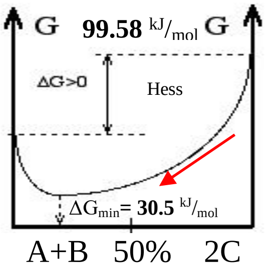
**bb** $\mathbf{ADP^{3-}+HPO_4^{2-}+H_3O^+=>ATP^{4-}+2H_2O}$; $\Delta G_{bbLehninger}=30{,}5\ ^{kJ}/_{mol}$; pH=7,36

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

$\Delta G_{Hess}=\Delta G°_{ATP4}+2\Delta G°_{H2O}-\Delta G°_{HPO42}-\Delta G°_{ADP3}-\Delta G°_{H3O}=\mathbf{99.58}\ ^{kJ}/_{mol}$;

$=\mathbf{-2267{,}64}-2*\mathbf{151{,}549}-(\mathbf{-1057{,}143-1399{,}9}-213{,}275)=\mathbf{99.58}\ ^{kJ}/_{mol}$;**Biothermodynamic** 2006; $[H_2O]/[H_3O^+]$ CRC 2010

Endothermic and endoergic $\mathbf{ADP^{3-}}$ phosphorilation reaction at pH 7,36 Hess free energy change negative $\Delta G_{phosphorilation}=\mathbf{99.58}\ ^{kJ}/_{mol}$, but minimizes $\Delta G_{min}= \Delta G_{bb}=30{,}5\ ^{kJ}/_{mol}$ 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 $\Delta G_{min}$.

Free energy change minimum reaching establishes equilibrium. Reactants

$\underline{\Delta G_H=\Delta G°_{ATP4-}+\Delta G°_{H2O}+\Delta G°_{H3CC=OCOO}-\Delta G°_{PyruvEnolP3-}-\Delta G°_{ADP3}-\Delta G°_{H3O-}}=\mathbf{-90.724}\ ^{kJ}/_{mol}$; $\mathbf{ADP^{3-}+HPO_4^{2-}+H_3O^+}$ -

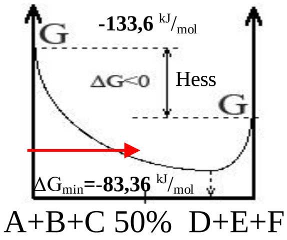
$=\mathbf{-2267{,}64-151{,}549}-474{,}44-(-1189{,}73\mathbf{-1399{,}9}-213{,}275)=\mathbf{-90.724}\ ^{kJ}/_{mol}$; product $\mathbf{ATP^{4-}+2H_2O}$ ;

$\mathbf{PyruvEnolP^{3-}}+ADP^{3-}+H_3O^+=>H_3CC=OCOO^-+ATP^{4-}+H_2O$; $\Delta G_{ab}=\Delta G_a+\Delta G_{bb}=-61{,}9+30{,}5=-31{,}4\ ^{kJ}/_{mol}$;

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

$K_{abb}= \mathbf{K_a\ K_b} =69902464988*0{,}000004535142=317017{,}6=\frac{[H_2O]\cdot[ATP^{4-}]\cdot[CH_3C=OCOO^-]}{[ADP^{3-}]\cdot[H_3O^+]\cdot[PyruvEnolP^{3-}]}$

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



Free energy change minimum establishes equilibrium.

reactants $PyruvEnolP^{3-}+\mathbf{ADP^{3-}+H_3O^+}$

products $\mathbf{H_3CC=OCOO^-+ATP^{4-}+H_2O}$

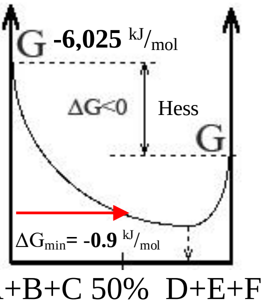
$\frac{[CH_3COO^-]\cdot[HSCoA^{4-}]\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[Acetyl\text{-}CoA^{4-}]}=1{,}4381$; $\mathbf{HPO_4^{2-}}+ADP^{3-}+Acetyl\text{-}CoA^{4-}=>ATP^{4-}+CH_3COO^-+HSCoA^{4-}$ ;

$\Delta G_H=\Delta G°_{ATP4-}+\Delta G°_{CH3COO-}+\Delta G°_{CoA2-}-\Delta G°_{HPO42}-\Delta G°_{ADP3}-\Delta G°_{Acetyl-CoA2-}=\mathbf{-6.025}\ ^{kJ}/_{mol}$;

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

$\mathbf{K_{abTotal}= K_a\ K_{bb}} =\underline{318243{,}5442}*0{,}000004535142=1.438142576$

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



reactants $\mathbf{HPO_4^{2-}}+ADP^{3-}+Acetyl\text{-}CoA^{4-}$

Free energy change minimum reaching establishes equilibrium.

products $ATP^{4-}+CH_3COO^-+HSCoA^{4-}$

$\mathbf{\Delta G_{total}=\Delta G_a+\Delta G_b=\Delta G_{ab}}=30{,}5087-31{,}409= -0{,}9003\ ^{kJ}/_{mol}$;

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

$AcetylCoA^{2-}+H_2O \Rightarrow CH_3COOH+HSCoA^{2-}$; $\Delta G_{aL}=-21{,}45$ $^{kJ}/_{mol}$; $\mathbf{K}_{aL}=\mathbf{K}_{Lehninger}/[\mathbf{H_2O}]=5727{,}95$

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

$\Delta\mathbf{G}_{aL}=-\mathbf{R}\bullet\mathbf{T}\bullet\mathbf{ln}(\mathbf{K}_{aL})$=-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, $Acetyl\text{-}CoA^{3-}+2H_2O \Rightarrow CH_3COO^-+HSCoA^{3-}+H_3O^+$

| | | | |
|---|---|---|---|
| **AcetylCoA**$^{3-}$ | - | - | **-51,8968** |
| **AcetylCoA**$^{3-}$ | - | - | -58,06 |
| HSCoA$^{3-}$ | - | - | -7,26 |
| **HSCoA**$^{3-}$ | **BioThe** | **rmod**06 | **-5,6616** |
| $\mathbf{H_3CCOO^-}$ | **-486,836** | **-813,043** | **-241,663** |
| $\mathbf{C_{16}H_{32}O_{2s}}$ | -891.5 | 452.4 | - |
| $\mathbf{C_{16}H_{32}O_{2liqui}}$ | -838.1 | - | - |
| Palmitate- | - | | -1003,54 |
| Palmitate- | - | | **-1067,238** |
| $\mathbf{H_3CCOO^-}$ | -486,84 | 82,23 | -247,83 |
| $\mathbf{H_3CCOO^-}$ | -485,64 | 87,58 | -369,37 |
| **PalmtylCoA**$^{3-}$ | PalmitateCoA | - | **-784,9391** |
| $\mathbf{H_3CCOOH}$ | -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** |
| $\mathbf{H_3O^+}$ | -285,81 | -3,854 | -213,275 |
| $\mathbf{H_2O}$ | -285,85 | 69,9565 | -237,191 |
| $\mathbf{H_2O}$ | **-286,65** | **-453,188** | **-151,549** |

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

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

$\mathbf{K}_a=\mathbf{K}_{Leninge}$=exp(31400/8,3144/298,15)=317017,64

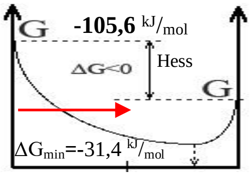
$\mathbf{K}_{aL}=\mathbf{K}_{Lehninger}/[\mathbf{H_2O}]$=317017,6/55,346=5727,95= $\frac{[CH_3COOH]\cdot[HSCoA^{2-}]}{[H_2O]\cdot[Acetyl\text{-}CoA^{2-}]}$

$\mathbf{K}_a=\mathbf{K}_{Lehninge}$=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 $\Delta\mathbf{G}_{Hess}$=**-105,6** $^{kJ}/_{mol}$ , but minimizes $\Delta\mathbf{G}_{min}=\Delta\mathbf{G}_a=-31{,}4$ $^{kJ}/_{mol}$ reaching equilibrium mixture Le Chatelier principle is Prigogine attractor free energy minimum $\Delta G_{min}$

$Acetyl\ CoA^{3-}+2H_2O$



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

$PalmitCoA^{3-}+2H_2O$ reaktanti _

$CH_3(CH_2)_{14}COO^-+$ $+HSCoA^{3-}+H_3O^+$; produkti.

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

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

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

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

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

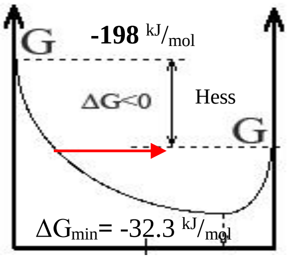
$\mathbf{K}_a=\mathbf{K}_{Lehninger}$=455782,655095979= $\frac{[CH_3(CH_2)_{14}COO^-]\cdot[HSCoA^{3-}].[H_3O^+]}{[H_2O]^2\cdot[Palmitate\text{-}CoA^{3-}]}$

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

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

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

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



A+2B 50% C+D+E

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

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

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

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

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

**ppbc)** $CH_3COO^-+HSCoA^{4-}+ATP^{4-}+2H_2O \Rightarrow Acetyl\text{-}CoA^{4-}+AMP^{2-}+\mathbf{HPO_4^{2-}}+\mathbf{HPO_4^{2-}}+\mathbf{H_3O^+}$; $\Delta\mathbf{G}_{Lehnin}$=**-33.4** $^{kJ}/_{mol}$;

$\Delta G_{abc}$=**-45.6-19.2+31.4=-33.4** $^{kJ}/_{mol}$, $\mathbf{K}_{abc}$=2310,5736*97462087,2480605*0,0000031544=710349,826891739:

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

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

THERMODYNAMICS Exercise V h Palmtyl$\mathbf{CoA^{4-}}$ hydrolysis to $\mathbf{HSCoA^{4-}}$

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

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

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

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

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

Hydrolisis equilibrium of $PalmitCoA^{3-}+2H_2O \Rightarrow CH_3(CH_2)_{14}COO^-+HSCoA^{3-}+H_3O^+$; $\Delta G_{Lehninger}=-32.3$ $^{kJ}/_{mol}$; pH=7,36

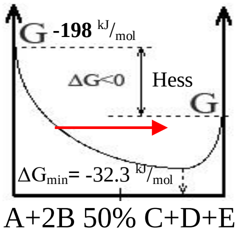
| | | | |
|---|---|---|---|
| $HSCoA^{4-}$ | - | - | -7,26 |
| $\mathbf{HSCoA^{3-}}$ | - | - | **-5,6616** |
| PalmitateCoA | -999,745 | Palmitate- | -1003,54 |
| PalmitateCoA | **-784,9391** | Palmitate- | **-1067,238** |
| $\mathbf{C_{16}H_{32}O_{2s}}$ | -891,5 | 452,4 | -1026,383 |
| $\mathbf{C_{16}H_{32}O_{2li}}$ | -838.1 | - | - |
| $\mathbf{H_3O^+}$ | -285,81 | -3,854 | -213,275 |
| $\mathbf{H_2O}$ | -285,85 | 69,9565 | -237,191 |
| $\mathbf{H_2O}$ | **-286,65** | **-453,188** | **-151,549** |
| $\mathbf{HP_2O_7^{3-}}$ | **-2291**,04 | **-1181,25** | **-1938,85** |
| $\mathbf{HP_2O_7^{3-}}$ | -2247,8 | 46 | -1940,66 |
| $\mathbf{H_2P_2O_7^{2-}}$ | - | - | **-1952,27** |

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

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

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

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



$\mathbf{ATP^{3-}+H_2O \Rightarrow AMP^-+H_2P_2O_7^{2-}}$; pH<6,72

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

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

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

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

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

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

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

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

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

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

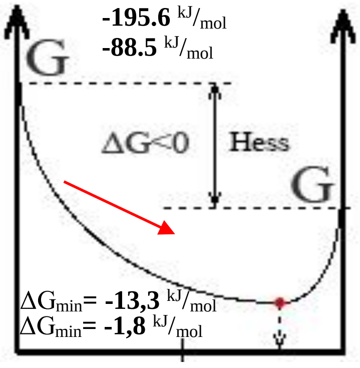
**abc)** $CH_3(CH_2)_{14}COO^-+HSCoA^{3-}+\mathbf{ATP^{4-}} \Rightarrow \mathbf{HP_2O_7^{3-}+AMP^{2-}}+PalmitateCoA^{3-}$;

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

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

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

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



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

$\Delta G_{bbaLehninger}=\Delta G_{bb}+\Delta G_a=30{,}5-32{,}3=-1.8$ $^{kJ}/_{mol}$; reactants_ $ADP^{3-}+HPO_4^{2-}+Palmitate\text{-}CoA^{4-}$

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

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

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

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

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

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

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

$\Delta G_{Hess}=\Delta G^\circ_{HSCoA2}+\Delta G^\circ_{Palmitate}-(\Delta G_{PalmitateCoA4}+\Delta G_{H2O})$ =**-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

$\Delta G_{eqLehn}$=**-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; $\Delta G_{Lenin}$=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(-$\Delta G_H$ /R/T)=EXP(-32300/8,3144/298,15)=2,194*$10^{-6}$=

$$\frac{[H_2O]^2\cdot[\text{Palmitate-CoA}^{3-}]}{[CH_3(CH_2)_{14}COO^-]\cdot[HSCoA^{3-}]\cdot[H_3O^+]}$$

$\Delta G_c$=**-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;

$\Delta G_{Hess}=2\Delta G^\circ_{H2PO4-}-\Delta G^\circ_{H2P2O72-}-\Delta G^\circ_{H2O}$=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** $HP_2O_7^{3-}+2H_2O$=>$HPO_4^{2-}+HPO_4^{2-}+H_3O^+$+$\Delta$G+**Q;** pH=7,36; $\Delta G_{LeningeH}$=-19,2 kJ/mol;

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

$\Delta G_a$=**-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=

$$\frac{[HPO^{2-}]^2\cdot[H_3O^+]}{[H_2O]^2\cdot[HP_2O_7^{3-}]}$$

$\Delta G_{Habb}=\Delta G^\circ_{Glycerol}+\Delta G^\circ_{ATP4}+\Delta G^\circ_{H2O}-\Delta G^\circ_{ADP3}-\Delta G^\circ_{Glyol3P}-\Delta G^\circ_{H3O}$=**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$^{2-}$+$H_2O$+$\Delta$G+**Q**=>Glycerol+$HPO_4^{2-}$ ; pH=7.36;

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

Glycerol1P$^{2-}$+$ADP^{3-}+H_3O^+$=>Glycerol+$ATP^{4-}$-+$H_2O$;$\Delta G_{abb}$=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>

$\Delta G_{HabbL}=\Delta G^\circ_{Glyc}+\Delta G^\circ_{ATP4}-\Delta G^\circ_{ADP3}-\Delta G^\circ_{Glyol3P}$=**-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+$HPO_4^{2-}$+$\Delta$G+**Q**; $\Delta G_{Lehninger}$=-15,9 kJ/mol

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

=-426,32-1089,28-(**-1293,1-151,549**)= **-70.951** kJ/mol exoergic

$\Delta H_{Hess}=\Delta H^\circ_{Fruc}+\Delta H^\circ_{HPO42-}-\Delta H^\circ_{Fruc6P}-\Delta H^\circ_{H2O}$=**-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);

$\Delta S_{Hess}=\Delta S^\circ_{Fruc}+\Delta S^\circ_{HPO42-}-\Delta S^\circ_{Fruc6P}-\Delta S^\circ_{H2O}$=**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•$\Delta S_{total}$=**0,047606** *298,15=**14.194** kJ/mol T$\Delta$Sn <u>dispersed</u>

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

$\Delta G_{Habb}=\Delta G^\circ_{Fruc}+\Delta G^\circ_{ATP4}+\Delta G^\circ_{H2O}-\Delta G^\circ_{ADP3}-\Delta G^\circ_{Fruc6P}-\Delta G^\circ_{H3O}$=**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

$\Delta G_{Habb}=\Delta G^\circ_{Fruc}+\Delta G^\circ_{ATP4}-\Delta G^\circ_{ADP3}-\Delta G^\circ_{Fruc6P}$=**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 $\Delta H_H$ $\Delta S_H$ $\Delta G_H$ 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* $\Delta H^\circ_H$ $^{kJ}/_{mol}$ $\Delta S^\circ_H$ $^{J}/_{mol/K}$ $\Delta G^\circ_H$ , $^{kJ}/_{mol}$ ; Glycerol-3-phosphate$^{-}$+$\mathbf{H_2O}$+ΔG+**Q**=>Glycerol+ $\mathbf{H_2PO_4^-}$;pH<7.199

| *Substance* | $\Delta H^\circ_H$ $^{kJ}/_{mol}$ | $\Delta S^\circ_H$ $^{J}/_{mol/K}$ | $\Delta G^\circ_H$ , $^{kJ}/_{mol}$ |
|---|---|---|---|
| $\mathbf{H_3O^+}$ | -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$^{4--}$+$H_2O$;$\Delta \mathbf{G}_{abb}$=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=<u>0,0102670561193 77</u>
$\Delta G_{HabbL}=\Delta G^\circ_{\mathbf{Glyc}}+\Delta G^\circ_{ATP4}-\Delta G^\circ_{ADP3}-\Delta G^\circ_{\mathbf{Glyol3P}}$=**-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

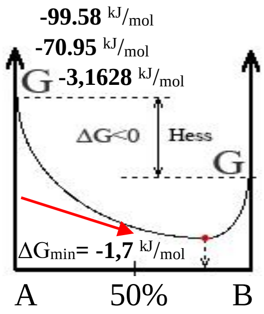
**ADP$^{2-}$+$H_2PO_4^-$=>ATP$^{3-}$+$H_2O$**; $\Delta \mathbf{G}_{Lehninger}$ = 20,55 $^{kJ}/_{mol}$; 2,26<pH<6,72
$\mathbf{K}_{Lehninger}$**=exp(-**$\Delta \mathbf{G}_{Lehninger}$**/R/T**)=exp(-30500/8,3144/298,15)=4,535*10$^{-6}$;
$\mathbf{K}_{bL}$**=[$H_2O$]K**$_{Lehninger}$= 0,000004535142* 55,34573393= 0,000251001
**bb ADP$^{3-}$+HPO$_4^{2-}$+$H_3O^+$=>ATP$^{4-}$+2 $H_2O$**; pH=7.36; $\Delta \mathbf{G}_{bb}$=30,5 $^{kJ}/_{mol}$;
$\mathbf{K}_{bb}=\mathbf{K}_{Lehninger}$**=exp(-**$\Delta \mathbf{G}_{Lehning}$**/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(-**$\Delta \mathbf{G}_{Lehninger}$**/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;

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

Le Chatelier principle is Prigogine attractor Free energy change minimum $\Delta G_{min}$ 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* | $\Delta H^\circ_H\ ^{kJ}/_{mol}$ | $\Delta S^\circ_H\ ^{J}/_{mol/K}$ | $\Delta G^\circ_H\ ^{kJ}/_{mol}$ |
|---|---|---|---|
| **$H_3O^+$** | -285,81 | -3,854 | -213,275 |
| **$H_2O$** | -285,85 | 69,9565 | -237,191 |
| **$H_2O$** | **-286,65** | **-453,188** | **-151,549** |
| $(H_3CCO)_2O$ | -624,4 | 658,853 | -728,91 |
| $(H_3CCO)_2O$ | $\Delta G^\circ_{(H3CCO)2O}$ | -728,91 | -728,91 |
| $H_3CCOO^-$ | - | - | -247.83 |
| $H_3CCOO^-$ | **-486,836** | **-822,3** | **-241,663** |
| $H_3C$-$COOH$ | -484,09 | 159,83 | -531,743 |

$=2*-531{,}743-(-728{,}91-237{,}191)=-97.385\ ^{kJ}/_{mol}$;

CRC10; $\Delta G_H=2\Delta G^\circ_{CH3COOH}-\Delta G^\circ_{(H3CCO)2O}-\Delta G^\circ_{H2O}=-97.385\ ^{kJ}/_{mol}$;

CRC10; $2\Delta G^\circ_{CH3COOH}+91{,}1-\Delta G^\circ_{H2O}=\Delta G^\circ_{(H3CCO)2O}=-728{,}91\ ^{kJ}/_{mol}$;

**B06**; $\Delta H_{Hess}=2*-531{,}743-(-728{,}91-237{,}191)=-97.385\ ^{kJ}/_{mol}$;

CRC10; $\Delta H_{Hess}=2\Delta H^\circ_{CH3COOH}-\Delta H^\circ_{(H3CCO)2O}-\Delta H^\circ_{H2O}=-57.93\ ^{kJ}/_{mol}$;

$\Delta S_H=2\Delta S^\circ_{CH3COOH}-\Delta S^\circ_{(H3CCO)2O}-\Delta S^\circ_{H2O}=113{,}995\ ^{J}/_{mol/K}$;

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

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

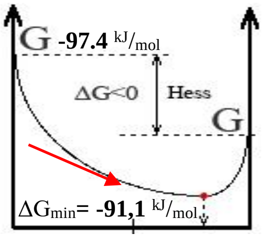
$\Delta G_H=\Delta H_H-T*\Delta S_H=-57{,}93-298{,}15*0{,}113995=-91{,}92\ ^{kJ}/_{mol}$ exoergic

$\Delta S_{total}=\Delta S_H+\Delta S_{dispeHsed}=191{,}615+113{,}995=305{,}61\ ^{J}/_{mol/K}$; $T\bullet\Delta S_{total}=0{,}30561*298{,}15=91{,}12\ ^{kJ}/_{mol}$ TΔSn <u>dispersed</u>

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

Exothermic and exoergic **$(H_3CCO)_2O$** hydrolize Hess free energy change negative at pH<4,76 as **$CH_3COOH$** $\mathbf{\Delta G_{hydrolise}}$ = **-97.4** $^{kJ}/_{mol}$ , but minimizes $\mathbf{\Delta G_{min}=\Delta G_{eq}}=-91{,}1\ ^{kJ}/_{mol}$ reaching equilibrium mixture

$$\underline{9{,}12*10^{15}}=10^{15{,}96}=\mathbf{K_{eq}}=\frac{[CH_3COOH]^2}{[CH_3COOOCCH_3]\cdot[H_2O]}$$



A+B 50% 2C

Products 2**$CH_3COOH$**

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ 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 **$H_3O^+$**; $\Delta G_H=217{,}26\ ^{kJ}/_{mol}$; at pH=7,36;

$\Delta G_{Hess}=2\Delta G^\circ_{CH3COO}+2\Delta S^\circ_{H3O}-\Delta G^\circ_{(H3CCO)2O}-3\Delta G^\circ_{H2O}=2*\mathbf{-241{,}663+2*}-213{,}275-(-728{,}91+3*\mathbf{-151{,}549})=\mathbf{273.7}\ ^{kJ}/_{mol}$;

$=2*\mathbf{-241{,}663+2*}-213{,}275-(-728{,}91+3*\mathbf{-151{,}549})=\mathbf{273.7}\ ^{kJ}/_{mol}$ endoergic

$\Delta H_H=2\Delta H^\circ_{CH3COO}+2\Delta S^\circ_{H3O}-\Delta H^\circ_{(H3CCO)\,2O}-3\Delta H^\circ_{H2O}=\mathbf{-60{,}942}\ ^{kJ}/_{mol}$; $\Delta S_{dispeHse}=-\Delta H_H/T=\mathbf{60{,}942}/298{,}15=\mathbf{204{,}4}\ ^{J}/_{mol/K}$;

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

$\Delta S_H=2\Delta S^\circ_{CH3COO-}+2\Delta S^\circ_{H3O}-\Delta S^\circ_{(H3CCO)\,2O}-3\Delta S^\circ_{H2O}=\Delta S_{total}=\Delta S_H+\Delta S_{dispeHsed}=\mathbf{-951{,}597+204{,}4=-747{,}197}\ ^{J}/_{mol/K}$;

$=2*\mathbf{-822{,}3+2*}-3{,}854-(658{,}853+3*\mathbf{-453{,}188})=\mathbf{-951.597}\ ^{J}/_{mol/K}$;

$\Delta G_H=\Delta H_H-T*\Delta S_H=\mathbf{-60{,}942}-298{,}15*-0{,}\mathbf{9516=222.777}\ ^{kJ}/_{mol}$;$T\Delta S_{total}=-0{,}747197*298{,}15=-222.777\ ^{kJ}/_{mol}$ TΔSn <u>dispersed</u>

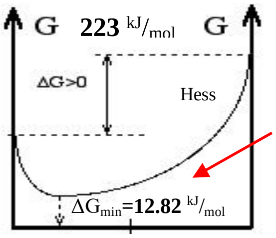
$\mathbf{\Delta G_{eq}=-R\bullet T\bullet ln(K_{eq})}=-8{,}3144*298{,}15*\mathbf{ln}(0{,}0056732)/1000=12{,}82107402328\ ^{kJ}/_{mol}$,,

$$\mathbf{K_{eq}=K_{Lehninger}}[H_3O^+]^2/[H_2O]^2=9{,}12*10^\wedge15*10^\wedge(^{-7{,}36*2})/55{,}34573393^\wedge2=0{,}0056732=\frac{[CH_3COO^-]^2\cdot[H_3O^+]^2}{[CH_3COOOCCH_3]\cdot[H_2O]^3}$$

Endothermic and endoergic anhydride hydrolysis Hess free energy change $\mathbf{\Delta G_{hydrolyse}}$ positive 223 $^{kJ}/_{mol}$ , but minimizes up to $\mathbf{\Delta G_{min}=\Delta G_{eq}}=12.82\ ^{kJ}/_{mol}$ reaching equilibrium

$$\text{mixture } K_{eq}=\frac{[CH_3COO^-]^2\cdot[H_3O^+]^2}{[CH_3COOOCCH_3]\cdot[H_2O]^3}=0{,}0056732.$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ reaching . Free energy change minimum reaching establishes equilibrium.



Reactants **$(H_3CCO)_2O$**+3**$H_2O$** products 2**$CH_3COO^-$**+2 **$H_3O^+$**

A+3B 50% 2C+2D

$H_2P_2O_7^{2-}+H_2O=\mathbf{H_3O^+ + HP_2O_7^{3-}}$; $\Delta G_{Hess}=\Delta G^\circ_{H3O+}+\Delta G^\circ_{HOPO2OPO2O3}-\Delta G^\circ_{H2OPO2OPO2O2-}-\Delta G^\circ_{H2O}=\mathbf{25.73}\ ^{kJ}/_{mol}$ ;

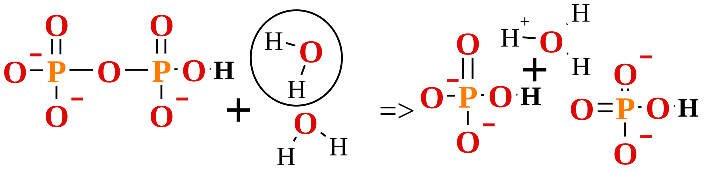
$=-213{,}275\mathbf{-1938{,}85}-(-1940{,}66-237{,}191)=\mathbf{25.73}\ ^{kJ}/_{mol}$ ;

$\mathbf{\Delta G_{eq}=-R\bullet T\bullet ln(K_{eq})}=-8{,}3144*298{,}15*\mathbf{ln}(10^\wedge(^{-8{,}463}))/1000=48{,}31\ ^{kJ}/_{mol}$,

$$\mathbf{K_{eq}=K_{H2P2O72}}/[\mathbf{H_2O}]=10^{-6.72}/55{,}34573393=3{,}4436*10^{-9}=10^{-8{,}463}=\frac{[H_3O^+]\cdot[HP_2O_7^{3-}]}{[H_2O]\cdot[H_2P_2O_7^{2-}]}\ ;$$

THERMODYNAMICS Exercise V e **Pyrophosphate** hydrolysis to $HPO_4^{2-}$ + $HPO_4^{2-}$

Calculate $\Delta H_H$, $\Delta S_H$, $\Delta G_H$ 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 |
| $H_3P_2O_7^-=H^++H_2\ P_2O_7^{2-}$ 7 | 2,26 | -5,0 | -130 |
| $H_2\ P_2O_7^{2-}=H^++\mathbf{HP_2O_7^{3-}}$ | 6,72 | 0,5 | -136 |
| $\mathbf{HP_2O_7^{3-}}=H^++P_2O_7^{4-}$ | **9,46** | 1,4 | -141 |

1.$\Delta H_{Hess}=\Delta H°_{products}-\Delta H°_{reactants}$; $\mathbf{HP_2O_7^{3-}}+2H_2O\Rightarrow HPO_4^{2-}+HPO_4^{2-}+\mathbf{H_3O^+}$; $\Delta G_{LehningeHpp}=-19,2\ ^{kJ}/_{mol}$; pH=7,36

*Substance* $\Delta H°_H$, $^{kJ}/_{mol}$ $\Delta S°_H$, $^{J}/_{mol/K}$ $\Delta G°_H$ , $^{kJ}/_{mol}$ ; $\mathbf{HP_2O_7^{3-}}+ADP^{3-}\Rightarrow HPO_4^{2-}+ATP^{4-}$; $\Delta G_{abbpp}=11,3\ ^{kJ}/_{mol}$; 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 |

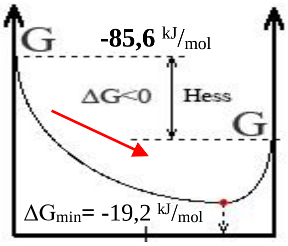
Mishchenko ; $\Delta G_{abbpp}=\Delta G_{app}+\Delta G_{bb}=-19,2+30,5=11,3\ ^{kJ}/_{mol}$;

$\Delta G_{Hess}=\Delta G°_{H3O}+2\Delta G°_{HPO42}-\Delta G°_{HOPO2OPO2O2}-2\Delta G°_{H2O}=\mathbf{-85,6}\ ^{kJ}/_{mol}$ ;

$=-213,275+2*\mathbf{-1057,143}-(\mathbf{-1938,85}+2*\mathbf{-151,549})=\mathbf{-85,6}\ ^{kJ}/_{mol}$;

Endothermic and endoergic $\mathbf{HPO_4^{2-}}$ transfer from $\mathbf{HP_2O_7^{2-}}$ Hess free energy change positive at pH=7,36 $\Delta G_{Hess}=\mathbf{-85,6}$ , but minimizes $\Delta G_{min}=\Delta G_{eq}=-19,2\ ^{kJ}/_{mol}$ reaching equilibrium

$$K_{app}=K_{Lehningepp}=2310,57=\frac{[HPO_4^{2-}]^2\cdot[H_3O^+]}{[H_2O]^2\cdot[HP_2O_7^{3-}]}\cdot$$



A+2B 50% 2C+D
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 $\Delta G_{min}$ reaching. Products**.** Free energy change minimum reaching establishes equilibrium.

$$\mathbf{K_{app}}=\mathbf{K_{Lehningerpp}=exp(-\Delta G_{Lehningerpp}/R/T)}=exp(19200/8,3144/298,15)=2310,57=\frac{[HPO_4^{2-}]^2\cdot[H_3O^+]}{[H_2O]^2\cdot[HP_2O_7^{3-}]}$$

$H_2P_2O_7^{2-}+H_2O=\mathbf{H_3O^+}+\mathbf{HP_2O_7^{3-}}$;

$$\mathbf{K_{eq}}=\mathbf{K_{H2P2O72}}/[\mathbf{H_2O}]=10^{-6,72}/55,3457=3,4436*10^{-9}=10^{-8,463}=\frac{[H_3O^+].[H\ P_2O_7^{3-}]}{[H_2O]\cdot[H_2P_2O_7^{2-}]}$$

$\mathbf{H_2P_2O_7^{2-}}+H_2O\Rightarrow H_2PO_4^-+H_2PO_4^-$; $\Delta G_{Lehninger}=-19,2\ ^{kJ}/_{mol}$;without 6,72<pH<7,199;

$$\mathbf{K_{pp}}=\mathbf{K}_{Lehningerpp}/[\mathbf{H_2O}]=2310,57/55,34573393=41,748=\frac{[H_2PO_4^-].[H_2PO_4^-]}{[H_2O]\cdot[H_2P_2O_7^{2-}]}$$

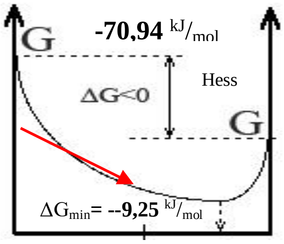
$\mathbf{\Delta G_{ppL}=-R\bullet T\bullet ln(K_{eqL})}=-8,3144*298,15*\mathbf{ln}(41,74799819)=\mathbf{-9,251}\ ^{kJ}/_{mol}$ ,

$\Delta G_{Hess}=2\Delta G°_{H2PO4-}-\Delta G°_{H2P2O72-}-\Delta G°_{H2O}=\mathbf{-70,94}\ ^{kJ}/_{mol}$; $=2*-1130,2-(\mathbf{-1952,27}-237,191)=\mathbf{-70,94}\ ^{kJ}/_{mol}$;

Exothermic and exoergic $\mathbf{H_2P_2O_7^{2-}}$ hydrolytic Hess free energy change to $H_2PO_4^-$ $+HPO_4^{2-}$ negative $\Delta G_{Hess}=\mathbf{-70,94}\ ^{kJ}/_{mol}$ , but minimizes reaching equilibrium mixture $\mathbf{\Delta G_{min}}=\Delta G_{eqL}=\mathbf{-9,251}\ ^{kJ}/_{mol}$ without pH<7,199

$$41,748=\mathbf{K_{pp}}=\frac{[H_2PO_4^-].[H_2PO_4^-]}{[H_2O]\cdot[H_2P_2O_7^{2-}]}$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$. Free energy change minimum reaching establishes equilibrium. $\mathbf{K_{pp}}$ =41,748;



A+B 50% 2C
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; $\Delta G_{abbppPH}=21,25\ ^{kJ}/_{mol}$;

$\mathbf{K}_{abbppPH}=\mathbf{K}_{abbpp}/[\mathbf{H_2O}]=\underline{0,01047878}/55,3457=0,0001893$

$\Delta G_{abbppPH}=\mathbf{-R\bullet T\bullet ln}(\mathbf{K}_{abbppPH})=-8,3144*298,15*\mathbf{ln}(0,0001893)/1000=21,25\ ^{kJ}/_{mol}$;

$\mathbf{K}_{abbppL}=\mathbf{exp(-\Delta G}_{Lehninger}\mathbf{/R/T)}=exp(-11300/8,3144/298,15)=\underline{0,01047878}$

$\mathbf{K}_{abL}=\mathbf{K}_{aL}\mathbf{K}_{bL}=41,748*0,000250942=0,010476327$;

$\Delta G_{abbppL}=\mathbf{-R\bullet T\bullet ln}(\mathbf{K}_{abbppL})=-8,3144\bullet 298,15\bullet\mathbf{ln}(\underline{0,01047878})=11,3\ ^{kJ}/_{mol}$;

$\mathbf{HP_2O_7^{3-}}+\mathbf{ADP^{3-}}\Rightarrow\mathbf{HPO_4^{2-}}+\mathbf{ATP^{4-}}$; pH=7,36; $\Delta G_{Lehninger}=30,5+(-19,2)=11,3\ ^{kJ}/_{mol}$;;

$\Delta G_{Hess}=\Delta G°_{HPO42-}+\Delta G°_{ATP4-}-\Delta G°_{HP2O73-}-\Delta G°_{ADP3-}=\mathbf{-1057,143-2267,64-(-1938,85-1399,9)=13,967}\ ^{kJ}/_{mol}$;

| | | | |
|---|---|---|---|
| **$H_3O^+$** | -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** |

$\Delta H_{Hess}=\Delta H^\circ_{\mathbf{Gln}}+\Delta H^\circ_{\mathbf{H2O}}-\Delta H^\circ_{Glu-}-\Delta H^\circ_{NH4+}=\mathbf{19,5}\ {}^{kJ}/_{mol}$

$=\mathbf{-809,12-286,65}-(\mathbf{-982,77}-132,5)=\mathbf{19,5}\ {}^{kJ}/_{mol}$ endothermic

$\Delta S_{Hess}=\Delta S^\circ_{\mathbf{Gln}}+\Delta S^\circ_{\mathbf{H2O}}-\Delta S^\circ_{Glu-}-\Delta S^\circ_{NH4+}=\mathbf{-842.48}\ {}^{J}/_{mol/K}$

$=\mathbf{-2379,04-453,188}-(\mathbf{-2103,15}+113,4)=\mathbf{-842.478}\ {}^{J}/_{mol/K}$

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=\mathbf{-19,5}\ -298,15*-0,\mathbf{84248}=\mathbf{231.685}\ {}^{kJ}/_{mol}$; endoergic

**a**)$Glu^-+NH_4^+=>Gln+H_2O$; $\Delta G_{bLehninger}=\mathbf{14,2}\ {}^{kJ}/_{mol}$; pH=7,36;

$K_{aLehningeH}=\mathbf{exp(-\Delta G_{aLehninger}/R/T)}=\exp(14200/8,3144/298,15)=307.43$

$\Delta G_{Hess}=\Delta G^\circ_{\mathbf{Gln}}+\Delta G^\circ_{\mathbf{H2O}}-\Delta G^\circ_{Glu-}-\Delta G^\circ_{NH4+}=\mathbf{-99,8112-151,549}-(\mathbf{-355,712}-79,3)=\mathbf{183.65}\ {}^{kJ}/_{mol}$;

$K_{bLehningeH}=\mathbf{exp(-\Delta G_{bLehninger}/R/T)}=\exp(-14200/8,3144/298,15)=\underline{0,003252737}=\frac{[Gln]\cdot[H_2O]}{[Glu^-]\cdot[NH_4^+]}$

Endoergic Glu amination to Gln Hess free energy change $\Delta \mathbf{G_{Hess}}$ positive **183.65** ${}^{kJ}/_{mol}$ ,

$Gln+H_2O=>Glu^-+NH_4^+$; $\Delta G_{aLehninger}=-14.2\ {}^{kJ}/_{mol}$; $\Delta G_{Hess}=\mathbf{-183.65}\ {}^{kJ}/_{mol}$; $K_{aLehninger}=307.43=\frac{[Glu^-]\cdot[NH_4^+]}{[Gln]\cdot[H_2O]}$

but minimizes up to $\Delta \mathbf{G_{min}}=\Delta G_{aLehninger}=\mathbf{14.2}\ {}^{kJ}/_{mol}$ reaching equilibrium mixture:

$K_{aLehninger}=\underline{0,003252737}=[Glu^-]*[NH_4^+]/[Gln]*[H_2O]$. Exoergic Glu amination to Gln with **$ATP^{4-}$** free energy change $\Delta \mathbf{G_{Hess}}=\mathbf{-40,2}\ {}^{kJ}/_{mol}$ negative at pH<7,199, but minimizes reaching equilibrium mixture

| | | | |
|---|---|---|---|
| **$AMP^{2-}$** | - | - | -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** |

$\Delta \mathbf{G_{min}}=\Delta \mathbf{G}_{abL}=\mathbf{-6,35}\ {}^{kJ}/_{mol}$

$\frac{[H_2PO_4^-]\cdot[ADP^{2-}]\cdot[Gln]}{[Glu^-]\cdot[NH_4^+]\cdot[ATP^{3-}]}=12.959=K_{abLehninger}$ .

**a** $ATP^{3-}+H_2O=>ADP^{2-}+H_2PO_4^-$;$\Delta \mathbf{G_{bl}}=\mathbf{-20,55}\ {}^{kJ}/_{mol}$;

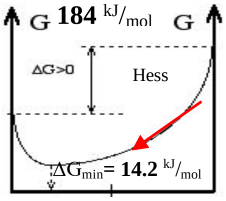
$K_{bLehninger}=\exp(20550/8,3144/298,15)=3984.$

$\Delta \mathbf{G}_{aLehninger}=\mathbf{-RTln(K}_{aLehninger}\mathbf{)}=$

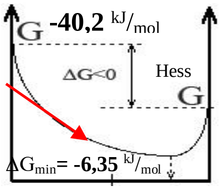
$=-8,3144\bullet298,15\bullet\mathbf{ln}(3984)=\mathbf{-20,55}\ {}^{kJ}/_{mol}$;

$K_a=K_{Lehninger}=\mathbf{exp(-\Delta G_{Lehninger}/R/T)}=$

$=\exp(30500/8,3144/298,15)=220500$



A+B 50% C+D



$\Delta G_{Hess}=\Delta G^\circ_{H2PO4}+\Delta G^\circ_{\mathbf{Gln}}+\Delta G^\circ_{ADP2}-\Delta G^\circ_{NH4}-\Delta G^\circ_{Glu}-\Delta G^\circ_{ATP3}=20.292\ {}^{kJ}/_{mol}$;

$=-1137,3-120,36-1424,7-(-79,3\mathbf{-355,712-2267,64})=20.292\ {}^{kJ}/_{mol}$;

$K_{aLehninger}=K_{Lehninger}/[\mathbf{H_2O}]=220500/55,34573393=3984=\frac{[H_2PO_4^-]\cdot[ADP^{2-}]}{[H_2O]\cdot[ATP^{3-}]}$

pH<7,199;$Glu^-+NH_4^++ATP^{3-}=>Gln+ADP^{2-}+H_2PO_4^-$;$\Delta \mathbf{G}_{abL}=\mathbf{14,2-20,55=-6,35}\ {}^{kJ}/_{mol}$

pH<7,199; $K_{abLehninger}=K_{aLehninger}*K_{bLehninger}=3984*0,003252737=12.959=\frac{[H_2PO_4^-]\cdot[ADP^{2-}]\cdot[Gln]}{[Glu^-]\cdot[NH_4^+]\cdot[ATP^{3-}]}$

$\Delta \mathbf{G}_{abL}=\mathbf{-R\bullet T\bullet ln(K}_{abL})=-8,3144*298,15*\mathbf{ln}(12,958904208)=\mathbf{-6.35}\ {}^{kJ}/_{mol}$;pH<7,199

$\Delta H_{Hess}=\Delta H^\circ_{H2PO4-}+\Delta H^\circ_{\mathbf{Gln}}+\Delta H^\circ_{ADP3}-\Delta H^\circ_{NH4}-\Delta H^\circ_{Glu-}-\Delta H^\circ_{ATP4}=\mathbf{-6,75}\ {}^{kJ}/_{mol}$;

$=-1302,6\mathbf{-809,12-2627,4}-(-132,5\mathbf{-982,77-3617,1})=\mathbf{-6,75}\ {}^{kJ}/_{mol}$ exo

$\Delta S_{Hess}=-\Delta S^\circ_{H2PO4-}+\Delta S^\circ_{\mathbf{Sln}}+\Delta S^\circ_{ADP3}-\Delta S^\circ_{NH4}-\Delta S^\circ_{Slu-}-\Delta S^\circ_{ATP4}=\mathbf{112,2}\ {}^{J}/_{mol/K}$;

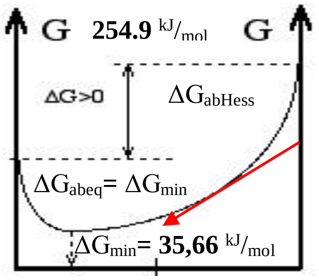
$=92,5\mathbf{-2379,04-4117,11}-(113,4\mathbf{-2103,15-4526,1})=\mathbf{112,2}\ {}^{kJ}/_{mol}$ exo

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=\mathbf{-6,75}\ -298,15*0,\mathbf{1122}=\mathbf{-40,2}\ {}^{kJ}/_{mol}$ endoergic;

$Glu^-+NH_4^++ATP^{4-}+H_2O=>Gln+ADP^{3-}+HPO_4^{2-}+H_3O^+$; $\Delta \mathbf{G}_{ab}=66,16-30,5=35.66\ {}^{kJ}/_{mol}$;

$\Delta H_{Hess}=\mathbf{-809,12-2627,4-1298,89}-285,81-(\mathbf{-982,77}-132,5\mathbf{-3617,1}-285,85)=-3\ {}^{kJ}/_{mol}$;

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=\mathbf{-3}\ -298,15*-0,\mathbf{8649}=\mathbf{254.9}\ {}^{kJ}/_{mol}$;



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

$K_{abL}=\mathbf{K_a*K_{bLehninger}}=220500*0,003252737=717.23=\frac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[Gln]\cdot[H_3O^+]}{[Glu^-]\cdot[NH_4^+]\cdot[ATP^{4-}]\cdot[H_2O]}$

$\Delta S_{Hess}=\mathbf{-2379,04-4117,11-810,792}-3,854-(\mathbf{-2103,15+}113,4\mathbf{-4526,1}+69,9565)=\mathbf{-864.9}\ {}^{J}/_{mol/K}$;

$\Delta G_{Hess}=\Delta G^\circ_{\mathbf{Gln}}+\Delta G^\circ_{ADP3}+\Delta G^\circ_{HPO42}+\Delta H^\circ_{H3O}-\Delta G^\circ_{Glu}-\Delta G^\circ_{NH4}-\Delta G^\circ_{ATP4}-\Delta G^\circ_{\mathbf{H2O}}=\mathbf{84,0718}\ {}^{kJ}/_{mol}$;

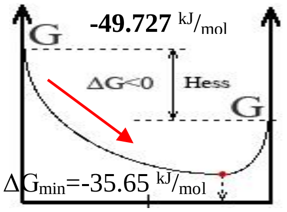
$\Delta G_H=\mathbf{-99,8112-1057,143-1399,9}-213,275-(\mathbf{-355,712}-79,3\mathbf{-2267,64-151,549})=\mathbf{84,072}\ {}^{kJ}/_{mol}$;

$\Delta \mathbf{G^o}_{abHess}=(\Delta G^\circ_{Hess})\ \mathbf{84,07}((\Delta H^\circ_{Hess},\Delta S^\circ_{Hess})\mathbf{254.9})\ {}^{kJ}/_{mol}$; $\Delta \mathbf{G}_{ab}=66,16-30,5=35.66\ {}^{kJ}/_{mol}$;

**$ATP^{3-}+H_2O$=>$AMP^{1-}+H_2P_2O_7^{2-}$**; $\Delta G_{Lehningerppm}=-35{,}65\ ^{kJ}/_{mol}$ ; $K_{Lehninge_{rppm}}=K_{Lehninger}/[H_2O]=1760968$; pH<6,72;

$\Delta G_{Hess}=\Delta G°_{H2P2O73-}-\Delta G°_{AMP2-}-\Delta G°_{ATP4-}-\Delta G°_{H2O}$ =**-1938,85-530,066-(-2267,64-151,549)**= **-49.727** $^{kJ}/_{mol}$;

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



Exothermic and exoergic **$ATP^{4-}$** hydrolize Hess free energy change negative as **$H_2P_2O_7^{2-}$** $\Delta G_{Hess}$=**-63.15** $^{kJ}/_{mol}$ , but minimized $\Delta G_{min}=\Delta G_{Lehningerppm}=-35.65\ ^{kJ}/_{mol}$ reaching equilibrium mixture: $K_{mppL}=K_{Leninger}/[H_2O]=1760959{,}91125033=$

$$\frac{[H_2P_2O_7^{2-}]\cdot[AMP^{1-}]}{[H_2O]\cdot[ATP^{3-}]}$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.

A+B 50% C+D
reactants $ATP^{3-}+H_2O$
products **$AMP^{1-}+H_2P_2O_7^{2-}$**

**ppm) $ATP^{4-}+2H_2O$=>$AMP^{2-}+HP_2O_7^{3-}+H_3O^+$**; $\Delta G_{Lehninger}=-45{,}6\ ^{kJ}/_{mol}$ ;at pH=7,36;

$\Delta G_{Hess}=\Delta G°_{H3O}+\Delta G°_{HP2O73}+\Delta G°_{AMP2}-\Delta G°_{ATP4}-2\Delta G°_{H2O}$=-213,275-**1938,85-530,066-(-2267,64**+2*-**151,549)=-111,45** $^{kJ}/_{mol}$;

$K_{ab}=K_{Leninger}=\exp(45600/8{,}3144/298{,}15)=97462087{,}2480605$; $\Delta S_{dispersed}=-\Delta H_H/T$=**24,79**/298,15=**83,15** $^{J}/_{(mol\ K)}$;

$\Delta H_{Hess}=\Delta H°_{H3O}+\Delta H°_{HP2O73}+\Delta H°_{AMP2}-\Delta H°_{ATP4}-2\Delta H°_{H2O}$=-285,81**-2291,04-1638,34-(-3617,1**+2*-**286,65)=-24,79** $^{kJ}/_{mol}$;

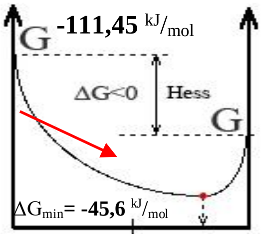
$\Delta S_{Hess}=\Delta S°_{H3O}+\Delta S°_{HP2O73}+\Delta S°_{AMP2}-\Delta S°_{ATP4}-2\Delta S°_{H2O}$=-3,854**-1181,25-3717,19-(-4526,1**+2*-**453,188)**= **530,182** $^{J}/_{(mol\ K)}$;

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}$=**-24,79** -298,15*0,**530182=-182,9** $^{kJ}/_{mol}$ exoergic;

$\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}$=**530,182+83,15=613,332** $^{J}/_{mol/K}$; $T\bullet\Delta S_{total}$=**0,613332***298,15=**182,86** $^{kJ}/_{mol}$ TΔSn <u>dispersed</u>

Equilibrium reached by free energy change minimum at compounds mixture ratio in Prigogine attractor expression is favored grater as one

$$1 < K_{Lehningeppm}=\exp(-\Delta G_{Lehninger}/R/T)=\exp(45600/8{,}3144/298{,}15)=97462087{,}2480605=\frac{[HP_2O_7^{3-}]\cdot[AMP^{2-}]\cdot[H_3O^+]}{[H_2O]^2\ \cdot[ATP^{4-}]}$$



Exothermic, exoergic pyrophosphate hydrolysis Hess free energy change $\Delta G_{Hess}$ is negative **-111,45** $^{kJ}/_{mol}$ , but minimized up to $\Delta G_{min}=\Delta G_{Lehningerppm}=-45{,}6\ ^{kJ}/_{mol}$ reaching

$$\text{equilibrium mixture } K_{Lehningeppm}=\frac{[HP_2O_7^{3-}]\cdot[AMP^{2-}]\cdot[H_3O^+]}{[H_2O]^2\ \cdot[ATP^{4-}]}=97462087{,}2480605.$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$. Free energy change minimum reaching establishes equilibrium.

A+2B 50% C+D+E
reactants $ATP^{4-}+2H_2O$
products
**$AMP^{2-}+HP_2O_7^{3-}+H_3O^+$**

**$H_2P_2O_7^{2-}$**$+H_2O$=>$H_2PO_4^-+H_2PO_4^-$; $\Delta G_{pp}$=**-70,94** $^{kJ}/_{mol}$; without 6,72<pH<7,199;

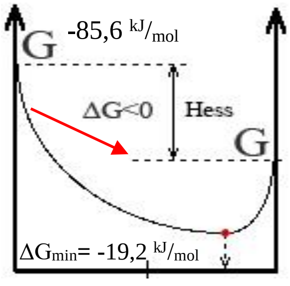
$\Delta G_{Hess}=2\Delta G°_{H2PO4}-\Delta G°_{H2P2O72}-\Delta G°_{H2O}$=2*-1130,2-(**-1952,27**-237,191)=**-70,94** $^{kJ}/_{mol}$;

$$K_{pp}=K_{Lehningerpp}/[H_2O]=2310{,}57/55{,}34573393=41{,}748=\frac{[H_2PO_4^-]^2}{[H_2O].[H_2P_2O_7^{2-}]};$$

$\Delta G_{ppL}=-R\bullet T\bullet\ln(K_{eqL})=-8{,}3144*298{,}15*\ln(41{,}74799819)$= **-9,251** $^{kJ}/_{mol}$ ,

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

$$K_{app}=K_{Lehningepp}=\exp(-\Delta G_{Lehninger}/R/T)=\exp(19200/8{,}3144/298{,}15)=2310{,}57=\frac{[HPO_4^{2-}]^2\cdot[H_3O^+]}{[H_2O]^2\cdot[HP_2O_7^{3-}]}$$



$\Delta G_{Hess}=\Delta G°_{H3O}+2\Delta G°_{HPO42}-\Delta G°_{HOPO2OPO2O2}-2\Delta G°_{H2O}$=**-85,6** $^{kJ}/_{mol}$ ;
=-213,275+2***-1057,143-(-1938,85**+2***-151,549)=-85,6** $^{kJ}/_{mol}$
Eksoergic pyrophosphate **$HP_2O_7^{3-}$** hydrolysis Hess free energy change at pH=7,36

$\Delta G_{Hess}$ negative **-85,6** $^{kJ}/_{mol}$, but minimized $\Delta G_{min}=\Delta G_{eq}=-19{,}2\ ^{kJ}/_{mol}$ reaching

$$\text{equilibrium mixture } K_a=\frac{[HPO_4^{2-}]^2\cdot[H_3O^+]}{[H_2O]^2\cdot[HP_2O_7^{3-}]}=2310{,}57.$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium.

A+2B 50% C+2D
reactants **$HP_2O_7^{3-}+2H_2O$**
products **2** $HPO_4^{2-}+H_3O^+$

**pp)** $\mathbf{HP_2O_7^{3-}+2\,H_2O=>HPO_4^{2-}+HPO_4^{2-}+H_3O^+}$; $\Delta\mathbf{G}_{ppLehninger}\mathbf{= -19.2}$ $^{kJ}/_{mol}$; $\Delta\mathbf{G}_{ppHess}=\mathbf{-85.6}$ $^{kJ}/_{mol}$;

**b)** $ATP^{4-}+2H_2O=>AMP^{2-}+$ $\mathbf{HP_2O_7^{3-}}$$+H_3O^+$; $\Delta\mathbf{G}_{bLehninger}\mathbf{=-45.6}$ $^{kJ}/_{mol}$; $\Delta\mathbf{G}_{bHess}=\mathbf{-111,45}$ $^{kJ}/_{mol}$;

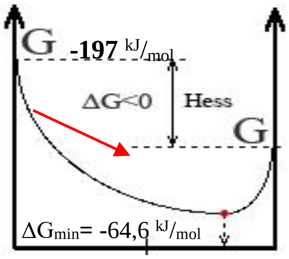
**ppb)** $ATP^{4-}+4H_2O=>AMP^{2-}+\mathbf{HPO_4^{2-}+HPO_4^{2-}}+2\mathbf{H_3O^+}$; $\Delta\mathbf{G}_{ppbL}\mathbf{=-64.6}$ $^{kJ}/_{mol}$; $\Delta\mathbf{G}_{ppHess}=\mathbf{-197,05}$ $^{kJ}/_{mol}$;

$\Delta\mathbf{G}_{ppbH}\mathbf{=}\Delta\mathbf{G}_{ppH}\mathbf{+}\Delta\mathbf{G}_{bH}\mathbf{=-85,6-111,45= -197,05}$ $^{kJ}/_{mol}$ ;

$\Delta G_{Hess}=\Delta G°_{AMP2-}+2\Delta G°_{\mathbf{H3O}}+\mathbf{2}\Delta G°_{\mathbf{HPO42}}\mathbf{-}\Delta G°_{\mathbf{ATP4}}\mathbf{-}4\Delta G°_{\mathbf{H2O}}\mathbf{=-197}$ $^{kJ}/_{mol}$ ;

$=\mathbf{-530,066}-2*213,275+2*\mathbf{-1057,143-(-2267,64}+4*\mathbf{-151,549})\mathbf{=-197.066}$ $^{kJ}/_{mol}$

Exothermic and exoergic $ATP^{4-}+4H_2O$ hydrolise Hess free energy change negative $\Delta\mathbf{G}_{Hess}\mathbf{=-197}$ $^{kJ}/_{mol}$ , but $\Delta\mathbf{G}_{\mathbf{min}}=$ $\Delta\mathbf{G}_{ppbL}\mathbf{=-64.6}$ $^{kJ}/_{mol}$; minimizes reaching equilibrium mixture $\mathbf{K}_{ppbLehninger}=207737828686.$



A+2B 50% 2C+D

reaktants $\mathbf{ATP^{4-}+4H_2O}$

products $AMP^{2-}+$ $HPO_4^{2-}+HPO_4^{2-}+\mathbf{2}H_3O^+$;

$$\mathbf{K}_{ppb}= \mathbf{K}_{Leningeppb}\mathbf{=exp(-}\Delta\mathbf{G}_{Lehningerppb}\mathbf{/R/T})=exp(64600/8,3144/298,15)= 207737828686= \frac{[HPO_4^{2-}]^2\cdot[H_3O^+]^2\cdot[AMP^{2-}]}{[H_2O]^4\cdot[ATP^{4-}]}$$

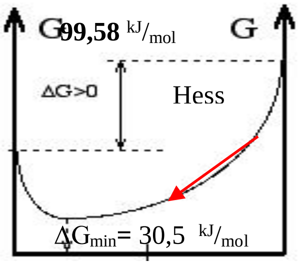
**bb)** $\mathbf{ADP^{3-}+HPO_4^{2--}+H_3O^+=>ATP^{4-}+2H_2O}$; $\Delta\mathbf{G}_{\mathbf{bb}Lehninger}=30,5$ $^{kJ}/_{mol}$;

$$\mathbf{K}_{bbLehningeH}\mathbf{=exp(-}\Delta\mathbf{G}_{bbLehningeH}\mathbf{/R/T})=exp(-30500/8,3144/298,15) =0.000004535142 = \frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$$

$\Delta G_{Hess}=\Delta G°_{\mathbf{ATP3}}\mathbf{-}2\Delta G°_{\mathbf{H2O}}\mathbf{-}\Delta G°_{\mathbf{ADP2}}\mathbf{-}\Delta G°_{HPO42}\mathbf{-}\Delta G°_{\mathbf{H3O}}=\mathbf{99,58}$ $^{kJ}/_{mol}$;

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

Endothermic and endoergic $\mathbf{ADP^{3-}}$ phosphorylation at pH = 7,36 Hess free energy change positive $\Delta\mathbf{G}_{\mathbf{transfer}}=$ **99,58** $^{kJ}/_{mol}$ , but minimizes to $\Delta\mathbf{G}_{\mathbf{min}}=$ $\Delta\mathbf{G}_{\mathbf{eq}}=30,5$ $^{kJ}/_{mol}$ reaching equilibrium mixture $\mathbf{K}_{bbLehningeH}=0.000004535142$: Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ reaching at equilibrium.



A+B+C 50% D+2E

Free energy change minimum reaching establishes equilibrium.

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

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

$\mathbf{HP_2O_7^{3-}+}ADP^{3-}=>HPO_4^{2-}\mathbf{+}ATP^{4-}$; $\Delta\mathbf{G}_{\mathbf{abbpp}}=\Delta\mathbf{G}_{\mathbf{app}}+\Delta\mathbf{G}_{\mathbf{bb}}=-19,2+30,5=11,3$ $^{kJ}/_{mol}$; pH=7,36

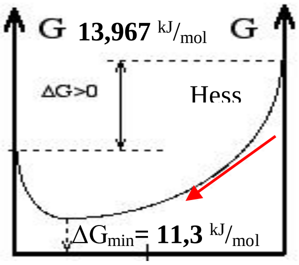
$\Delta G_H=\Delta G°_{HPO42}+\Delta G°_{ATP4}\mathbf{-}\Delta G°_{\mathbf{HP2O73}}\mathbf{-}\Delta G°_{ADP3-}=\mathbf{-1057,143-2267,64-(-1938,85-1399,9)=13,967}$ $^{kJ}/_{mol}$;

$\mathbf{K}_{\mathbf{abpp}}=\mathbf{K}_{\mathbf{app}}\mathbf{K}_{\mathbf{bbLehninger}}=2310,57*0,000004535142=0,010478763$

$\Delta\mathbf{G}_{\mathbf{abpp}}\mathbf{=-R\bullet T\bullet ln(K}_{\mathbf{abpp}}\mathbf{)}=-8,3144*298,15*\mathbf{ln}(0,010478763)/1000=\mathbf{11,3}$ $^{kJ}/_{mol}$;

Endothermic and endoergic phosphate transfer Hess free energy change positive $\Delta\mathbf{G}_{\mathbf{transfer}}=$ **13,967** $^{kJ}/_{mol}$ , but minimizes up to $\Delta\mathbf{G}_{\mathbf{min}}\mathbf{=}\Delta\mathbf{G}_{\mathbf{eq}}\mathbf{=11,3}$ $^{kJ}/_{mol}$ reaching equilibrium mixture: $\mathbf{K}_{\mathbf{abpp}}=0,010478763=\frac{[HPO_4^{2-}]\cdot[ATP^{4-}]}{[HP_2O_7^{3-}]\cdot[ADP^{3-}]}$ . Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ 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** $^{kJ}/_{mol}$;

$$\frac{[H_2O]\cdot[ATP^{3-}]}{[H_2PO_4^-]\cdot[ADP^{2-}]}$$

=**$K_{bbLehningeH}$=exp(-$\Delta G_{Lehninger}$/R/T)**=exp(-30500/8,3144/298,15) = 000004535142

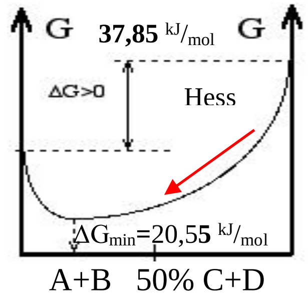
= **$K_{bL}$**= **$K_{bbLehninger}$[$H_2O$]** =0,000004535142*55,3457339 =0,000250993.

**$\Delta G_{bL}$= -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 **$\Delta G_{transfer}$=37,85** $^{kJ}/_{mol}$ , but minimizes up to **$\Delta G_{min}$=$\Delta G_{eq}$**=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 $\Delta G_{min}$ reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.



reactants $ADP^{2-}$+$H_2PO_4^-$
products **$ATP^{3-}$**+ $H_2O$;

**bb) $ADP^{3-}$+$HPO_4^{2--}$+$H_3O^+$=>$ATP^{4-}$+2$H_2O$**; $\Delta G_{bLehninger}$=30,5 $^{kJ}/_{mol}$; **$K_{bbLehn}$**=1/220500,2=0.000004535142;

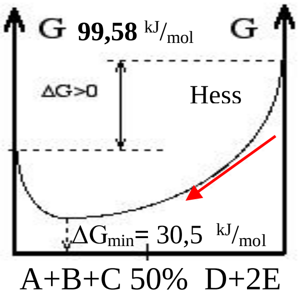
$\Delta G_{Hess}=\Delta G°_{ATP3}-2\Delta G°_{H2O}-\Delta G°_{ADP2}-\Delta G°_{HPO42}-\Delta G°_{H3O}$=**-1399,9-1057,143**-213,275-(**-2267,64+2*-151,549**)=**99,58** $^{kJ}/_{mol}$;

**$K_{bbLehningeH}$=exp(-$\Delta G_{Lehninger}$/R/T)**=exp(-30500/8,3144/298,15) = 0.000004535142 .

$$\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$$ =**$K_{bbLehningeH}$=exp(-$\Delta G_{Lehninger}$/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 **$\Delta G_{transfer}$**= **99,58** $^{kJ}/_{mol}$ , but minimizes to **$\Delta G_{min}$**= **$\Delta G_{eq}$**= 30,5 $^{kJ}/_{mol}$ reaching equilibrium mixture

$$K_{bbLehningeH}=0.000004535142=\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$$ : Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.



reactants_ **$ADP^{3-}$+$HPO_4^{2-}$+$H_3O^+$**
products $ATP^{4-}$+2$H_2O$

**b0)** $\mathbf{ATP^{3-}+H_2O \Rightarrow ADP^{2-}+H_2PO_4^-}$; $\Delta \mathbf{G}_{b0LehningeH}=-20{,}55\ ^{kJ}/_{mol}$; $\mathbf{K}_{b0Lehninger}=\mathbf{K}_{\mathbf{b}Lehninger}/[\mathbf{H_2O}]=3984$; without pH=?

$\Delta G_{Hess}=\Delta G^\circ_{ADP3}+\Delta G^\circ_{HPO42}-\Delta G^\circ_{ATP4}-\Delta G^\circ_{H2O}=\mathbf{-1399{,}9-1057{,}143}-(\mathbf{-2267{,}64-151{,}549})=\mathbf{-37{,}854}\ ^{kJ}/_{mol}$;

$$\mathbf{K}_{b0Lehninger}=\mathbf{K}_{\mathbf{b}Lehninger}/[\mathbf{H_2O}]=220500{,}2/55{,}3457=3984{,}1=\frac{[H_2PO_4^-]\cdot[ADP^{3-}]}{[H_2O]\cdot[ATP^{4-}]}$$

$$\Delta \mathbf{G}_{b0LehningeH}=\mathbf{-R\bullet T\bullet ln}(\mathbf{K}_{b0LehningeH})=-8{,}3144*310{,}15*\mathbf{ln}(3984{,}052962)/1000=-21{,}38\ ^{kJ}/_{mol};$$

**b)** $\mathbf{ATP^{4-}+2H_2O \Rightarrow ADP^{3-}+HPO_4^{2-}+H_3O^+}$; $\Delta \mathbf{G}_{\mathbf{b}Lehninger}=-30{,}5\ ^{kJ}/_{mol}$; $\mathbf{K}_{\mathbf{b}Lehninger}=K_{Lehninger}[\mathbf{H_2O}]/[\mathbf{H_3O^+}]=220500{,}2$;

$\Delta G_{Hess}=\Delta G^\circ_{ADP3}+\Delta G^\circ_{HPO42}+\Delta G^\circ_{H3O}-\Delta G^\circ_{ATP4}-2\Delta G^\circ_{H2O}=\mathbf{-1399{,}9-1057{,}143}-213{,}275-(\mathbf{-2267{,}64+2*-151{,}549})=\mathbf{-99{,}58}\ ^{kJ}/_{mol}$;

T=298,15 K (25° C);

$$\mathbf{K}_{\mathbf{b}Lehninger}=\mathbf{exp(-\Delta G}_{\mathbf{b}Lehninger}\mathbf{/R/T})=exp(30500/8{,}3144/298{,}15)=220500{,}2=\frac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_2O]^2[ATP^{4-}]}$$

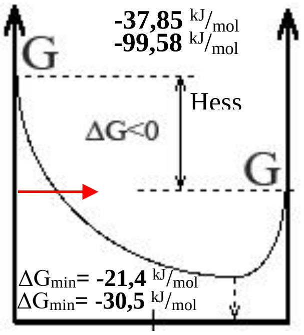
T=310,15 K (37° C); $\mathbf{K}_{LehningeH}=\mathbf{exp(-\Delta G}_{Lehninger}\mathbf{/R/T})=exp(30500/8{,}3144/310{,}15)=136983{,}2474$;

$$\Delta \mathbf{G}_{bLehningeH}=\mathbf{-R\bullet T\bullet ln}(\mathbf{K}_{bLehningeH})=-8{,}3144*310{,}15*\mathbf{ln}(136983{,}2474)/1000=-30{,}5\ ^{kJ}/_{mol};$$

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 $\Delta \mathbf{G_{min}}=\Delta \mathbf{G_{eq}}$ $-21{,}38\ ^{kJ}/_{mol}$ and $-30{,}5\ ^{kJ}/_{mol}$ reaching equilibrium mixture

$$\mathbf{K}_{b0Lehninger}=\mathbf{K}_{\mathbf{b}Lehninger}/[\mathbf{H_2O}]=3984{,}1=\frac{[H_2PO_4^-]\cdot[ADP^{3-}]}{[H_2O]\cdot[ATP^{4-}]}$$

$$\mathbf{K_{bLehninger}}=220500{,}2=\frac{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_2O]^2\cdot[ATP^{4-}]}.$$



Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ reaching at equilibrium mixture.

Free energy change minimum reaching establishes equilibrium.

$\Delta \mathbf{G_{Hess}}=\Delta G^\circ_{\mathbf{cHeatine}}+\Delta G^\circ_{\mathbf{HPO42}}-\Delta G^\circ_{\mathbf{PcHeatine}}-\Delta G^\circ_{\mathbf{H2O}}=107{,}69-1089{,}28-(-689{,}08-237{,}191)=-55{,}3\ ^{kJ}/_{mol}$;
$\Delta \mathbf{G_{Hess}}=107{,}69-1089{,}28-(-689{,}08-237{,}191)=-55{,}3\ ^{kJ}/_{mol}$;
$\Delta \mathbf{G_{Hess}}=\mathbf{126{,}1868}-1089{,}28-(\underline{\mathbf{-736{,}4}}-237{,}191)=10{,}5\ ^{kJ}/_{mol}$;

$\Delta G_{CRCHess}=\Delta G^\circ_{\mathbf{cHeatine}}+\Delta G^\circ_{\mathbf{ATP3}}-\Delta G^\circ_{\mathbf{PcHeatine1}}-\Delta G^\circ_{\mathbf{ADP2}}=-71{,}03\ ^{kJ}/_{mol}$; 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)** $ADP^{2-}+H_2O \Rightarrow AMP^{-}+H_2PO_4^{-}$;$\mathbf{\Delta G_{bd}=-22.85}$ $^{kJ}/_{mol}$; without pH=?

$\Delta G_{Hess}=\Delta G°_{H2PO4-}+\Delta G°_{AMP-}-\Delta G°_{ADP2-}-\Delta G°_{H2O}=\mathbf{-530{,}066}-1130{,}2-(\mathbf{-1399{,}9-151{,}549})=\mathbf{-108.8}$ $^{kJ}/_{mol}$;

$\mathbf{\Delta G_{bd}=-R \bullet T \bullet ln(K_{bd})}=-8{,}3144*298{,}15*\mathbf{ln}(10075{,}75322)/1000=-22{,}85$ $^{kJ}/_{mol}$;

$$\mathbf{K_{bd}=K_{bd Lehninger}/[H_2O]}=557649{,}957/55{,}34573393=10075{,}75=\frac{[H_2PO_4^-]\cdot[AMP^-]}{[H_2O]\cdot[ADP^{2-}]}$$

$\mathbf{\Delta G_{bd}=-R \bullet T \bullet ln(K_{bd})}=-8{,}3144*298{,}15*\mathbf{ln}(10075{,}75322)/1000=-22{,}85$ $^{kJ}/_{mol}$;

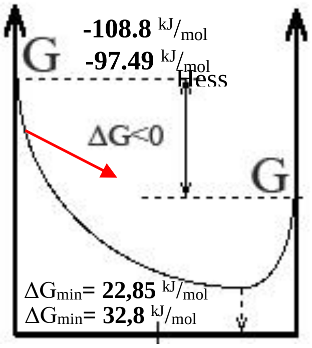
$$\mathbf{K_{bd Lehninger}=exp(-\Delta G_{Lehninger}/R/T)}=exp(32800/8{,}3144/298{,}15)=557649{,}957=\frac{[HPO_4^{2-}]\cdot[H_3O^+]\cdot[AMP^{2-}]}{[H_2O]^2\cdot[ADP^{3-}]}$$

**bd)** $\mathbf{ADP^{3-}+2H_2O \Rightarrow AMP^{2-}+HPO_4^{2-}+H_3O^{+}}$; pH=7,36; $\mathbf{\Delta G_{Lehninger}}=-32.8$ $^{kJ}/_{mol}$;

$\Delta G_{Hess}=\Delta G°_{H3O+}+\Delta G°_{HPO42-}+\Delta G°_{AMP2-}-\Delta G°_{ADP3-}-2\Delta G°_{H2O}=-213{,}275\mathbf{-1057{,}143-530{,}066}-(\mathbf{-1399{,}9}+2*(\mathbf{-151{,}549}))=\mathbf{-97{,}49}$ $^{kJ}/_{mol}$;

| | | | |
|---|---|---|---|
| **$H_3O^+$** | -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 $\mathbf{ADP^{3-}}$ hydrolise without pH=? and at pH=7,36 Hess free energy change negative $\Delta\mathbf{G_{hydrolise}}=\mathbf{-108.8}$ $^{kJ}/_{mol}$ and **-97,49** $^{kJ}/_{mol}$, but minimizes $\Delta\mathbf{G_{min}}=\Delta\mathbf{G_{bd}}=-22{,}85$ $^{kJ}/_{mol}$ and -32.8 $^{kJ}/_{mol}$ reaching equilibrium mixture $\mathbf{K_{bd}}=10075{,}75$ and $\mathbf{K_{bd Lehninger}}=557649{,}957$.



reactants $\mathbf{ADP^{2-}+H_2O}$ A+B 50% C+D

products $H_2PO_4^-+AMP^-$

reactants $\mathbf{ADP^{3-}+2H_2O}$ A+2B 50% C+D+E

products $AMP^{2-}+HPO_4^{2-}+H_3O^+$

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

Free energy change minimum reaching establicshes equilibrium.

**Am)** $AMP^{2-}+H_2O \Rightarrow Adenosine+HPO_4^{2-}$; $\mathbf{\Delta G_{Lehninger}=-14.2}$ $^{kJ}/_{mol}$; $\mathbf{K_{Am}}=exp(14200/8{,}3144/298{,}15)=307{,}43344$;

$$\frac{[HPO_4^{2-}]\cdot[Adenosin]}{[H_2O]\cdot[AMP^{2-}]}\ \mathbf{K_{Am}=K_{Lehninger}}=exp(14200/8{,}3144/298{,}15)=307{,}43344 \text{ at pH}=7{,}36 .$$

$\Delta G_{Hess}=\Delta G°_{adenosin}+\Delta G°_{HPO42}-\Delta G°_{AMP2}-\Delta G°_{H2O}=\mathbf{362{,}172}-1089{,}28-(\mathbf{-530{,}066-151{,}549})=\mathbf{-45.5}$ $^{kJ}/_{mol}$;

**AmL)** $AMP^{-}+H_2O \Rightarrow Adenosine+H_2PO_4^{---}$; at les pH<7.199 $\mathbf{\Delta G_{AmL}}=-14{,}2$ $^{kJ}/_{mol}$ .

$$\mathbf{K_{AmL}=K_{Lehninger}}=exp(14200/8{,}3144/298{,}15)=307{,}43344=\frac{[H_2PO_4^-]\cdot[Adenosin]}{[H_2O]\cdot[AMP^-]} .$$

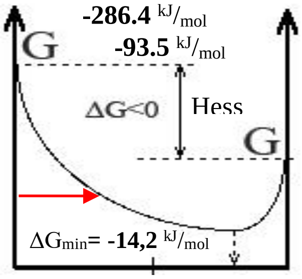
$\Delta G_{HessAmL}=\Delta G°_{adenosin}+\Delta G°_{H2PO4}-\Delta G°_{AMP}-\Delta G°_{H2O}=\mathbf{362{,}172}-1137{,}3-(\mathbf{-530{,}066-151{,}549})=\mathbf{-93.5}$ $^{kJ}/_{mol}$; pH<7.199;

$\Delta G_{HessAm}=\Delta H_{HessAm}-T*\Delta S_{HessAm}=\mathbf{-4{,}27}\ -298{,}15*0{,}\mathbf{946308}=\mathbf{-286.4}$ $^{kJ}/_{mol}$ exoergic;

Exothermic and exoergic Hess free energy change negative for $AMP^-$ at les pH<7.199 $\Delta\mathbf{G_{hydrolize}}=\mathbf{-286.4}$ $^{kJ}/_{mol}$ and $\mathbf{AMP^{2-}}$ hydrolyze **-93.5** $^{kJ}/_{mol}$ at pH=7,36, but minimizes to $\Delta\mathbf{G_{min}}=\Delta\mathbf{G}_{Am}=-14{,}2$ $^{kJ}/_{mol}$ at pH=7,36 reaching equilibrium mixture:

$$\mathbf{K_{AmL}}=307{,}4=\frac{[HPO_4^{2-}]\cdot[Adenosin]}{[H_2O]\cdot[AMP^{2-}]}$$

. Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ 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.

$\Delta H_{HessAm}=\Delta H°_{adenosin}+\Delta H°_{HPO42}-\Delta H°_{AMP}-\Delta H°_{H2O}=\mathbf{-626{,}66}-1302{,}6-(\mathbf{-1638{,}34-286{,}65})=\mathbf{-4.27}$ $^{kJ}/_{mol}$;

$\Delta S_{HessAm}=\Delta S°_{adenosin}+\Delta S°_{HPO42}-\Delta S°_{AMP}-\Delta S°_{H2O}=\mathbf{-3316{,}57}+92{,}5-(\mathbf{-3717{,}19-453{,}188})=\mathbf{946.308}$ $^{kJ}/_{K}/_{mol}$;

$\mathbf{H_2P_2O_7^{2-}}$+$ADP^{2-}$ =>$H_2PO_4^-$ +$ATP^{3-}$; 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** $^{kJ}/_{mol}$;

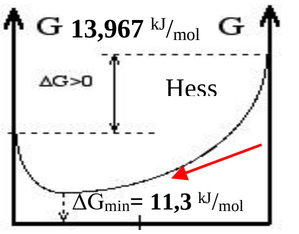
2. $\Delta S_{dispeHse}=-\Delta H_H/T$=**-2,45**/298,15=**-8,22** $^{J}/_{(mol\ K)}$; $\Delta S_{total}=\Delta S_H+\Delta S_{dispeHsed}$=**-38,532-8,2173=-46,75** $^{J}/_{mol/K}$

$\Delta S_H=\Delta S°_{HPO42-}+\Delta S°_{ATP4-}-\Delta S°_{HP2O73-}-\Delta S°_{ADP3-}$=**-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(-Δ**$\mathbf{G}_{Lehninger}$**/R/T)**=exp(-11300/8,3144/298,15)=0,01047878;

$\Delta \mathbf{G}_{abbppL}$**=-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 $\Delta \mathbf{G}_{\mathbf{min}}$=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 $\Delta G_{min}$ reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.



A+B 50% C+D

reactants $HP_2O_7^{3-}$+$ADP^{3-}$

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

| *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** |
| $\mathbf{ADP^{3-}}$ | -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** |
| $Pcreatine^{2-}$ | **-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 $^{kJ}/_{mol}$;

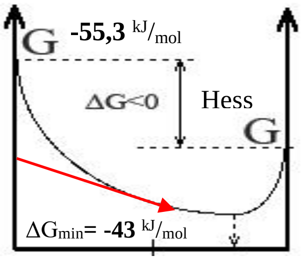
$\Delta G_{Hess}=\Delta G°_{cHeatine}+\Delta G°_{HPO42}-\Delta G°_{PcHeatine}-\Delta G°_{H2O}$ = -55,32 $^{kJ}/_{mol}$;

$\Delta G_{Hess}$ =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**=$\Delta G°_{Pcreatine}$= **-736,4** $^{kJ}/_{mol}$

Exothermic and exoergic $Pcreatin^{2-}$ hydrolise Hess free energy change negative at pH=7,36 $\Delta \mathbf{G}_{hydrolise}$ =-55,3 $^{kJ}/_{mol}$ , but minimizes $\Delta \mathbf{G}_{min}=\Delta \mathbf{G}_{Lehninge}$= -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=$\Delta G°_{Pcreatine}$=-703,4 $^{kJ}/_{mol}$

$_{Lehninger}\Delta G_{Pcreatine}$=43+107,69-1089,28+237,191=$\Delta G°_{Pcreatine}$= -701,4 $^{kJ}/_{mol}$;

$\frac{[creatine]\cdot[HPO_4^{2-}]}{[Pcreatine^{2-}]\cdot[H_2O]}$ $\mathbf{K}_{CARLSON}$**=exp(-Δ**$\mathbf{G}_{Carlson}$**/R/T)**=exp(41000/8,3144/298,15)=15238538,963622

=$\mathbf{K}_{Lehninge}$**=exp(-Δ**$\mathbf{G}_{Lehninger}$**/R/T)**=exp(43000/8,3144/298,15)=34145290,2951607;

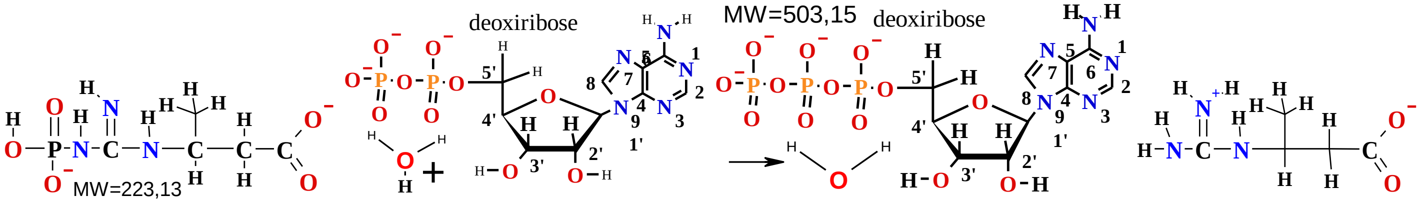
$\Delta \mathbf{G}_{Ellington}$**=-R•T•ln(K**$_{Ellington}$)=-8,3144*308***ln**(3,46*10^7)/1000=**-44,45** $^{kJ}/_{mol}$;

$\frac{[creatine]\cdot[ATP^{3-}]}{[Pcreatine^-]\cdot[ADP^{2-}]}$ =$\mathbf{K}_{CRC}$=1/(5,78*10^(-3))=173 (310,15 K);pMg=2,47;pH=<7,199;

$Pcreatine^{2-}$+$\mathbf{ADP^{3-}}$+$\mathbf{H_3O^+}$=>creatine+$\mathbf{ATP^{4-}}$+$\mathbf{H_2O}$; 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(**$K_aK_{bb}$)=-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;



$PCr^{2-}+ADP^{3-}+H_3O^+ \Rightarrow Cr+ATP^{4-}+H_2O$;pH=7,36; $Pcreatine^{-}+ADP^{2-} \Rightarrow creatine+ATP^{3-}$; pH<7,199 .

$$\frac{[creatine^{-}]\cdot[ATP^{4-}]\cdot[H_2O]}{[Pcreatine^{2-}]\cdot[ADP^{3-}]\,[H_3O^+]}$$

$\Delta G_{abb}=\Delta G_a+\Delta G_{bb}=-43+30,5= -12,5\ ^{kJ}/_{mol}$;

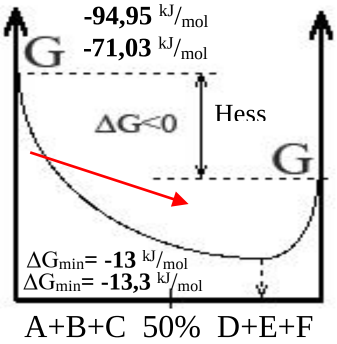
$=K_{abbLehninger}=K_aK_{bb}=34145290,295*0,000004535142=154,854$; at pH=7,36.

$\Delta G_{abbLehninger}=-R\bullet T\bullet \ln(K_aK_{bb})=-8,3144*298,15*\ln(154,854)/1000= -12,5\ ^{kJ}/_{mol}$;

$\Delta G_{abbHess}=\Delta G°_{cHeatine}+\Delta G°_{ATP4-}+\Delta G°_{H2O} -\Delta G°_{PcHeatine2}-\Delta G°_{ADP3} -\Delta G°_{H3O} = -94,946\ ^{kJ}/_{mol}$; 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 $ATP^{4-}$ kinase Hess free energy change negative at pH=7,36 and pH<7,199 $\Delta G_{abb}=-94,946\ ^{kJ}/_{mol}$ and $\Delta G_{CRC}=-71,03\ ^{kJ}/_{mol}$, but minimizes to $\Delta G_{min}= \Delta G_{abbLehninger}= -12,5\ ^{kJ}/_{mol}$ and $\Delta G_{CRC}= -13,3\ ^{kJ}/_{mol}$ 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 $\Delta G_{min}$ reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.

reactants $PCr^{2-}+ADP^{3-}+H_3O^+$

$\Delta G_{abbLehninger}=-R\bullet T\bullet \ln(K_{abb})=-8,3144*310,15*\ln(154,854)/1000=-13\ ^{kJ}/_{mol}$; products (creatine) $Cr+ATP^{4-}+H_2O$

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), $[Pcreatine^{3-}]/[ATP^{4-}]$= 3 to 4 and $[Pcreatine^{3-}]/[creatine^{-}]$= 2,5, $[ATP^{4-}]/[ADP^{3-}]=10^2$ 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 $\Delta G_{Hess}= -94,95\ ^{kJ}/_{mol}$ minimized reaching equilibrium mixture of compounds $\Delta G_{abb}= -13\ ^{kJ}/_{mol}$:

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,$[ATP^{4-}]$=8,05 mM,$[ADP^{3-}]$=0,93 mM un $[H_2O]$=55,1398 M, $[H_3O^+]=10^{-7,36}$ 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:

$$K_{Homeostasis}=\frac{[creatine^{-}]\cdot[ATP^{4-}]\cdot[H_2O]}{[Pcreatine^{2-}]\cdot[ADP^{3-}]\,[H_3O^+]}=\frac{28\bullet 10^{-9}\bullet 8.05\bullet 10^{-5}\bullet 55.1398}{28\bullet 10^{-3}\bullet 9,3\bullet 10^{-3}\bullet 10^{-7.36}}=10,9339760517278;\ \ln(10,934)=2,3919 .$$

$\Delta G_{Homeostasis}=\Delta G_{eq}+R\bullet T\bullet \ln K_{Homeostasis}$ 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,$[ATP^{4-}]$=8,05 mM, $[ADP^{3-}]$=0,93 mM un $[H_2O]$=55,1398 M, $[H_3O^+]=10^{-7,36}$ 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

$$K_{Homeostasis}=\frac{[creatine^{-}]\cdot[ATP^{4-}]\cdot[H_2O]}{[Pcreatine^{2-}]\cdot[ADP^{3-}]\,[H_3O^+]}=\frac{28\bullet 10^{-8}\bullet 8.05\bullet 10^{-5}\bullet 55.1398}{28\bullet 10^{-3}\bullet 9,3\bullet 10^{-3}\bullet 10^{-7.36}}=109,339760517278;\ \ln(109,34)= 4,6945 .$$

$\Delta G_{Homeostasis}=\Delta G_{eq}+R\bullet T\bullet \ln K_{Homeostasis}$ 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)** $ADP^{2-}+H_2PO_4^- \Rightarrow ATP^{3-}+H_2O$; $ADP^{3-}+HPO_4^{2--}+H_3O^+ \Rightarrow ATP^{4-}+2H_2O$; $\Delta G_{bLehninger}=30,5\ ^{kJ}/_{mol}$;

$$\frac{[H_2O]\cdot[ATP^{4-}]}{[H_2PO_4^-]\cdot[ADP^{3-}]}$$

$=K_{bbL}= K_{bbLehninger}[H_2O]=0,000004535142*55,3457339 =0,000251001$ .

$\Delta G_{bHL}=-R\bullet T\bullet \ln(K_{bL})=-8,3144\bullet 298,15\bullet \ln(0,000251001)=20,5512\ ^{kJ}/_{mol}$;

$$\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$$

$=K_{bb}=K_{bbLehninger}=\exp(-\Delta G_{Lehninger}/R/T)=\exp(-30500/8,3144/298,15) =0,000004535142$;

$\Delta G_{bLehninger}=30,5\ ^{kJ}/_{mol}$;

# 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 $\Delta H_H$ $\Delta S_H$ $\Delta G_H$ at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? Will be **exoergic** or **endoergic**! $\Delta G_{Lehninger}$= -13,8 kJ/mol;**$Glc6P^{2-}+H_2O \Rightarrow Glc+HPO_4^{2-}$**;pH=7,36;**$\Delta G_H$**= **-**38,55 kJ/mol;

$\Delta G_{Lehninger}$=13,8 kJ/mol; **$Glc+HPO_4^{2-} \Rightarrow Glc6P^{2-}+H_2O$**; pH=7,36; **$\Delta G_H$**=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; **$Glc+HPO_4^{2-} \Rightarrow Glc6P^{2-}+H_2O$**; 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;

**$\Delta G_{a22}$**$_{Lehninger}$=+13,8 kJ/mol; **$\Delta G_b$**$_{Lehninger}$=-30,5 kJ/mol;

**$Glc+ATP^{4-}+H_2O \Rightarrow Glc6P^{2-}+ADP^{3-}+H_3O^+$**; **$\Delta G_{a22b}$**=-16,7 kJ/mol

**$\Delta G_{a22b}=\Delta G_{a22}+\Delta G_{b}$**$_{Lehninger}$**=**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=

$$\frac{[Glc6P^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[Glc]\cdot[H_2O]\cdot[ATP^{4-}]}$$

**$\Delta G$**$_{a22b}$=-8,3144*298,15***ln**(842,82)/1000=-16,7 kJ/mol

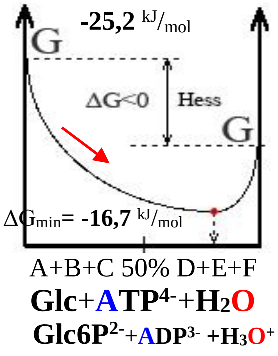
310,15 K; **K**$_{a22b310}$=**K$_{a22}$K$_{bLehninger}$**=0,004741*136983,25=649,438; **K**$_{a22Lehninger310}$=0,004741;

**$\Delta G_{eq}$**=-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 $\Delta G_{min}$ reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.

**$Glc+ATP^{4-}+H_2O \Rightarrow Glc1P^{2-}+ADP^{3-}+H_3O^+$**; **$\Delta G$**$_{Lehnin}$=-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;

**$Glc+ HPO_4^{2-} \Rightarrow Glc1P^{2-}+H_2O$**; $^-$;$\Delta G_{Lehninger}$=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;

$Glc1P^{2-} \Rightarrow Glc6P^{2-}$;**$\Delta G$**$_{Lehninger}$=-7,02 kJ/mol; **K$_{eq}$=[$Glc6P^{2-}$]/[$Glc1P^{2-}$=**17;**$\Delta G_{eq}$**=-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;

$\Delta G_b$=-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 $\Delta H_H$ $\Delta S_H$ $\Delta G_H$ at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? Will be **exoergic** or **endoergic**!

a22 $\Delta G_{Lehninger}=+20,9\ ^{kJ}/_{mol}$; **Glc**+**$HPO_4^{2-}$**+ΔG**+Q**=> **Glc1P$^{2-}$+$H_2O$**; pH=7,36; $\Delta G_{Hess}$=**36,1** $^{kJ}/_{mol}$;

a2 $\Delta G_{Lehninger}=-20,9\ ^{kJ}/_{mol}$; **Glc1P$^{2-}$+$H_2O$=>Glc**+**$HPO_4^{2-}$**+ΔG**+Q**; pH=7,36; $\Delta G_{Hess}$= **-36,1** $^{kJ}/_{mol}$ ;

| *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** |
| **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** |

$\Delta G_{Hess}=\Delta G°_{H2O}+\Delta G°_{Glc1P}-\Delta G°_{Glc}-\Delta G°_{HPO42}$=**36,113** $^{kJ}/_{mol}$ **endoergic**

=**-151,549-1289,221**-(-419,74**-1057,143**)=**36,113** $^{kJ}/_{mol}$

$K_{a22Lehninger}$=EXP(-20900/8,3144/298,15)= 0,000217997;

$\Delta G_H=\Delta G°_{Glc}+\Delta G°_{HPO42}-\Delta G°_{H2O}-\Delta G°_{Glc1P}$= **-36,113** $^{kJ}/_{mol}$ **exoergic**

=-419,74**-1057,143**-(**-151,549-1289,221**)=**-36,113** $^{kJ}/_{mol}$

$K_{a2Lehninger,}$=EXP(20900/8,3144/298,15)=4587,215687;

**Glc**+**$ATP^{4-}$+$H_2O$=>Glc1P$^{2-}$+$ADP^{3-}$+$H_3O^+$**; pH=7,36; I=0,2 M.

$K_{a22b}=K_{a22}K_b$=0,000217997*220500,2=48,07;

**$\Delta G_{a22b}$=-R•T•ln($K_{a22b}$)**=-8,3144*298,15***ln**(48,0684)=-9,6 $^{kJ}/_{mol}$;

**Glc1P$^{2-}$+$ADP^{3-}$**+**$H_3O^+$**=> **Glc**+**$ATP^{4-}$**+**$H_2O$**; pH=7,36; I=0,2 M.

$K_{a2b}=K_{a2}K_b$=4587,215687*4,54*10^(-6)=0,02083

**$\Delta G_{a2b}$=-R•T•ln($K_{a2b}$)**=-8,3144*298,15***ln**(0,02083)=9,6 $^{kJ}/_{mol}$

$$K_{a2b}=K_{a2}K_b=0,02083=\frac{[Glc]\cdot[H_2O]\cdot[ATP^{4-}]}{[Glc1P^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}$$

Lehningera līdzsvars ; **$ATP^{3-}$+$H_2O$<=>$ADP^{2-}$+$H_2PO_4^-$**; $K_{Lehninger}$=0,0001739; without pH=7,36;

**$\Delta G_{Lehninger}$=-R•T•ln($K_{Lehninger}$)**=-8,3144*298,15***ln**(0,0001739)=**21,46** $^{kJ}/_{mol}$ ;

$$K_{Lehninger}=K_{bLehninger}*[H_3O^+]/[H_2O]=220500,2*10^{(-7,36)}/55,3457=0,0001739=\frac{[H_2PO_4^-]\cdot[ADP^{3-}]}{[H_2O]\cdot[ATP^{4-}]}$$

$\Delta G_H=\Delta G°_{ADP3}+\Delta G°_{H2PO4}-\Delta G°_{ATP4}-\Delta G°_{H2O}$=**-1399,9-1057,143**-(**-2267,64**-237,191)=47,79 $^{kJ}/_{mol}$;

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

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

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

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

abb **Glc1P$^{2-}$+$ADP^{3-}$**+$H_3O^+$ => **Glc**+**$ATP^{4-}$**+$H_2O$; **$\Delta G_{a2b}$= $\Delta G_{a2}$+ $\Delta G_b$=-20,9**+30,5= **9,6** $^{kJ}/_{mol}$ ;

sum **Glc**+**$ATP^{4-}$**+$H_2O$=>**Glc1P$^{2-}$+$ADP^{3-}$**+$H_3O^+$+ΔG**+Q**; **$\Delta G_{a22b}$= $\Delta G_{a22}$+ $\Delta G_b$=**20,9 +-30,5= **-9,6** $^{kJ}/_{mol}$ ;

$\Delta G_{Hess}=\Delta G°_{ADP3}+\Delta G°_{Glc1P}+\Delta G°_{H3O}-\Delta G°_{Glc}-\Delta G°_{ATP4}-\Delta G°_{H2O}$= **-38,607** $^{kJ}/_{mol}$;

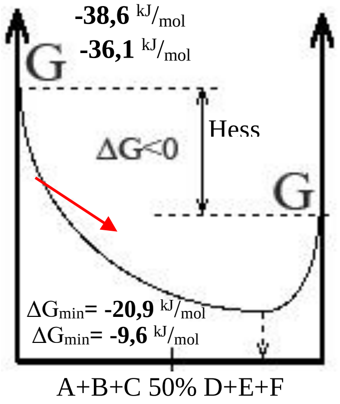
=**-1399,9-1289,221**-213,275-(-419,74-2292,5-**151,549**)=**- 38,607** $^{kJ}/_{mol}$;

**$\Delta G_{a22b}$=- R•T•ln($K_{a22b}$)** =-8,3144*298,15***ln**(3,79204*$10^{-8}$)= 42,36 $^{kJ}/_{mol}$.

Exothermic, exoergic **Glc1P$^{2-}$** dephosphorylation – phosphorilation Hess free energy change is negative **$\Delta G_{dephosphorylation}$**= **-36,113** and **-38,607** $^{kJ}/_{mol}$, but minimizes reching equilibrium **$\Delta G_{min}$=$\Delta G_{a2Lehninger}$**=-20,9 $^{kJ}/_{mol}$ and **$\Delta G_{a22b}$**=-9,6 $^{kJ}/_{mol}$ mixture

$$K_{a2Lehninger,}=4587=\frac{[Glc]\cdot[HPO_4^{2-}]}{[Glc1P^{2-}]\cdot[H_2O]}\ \text{and}\ K_{a22b}=\frac{[Glc1P^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[Glc].[H_2O]\cdot[ATP^{4-}]}=48,07$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum **$\Delta G_{min}$** reaching. Free energy minimum reaching establishes equilibrium.



reactants **Glc1P$^{2-}$**+ $H_2O$

products **Glc**+ **$HPO_4^{2-}$**

$ADP^{2-}+H_2PO_4^{-}$=>$ATP^{3-}+H_2O$; $\Delta G_{Lehninger}$ = 20,55 $^{kJ}/_{mol}$; bez pH=?;

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

**bb)** $\mathbf{ADP^{3-}+HPO_4^{2--}+H_3O^{+}}$**=>**$\mathbf{ATP^{4-}+2H_2O}$; $\Delta G_{bLehninger}$=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•T•ln**($K_{bL}$)=-8,3144*298,15***ln**(0,000250993)/1000= 20,5512 $^{kJ}/_{mol}$;

$$\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^{+}]}$$

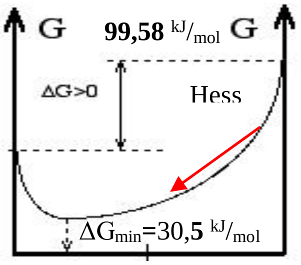
$K_{bbLehningeH310}$**=exp(-**$\Delta G_{Lehninger}$**/R/T**)=exp(-30500/8,3144/310,15) = 0,000004535142

=$K_{bbLehningeH}$**=exp(-**$\Delta G_{Lehninger}$**/R/T**)=exp(-30500/8,3144/298,15) = 0,000004535142

$K_{bbLehnH}$=1/220500,2=0,000004535142;

$\Delta G_{Hess}=\Delta G°_{ATP3}-2\Delta G°_{H2O}-\Delta G°_{ADP2}-\Delta G°_{HPO42}-\Delta G°_{H3O}$=**-1399,9-1057,143**-213,275-(**-2267,64+2*-151,549**)=**99,58** $^{kJ}/_{mol}$;

Endothermic and endoergic **ADP**$^{3-}$ phosphorilation Hess free energy change positive at pH 7,36 $\Delta G_{hydrolise}$=**99,58** $^{kJ}/_{mol}$ , but minimizes $\Delta G_{min}=\Delta G_{bbLehningeH}$=30,5 $^{kJ}/_{mol}$ reaching equilibrium mixture: 0,000004535142=$K_{bbLehningeH}$= $\frac{[H_2O]^2\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^{+}]}$. Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ reaching mixture of equilibrium. Free energy change minimum reaching establishes equilibrium.



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aa $\Delta G_{Lehninger}$=13,8 $^{kJ}/_{mol}$; **Glc**+$\mathbf{HPO_4^{2-}}$**+ΔG+Q=>** $\mathbf{Glc6P^{2-}+H_2O}$; pH=7,36; reactants $\mathbf{HPO_4^{2-}+H_3O^{+}+ADP^{3-}}$

$K_{aaLehninger}$=EXP(-13800/8,3144/298,15)=0,003822314; product s $\mathbf{2H_2O}$ **+**$\mathbf{ATP^{4-}}$

$K_{aaLehninger}$=EXP(-13800/8,3144/310,15)= 0,0047409841; **T=310.15 K**

$\Delta G_{aaHess}=\Delta G°_{Glc6P}+\Delta G°_{H2O}-\Delta G°_{Glc}-\Delta G°_{HPO42}$=**-1296,262**+((**-151,549**-237,191)/2)-(-419,74-1089,28)= **18.39** $^{kJ}/_{mol}$

$\Delta G_{aaHess}=\Delta G°_{Glc6P}+\Delta G°_{H2O}-\Delta G°_{Glc}-\Delta G°_{HPO42}$=**-1296,262-151,549**-(-419,74-1089,28)= **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 $^{kJ}/_{mol}$

$\Delta G_{aaHess}=\Delta G°_{Glc6P}+\Delta G°_{H2O}-\Delta G°_{Glc}-\Delta G°_{HPO42}$=**-1296,262-151,549-(-402,05-1057,143)**= **11,38** $^{kJ}/_{mol}$

aa2 $\Delta G_{Lehninger}$=-13,8 $^{kJ}/_{mol}$; $\mathbf{Glc6P^{2-}+H_2O}$**=>Glc+**$\mathbf{HPO_4^{2-}}$; pH=7,36; $\Delta G_{aa2Hess}$= **-18.39** $^{kJ}/_{mol}$ ;

$\Delta G_{aa2Hess}=\Delta G°_{Glc}-\Delta G°_{HPO42}-\Delta G°_{Glc6P}-\Delta G°_{H2O}$=-419,74-1089,28-(**-1296,262**+((**-151,549**-237,191)/2))= **-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;

**Glc+**$\mathbf{ATP^{4-}+H_2O}$**=>**$\mathbf{Glc6P^{2-}+ADP^{3-}+H_3O^{+}}$; $\Delta G_{Lehninger}$=-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•T•ln**($K_{aLb}$)=-8,3144*298,15***ln**(842,82)=-16.7 $^{kJ}/_{mol}$;

$\Delta G_{abHess}=\Delta G°_{Glc6P-}+\Delta G°_{ADP3}+\Delta G°_{H3O}-\Delta G°_{H2O}-\Delta G°_{ATP4}-\Delta G°_{Glc}$=**-25,2** $^{kJ}/_{mol}$ $^{kJ}/_{mol}$

=**-1399,9**-1318,92-213,275-(**-402,05-2267,64**-237,191)= **-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 ; ↓$\Delta G_{Lehninger}$=16,7 $^{kJ}/_{mol}$;

aaLbb $\mathbf{Glc6P^{2-}+ADP^{3-}+H_3O^{+}}$**=>Glc+**$\mathbf{ATP^{4-}+H_2O}$; $K_{aLbb}$=261,62*0,000004535142=0,00118648385004;

Endothermic and endoergic phosphorilation Hess free energy change positive $\Delta G_{phosphoHilation}$=**25.2** $^{kJ}/_{mol}$ negative, but minimized $\Delta G_{min}=\Delta G_{eq}$=**16.7** $^{kJ}/_{mol}$ reaching equilibrium mixture 298,15 K:

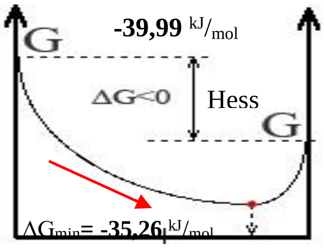
$K_{aLbb\_298}$=261,62*0,000004535142=0,00118648385004=$\frac{[H_2O]\,[ATP^{4-}]\,[Glc]}{[Glc6P^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^{+}]}$

$\Delta G_{Hess}=\Delta G°_{Glc}+\Delta G°_{ATP4}+\Delta G°_{H2O}-\Delta G°_{ADP3}-\Delta G°_{Glc6P}-\Delta G°_{H3O}$=**-25,2** $^{kJ}/_{mol}$

=**-402,05-2267,64**-237,191-(**-1399,9**-1318,92-213,275)=**25.2** $^{kJ}/_{mol}$;

$\Delta G_{aaLbb}$=-RT**ln**($K_{aaLbb}$)=-8,3144*298,15***ln**(0,00118648385004)=**16.7** $^{kJ}/_{mol}$; reactants $\mathbf{Glc6P^{2-}+ADP^{3-}+H_3O^{+}}$

$K_{aLb\_310}$=210,9*0,0000073001623=0,00153960422907; products **Glc+**$\mathbf{ATP^{4-}+H_2O}$;



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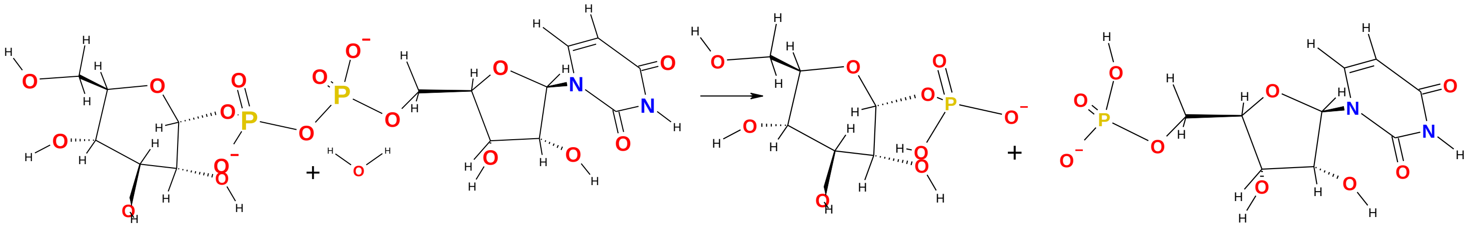
Le Chatelier principle is Prigogine attractor for Free energy change minimum **ΔG**$_{min}$ reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.

$\Delta G_{aaLbb310}$=-RT**ln**($K_{aaLbb310}$)=-8,3144*310,15***ln**(0,00153960422907)/1000=**16.7** $^{kJ}/_{mol}$

$UDPGlc^{2-}+H_2O \Rightarrow UMP^{1-}+Glc1phosphate^{1-}$; $\Delta G_{LehningeH}=-43$ $^{kJ}/_{mol}$; without pH=?



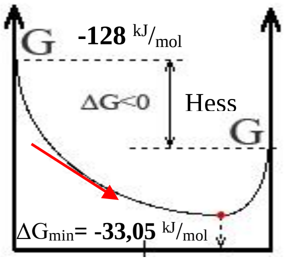
$K_{Lehninger}=EXP(-\Delta G_L/R/T)=EXP(43000/8{,}3144/298{,}15)=EXP(17{,}346)=34145290=10^{-pKeq}=10^{7{,}75333}$,

$$K_{Lehninger}=EXP(-\Delta G_L/R/T)=EXP(43000/8{,}3144/298{,}15)=EXP(17{,}346)=\frac{[Glc1P^{-}]\cdot[UMP^{-}]}{[UDP^{2-}Glc]\cdot[H_2O]}=34145290$$

$|\Delta G_{aLehninger}=-43|$ $^{kJ}/_{mol}<|\Delta G_{Hess}=\Delta G_{UMP1}+\Delta G_{Glc1phosphate1}-\Delta G°_{UDPGlc2}-\Delta G°_{H2O}=\mathbf{-128{,}642}$ $^{kJ}/_{mol}|$;

$\Delta G_H=\Delta G_{LehningeH}-\Delta G°_{H2O}$(BioThermodybamic 2006)$+\Delta G°_{H2O}$(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=? $\Delta G_{hydrolise}=\mathbf{-128{,}642}$ $^{kJ}/_{mol}$ , but minimizes reaching equilibrium mixture :$\Delta G_{min}=\Delta G_{eq}=\mathbf{-43}$ $^{kJ}/_{mol}$



$$K_{Lehninger}=EXP(-\Delta G_{Lehni}/R/T)=EXP(43000/8{,}3144/298{,}15)=34145290=\frac{[Glc1P^{-}]\cdot[UMP^{-}]}{[UDP^{2-}Glc]\cdot[H_2O]}.$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ reaching at equilibrium.

Free energy change minimum reaching establishes equilibrium.

Reactants $UDPGlc^{2-}+H_2O$

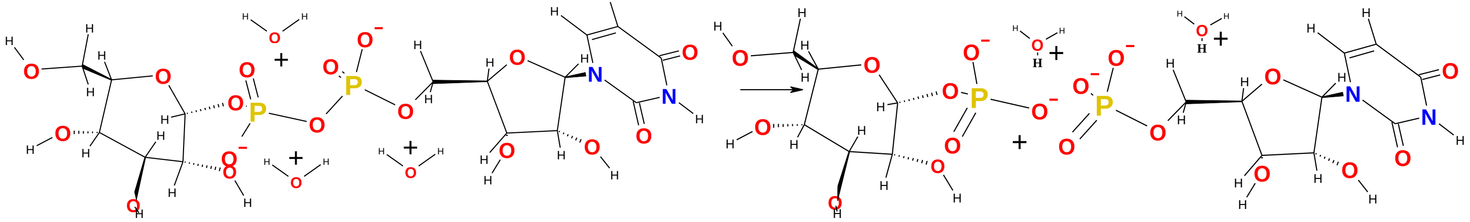
products $UMP^{1-}+Glc1phosphate^{1-}$;

$UDPGlc^{2-}+3H_2O \Rightarrow UMP^{2-}+Glc1phosphate^{2-}+2H_3O^+$;pH=7,36

$\Delta G_H=\Delta G_{UMP2}+\Delta G_{Glc1phosphate2}+2\Delta G°_{H3O}-\Delta G°_{UDPGlc2}-3\Delta G°_{H2O}=\ )=\mathbf{-14{,}9}$ $^{kJ}/_{mol}$; pH=7,36

$\Delta G_H=\Delta G_{LehningeH}+2\Delta G°_{H3O}-3\Delta G°_{H2O}=-43-2*213{,}275-(3*\mathbf{-151{,}549})=\mathbf{-14{,}9}$ $^{kJ}/_{mol}$; pH=7,36;

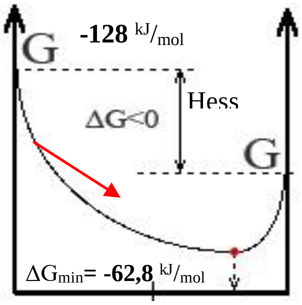
Alberty,Robert A.,Biochemical Thermodynamics: Applications of Mathematica, © 2006,Masachusetts Techn Inst.



$K_a=K_{Lehninger}*[H_2O]^2=34145290*55{,}3457339\wedge^2=104592153973{,}017=10\wedge^{11.019}$;

$\Delta G_a=-R\bullet T\bullet \ln(K_a)=-8{,}3144*298{,}15*\ln(104592153973{,}017)/1000=\mathbf{-62{,}8}$ $^{kJ}/_{mol}$;

Exothermic and exoergic $UDPGlc^{2-}$ hydrolise reaction free energy change negative at pH 7,36 $\Delta G_{hydrolise}=\mathbf{-128}$ $^{kJ}/_{mol}$ , but minimizes reaching equilibrium mixture : $\Delta G_{min}=\Delta G_{eq}=\mathbf{-62.8}$ $^{kJ}/_{mol}$



$$104592153973{,}017=K_a=\frac{[Glc1P^{2-}]\cdot[UMP^{2-}]\cdot[H_3O^+]^2}{[UDP^{2-}Glc]\cdot[H_2O]^3}.$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ 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**SCoA**$^{4-}$ $O_2$ $H_2O_2$ 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**S**CoA**$^{4-}$**+**$O_{2aqua}$**+**$H_3O^+$**=>fumarate**$^{2-}$**+HSCoA**$^{3-}$**+** $H_2O_{2aqua}$**+**$H_2O$+ΔG;

| *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**

**Succinat**$^{2-}$**+**$O_{2aqua}$**=>fumarate**$^{2-}$**+**$H_2O_{2aqua}$+ΔG

$\Delta G_H=\Delta G°_{fumarat2-}+\Delta G°_{H2O2}-\Delta G°_{O2}-\Delta G°_{Succinat2-}$=**-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** $\Delta G_{Hess}$= **-61.82** $^{kJ}/_{mol}$. at pH=7.36 exoergic

Ox $O_{2aqua}$ **+2**$H_3O^+$**+2e**$^-$**=**$H_2O_{2aqua}$ **+2**$H_2O$; **E°** $_{OxO2}$=0.4495 V Thermodynamic University Alberta

Red **Succinate**$^{2-}$**+2**$H_2O$ **= Fumarate**$^{2-}$**+2**$H_3O^+$ **+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** $^{kJ}/_{mol}$;

**K**$_{eq}$**=exp(-**$\Delta G_{eq}$**/R/T)**=exp(382565.95/8.3144/298.15)=5057721 ;

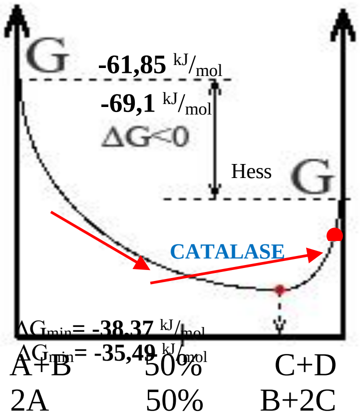
Exoergic dehydrogenation reaction favored reactants conversion to:

**Succinat**$^{2-}$**+**$O_{2aqua}$ =>**fumarate**$^{2-}$**+**$H_2O_{2aqua}$**+Q+ΔG;**

Exoergic CATALASE erase **2H-O-O-H** peroxide **2**$H_2O_{2aq}$**=>**$O_{2aqua}$**+2**$H_2O$**+Q+ΔG** to $O_{2aqua}$ and **2**$H_2O$ . Complex reaction sequence favors stabile unsaturated double bond product **H>C=C<H** efficiency ● 100% as erasing molecules to

zero 0=[$H_2O_2$]: $K_{eq}$=5057721= $\dfrac{[\text{Fumarate}^{2-}]\cdot[H_2O_2]\swarrow \text{CATALASE}}{[\text{Succinate}^{2-}]\cdot[O_2]}$ =5057721,

$K_{eq}$=90471011.97= $\dfrac{[\text{UbiQuinOx}]\cdot[H_2O_2]\swarrow \text{CATALASE}}{[\text{UbiQuinRed}]\cdot[O_2]}$ .



Formation $H_{2gas}$+$O_{2gas}$=>$H_2O_2$ ; **ΔG**°$_{UnivAlberta}$=-134,03 $^{kJ}/_{mol}$ ; **ΔG**°$_{Alberty}$=**-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** $^{kJ}/_{mol}$)

**UbiQuinRed**$^-$ **+**$O_{2aqua}$ **=>UbiQuinOx+**$H_2O_{2aqua}$+ΔG+**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 $O_{2aqua}$ **+2**$H_3O^+$**+2e**$^-$**=**$H_2O_{2aqua}$ **+2**$H_2O$; **E°** $_{OxO2}$=0.4495 V Thermodynamic University Alberta

Red **Ubiquinol+2**$H_2O$ **= Ubiquinone+2**$H_3O^+$ **+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(-$\Delta G_{eq}$/R/T)=EXP(**35490**/8.3144/298,15)=1650539;????

Red: **Ubiquinol6+2**$H_2O$ **= Ubiquinone6+2**$H_3O^+$ **+2e**$^-$; **E°**$_{Red}$**=E°**$^2_{H2O}$**=-0.845 V**; Thermodynamic CRC 2010 **E°**=-1.05 V;

**E°**$^2_{H2O}$ **=-1.05**+0.10166+0.0591/2*log([$H_2O$]$^2$)=(**-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 $\Delta H_H$ $\Delta S_H$ $\Delta G_H$ 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$^{3-}$+$H_2O$**; $\Delta G_{Lehninger}$ = 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;

$\Delta G_{eq}=-R\bullet T\bullet \ln(K_{eq})$=-8,3144•298,15•**ln**(0,000250993)=20,55 $^{kJ}/_{mol}$;

$$K_{bHL}=K_{bbLehninger}[H_2O]=0,000250993=\frac{[H_2O]\cdot[ATP^{3-}]}{[H_2PO_4^-][ADP^{2-}]}$$

**bb ADP$^{3-}$+$HPO_4^{2-}$+$H_3O^+$=>ATP$^{4-}$+2$H_2O$**;

$\Delta G_{bbLehninger}$=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$^{4-}$;

$\Delta G_H=\Delta G°_{CH3COO}+\Delta G°_{CoA2}+\Delta G°_{ATP4}-\Delta G°_{Acetyl\text{-}CoA2}-\Delta G°_{ADP3\text{-}}-\Delta G°_{HPO42}$= **-5,4348** $^{kJ}/_{mol}$;

=**-2267,64-240,963-5,7716-(-1057,143-1399,9-51,8968)**= **-5,4348** $^{kJ}/_{mol}$;

$$K_{abb}=K_aK_{bbLehningeH}=317017,64*0,000004535142=1,43772001390488=\frac{[CH_3COO^-]\cdot[HSCoA^{4-}]\cdot[ATP^{4-}]}{[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[Acetyl\text{-}CoA^{4-}]}$$

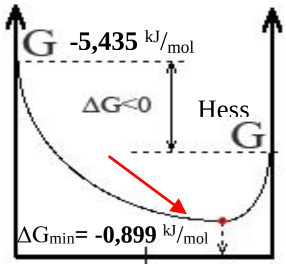
$\Delta G_{abb}=\Delta G_a+\Delta G_{bb}$=-31,409+30,51= -0,899 $^{kJ}/_{mol}$;

$\Delta G_{abb}=-R\bullet T\bullet \ln(K_{abb})$=-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 $\Delta G_{esterification}$= **-5,435** $^{kJ}/_{mol}$, but minimizes $\Delta G_{min}=\Delta G_{abb}$= **-0,899** $^{kJ}/_{mol}$ reaching equilibrium mixture:

$K_{abb}=K_aK_{bbLehningeH}$=317017,64* 0,000004535142=1,43772;

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ 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 **2$H_2O$ +ATP$^{4--}$**

# THERMODYNAMICS Exercise V l **Glyc31P=Glyc3P** hydrolysis

Calculate $\Delta H_H$ $\Delta S_H$ $\Delta G$ at standard conditions (298.15 K). Reaction is **exothermic** , **athermic**, **endothermic**? Glycerate dephosphorilation **Glyc31P=Glyc3P** $^-$ with water! **Exoergic** or **endoergic**! Reactants **=>** products

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$^{4-}$+2$H_2O$=>Glycerat3P$^{3-}$+$HPO_4^{2-}$+$H_3O^+$+ΔG+Q;** pH=7,36

| *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** |
| 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

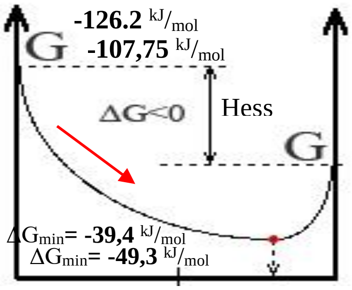
**$\Delta G_{aL}$=-R•T•ln($K_{aL}$)**=-8,3144*298,15***ln**(7833705,111)= -39,351 $^{kJ}/_{mol}$

$\Delta G_{Hess}=\Delta G°_{\mathbf{Glyc3P}}+\Delta G°_{\mathbf{H2PO4}}-\Delta G°_{\mathbf{Glyc31P}}-\Delta G°_{\mathbf{H2O}}$=**-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 $\Delta G_{aL}$=**-39,4** $^{kJ}/_{mol}$ and at pH=7,36 to **$\Delta G_{aLehninger}$=-49,3** $^{kJ}/_{mol}$ reaching equilibrium mixture **$\Delta G_{min}$**:



$$\frac{[HPO_4^{2-}]\cdot[H_3O^+]\cdot[\text{Glycerat3}P^{3-}]}{[H_2O]^2\cdot[\text{Glycerat13}P^{4-}]}=433562158{,}5=K_{aLehninger}$$ ; $K_{aL}$=**K**$_{aLehninger}$/[$H_2O$]=7833705; A+2B 50% C+D+E

$\Delta G_{Hess}=\Delta G°_{\mathbf{H3O+}}+\Delta G°_{\mathbf{Glyc3P}}+\Delta G°_{\mathbf{HPO42-}}-\Delta G°_{\mathbf{Glyc31P}}-2\Delta G°_{\mathbf{H2O}}$=**-107.75** $^{kJ}/_{mol}$;
=-213,275**-1347,73-1057,143**-(-2207,30+2***-151,549**)=**-107.75** $^{kJ}/_{mol}$ .

Reactants Glycerat31P$^{4-}$+2HO
products Glycerat3P$^{3-}$+$HPO_4^{2-}$+$H_3O^+$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ reaching equilibrium . Free energy change minimum reaching establishes equilibrium.

pH<7,199; **PyruvEnolP$^{2-}$+$H_2O$**=>$H_3CC$=OCOO$^-$+**$H_2PO_4^-$;**

$\Delta G_{Hess}=\Delta G°_{H3CC=OCOO}+\Delta G°_{\mathbf{H2PO4}}-\Delta G°_{PyruvEnolP3}-\Delta G°_{\mathbf{H2O}}$=-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;

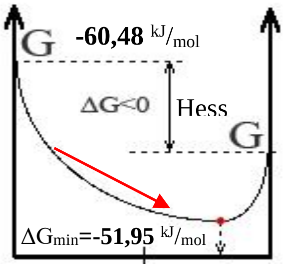
$\Delta G_H=\Delta G°_{H3CC=OCOO}+\Delta G°_{\mathbf{HPO42}}-\Delta G°_{PyruvEnolP3}-\Delta G°_{\mathbf{H2O}}$ =**-344,62-1057,14**-(-1189,73 **-151,549**)=**-60,481** $^{kJ}/_{mol}$ .

**K**$_{Lehninger}$**=exp(-Δ$G_{Lehninger}$/R/T)**=exp(61900/8,3144/298,15)=69902464988

**$K_{aL}$=K**$_{Lehninger}$/[**$H_3O^+$**]=69902464988/55,3457339=1263014510

$\Delta G_a$=-R•T•ln($K_a$)=-8,3144*298,15*ln(1263014510)/1000= **-51,95** $^{kJ}/_{mol}$;

Exoergic **PyruvEnolP$^{3-}$** hydrolise Hess free energy change $\Delta G_{Hess}$ at pH 7,36 negative **-60,48** $^{kJ}/_{mol}$, but minimizes $\Delta G_{min}=\Delta G_{eq}$= **-51,95** $^{kJ}/_{mol}$ reaching equilibrium mixture: $$\frac{[CH_3C{=}OCOO^-]\cdot[HPO_4^{2-}]}{[H_2O]\ \cdot[\text{PyruvEnolP}^{3-}]}$$ =1263014510=$K_a$ **;** Le Chatelier principle is Prigogine attractor for Free energy change minimum **$\Delta G_{min}$** 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 $\Delta H_H$ $\Delta S_H$ $\Delta G$ 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**! <u>Reactants</u> => <u>products</u>
Lehninger 2000 $\Delta G_{Lehninger}$= -13,8 $^{kJ}/_{mol}$; **Glc6P$^{2-}$+$H_2O$ => Glc+$HPO_4^{2-}$+Q+ΔG**; pH=7,36; **$\Delta G_H$**=-11,38 $^{kJ}/_{mol}$
$\Delta G_{Lehninger}$=-20,9 $^{kJ}/_{mol}$; **Glc1P$^{2-}$+$H_2O$ => Glc+$HPO_4^{2-}$**+ΔG+**Q**;;pH=7,36;**$\Delta G_H$**=-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•$\Delta S_{Hess}$;

$\Delta G_H=\Delta G°_{Glc}+\Delta G°_{HPO42-}-\Delta G°_{H2O}-\Delta G°_{Glc6P}$=**-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•$\Delta S_{total}$=38,29*298,15=11,42; $^{kJ}/_{mol}$ <u>spontaneouse</u>
$\Delta H_{H1}=\Delta H°_{Glc}+\Delta H°_{HPO42-}-\Delta H°_{H2O}-\Delta H°_{Glc1P}$ =**-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($-\Delta G_H$/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
**$\Delta G_{eq1}$= -R•T•ln($K_{eq1}$)**=-8,3144*298,15***ln**(4,727)/1000= **-3,851** $^{kJ}/_{mol}$ ; **-3,45** $^{kJ}/_{mol}$
**$K_{Lehmiger1}$**=EXP($-\Delta G_H$ /R/T)=EXP(20900/8,3144/298,15)=4587,22; 3310,4

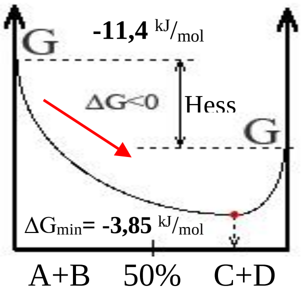
$$\frac{[Glc]\cdot[HPO_4^{2-}]}{[Glc1P^{2-}]\cdot[H_2O]}$$

=**$K_{eq1}$**=82,883;0, 59,813; 298,15, 310,15; **$K_{eq1}$**=$K_{Lehmiger1}$/[**$H_2O$**]= 4587,22/55,3457339=82,883
**$\Delta G_{eq1}$= -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($-\Delta G_{L66}$/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 .
**$\Delta G_{eq66}$=-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 **$\Delta G_{min}$ = $\Delta G_{eq}$ = -3,851** $^{kJ}/_{mol}$ reaching equilibrium $K_{eq}$=**4,727 .**

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

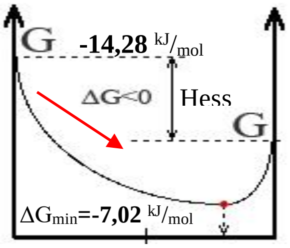


Glc6P$^{2-}$+$H_2O$ reactants
products Glc+$HPO_4^{2-}$

**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

**$\Delta G_{eq}$ = - 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 $\Delta G_{total}$=**11,42-19,63** $^{kJ}/_{mol}$ = **-8,21** $^{kJ}/_{mol}$ , but minimized to **$\Delta G_{eq}$ = -7,02** $^{kJ}/_{mol}$ reaching equilibrium **$\Delta G_{min}$** .Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ 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* | $\Delta H°_{Hess}$, ${}^{kJ}/_{mol}$ | $\Delta S°_{Hess}$, ${}^{J}/_{mol/K}$ | $\Delta G°_{Hess}$, ${}^{kJ}/_{mol}$ |
|---|---|---|---|
| $H_3O^+$ | -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 |

$\Delta H_H = \Delta H°_{CO2aq} - \Delta H°_{CO2gas} = -413.7976 + 393.509 = -20.3\ {}^{kJ}/_{mol}$
$\Delta S_{Hess} = \Delta S°_{CO2aqua} - \Delta S°_{CO2gas} = 117.57 - 213.74 = -96.17\ {}^{J}/_{mol/K}$;
$= 117.57 + 69.9565 - (213.74 + 69.9565) = -96.17$....... ${}^{J}/_{mol/K}$
$\Delta G_H = \Delta H_H - T*\Delta S_H = -20.3 + 298.15*0.09617 = 8.385\ {}^{kJ}/_{mol}$;
$\Delta G_{sp} = \Delta G°_{CO2aq} - \Delta G°_{CO2gas} = -385.98 + 394.359 = 8.379\ {}^{kJ}/_{mol}$
$K_{sp} = EXP(-\Delta G_{sp}/R/T) = EXP(-8379/8.3144/298.15) = 0.034045$

$$K_{sp} = 0.0341 = \frac{X_{CO_2\,aqua}}{[CO_2\ gas]} = \frac{[CO_2\ aqua]}{[CO_2\ gas]\cdot[H_2O]}$$ 100% mol fraction

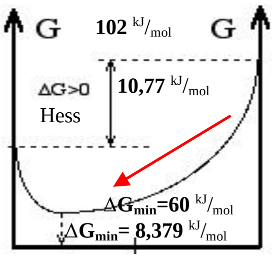
$[CO_{2gas}] = 1$; $[CO_{2aqua}] = K_{sp}[H_2O] = 0.034*55.346 = 1.878$ M
Air 0.04% $[CO_{2gas}] = 0.0004$; $[CO_{2aqua}] = K_{sp}*[CO_2\uparrow_{gas}]*[H_2O] = 0.034045*0.0004*55.3457339 = 0.000754$ M;

Hydrolysis reaction $CO_{2aqua} + 2H_2O + \Delta G + Q \xrightarrow{CA} H_3O^+ + HCO_3^-$ and acid neutralisation equilibrium
$\Delta H_H = \Delta H°_{H3O} + \Delta H°_{HCO3} - 2\Delta H°_{H2O} - \Delta H°_{CO2} = -285.81\mathbf{-692.4948}-(2*-285.85-413.7976) = 9.7576$..........${}^{kJ}/_{mol}$;
$\Delta S_{dispersed} = -\Delta H_{Hess}/T = -9.7576/298.15 = -32.727$.......${}^{J}/_{mol/K}$; **endothermic**.........................
2. $\Delta S_{Hess} = \Delta S°_{H3O} + \Delta S°_{HCO3} - 2\Delta S°_{H2O} - \Delta S°_{CO2} = -3.854 + 98.324 - (2*69.9565 + 117.5704) = -163.0134$..........${}^{J}/_{mol/K}$;
$\Delta S_{total} = \Delta S_{Hess} + \Delta S_{dispersed} = -32.727 - 163.0134 = -195.169$........${}^{J}/_{mol/K}$;
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 $T\Delta Sn \leftarrow$ <u>accumulated free energy</u> **endoergic**...........
3. $\Delta G_{Hess} = \Delta G°_{H3O} + \Delta G°_{HCO3} - 2\Delta G°_{H2O} - \Delta G°_{CO2} = -213.2746\mathbf{-544.9688}-(2*-237.191-385.98) = 102\ {}^{kJ}/_{mol}$;
$\Delta G_{Absolute} = G_{H3O} + G_{HCO3} - (2G_{H2O} + G_{CO2qua}) = 22.44 + 46.08 - (2*0 + 8.379) = \mathbf{60.14}\ {}^{kJ}/_{mol}$ ;

Thermodynamic unfavored $\dfrac{[HCO_3^-]_{aqua}\cdot[H_3O^+]}{[CO_2]_{aqua}\cdot[H_2O]^2} = K_{eqCA} = K_{HCO3}/[H_2O]^2 = 10^{\wedge(-7.0512)}/55.3457339^{\wedge 2} = 2.906*10^{-11}$

$\Delta G_{eqCA} = -R\bullet T\bullet \ln(K_{eqCA}) = -8.3144*298.15*\ln(2.906*10^{\wedge(-11)}) = \mathbf{60.}14\ {}^{kJ}/_{mol}$.
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 $\Delta G_{min}$ 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 $CO_{2aqua} + OH^- => HCO_3^- + \Delta G(\mathbf{-39.7}\ {}^{kJ}/_{mol}) + \Delta H(\mathbf{-48.68}\ {}^{kJ}/_{mol})$.
$\Delta H_{Hess} = \Delta H°_{HCO3} - \Delta H°_{CO2} - \Delta H°_{OH} = \mathbf{-692.4948}-(-413.7976-230.015) = \mathbf{-48.68}\ {}^{kJ}/_{mol}$; **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. $\Delta S_{Hess} = \Delta S°_{HCO3} - \Delta S°_{CO2} - \Delta S°_{OH} = \mathbf{-494.768}-(117.5704-10.9) = \mathbf{-601.44}\ {}^{J}/_{mol/K}$;
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 $T\Delta Sn \leftarrow$ <u>accumulated</u> energy in products .
3. $\Delta G_{Hess} = \Delta G°_{HCO3} - \Delta G°_{CO2} - \Delta G°_{OH} = \mathbf{-544.9688}-(-385.98-157.2) = -1.7888\ {}^{kJ}/_{mol}$; 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

$$\frac{[HCO_3^-]}{[CO_2]_{aqua}\cdot[OH^-]}$$

$K_{eqOH} = K_{eqCA}/K_{H2O} = 2.993*10^{\wedge}(^{-11})/3.26/10^{\wedge(-18)} = 9180981.6$; Reversible CA present;
$= K_{eqOH} = K_{eqCA}/K_{H2O} = 9180981.6$; Ratio $K_{eqOH}[OH^-] = 9180981.6*10^{\wedge(-6.64)} = 2.103 =$
$\Delta G_{OH} = -R\bullet T\bullet \ln(K_{eqOH}[OH^-]) = -8.3144*298.15*\ln(2.1032413768)/1000 = \mathbf{-1.84}\ {}^{kJ}/_{mol}$

$$\frac{[HCO_3^-]}{[CO_2]_{aqua}}$$

$[HCO_3^-] = K_{eq}[OH^-]*[CO_{2aqua}] = 2.103*0.00075125 = 0.00158$ 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,):

$[\mathbf{CO_2}_{aqua}]=\mathbf{K}_{eq}*[\mathbf{CO_2}{\uparrow}_{air}]=1{,}878*0{,}0004=0{,}0007512$ 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 direct for oxidation$\mathbf{\Rightarrow H_3O^+ + HCO_3^-} \Rightarrow \mathbf{CO_2}_{aqua}+2\mathbf{H_2O+Q}+\mathbf{\Delta G}$

| *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 |

$\Delta G_{Hess}=2\Delta G°_{\mathbf{H2O}}+\Delta G°_{\mathbf{CO2}}-\Delta G°_{\mathbf{H3O}}-\Delta G°_{\mathbf{HCO3}}=\mathbf{-102}\ ^{kJ}/_{mol}$

$=2*-237{,}191-385{,}98-(-213{,}2746\mathbf{-544{,}9688})=\mathbf{-102}\ ^{kJ}/_{mol}$;

$\Delta H_H=2\Delta H°_{\mathbf{H2O}}+\Delta H°_{\mathbf{CO2}}-\Delta H°_{\mathbf{H3O}}-\Delta H°_{\mathbf{HCO3}}=\mathbf{-7{,}1928}\ ^{kJ}/_{mol}$

$=2*-285{,}85-413{,}7976-(-285{,}81\mathbf{-692{,}4948})=\mathbf{-7{,}1928}\ ^{kJ}/_{mol}$

$\Delta S_{dispersed}=-\Delta H_{Hess}/T=\mathbf{7{,}1928}/298{,}15=\mathbf{24{,}125}\ ^{J}/_{mol/K}$;

$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}=\mathbf{756{,}1054+24{,}125=780{,}23}\ ^{J}/_{mol/K}$;

$\Delta G_H=\Delta H_H-T*\Delta S_H=\mathbf{-7{,}193}-298{,}15*0{,}\mathbf{7561=-232{,}6}\ ^{kJ}/_{mol}$ ;

$\Delta S_{Hess}=2\Delta S°_{\mathbf{H2O}}+\Delta S°_{\mathbf{CO2}}-\Delta S°_{\mathbf{H3O}}-\Delta S°_{\mathbf{HCO3}}=\mathbf{756{,}1054}\ ^{J}/_{mol/K}$

$=2*69{,}9565+117{,}5704-(-3{,}854\mathbf{-494{,}768})=\mathbf{756{,}1054}\ ^{J}/_{mol/K}$

$T\bullet\Delta S_{total}=0{,}\mathbf{78023}^{*}298{,}15\ K=\mathbf{232{,}63}\ ^{kJ}/_{mol}$ ; bound TΔSn accumulate energy **endoergic, non spontaneous**

CAII; RBCs, kidney, osteoclasts, eye, GI tract, lung, brain, and testis; Cytosol; Glaucoma, epilepsy, edema, altitude sickness; $\mathbf{k_{cat}}=1{,}4\times10^6(s^{-1})$; $\mathbf{k_{1CO2}}_{aqua}=1{,}5\times10^8(M^{-1}\,s^{-1})$; **Biomed Res Int. 2015**;2015:453543. Review Article **3KS3,**
$\mathbf{v1=k_{1CO2}}_{aqua}[\mathbf{CO_2}_{aqua}]=1{,}5*10^{\wedge 8}*0{,}0007512=112680\ s^{-1}$; as $\mathbf{v1}=k_{cat}/K_M\mathbf{*}[E_i][S_i]$ ; $[E_i]=1$ M; $S_i=[\mathbf{CO_2}_{aqua}]$;

CAII: $\mathbf{CO_2}_{aqua}+2\mathbf{H_2O+\Delta G+Q=v1}\overset{CA}{\underline{\ \ }}\mathbf{>H_3O^+ + HCO_3^-}$ ; pH=7,36,

$k_2=\mathbf{k_{1CO2}}_{aqua}/\mathbf{K}_{eqCA}=1{,}5*10^{\wedge 8}/2{,}9016/10^{\wedge(-11)}=\mathbf{5.17*10^{\wedge 18}}\ s^{-1}=\mathbf{10^{\wedge 18{,}7}\ M^{-2}}s^{-1}$;

Neutralisation velocity constant $k_2=\mathbf{10^{\wedge 18{,}7}\ M^{-2}}s^{-1}$; $H_3O^++HCO_3^-\Rightarrow CO_2{}_{\mathbf{aqua}}\mathbf{+2}H_2O$ **;.**

$K_a=\mathbf{K_{eqCA}*[H_2O]^2=}2{,}902*10^{\wedge(-11)}\mathbf{*}(55{,}3457339)^{\wedge 2}=8{,}892*10^{\wedge(-8)}=10^{\wedge(-7{,}0512)}$; $\mathbf{K_{eqCA}}=\dfrac{[HCO_3^-]\ \cdot[H_3O^+]}{[CO_2]_{aqua}\cdot[H_2O]^2}$

Neutralisation $\mathbf{H_3O^+ + HCO_3^- \Rightarrow CO_2}_{aqua}\mathbf{+2H_2O}$ velocity according bicarbonate concentration in ocean

$pOH_{ocean}=5{,}9$; $pH_{ocean}=8{,}1$; $[HCO_3^-]=0{,}003$ M; Haack Weltmeer Atlas 1969:

$v_2=k_2\mathbf{\bullet}[H_3O^+]\mathbf{[}HCO_3^-\mathbf{]=10^{\wedge 18{,}7}*}10^{\wedge(-8{,}1)}*0{,}003=119432151\ s^{-1}$;

Extra Mitochondrial pH=5 $v_2=k_2\mathbf{\bullet[}H_3O^+\mathbf{][}HCO_3^-\mathbf{]=10^{\wedge 18{,}7}*}10^{\wedge(-5)}*0{,}0154=771828339786\ s^{-1}$;

Neutralisation velocity constant is greater the slow hydroxide anions reaction $\mathbf{k_{1OH}}=1{,}5\times10^2\ M^{-2}s^{-1}$;

$\mathbf{HCO_3^- \Rightarrow CO_2}_{aqua}+\mathbf{OH^-}+\Delta G+Q$ decomposition reaction: $k_{HCO3}=1{,}5*10^{\wedge 2}/9180981{,}6=0{,}000016338\ M^{-1}s^{-1}$;

$K_{eqOH}=k_{1OH}/k_{HCO3}=[HCO_3^-]/[CO_2{}_{aqua}]/[OH^-]=1{,}5*10^2\ M^{-2}s^{-1}/k_{HCO3}=8914110.$

$v_{HCO3}=k_{HCO3}*[HCO_3^-]=0{,}00001683*0{,}0154=0{,}000000259182\ s^{-1}$;

$\mathbf{CO_2}_{aqua}+\mathbf{OH^- \Rightarrow HCO_3^-}$: $v_{1OH}=k_{1OH}*[CO_2{}_{aqua}]*[OH^-]=1{,}5*10^{\wedge 2}*0{,}0076*10^{\wedge(-6{,}63)}=0{,}000000267$; $s^{-1}$;

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** $\mathbf{K_{eqOH}=K_{eqCA}/K}_{H2O}=2{,}993*10^{\wedge(-11)}/3{,}26/10^{\wedge(-18)}=9180981{,}6=\dfrac{[HCO_3^-]}{[CO_2]_{aqua}\cdot[OH^-]}$

$\mathbf{\Delta G_{eqOH}=-R\bullet T\bullet ln(K_{eqOH})}=-8{,}3144*298{,}15*\mathbf{ln}(9180981{,}6)/1000=-39.7\ ^{kJ}/_{mol}$ ; Unfavored equilibrium.

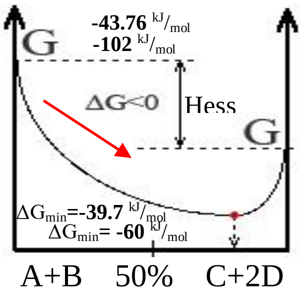
$\Delta G_{Hess}=\Delta G°_{\mathbf{HCO3}}-\Delta G°_{\mathbf{O\ H}}-\Delta G°_{\mathbf{CO2}}=-586{,}93988-(-157{,}2-385{,}98)=-43.76\ ^{kJ}/_{mol}$;

$\mathbf{K_{eqOH}=K_{eqCA}/K}_{H2O}=2{,}993*10^{\wedge(-11)}/3{,}26/10^{\wedge(-18)}=9180981{,}6$; $\mathbf{K_{eqHCO3}=1/K_{eqOH}}=1/9180981{,}6=0.0000001089$;

Neutralisation is faster 34463449218 times over carbonic anhydrase CA driven velocity $\mathbf{k_{1CO2}}_{aqua}=1{,}5*10^8\ M^{-1}\ s^{-1}$;

$1/\mathbf{K}_{eqCA}=k_2/\mathbf{k_{1CO2}}_{aqua}=\mathbf{10^{\wedge 18{,}7}}/1{,}5/10^{\wedge 8}=33412482242$; $\mathbf{K}_{eqCA}=\mathbf{k_{1CO2}}_{aqua}/k_2=1{,}5*10^{\wedge 8}/\mathbf{10^{\wedge 18{,}7}}=2{,}993*10^{\wedge(-11)}$**;**

Exothermic and exoergic neutralization $\mathbf{H_3O^+ + HCO_3^- \Leftrightarrow CO_2}_{aqua}+2\mathbf{H_2O}$ 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 $\mathbf{K_{eqHCO3}=1/K_{eqOH}}=1/9180981{,}6=0.0000001089$ equilibrium mixture $\mathbf{K_{eqOH}=K_{eqCA}/K}_{H2O}=9180981{,}6.$

Le Chatelier principle is Prigogine attractor free energy change minimum reaching $\Delta G_{min}$ at mixture. Free energy minimum reaching establishes equilibrium.

$\mathbf{\Delta G_{1/eqOH}=-R\bullet T\bullet ln(1/K_{eqOH})}=-8{,}3144*298{,}15*\mathbf{ln}(34463449218)/1000=-60\ ^{kJ}/_{mol}$ ;

$\mathbf{CO_2}_{aqua}+\mathbf{OH^-}$ ; $\mathbf{H_3O^+ + HCO_3^-}$ reactants products $CO_2{}_{\mathbf{aqua}}\mathbf{+2}H_2O$**;**

Protolysis of water pH=pOH=7 $G_{H3O++OH-}=G_{H3O+}+G_{OH}=22.44+77.36=99.8\ ^{kJ}/_{mol}$

CA $G_{\mathbf{H3O+HCO3}}=G_{\mathbf{H3O+}}+G_{\mathbf{HCO3-}}=22.44+46.08=\Delta\mathbf{G}_{spCO2aqua}+\Delta\mathbf{G}_{eqCO2aqua}=8.379+60.14=68.52\ ^{kJ}/_{mol}$ . [1,8,14]

# THERMODYNAMICS Exercise VIII Glycine+glycine→ glycylglycine dipeptide synthesis

Calculate $\Delta H_H$ $\Delta S_H$ $\Delta G_H$ 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. $\Delta H_{Hess}=\Delta H^\circ_{\mathbf{GlyGly}}+\Delta H^\circ_{\mathbf{H2O}}-2\,\Delta H^\circ_{\mathbf{Gly}}$=-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 $^{J}/_{mol/K}$;

$\Delta S_{Hess}=\Delta S^\circ_{\mathbf{Gly\text{-}Gly}}+\Delta S^\circ_{\mathbf{H2O}}-2\,\Delta S^\circ_{\mathbf{Gly}}$ =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 COOH 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 $\Delta H_H$ =4,0 $^{kJ}/_{mol}$ ; $\Delta S_H$= -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**

$K_{COOH}=10^{-2,351}=\dfrac{[H^+]\cdot[H_3N^+CH_2COO^-]Gly}{[H_3N^+CH_2COOH]}$ ; $K_{eq}=K_{COOH}/[\mathbf{H_2O}]=10^{-2,351}/55,33=10^{-4,094}=\dfrac{[H_3O^+]\cdot[H_3N^+CH_2COO^-]Gly}{[H_2O]\cdot[H_3N^+CH_2COOH]}$

$\Delta\mathbf{G_{eq}=-R\bullet T\bullet ln(K_{eq})}$=-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; $\Delta H_{Hess}$<=44,2 $^{kJ}/_{mol}$; $\Delta S_{Hess}$<= -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**

$K_{COOH}=10^{-9,78}=\dfrac{[H^+]\cdot[H_2NCH_2COO^-]}{\cdot[H_3^+NCH_2COO^-]Gly}$ ; $K_{eq}=K_{H3N+}/[\mathbf{H_2O}]=10^{-9,78}/55,33=10^{-11,523}=\dfrac{[H_3O^+]\cdot[H_2NCH_2COO^-]}{[H_2O]\cdot[H_3^+NCH_2COO^-]Gly}$

$\Delta\mathbf{G_{eq}=-R\bullet T\bullet ln(K_{eq})}$=-8,3144•298,15•**ln**($10^{-11,523}$)=-65,773+23,37 = **-42,403** $^{kJ}/_{mol}$,

Glycylglycine carboxylic acid COOH protolysis constant: $pK_{COOH}$=3,14;$\Delta H_{Hess}$=0,11 $^{kJ}/_{mol}$; $\Delta S_{Hess}$=-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);

$K_{COOH}=10^{-3,14}=\dfrac{[H^+]\cdot[H_3N^+GlyGlyCOO^-]Gly}{[H_3N^+GlyGly\,COOH]}$ ; $K_{eq}=K_{COOH}/[\mathbf{H_2O}]=10^{-3,14}/55,33=10^{-4,883}=\dfrac{[H_3O^+]\cdot[H_3N^+GlyGlyCOO^-]Gly}{[H_2O]\cdot[H_3N^+GlyGly\,COOH]}$

$\Delta\mathbf{G_{eq}=-R\bullet T\bullet ln(K_{eq})}$=-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; $\Delta H_{Hess}$=43,4 $^{kJ}/_{mol}$; $\Delta S_{Hess}$=-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)=

$K_{H3N+}=10^{-8,265}=\dfrac{[H^+]\cdot[H_2N\,GlyGly\,COO^-]}{[H_3N^+GlyGlyCOO^-]Gly}$ ; $K_{eq}=K_{H3N+}/[\mathbf{H_2O}]=10^{-8,265}/55,33=10^{-10,01}=\dfrac{[H_3O^+]\cdot[H_2N\,GlyGly\,COO^-]}{[H_2O]\cdot[H_3N^+GlyGlyCOO^-]Gly}$

$\Delta\mathbf{G_{eq}=-R\bullet T\bullet ln(K_{eq})}$=-8,3144•298,15•**ln**($10^{-10,01}$)=-57,137+27,873= **-29,262** $^{kJ}/_{mol}$,

| *Substance* | $\Delta H^\circ_H$ $^{kJ}/_{mol}$ | $\Delta S^\circ_H$ $^{J}/_{mol/K}$ | $\Delta G^\circ_H$ $^{kJ}/_{mol}$ | **I=0,1 M** | I=0.2 M | Protolysis increases $\Delta G^\circ_H$ $^{kJ}/_{mol}$ |
|---|---|---|---|---|---|---|
| **Gly**$_{aqua}$ | -554,56 | 76,45 | -180,13 | **-177,07** | -176,08 | =-176,08-**42,403**=-218,48 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **$GlyGly_{aq}$** | -790,99 | -1 | -200,55 | **-195,65** | -194,07 | =-194,07-**29,262**=-223,332 |
| **$Gly_{aqua}$** | **-525,06** | **-1204,952** | **-165,8056 ; I=1 M** | | - | **=-165,8056-42,403=-208,209** |
| **$GlyGly_{aq}$** | **-737,55** | **-1877,952** | **-177,6324 ; I=1 M** | | - | **=-177,6324-29,262=-206,8944** |
| $H_3NCH_2COO$- | **-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** |
| $H_3N$glyglyCOO- | **-738,3** | **-2455,3** | 27,873 | $pK_a$<3,14 | - | 27,873 |
| $H_3N$glyglyCOO- | **-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;

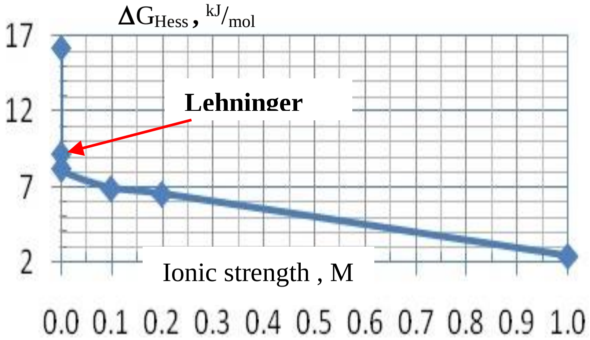
$\Delta S_H=\Delta S°_{GlyGly}+\Delta S°_{H2O}-2\Delta S°_{Gly}$=-1877,952-453,188-(2*-1204,952)=78,764 J/mol/K;=-1933,95-453,188-(2*-1695,3)=1003,5 J/mol/K;

$\Delta S_{disperse}=-\Delta H_H/T$=**-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

$\Delta G_{Hess}$**=46,145-298,15*0,10035=16,2265** kJ/mol protolīze;I=0 M

$\Delta G_{Heq}$=-200,55**-151,549**-(2*-180,13)= **8,161** kJ/mol endoergic;I=0 M

$\Delta G_{Heq}$=**-195,65-151,549**-(2***-177,07**)=**6,941** kJ/mol endoergic;I=0,1 M

$\Delta G_{Heq}$=-194,07**-151,549**-(2*-176,08)=**6,541** kJ/mol endoergic;I=0,2 M

$\Delta G_{Heq}$=**-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 .

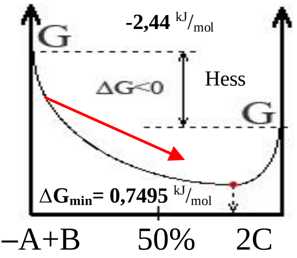
**$K_{0,2M}$=exp(-$\Delta G_{0,2M}$/R/T)**=exp(6541/8,3144/298,15)=13,994;pH=7,36; **$\Delta G_{0,2M}$=**-8,3144*298,15***ln**(14)=**-6,54** kJ/mol

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** **$\Delta G_{min}$= $\Delta G_{0,2M}$=-6,54** kJ/mol; **$K_{0,2M}$=13,994**.

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.

Reactants **$Gly\text{-}Gly_{aqua}+H_2O$=>$Gly_{aqua}+Gly_{aqua}$** products



$\Delta G_{bLehninger}=-R\cdot T\cdot \ln(K_{bLehninger})=-8{,}3144*298{,}15*\ln(220500{,}2)/1000=-30{,}5\ ^{kJ}/_{mol};$

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

$\Delta G_{Lehninger}=-R\cdot T\cdot \ln(K_{Lehninger})=-8{,}3144*298{,}15*\ln(0{,}0001739)/1000=\mathbf{21{,}46}\ ^{kJ}/_{mol}.$

$pH<7{,}199.\ ATP^{3-}+H_2O\Rightarrow ADP^{2-}+H_2PO_4^-;\ K_{Lehninger}=K_{bLehninger}*[H_3O^+]/[H_2O]=0{,}0001739=\dfrac{[H_2PO_4^-]\cdot[ADP^{2-}]}{[H_2O]\cdot[ATP^{3-}]};$

$\Delta G_H=\Delta G°_{ADP3}+\Delta G°_{HPO42}-\Delta G°_{ATP4}-\Delta G°_{H2O}=-1399{,}9-1057{,}143-(-2267{,}64-237{,}191)=\mathbf{47{,}79}\ ^{kJ}/_{mol};$

**b)** $ATP^{4-}+2H_2O\Rightarrow ADP^{3-}+HPO_4^{2-}+H_3O^+;\ \Delta G_{bLehninger}=-30{,}5\ ^{kJ}/_{mol};\ K_{bLehninger}=K_{Lehninger}[H_2O]/[H_3O^+]=220500{,}2;$

$\Delta G_H=\Delta G°_{ADP3}+\Delta G°_{HPO42}+\Delta G°_{H3O}-\Delta G°_{ATP4}-2\Delta G°_{H2O}=-1399{,}9-1057{,}143-213{,}275-(-2267{,}64+2*-151{,}549)=\mathbf{-99{,}58}\ ^{kJ}/_{mol};$

**a)** $Gly_{aq}+Gly_{aq}\Rightarrow Gly\text{-}Gly_{aq}+H_2O;\ \Delta G_{0,2M}=6{,}54\ ^{kJ}/_{mol};\ K_{0,2M}=\exp(-6541/8{,}3144/298{,}15)=\mathbf{0{,}07146}.$

$K_{0,2Mhydrolyse}=1/K_{0,2M}=1/0{,}07146=13{,}994;$

**ab)** $Gly_{aq}+Gly_{aq}+ATP^{4-}+H_2O\Rightarrow GlyGly_{aq}+ADP^{3-}+HPO_4^{2-}+H_3O^+;\Delta G_{ab}=\Delta G_{0,2M}+\Delta G_{bLehninger}=6{,}54-30{,}5=-23{,}96\ ^{kJ}/_{mol};$

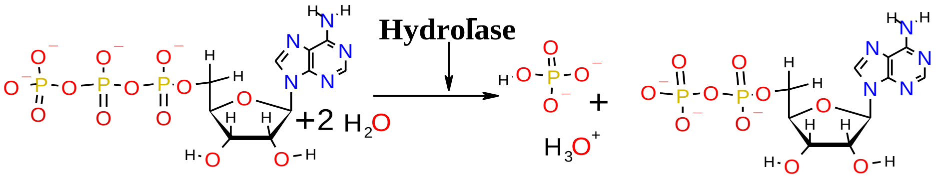
$\Delta G_H=\Delta G°_{Gly\text{-}Gly}+\Delta G°_{ADP3}+\Delta G°_{HPO42}+\Delta G°_{H3O}-2\Delta G°_{Gly}-\Delta G°_{ATP4}-\Delta G°_{H2O}=$

$=-177{,}632-1399{,}9-1057{,}143-213{,}275-(2*-165{,}806-2267{,}64-151{,}549)=\mathbf{-97{,}15}\ ^{kJ}/_{mol};$

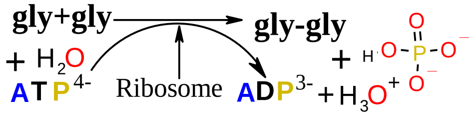
$=-177{,}632-1399{,}9-1057{,}143-213{,}275-(2*-165{,}806-2267{,}64-151{,}549)=-97{,}15\ ^{kJ}/_{mol};$

| *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** |
| $Gly_{aqua}$ | -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)** $Gly_{aq}+Gly_{aq}\Rightarrow Gly\text{-}Gly_{aq}+H_2O;\ \Delta G_{0,2M}=6{,}54\ ^{kJ}/_{mol};$



**ab)** $Gly_{aq}+Gly_{aq}+ATP^{4-}+H_2O\Rightarrow GlyGly_{aq}+ADP^{3-}+HPO_4^{2-}+H_3O^+;$
$\Delta G_{ab}=\Delta G_{0,2M}+\Delta G_{bLehninger}=6{,}54-30{,}5=-23{,}96\ ^{kJ}/_{mol};$
Peptide bond synthesis in Ribosomes.

$K_{eq}=K_{0,2M}K_b=\mathbf{0{,}07146}*220500{,}2=[GlyGly]*[ADP^{3-}]*[HPO_4^{2-}]*[H_3O^+]/[Gly]^2/[ATP^{4-}]/[H_2O]=15756{,}9.$

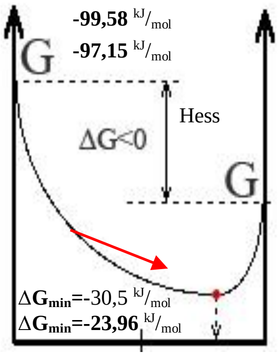
$$K_{eq\_a0,2Mb}=K_{0,2M}K_b=\frac{[H_3N^+GlyGlyCOO^-]Gly\cdot[HPO_4^{2-}]\cdot[ADP^{3-}]\cdot[H_3O^+]}{[H_3N^+CH_2COO^-]Gly^2\cdot[H_2O]\cdot[ATP^{4-}]}=\mathbf{15756{,}944}.$$

$\Delta G_{eqLehninger}=-R\cdot T\cdot \ln(K_{eqLehninger})=-8{,}3144*298{,}15*\ln(15756{,}944)/1000=\mathbf{-23{,}959}\ ^{kJ}/_{mol}.$

$K_{eqLehninger}=K_{Lehninger}[H_2O]/[H_3O^+]=0{,}000012428*55{,}3457/10^{\wedge(-7,36)}=\mathbf{15756{,}944}.$

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 $\Delta G_{min}$ 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 $\Delta H_H$ $\Delta S_H$ $\Delta G_H$ 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; **$\Delta G_H$**= **-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* | $\Delta H^\circ_H$ $^{kJ}/_{mol}$ | $\Delta S^\circ_H$ $^{J}/_{mol/K}$ | $\Delta G^\circ_H$ $^{kJ}/_{mol}$ |
|---|---|---|---|
| **$H_2O$** | -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**

$\Delta G_{ALBERTY}=\Delta G^\circ_{\mathbf{Glc}}+\Delta G^\circ_{\mathbf{Gal}}-\Delta G^\circ_{\mathbf{Lactoze}}-\Delta G^\circ_{\mathbf{H2O}}=\mathbf{-402{,}052-395{,}08-(-625{,}27-151{,}549)}=\mathbf{-20{,}3}$ $^{kJ}/_{mol}$ **exoergic**;

$\Delta G_{ALBERTY}=2\Delta G^\circ_{\mathbf{Glc}}-\Delta G^\circ_{\mathbf{Maltose}}-\Delta G^\circ_{\mathbf{H2O}}=2*\mathbf{-402{,}05-(-632{,}6312-151{,}549)}=\mathbf{-19{,}92}$ $^{kJ}/_{mol}$ **exoergic**;

1. $\Delta H_H=2\Delta H^\circ_{\mathbf{Glc}}-\Delta H^\circ_{\mathbf{MaltoHe}}-\Delta H^\circ_{\mathbf{H2O}}=2*\mathbf{-1267{,}13-(-2247{,}12-151{,}549)}=\mathbf{-135{,}591}$ $^{kJ}/_{mol}$ **exothermic** ;

2. $\Delta S_{disperse}=\Delta H_H/T=\mathbf{-135{,}591}/298{,}15=\mathbf{454{,}774442}$ $^{J}/_{(mol\ K)}$ ;

2. $\Delta S_H=2\Delta S^\circ_{\mathbf{Glc}}-\Delta S^\circ_{\mathbf{Maltose}}-\Delta S^\circ_{\mathbf{H2O}}=2*\mathbf{-2901{,}49-(-5415{,}032-453{,}188)}=\mathbf{65{,}24}$ $^{J}/_{mol/K}$;

3.$\Delta S_{total}=\Delta S_H+\Delta S_{disperse}=\mathbf{454{,}774442+65{,}24}=\mathbf{520{,}0144442}$ $^{J}/_{(mol\ K)}$ ;

$\Delta G_H=\Delta H_H-T*\Delta S_H=\mathbf{-135{,}591}-298{,}15*0{,}\mathbf{06524}=\mathbf{-155{,}0423}$ $^{kJ}/_{mol}$ **exoergic** ;

3. $T\bullet\Delta S_{total}=\mathbf{520{,}0144442}*298{,}15=\mathbf{155{,}0423}$ $^{kJ}/_{mol}$ $T\Delta S_{total}$ bound energy dispersed **spontaneous**.

$\mathbf{K}_{Lehninger}=\mathbf{exp(-\Delta G_{Lehninger}/R/T)}=exp(15500/8{,}3144/298{,}15)=519{,}4=10^{2{,}7155}$

$$K_{eq}=\mathbf{K}_{Lehninge}=519{,}4=\frac{[Glc]\cdot[Glc]}{[Maltose]\cdot[H_2O]}$$

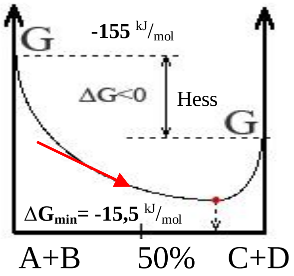
Prigogine attractor minimum $\Delta \mathbf{G_{min}}=\Delta G_{eq}=\mathbf{-19{,}9}$ $^{kJ}/_{mol}$ ; $\Delta G_{Lehninger}$=-15,5 $^{kJ}/_{mol}$; **$\Delta G_{Hess}$**= **-155** $^{kJ}/_{mol}$;

Endothermic and exoergic hydrolysis Hess free energy change negative

$\Delta \mathbf{G_{hydrolysis}}$ = **-155** $^{kJ}/_{mol}$ , but Prigogine attractor favored equilibrium constant

free energy change minimum $\longrightarrow$ $\mathbf{\Delta G_{min}=\Delta G_{eq}=-15{,}5}$ $^{kJ}/_{mol}$;

$$\text{at reaching equilibrium } K_{eq}=\frac{[Glc]\cdot[Glc]}{[Maltose]\cdot[H_2O]}=\mathbf{519{,}4;}$$



Maltose+**$H_2O$**

Reactants and products
Glc+Glc .

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ 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 $\Delta H_H$ $\Delta S_H$ $\Delta G_H$ 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; $\Delta G_{Hess}$= **-20,3** $^{kJ}/_{mol}$ ; I=0,25 M

**BioThermodyn 2006** pH=7,36 <u>reactants</u> <=> <u>products</u> ;

| *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•$\Delta S_{total}$=**520,0144442***298,15=**155,0423** $^{kJ}/_{mol}$ T$\Delta S_{total}$ <u>bound energy dispersed</u> **spontaneous**.

**$K_{Leninger}$=exp(-$\Delta G_{Leninger}$/R/T**)=exp(20300/8,3144/298,15)=3601

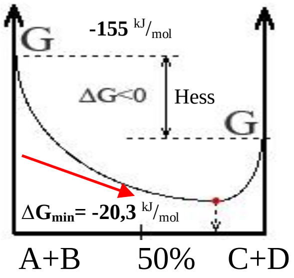
$$K_{eq}=\mathbf{K}_{Leninge}=3601=\frac{[Glc]\cdot[Gal]}{[Laktoze]\cdot[H_2O]}$$

Prigogine attractor minimum $\Delta$**$G_{min}$=**$\Delta G_{eq}$=-15.9 $^{kJ}/_{mol}$ ; $\Delta G_{Lehninger}$=-15,9 $^{kJ}/_{mol}$; **$\Delta G_{Hess}$**= **-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 $\Delta G_{min}$ 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* | $\Delta H°_H$ kJ/mol | $\Delta S°_H$ J/mol/K | $\Delta G°_H$ 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 |

$$Q+H_3O^++HCO_3^-\overset{\underline{\text{channals } H^+;\ HCO_3^-}}{=\!=\!=\!>}H_2O+H_2O_{gas}+CO_{2gas}+\Delta G$$

$\Delta H_H=\Delta H°_{H2O}+\Delta H°_{H2Ogas}+\Delta H°_{CO2gas}-\Delta H°_{H3O}-\Delta H°_{HCO3}=54,546\ ^{kJ}/_{mol}$;

$=-285,85-241,8352-393,509-(-285,81-689,93)=54,546\ ^{kJ}/_{mol}$ **endoth**

$\Delta G_H=\Delta G°_{H2O}+\Delta G°_{H2Ogas}+\Delta G°_{CO2gas}-\Delta G°_{H3O}-\Delta G°_{HCO3}=-59,935\ ^{kJ}/_{mol}$

$=-237,191-228,6-394,359-(-213,275-586,94)=-59,935\ ^{kJ}/_{mol}$ **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**

$\Delta S_{Hess}=\Delta S°_{H2O}+\Delta S°_{H2O}\uparrow_{gas}+\Delta S°_{CO2}\uparrow_{gas}-\Delta S°_{H3O}-\Delta S°_{HCO3}=377,966\ ^{J}/_{mol/K}$

$=69,956+188,74+213,74-(-3,854+98,324)=353,652-94.47=+377,966\ ^{J}/_{mol/K}$;

$T\bullet\Delta S_{total=}195,016\ ^{J}/K/_{mol}\bullet 298,15\ K=$**+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 **$HCO_3^-$**: $\Delta G_{HCO3}=RT\ln([HCO_3^-]_{right}/[HCO_3^-]_{left})$

$\Delta S_H=-R\ln(10^{-5,5}/0,02754)=75,42909\ ^{J}/_{mol/K}$...............

$\Delta S_{HCO3}=-R\ln(0,0154/0,0338919)=6,55847$............. $^{J}/_{mol/K}$

$\Delta S_H=377,966+75,42909+6,55847=459,954\ ^{J}/_{mol/K}$..........

$\Delta G_H=RT\ln(10^{-5,5}/0,02754)=-22,48918\ ^{kJ}/_{mol}$.......

$\Delta G_{HCO3}=RT\ln(0,0154/0,0338919)=-1,9554^{kJ}/_{mol}$..........

$\Delta G_H=\Delta H_H-T*\Delta S_H=+54,546-298,15*0,459954=-82,589$..............$^{kJ}/_{mol}$; **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 $\Delta H_H$ $\Delta S_H$ $\Delta G_H$ 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**! **$H_3O^++HCO_3^-\xleftrightarrow{\text{Membrane}}H_2O+H_2CO_3+\Delta G+Q$**.

| *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 |
| **$HCO_3^-$** | -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 |

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

$\Delta G_{Hess}=\Delta H_{Hess}-T\bullet\Delta S_{Hess}$

$H_{Hess}=\Delta H°_{H2O}+\Delta H°_{H2CO3}-\Delta H°_{H3O}-\Delta H°_{HCO3}=$**-7,9952** $^{kJ}/_{mol}$;

$=-285,85-699,65-(-285,81-689,93)=-9.76\ ^{kJ}/_{mol}$ **exothermic**....

=**-286,65**-699,65-(-285,81-**692,4948**)= **-7,9952** $^{kJ}/_{mol}$

$\Delta G_{Hess}=\Delta G°_{H2O}+\Delta G°_{H2CO3}-\Delta G°_{H3O}-\Delta G°_{HCO3}=$**-148,8** $^{kJ}/_{mol}$

$=-237,191-755,47-(-213,275-586,94)=-192,4\ ^{kJ}/_{mol}$ **exoergic**

=**-151,549**-755,47-(-213,275-**544,9688**)=**-148,8** $^{kJ}/_{mol}$ **exoergic**

$\Delta S_{Hess}=\Delta S°_{H2O}+\Delta S°_{H2CO3}-\Delta S°_{H3O}-\Delta S°_{HCO3}=$**232,4** $^{J}/_{mol/K}$;

$=69,956+187-(-3,854+98,324)=162,486\ ^{J}/_{mol/K}$;

$\Delta S_{total}=\Delta S_H+\Delta S_{dispersed}=$**26,816+232,4=259,216** $^{J}/_{mol/K}$; =**-453,188**+187-(-3,854**-494,768**)=**232,4** $^{J}/_{mol/K}$;

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}=$**-7,9952**-298,15*0,**2324**=**-77,3** $^{kJ}/_{mol}$ ; **exoergic**.

$T\bullet\Delta S_{total}=$**0,259216** $^{J}/K/_{mol}\bullet$298,15 K=**+77,3** $^{kJ}/_{mol}$ ; $\Delta S_{dispersed}=-\Delta H_H/T=$**7,9952**/298,15=**26,82** $^{J}/_{mol/K}$;

bound TΔSn← <u>dispersed-lost energy into products and surrounding</u>

THERMODYNAMICS Exercise XIII, XIV. $O_2\uparrow$gas respiration through membrane aquaporins to form $O_{2aqua-Blood}$

AIR $O_2\uparrow$gas assimilation reaction for human body respiration through membrane aquaporins to form concentration. **endoergic $\Delta G$+$O_2\uparrow_{gas\ AIR}$+$H_2O\overset{Aquporin}{=>}O_{2aqua-Blood}$+Q** ; **$O_{2aqua}$+Q=>$O_{2gas}$+$H_2O$+$\Delta G$ exoergic**

| *Substance* | $\Delta H°_H$ kJ/mol | $\Delta S°_H$ J/mol/K | $\Delta G°_H$ kJ/mol |
|---|---|---|---|
| ***$O_{2aqua}$*** | **-11.70** | **-94,2** | **16,40** |
| ***$O_{2aqua}$*** | -11.715 | 110,876 | 16,4 |
| **$O_2\uparrow_{gas}$** | 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** |

$\Delta G_{Hess}=\Delta G°_{O2aqua}-\Delta G°_{O2gas}-\Delta G°_{H2O}=\mathbf{16.4}-(0-\mathbf{151,549})=\mathbf{168}$ kJ/mol;

Alberty [8];$\Delta G_{HAlberty}=G_{O2aqua}-G_{O2gas}-G_{H2O}=\mathbf{330-303-0=27}$ kJ/mol;

$\Delta H_H=\Delta H°_{O2aqua}-\Delta H°_{O2gas}-\Delta H°_{H2O}=\mathbf{-11.7}-0+\mathbf{286,65=274,95}$ kJ/mol;

$\Delta S_{dispersed}=-\Delta H_{Hess}/T=\mathbf{-274,95}/298.15=\mathbf{-922,2}$ J/mol/K ;

$\Delta S_{Hess}=\Delta S°_{O2aq}-\Delta S°_{O2gas}-\Delta S°_{H2O}=\mathbf{-164,2}$ J/mol/K

$=110,876-205,152-69,9565=\mathbf{-164,2}$ J/mol/K

$\Delta G_H=\Delta H_H-T*\Delta S_H=\mathbf{274,95}-298,15*-0,\mathbf{1642=323,9}$ kJ/mol **endoergic**;

$\Delta S_{total}=\Delta S_H+\Delta S_{izkliede}=-164,2\ \mathbf{-922,2}=-1086,4$ J/mol/K ;

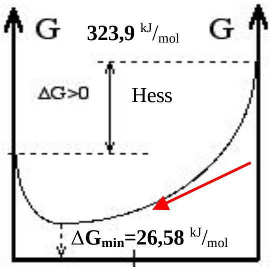
$T\bullet\Delta S_{kopējā}=-1,0864$ kJ/K/mol•298,15K= **-323,9** kJ/mol; bound TΔSn← accumulate energy non-**spontaneous**

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 $\mathbf{K_{sp}}=\frac{[O_{2\ aqua}]}{[O_{2\ gas}]\cdot[H_2O]}=\mathbf{K_{O2}}/[\mathbf{H_2O}]=1.22*10^{-3}/55.3=2.205*10^{-5}$ and ratio $\frac{[O_{2\ aqua}]}{[O_{2\ gas}]}=\mathbf{K_{O2}}$ 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 $\mathbf{\Delta G_{sp}=-R\bullet T\bullet ln(K_{sp})}=-8.3144*298.15*\ln(2.205*10^{-5})=-8.3144*298.15*6.414=\mathbf{26.58}$ kJ/mol;

Hess law **is** exothermic and endoergic oxygen water solubility free energy change positive $\mathbf{\Delta G_{solubility}=323,9}$ kJ/mol ,



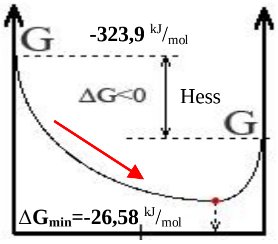
A+B 50% C+D
reactants $O_2\uparrow_{gas}+H_2O$
product $O_{2aqua}$.

but minimized at equilibrium $\mathbf{K_{sp}}=\frac{[O_{2\ aqua}]}{[O_{2\ gas}]\cdot[H_2O]}=2.205*10^{-5}=10^{-4.66}$ free energy change value $\mathbf{\Delta G_{min}=\Delta G_{eq}=26.58}$ kJ/mol . Le Chatelier principle is Prigogine attractor for free energy change minimum $\Delta G_{min}$ reaching the equilibrium.

Evapration $\mathbf{K_{eq}}=\frac{[O_{2\ gas}]\cdot[H_2O]}{[O_{2\ aqua}]}=[\mathbf{H_2O}]/\mathbf{K_{O2}}=55,3457339/1,22/10^{\wedge(-3)}=45365,4$;

Hess endothermic and exoergic oxygen $O_{2gas}$ evaporation free energy change is negative $\mathbf{\Delta G_{Hess}=-323,9}$ kJ/mol , but minimized by evaporation equilibrium state $\mathbf{\Delta G_{min}=\Delta G_{eq}=-R\bullet T\bullet ln(K_{eq})}=-8,3144*298,15*\ln(45365,35566)=\mathbf{-26,58}$ kJ/mol reaching the equilibrium state $\mathbf{K_{eq}}=45365,4$ - the Prigogine attractor for non equilibrium states. Free energy change minimum reaching establishes equilibrium. Solubility from air $\mathbf{[O_{2aqua}]}=9.77\cdot10^{-5}$ 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 $\mathbf{K_{O2Asins}}=[O_{2aqua}]/[O_{2gas}]=9.768\cdot10^{-5}/0.2095=4.663*10^{-4}=10^{-3.3314}=10^{pK}$ 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 $\Delta H_H=\Delta H°_{O2gas}+\Delta H°_{H2O}-\Delta H°_{O2aqua}=\mathbf{-286,65+0-11,7=-274,95}$ kJ/mol is exothermic exoergic $\Delta G_H=\Delta H_H-T*\Delta S_H=\mathbf{11.7}-298.15*\mathbf{0.399352=-77.55}$ kJ/mol.

Alberty [8] free energy for hydrogen gas $G°_{H2gas}=\mathbf{85.64}$ kJ/mol lets appreciate oxygen Free energy for gas and aqua $G_{O2gas}=\mathbf{303.1}$ kJ/mol and $G_{O2aqua}=\mathbf{329.68}$ kJ/mol ,

Photosynthesis restore global atmospheric attractor $[O_{2gas\_AIR}]=0.2095$ mol fraction of oxygen. At equilibrium water concentration $[O_{2aqua}]=[O_{2gas\_AIR}]*[\mathbf{H_2O}]/\mathbf{K_{sp}}=0.2095*55.3/45365=0.0002556$ 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 $2H_2O_2 \Rightarrow O_{2aqua}+2H_2O+Q+\Delta G$ ;

| *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 | 0 |
| $G_{CO2gr}$ | $G_{gr}$ | - | **91.26** |
| $CO\uparrow_{gas}$ | -110.525 | 197.674 | -137.2 |
| $CO_2\uparrow_{gas}$ | **-393.5** | **2.9** | **-394.36** |
| $CO_{2aq}$ | -413.8 | 117.5704 | -385.98 |
| $HCO_3^-$ | **-692.495** | **-494.768** | **-544.9688** |
| $H_{2aq}$ | **-5.02** | **-363.92** | **103.24** |
| $H_{2gas}$ | **-0.82** | **-283.82** | **85.64** |
| $H_{2gas}$ | 0 | 130.68 | 0 |
| $H_{atomic}$ | 218.0 | 114.7 | 203.3 |
| $OH^-$ | -230.00 | -10.539 | -157.2 |
| $O_2\uparrow_{gas}$ | 0 | 205.152 | 0 |
| $O_{2aqua}$ | -11.715 | 110.876 | 16.4 |
| $O_{2aqua}$ | **-11.7** | **-94.2** | **16.4** |
| $H_2O_{2aqua}$ | **-191.99** | **-481.688** | **-48.39** |
| $H_2O_{2(aq)}$ | -191.17 | 143.9 | -134.03 |
| $H_2O$ | -285.85 | 69.9565 | -237.191 |
| $H_2O$ | **-286.65** | **-453.188** | **-151.549** |
| $H_2O\uparrow_{gas}$ | -241.8352 | 188.74024 | -228.6 |
| $CH_{4aq}$ | **-90.69** | **-763.476** | **136.95** |
| $CH_{4gas}$ | **-76.46** | **-648.44** | **120.56** |
| $CH_{4gas}$ | -74.6 | 186.3 | -50.5 |

$\Delta G_{eqStandard}=(E^\circ_{Red}-E^\circ_{Ox})*F*n=(0.89916 -2.08366)* 96485*2=-228.6$ kJ/mol

$\Delta G_{eqStandard}=G_{O2\ aqua}+G_{O2sp}+2*G_{H2OBioChemistry}-2*G_{H2O2}=-228.6$ kJ/mol;

carbon (graphite) $G_{gr}=91.26$ kJ/mol;

$=303.1+26.58+2*85.65-(2*G_{H2O2})=-228.6$ kJ/mol; **Alberty**

$G_{H2O2}=(G_{O2aqua}+G_{O2sp}+2G_{H2O\_Biochemistry}-\Delta G_{eqStandard})/2=364.79$ kJ/mol

$364.79$ kJ/mol $=729.58/2=(303.1+26.58+2*85.65+228.6)/2=\Delta G_{H2O2}$;

$G_{CgrCH4gas}=G_{CO2gr}=-G_{Hess\_CO2gas}-G_{O2gas}=394.36-\underline{303.1}=91.26$ kJ/mol ;

$G^\circ_{H2aq}=\underline{103.24}$ kJ/mol; **Alberty** R.A. Biochem. Thermodynamic's, 2006.

$G^\circ_{H2gas}=\underline{85.64}$ kJ/mol; **Alberty** R.A. Biochem. Thermodynamic's, 2006

$G_{O2gas}=303.1$ kJ/mol; $H_{2gas}+1/2O_{2gas}\Rightarrow H_2O$; $G^\circ_{H2O}=-237.19$ kJ/mol;

$2H_{2gas}+O_{2aqua}\Rightarrow 2H_2O\Leftrightarrow H_3O^++OH^-$;

$\Delta G_{eqH2gas+O2gas}=(2G_{H2O}-2G^\circ_{H2gas}-G_{O2gas})/2=-474.38/2=-237.19$ kJ/mol ;

$\Delta G^\circ_{H2OHess}=2*0-2*85.64-303.1=-474.38/2=-237.19$ kJ/mol;

$G_{O2gas}=(-\Delta G^\circ_{H2OHess}-G^\circ_{H2gas})*2=(237.19-\underline{85.64})*2=\underline{303.1}$ kJ/mol;

Oxygen aqua $G_{O2aqua}=G_{O2gas}+G_{O2sp}=303.1+26.58=329.68$ kJ/mol ;

$G_{O2sp}=-\underline{R\bullet T\bullet\ln(K_{sp})}=26.58$ kJ/mo ; $\underline{K_{sp}}=2.205*10^{-5}$ ; 3rd page;[14]

$\Delta G_{HessH2O}=G^\circ_{H2O}-(-_{Hess}G^\circ_{H2}-_{Hess}G^\circ_{O2gas}/2)=-237.19-(0+0)=-237.19$ kJ/mol

BioChemic background zero $G_{CO2gasO2}=G_{H2O}=0$ kJ/mol;

$2G_{OH-}-G_{H2aq}-G_{O2aqua}=2G_{OH-}-103.24-329.68=$

$H_{2aq}+O_{2aq}+2e^-<=>2OH^-$; $E^\circ_{H2aqO2aq=2OH-}=???$ Volts

**BioTherm2006** Alberty R.A. $G_{H2O\_Biochemistry}=85,65$ kJ/mol

**BioTherm2006** Alberty R.A. Biochem. Thermodynamic's 463, 2006

$_{Hess}G_{O2gas}=0$; $_{Hess}G^\circ_{H2}=0$; $_{Hess}G^\circ_{gr}=0$; $_{Hess}G^\circ_{N2gas}=0$; $_{Hess}G^\circ_{Srombic}=0$;

Red $H_2O_2+2H_2O=O_{2aqua}+2H_3O^++2e^-$ ; absolūtā $E^\circ_{H2O2aqRed}=0,4495$ V Alberta University classic $E^\circ_{H2O2}=0,7975$ V;

$E_{Red}=E^\circ_{H2O2}+0,0591/2\bullet lg([O_{2aqua}]*[H_3O^+]^2/[H_2O_2]/[H_2O]^2)=0,4495+0,0591/2*lg(6*10^{\wedge(-5)}*10^{\wedge(-7,36*2)}/1/55,3^{\wedge2})=0,23643$ V

Oks $H_2O_2+2H_3O^++2e=4H_2O$;$E^\circ_{H2O2aqOx}=1,6855$ V [18];$[H_2O_2]=1$ M; $[O_{2aqua}]=6*10^{-5}$ M, $[H_3O^+]=10^{-7,36}$ M, $[H_2O]=55,3$ M

$E_{Ox}=E^\circ_{H2O2Ox}+0,0591/2\bullet log([H_2O]^4/[H_2O_2]/[H_3O^+]^2)=2,08366+0,0591/2*log(55,3\wedge4/10\wedge(-7,36*2)*1)=1,443$ V;

$\Delta G_{eqStandart}=(E_{Red}-E_{oOx})*F*n=(0,4495-1,6855)*96485*2=(-1,236)*96485*2=-238,51$ kJ/mol

$\Delta G_{Alberty}=-238,51$ kJ/mol; $\underline{G_{StandartaH2O2}=G_{O2aqua}+2*G_{H2O}+\Delta G_{Alberty}=(330+2*0+238,51)/2=568,5/2=284,25}$ kJ/mol ;

$\Delta G_{eqBioChem}=(E_{Red}-E_{oOx})*F*n=(-0,2132-1,0455)*96485*2=(-1,2066)*96485*2=-242,9......$ kJ/mol ;

$2*G_{H2O2}=G_{O2Biochem\_arteriaj}+2*G_{H2OBioChemistry}+\Delta G_{Alberty}\underline{=330+2*0+238,51=2*284,5=568,5}$ kJ/mol;;

Solubility $H_{2gas}+H_2O\Rightarrow H_{2aq}$ $\Delta G_{H2spAlberty}=G_{H2aq}-G_{H2gas}-G_{H2O\ Biochem}=103,24-85,64-85,6=-68,05$ kJ/mol **Alberty**:
$[H_{2aq}]/[H_{2gas}]/[H_2O]=K_{sp}=EXP(-\Delta G_{H2spAlberty}/R/T)=EXP(68050/8,3144/298,15)=10^{\wedge11,9}$. [8] **Alberty**
Solubility spontaneouse $[H_{2aq}]=K_{sp}*[H_2O]=10^{\wedge11,9}*55,3=10^{\wedge13,6}$ M, if $H_{2gas}$ mol fraction is one $[H_{2gas}]=1$ 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 $\Delta G_{Hess(Pt)H}=G_{H3O+}+G_{(Pt)}+G_{e-}-(G_{H2O}+G_{H(Pt)})=22,44+28,525+0-(0+41,2)=\underline{9,765}$ kJ/mol.
$\Delta G_{eq(Pt)H}=E^\circ_H\bullet F\bullet1=0.10166*96485/1000=9.81$ kJ/mol give equilibrium free energy change minimum of metallic hydrogen $\underline{(Pt)H}$ oxidation on zero scale $G_{(Pt)}+G_{e-}=G_{H2O}=G_{CO2gas}=0$ kJ/mol of indifferent $\underline{(Pt),}$ $+e^-$, water and $CO_{2gas}$ .
Hydrogen electrode thermodynamic standard potential $E^\circ_H=0.10166$ V is over classic zero $E^\circ_{Hclassic}=0$ Volts.
**Red:** $H_{2aq}+2\underline{(Pt)}\Leftrightarrow2\underline{(Pt)H}+H_2O$; $\Delta G_{Hess\_šķ(Pt)H}=2G_{H(Pt)}+G_{H2O}-(G_{H2aq}+2G_{(Pt)})=2*51,05+0-(103,24+2*38,375)=-\underline{77,89}$ kJ/mol.
$E^\circ_{H3O+}=-77,89*1000/96485/2=-0,4036$ V; $H_{2aq}+2\underline{(Pt)}\Leftrightarrow2\underline{(Pt)H}+H_2O$; $2H_3O^++2e^-\Leftrightarrow H_{2aq}+2H_2O$;
$K_{šķ(Pt)H}=[H_2O]*[\underline{(Pt)H}]^2/[H_{2aq}]/[\underline{(Pt)}]^2=EXP(-\Delta G_{(Pt)H}/R/T)=EXP(77890/8,3144/298,15=10^{13,65}$. [8]
**Ox:** $2H_3O^++2e^-+H_2O\Leftrightarrow H_{2aq}+2H_2O$;$\Delta G_{Hess\_H3O+}=2G_{H3O+}+2G_{e-}-(G_{H2aq}+G_{H2O})=-\underline{58,12}$ kJ/mol;$E^\circ_{H3O+}=-58,36*1000/96485/2=-0,302$ V
$\Delta E^\circ_{eqH3O+}=-0,4036-(-0,302)=0,40366$ V; $\Delta G_{eqH3O+}=\Delta E^\circ_{H3O+}\bullet F\bullet2=0,40366*96485*2=77,89$ kJ/mol; Metal hydrogen insoluble
$2\underline{(Pt)H}+H_2O\Leftrightarrow H_{2aq}+2\underline{(Pt)}$;$K_{šķ(Pt)H}=[H_{2aq}]/[\underline{(Pt)}]^2[H_2O]*[\underline{(Pt)H}]^2=EXP(-\Delta G_{(Pt)H}/R/T)=EXP(-77890/8,3144/298,15=10^{\wedge(-13,65)}$:
$\Delta G_{sp(Pt)H}=E^\circ_{sp(Pt)H}\bullet F\bullet2=-0.109*96485*2/1000=-21.0$ kJ/mol; $E^\circ_{sp(Pt)H}=-21.03*1000/2/96485=-0.109$ V; The mol fraction of Metallic hydrogen is one $[\underline{(Pt)H}]=1$ and $[\underline{(Pt)H}]^2=1$. The metallic hydrogen (Pt)H $[H_{2aq}]=K_{sp}*[H_2O]=10^{\wedge11,9}*55,3=10^{\wedge13,6}$ M created concentration and gas $[H_{2aq}]=K_{sp}*[H_2O]=10^{\wedge11,9}*55,3=10^{\wedge13,6}$ M hydrogen solubility, if $H_{2gas}$ mol fraction is one $[H_{2gas}]=1$ pure gas. 0,000771899 M in water, than minimal is $[H_{2gas}]=0,000771899$ M$/10^{\wedge13,6}$ 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

$$NADP^+ + NADH + H_3O^+_{in} + Q(\text{weak}) \xrightarrow{\text{Membrane}} NADPH + NAD^+ + H_3O^+_{out} + \Delta G(\text{weak});$$

| *Substance* | $\Delta H^\circ_H$, kJ/mol | $\Delta S^\circ_H$, J/mol/K | $\Delta G^\circ_H$ 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

$\Delta H_{Hess} = \Delta H^\circ_{NADPH} + \Delta H^\circ_{NAD} - \Delta H^\circ_{NADP} - \Delta H^\circ_{NADH} = 4{,}4$ 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

$\Delta S_H = \Delta S^\circ_{NADPH} + \Delta S^\circ_{NAD} - \Delta S^\circ_{NADP} - \Delta S^\circ_{NADH} = -4465{,}708-3766{,}008-(-4166{,}096-4081{,}784) = 16{,}164$ 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**.

$\Delta G_{Hess} = \Delta G^\circ_{NADPH} + \Delta G^\circ_{NAD} - \Delta G^\circ_{NADP} - \Delta G^\circ_{NADH} = 290{,}6776+1112{,}534-(228{,}052+1175{,}5732) = -0{,}4136$ 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 $E^\circ_{NADP} = -0{,}4135$ V;

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

$$NADP^+ + NADH + H_3O^+_{in} + Q(\text{weak}) \xrightarrow{\text{Membrane}} NADPH + NAD^+ + H_3O^+_{out} + \Delta G(\text{weak});$$

$$\Delta E^\circ = E^\circ_{NADH} - E^\circ_{NADH} = -0{,}4095-(-0{,}4135) = 0{,}004\ \text{V},\ n\ \text{is}\ 2;$$

$$\Delta G_{eq} = \Delta E^\circ \bullet F \bullet n = 0{,}004\ \text{V} \bullet 2\ \text{mol} \bullet 96485\ \text{C/mol} = (-0{,}4095-(-0{,}4135))^*2^*96485 = -R \bullet T \bullet \ln(K_{eq}) = 0{,}77188\ \text{kJ/mol}$$

$$\text{EXP}(-\Delta G_{eq\text{Aerobic}}/R/T) = \text{EXP}(-771{,}88/8{,}3144/298{,}15) = 0{,}7324 = K_{eq\text{Aerobic}};$$

$$K_{eq\text{Aerobic}} = \frac{[NAD^+] \cdot [NADPH] \cdot [H_3O^+]}{[NADH]\,[NADP^+]\,[H_3O^+]} = e^{-\frac{\Delta G_{eq\text{Aerobic}}}{R \bullet T}} = e^{-\frac{771{,}88}{8.314 \bullet 298.15}} = 0{,}7324;$$

Mitochondria channels

$H^+$ : $\Delta G_H = RT\ln([H_3O^+]_{right}/[H_3O^+]_{left})$ 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;

$Q + H_3O^+ + HCO_3^- \xrightarrow{\text{channaels } H_2O,\ H^+;\ HCO_3^-} H_2O + H_2O\uparrow_{gas} + CO_2\uparrow_{gas} + \Delta G.\text{exhale } H_2O\uparrow_{gas} + CO_2\uparrow_{gas};$

$\Delta S_{Hess} = \Delta S^\circ_{H2O} + \Delta S^\circ_{H2Ogas} + \Delta S^\circ_{CO2gas} - \Delta S^\circ_{H3O} - \Delta S^\circ_{HCO3} = 69{,}956+188{,}74+213{,}74-(-3{,}854+98{,}324) = 377{,}966$ J/mol/K;

channels $HCO_3^-$: $\Delta G_{HCO3} = RT\ln([HCO_3^-]_{right}/[HCO_3^-]_{left})$

$\Delta S_{HCO3} = 8{,}1344^*\ln(0{,}0154/0{,}0338919) = -6{,}55847$ 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. $NADH+H_3O^+ + O_{2aqua} \xleftrightarrow{FMN(B2vitamin)} NAD^+ + H_2O + H_2O_{2aqua} + Q$

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 |
| $NADH_{(aq)}$ | -1036,66 | -140,5 | - |
| $NADH_{(aq)}$ | **-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** |

$H_3O^+ + O_{2aqua} + NADH \overset{FMN(B2vitamin)}{=>} H_2O_{2aqua} + H_2O + NAD^+ + Q$

**BioChemistry Thermodynamic** 2006 Massachusetts Techn.Inst.

$\Delta H_H = \Delta H°_{H2O2} + \Delta H°_{H2O} + \Delta H°_{NAD} - \Delta H°_{H3O} - \Delta H°_{O2} - \Delta H°_{NADH} = \mathbf{-150}$ kJ/mol

$\Delta H_H = \mathbf{-191{,}99-286{,}65-1010{,}3}-(-285{,}81\mathbf{-11{,}70-1041{,}41}) = \mathbf{-150}$ kJ/mol;

$= -191{,}17-285{,}85-1007{,}48-(-285{,}81-11{,}715-1036{,}66) = 150{,}315$ kJ/mol;

$\Delta S_H = \Delta S°_{H2O2} + \Delta S°_{H2O} + \Delta S°_{NAD} - \Delta S°_{H3O} - \Delta S°_{O2} - \Delta S°_{NADH} = \mathbf{-521{,}05}$ J/mol/K

$= \mathbf{-481{,}688-453{,}188-3766{,}008}-(-3{,}854\mathbf{-94{,}2-4081{,}784}) = \mathbf{-521{,}05}$ J/mol/K;

$= 143{,}9+69{,}9565-183-(-3{,}854+110{,}876-140{,}5) = 64{,}3345$ J/mol/K;

$\Delta G_H = \Delta H_H - T*\Delta S_H = \mathbf{-150{,}02}-298{,}15*\mathbf{-0{,}52105} = \mathbf{5{,}33}$ kJ/mol; **endoergic**

$\Delta G_H = \Delta H_H - T*\Delta S_H = -150{,}315-298{,}15*0{,}064335 = -169{,}5$ kJ/mol; **exoergic**

$\Delta G_{Hess} = \Delta G°_{H2O2} + \Delta G°_{H2O} + \Delta G°_{NAD} - \Delta G°_{H3O} - \Delta G°_{O2} - \Delta G°_{NADH} =$

$\Delta G_{Hess} = -134{,}03+(-237{,}191\mathbf{-151{,}549})/2+\mathbf{1112{,}534}-(-213{,}275+\mathbf{16{,}4+1175{,}5732}) = \mathbf{-194{,}56}$ kJ/mol;;

$\Delta S_{dispersed} = -\Delta H_{Hess}/T = \mathbf{150}/298{,}15 = \mathbf{503{,}1}$ J/mol/K; $\Delta S_{dispersed} = -\Delta H_{Hess}/T = 150{,}315/298{,}15 = 504{,}1$ J/mol/K;

$\Delta S_{total} = \Delta S_{Hess} + \Delta S_{dispersed} = \mathbf{-521{,}1+503{,}1=-18}$ J/mol/K; $\Delta S_{total} = \Delta S_{Hess} + \Delta S_{dispersed} = 64{,}3345+504{,}1 = 568{,}44$ J/mol/K;

$T \bullet \Delta S_{total} = 0{,}5684345$ 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

$H_3O^+ + O_{2aqua} + NADH \overset{FMN(B2vitamin)}{=>} H_2O_{2aqua} + H_2O + NAD^+ + Q + \Delta G$

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: $G_{H2O2} = \underline{\mathbf{284{,}25}}$ kJ/mol; $G_{H3O+} + G_{HOO-} = 22.44 + \mathbf{337{,}8} = 360.24$ kJ/mol;

$\Delta E° = E°^2 - E_{H2O}°^1 = -0{,}4095-0.4495 = \mathbf{-0{,}859}$ **V**, **n** is **2**;

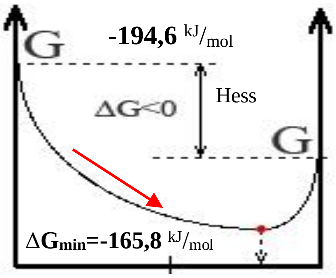
$\Delta G_{eq} = (E°^2 - E_{H2O}°^1) \bullet F \bullet n = \mathbf{-0{,}859*2*96485}$ C/mol $= (-0{,}4095-0.4495)\mathbf{*2*96485}$ C/mol $= -R \bullet T \bullet \ln(K_{eq}) = \mathbf{-165{,}8}$ kJ/mol;

$K_{eq}Aerobic = EXP(-\Delta G_{eq}Aerobi/R/T) = EXP(\mathbf{165761}/8{,}3144/298{,}15) = \mathbf{1{,}097*10^{29}}$;

$$K_{eq}Aerobic = \frac{[NAD^+] \cdot [H_2O_2]_{aqua} \cdot [H_2O]}{[NADH] \cdot [O_2]_{aqua} \cdot [H_3O^+]} = e^{-\frac{\Delta G_{eqAerobi}C}{R \bullet T}} = e^{-\frac{-165761}{8.314 \bullet 298.15}} = \mathbf{1{,}097*10^{29}};$$

Prigogine attractor favored equilibrium by Hess law solution **is** exothermic and exoergic oxidation of NADH free energy change is negative $\Delta G_{Hess}$ = **-194,56** kJ/mol , but minimized constant free energy change value $\Delta G_{min} = \Delta G_{eq} = \mathbf{-165{,}8}$ kJ/mol reaching equilibrium $K_{eq}Aerobic = \mathbf{1{,}097*10^{29}}$ ;

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ 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 $\mathbf{O_{2aqua} + 2H_2O + Q}$

High rate protolysis Peroxide anions $\mathbf{H^+ + HOO^-} >< \mathbf{^-OOH + H^+}$ 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**

$\Delta G_{AlbertyHomeostasis}=G_{O2Biochem\_arteriaj}+2*G_{H2OBioChemistry}-2*G_{H2O2}=\mathbf{88,04+2*85,64-2*\underline{284,25}=-309,18}$ $^{kJ}/_{mol}$;; **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 $\Delta G_{Hess}$</u>.

**Red**: $H_2O_2 + 2\,H_2O = O_2 + 2\,H_3O^+ + 2\,e^-$ ; $\mathbf{E°_{Red}=E°}_{H2O2}=0.4495$ V Alberta University classic $E_o$ =0,694 V;

**Ox**: $H_2O_2 + 2\,H_3O^+ + 2\,e = 4\,H_2O$ ; $\mathbf{E\,°_{Ox}}=1,6855$ V Suhotina classic $E_o$ =1,776 V

$\mathbf{2H_2O_{2(aq)}} \mathbf{=> O_{2aqua} + 2H_2O + Q + \Delta G}$;

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>$\Delta G_{AlbertyStandart}=G_{O2Biochem\_arteriaj}+2*G_{H2OBioChemistry}-2*G_{H2O2}=\mathbf{78,08+2*85,64-2*284,25=-238,5}$ $^{kJ}/$</u>$_{mol}$; **Alberty**

<u>$2G_{H2O2}=G_{O2aqua}+2*G_{H2O}+\Delta G_{AlbertyStandart}$ $\mathbf{=330+2*0+218,9}=2*\mathbf{284,25=}$</u>$\mathbf{548,9}$ $^{kJ}/_{mol}$;;

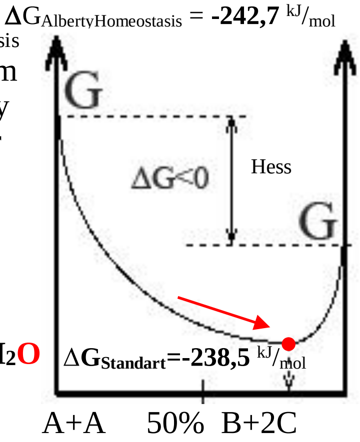
Free energy of activate homeostasis products referring to water and $\mathbf{CO_2}_{gas}$ zero $G_{H2O}=G_{CO2gas}=0$ $^{kJ}/_{mol}$ are peroxide, hydroxonium and anion of peroxide: $G_{H2O2}=\mathbf{\underline{284,25}}$ $^{kJ}/_{mol}$; $G_{H3O+}+G_{HOO-}=22.44+\mathbf{\underline{337,8}}=360,24$ $^{kJ}/_{mol}$

$\Delta G_{eqStandart}=(E_{Red}-E_{oOx})*\mathbf{F*n}=(0,4495-1,6855)*96485*2=(-1,24)*96485*2=\mathbf{-238,5}$ $^{kJ}/_{mol}$ ;

$$\mathbf{K_{eq}}_{Standart}=\frac{[O_2]_{aqua}\cdot[H_2O]^2}{[H_2O_2]^2_{aqua}}=\mathbf{K_{H2O2}=exp(-\Delta G_{eq}/R/T)}=exp(238510/8.3144/298.15)=10^{41,75}........$$

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 $\mathbf{K_{eq}}_{BioChem}=10^{41}$ Le Chatelier principle is Prigogine attractor free energy change minimum $\Delta G_{min}$ 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_$\mathbf{O_{2aqua}+2H_2O}$



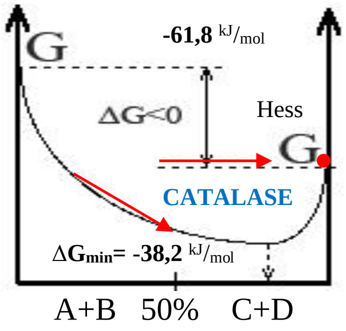
THERMODYNAMICS Exercise VII a succinat**SCoA**$^{4-}$ **$O_2$ $H_2O_2$** fumarate dehydrogenation reaction

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$^{2-}$+2$H_2O$=Fumarate$^{2-}$+2$H_3O^+$ +2e$^-$; E° $_{Red}$**=0.2512 V Lehninger 2000; Univ.Alberta 1997;
**Ox**: **$O_{2aqua}$+2$H_3O^+$+2e$^-$=$H_2O_{2aqua}$+2$H_2O$; E° $_{Ox}$**=0,4495 V; ΔE=(**E° $_{Red}$-E° $_{Ox}$**)=( 0,2512-0,4495)=-0,1983 V;
**$\Delta G_{min}=\Delta G_{eq}$**=(**E°$_{RedSuccinate}$-E°$_{OxO2}$**)***F*n**=(0,2512-0,4495)*96485*2=(-0,1983)* 96485*2=**-38,3** $^{kJ}/_{mol}$;
**$K_{eq}$**=**exp(-$\Delta G_{eq}$/R/T**)=exp(**38270**/8,3144/298,15)=5065991 **labvēlīgs** līdzsvars.
$\Delta G_{Hess}=\Delta G°_{H2O2}+\Delta G°_{fumarat}-\Delta G°_{O2}-\Delta G°_{Succinat}$=**-48,39-519,4688-(16,4-522,414)** = **-61,845** $^{kJ}/_{mol}$;

| *Substance* | $\Delta H°_{Hess}$, $^{kJ}/_{mol}$ | $\Delta S°_{Hess}$, $^{J}/_{mol/K}$ | $\Delta G°_{Hess}$, $^{kJ}/_{mol}$ |
|---|---|---|---|
| **$H_3O^+$** | -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** |

**$\Delta G_H=\Delta H_H-T*\Delta S_H$=-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 $\Delta G_{Hess}$ is negative **-61,8** $^{kJ}/_{mol}$ , but reachied minimum at equilibrium mixture **$\Delta G_{min}=\Delta G_{eq}$=-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 $\Delta G_{min}$

$$\text{at equilibrium mixture : } K_{eq}=\frac{[\text{Fumarate}^{2-}]\cdot[H_2O_2]\swarrow \text{CATALASE}}{[\text{Succinate}^{2-}]\cdot[O_2]}=5065991.$$

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;**
$\Delta G_{Hess}=\Delta G°_{UbiQuinOx}+\Delta G°_{H2O2}-\Delta G°_{O2}-\Delta G°_{UbiQuinRed}$=**-3853,8792-48,39-(16,4-3849,6004)**= **-69,07** $^{kJ}/_{mol}$
Ox: **$O_{2aqua}$ +2$H_3O^+$+2e$^-$=$H_2O_{2aqua}$ +2$H_2O$; E° $_{Ox}$**=0,4495 V University Alberta
Red: **Ubiquinol+2$H_2O$ = Ubiquinone+2$H_3O^+$ +2e$^-$; E° $_{Red}$**=0,2656 V Lehninger 2000 ;
**$\Delta G_{min}=\Delta G_{eq}$=(E°$_{Red}$-E°$_{Ox}$)*F*n**=(0,2656-0,4495)*96485*2=(-0,1839)* 96485*2= **-35,49** $^{kJ}/_{mol}$;
**$K_{eq}$**=**exp(-$\Delta G_{eq}$/R/T**)=exp(**35490**/8,3144/298,15)=90471395= 1650539 **labvēlīgs** līdzsvars .

????

Red: **Ubiquinol6+2$H_2O$=Ubiquinone6+2$H_3O^+$+2e**; absolūtais potenciāls **E°$_{Red}$=-1,2435 V**; **E°**$_{klasika}$=-1,05 V CRC 2012 ;
**$\Delta G_{min}=\Delta G_{eq}$=(E°$_{Red}$-E°$_{Ox}$)*F*n**=(**-1,2435**-0,4495)*96485*2=(-1,693)* 96485*2= **-336,6** $^{kJ}/_{mol}$;
**$K_{eq}$**=**exp(-$\Delta G_{eq}$/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>

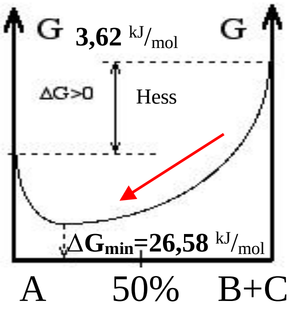
$$\frac{[Fumarat^{2-}]\cdot[H_2O]}{[Malat^{2-}]}=K_{eq}=K_{Lehninge}=\exp(-\Delta G_{eq}/R/T)=\exp(-3100/8{,}3144/298{,}15)=0{,}28635=10^{-0{,}543}$$ **unfavored**

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 $\Delta G_{Hess}$ 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 $\Delta G_{min}$ reacing at equilibrium mixture. Free energy minimum reaching establishes equilibrium.



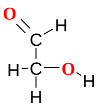
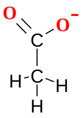
**$Malate^{2-}$** reactant
with **$Fumarate^{2-}$**$+H_2O$

=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(55,34573393^2)= **0,1030** V

## THERMODYNAMICS Exercise XVIII Glycolaldehyde $\mathbf{H_2C(OH)CHO}$ conversion to $\mathbf{H_3CCOO^-}$ $\mathbf{+H_3O^+ +Q}$

Glycolaldehyde $\mathbf{H_2C(OH)CHO}$ conversion to acetate $\mathbf{H_3CC{=}OO^-}$ $\mathbf{+H_3O^+ +Q}$ (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 + $\mathbf{H_3O^+ +Q}$

| *Substance* | $\Delta H^\circ_H$, $^{kJ}/_{mol}$ | $\Delta S^\circ_H$, $^{J}/_{mol/K}$ | $\Delta G^\circ_H$, $^{kJ}/_{mol}$ |
|---|---|---|---|
| $H_2C(OH)CHO$ | -212 | 272,5 | -313,83 |
| $\mathbf{H_2O}$ | **-286,65** | **-453,188** | **-151,549** |
| $\mathbf{H_2O_{(aq)}}$ | -285.85 | 69,9565 | -237,191 |
| $\mathbf{H_3O^+_{(aq)}}$ | -285.81 | -3,854 | -213,275 |
| $\mathbf{H_3CCOOH}$ | -484,3 | 159,8 | -389,9 |
| $\mathbf{H_3CCOO^-}$ | -486,84 | 82,23 | -247,83 |
| $\mathbf{H_3CCOO^-}$ | -485,64 | 87,58 | -369,37 |
| $\mathbf{H_3CCOO^-}$ | **-486** | **85,3** | **-240,963** |

Glycolaldehyde  $\mathbf{+H_2O}$=>  $\mathbf{+H_3O^+ +\Delta G+Q}$

$\mathbf{H_2C(OH)CHO+H_2O{=>}H_3CCOO^- +H_3O^+ +Q+\Delta G}$

$\Delta H_{Hess}=\Delta H^\circ_{H3CCOO-} + \Delta H^\circ_{\mathbf{H3O}} - \Delta H^\circ_{\mathbf{H2O}} + \Delta H^\circ_{H2C(OH)CHO} = {}^{kJ}/_{mol}$

$=-485{,}64-285{,}81-(-212-285{,}85)= -273{,}32-$ $^{kJ}/_{mol}$ **exothermic**

$=\mathbf{-486}-285{,}81-(-212\mathbf{-286{,}65})=$ $\mathbf{-273{,}16-}$ $^{kJ}/_{mol}$ **exothermic**

$\Delta S_{dispersed}=-\Delta H_H/T=\mathbf{273{,}16}/298{,}15=\mathbf{916{,}2}$ $^{J}/_{K/mol}$

$\Delta G_H=\Delta G^\circ_{\mathbf{CH3COO}}+\Delta G^\circ_{\mathbf{H3O}} -\Delta G^\circ_{\mathbf{H2O}}-\Delta G^\circ_{H2C(OH)CHO}=-31{,}624$ $^{kJ}/_{mol}$

$\Delta G_{Hess}=369{,}37-213{,}275-(-237{,}191-313{,}83)=-31{,}624$ $^{kJ}/_{mol}$ ;

$\Delta S_{Hess}=\Delta S^\circ_{\mathbf{CH3COO}}+\Delta S^\circ_{\mathbf{H3O}} -\Delta S^\circ_{\mathbf{H2O}}-\Delta S^\circ_{H2C(OH)CHO}=87{,}58-3{,}854-(69{,}9565+272{,}5)= -258{,}73$ $^{J}/_{mol/K}$ **;**

$\Delta S_{total}=\Delta S_{Hess}+\Delta S_{dispersed}=918{,}966-261{,}014 = 660{,}236$ $^{J}/_{mol/K}$;

$\Delta G_H=\Delta H_H-T^*\Delta S_H=\mathbf{-273{,}16}-298{,}15^*-0{,}25873=-196$ $^{kJ}/_{mol}$ **exoergic**

$T\bullet\Delta S_{total}=660{,}236^*298{,}15\ K= \mathbf{+196}$ $^{kJ}/_{mol}$;

bound $T\Delta Sn\leftarrow$<u>dispersed-lost energy $\Delta G_{reversereaction}$</u><u>$\leftarrow$</u>$Q=273{,}96$ $^{kJ}/_{mol}$.......**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 $2C+2*H_{2gas}+1{,}5O_{2gas}$=> $H_2COHCOOH$ ; $\Delta G_{H2COHCOOH}$=**-403,2968** $^{kJ}/_{mol}$ [8];
$\Delta G_{H2COHCOOH}=G_{H2COHCOOH}-(2G_{Cgraph}+2G_{H2gas}+1{,}5*G_{O2gas})$= **-403,2968** $^{kJ}/_{mol}$;
$G_{H2COHCOOH}$=**-403,2968+(2*91,26+**2***85,6+1,5*303)=404,9232** $^{kJ}/_{mol}$;
Glycolic acid $H_2COHCOOH+H_2O$<=>$H_2COHCOO^-+H_3O^+$; $pK_{a1}$=3,83; Wikipedia
$K_{eq}=[H_2COHCOO^-]*[H_3O^+]/[H_2COHCOOH]/[H_2O]=K_a/[H_2O]=10^{\wedge(-3{,}83)}/55{,}3=2{,}675*10^{\wedge(-6)}=10^{\wedge(-5{,}573)}$;

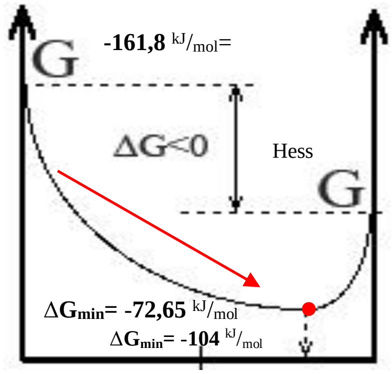
$\Delta G_{eqOHCCOOH}=-R\bullet T\bullet\ln(K_{aeq})=-8{,}3144*298{,}15*\ln(10^{\wedge(-5{,}573)})/1000$=**31,81** $^{kJ}/_{mol}$ .

$\Delta G_{eqOHCCOOH}=G_{OHCCOO}+G_{H3O+}-(G_{OHCCOOH}+G_{H2O})=G_{OHCCOO}$**+22,44-(404,9232+0)= 31,81** $^{kJ}/_{mol}$;
$G_{OHCCOO}=\Delta G_{eqOHCCOOH}-G_{H3O+}+(G_{OHCCOOH}+G_{H2O})$=**31,81-22,44+(404,9232+0)=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** |
| $H_3O^+{}_{(aq)}$ | -285.81 | -3,854 | -213,2746 |
| $NAD^+{}_{(aq)}$ | -1007,48 | -183 | - |
| $NAD^+{}_{(aq)}$ | **-1010,3** | **-3766,008** | **1112,534** |
| $H_3CCOOH$ | -484,09 | 159,83 | -531,743 |
| $H_3CCOO^-$ | -486,84 | 82,23 | -247,83 |
| $H_3CCOO^-$ | **-486** | **85,3** | **-240,963** |
| $H_2O$ | -285,85 | 69,9565 | -237,191 |
| $H_2O$ | **-286,65** | **-453,188** | **-151,549** |

$H_2COHCOOH+H_2O$<=> $H_2COHCOO+H_3O^+$;pKa=3,83
$G_{OHCCOO}=\Delta G_{eqOHCCOOH}-G_{H3O+}+(G_{OHCCOOH}+G_{H2O})$=**414,3** $^{kJ}/_{mol}$;

Exothermic, exoergic reduction Hess free energy change negative **-161,8** $^{kJ}/_{mol}$ or **-129,6** $^{kJ}/_{mol}$, but minimized **$\Delta G_{min}=\Delta G_{eq}$= -85** $^{kJ}/_{mol}$ or **-104** $^{kJ}/_{mol}$ reaching Prigogine attractor free energy change $G_{H3CCOOH}$=**-415,8** $^{kJ}/_{mol}$; $G_{H3CCOO}$=**430,46** $^{kJ}/_{mol}$; minimum $\Delta G_{min}$ at equilibrium mixture.



A+B+C 50% D+2E+F

Acetic acid Formation 61st page $2C+2H_{2gas}+O_{2gas}$=>H3CCOOH ; $\Delta G_{OHCCOOH}$=**-240,963** $^{kJ}/_{mol}$ [8];
$\Delta G_{H3CCOOH}=G_{H3CCOOH}-(2G_{Cgraph}+2G_{H2gas}+1*G_{O2gas})$=**-240,963** $^{kJ}/_{mol}$;
$G_{H3CCOOH}$=**-240,963+(2*91,26+**2***85,6+1*303)=415,8** $^{kJ}/_{mol}$;
Acetic acid H3CCOOH+$H_2O$<=>$OHCCOO^-+H_3O^+$; $pK_{a1}$=4,76; Wikipedia
$K_{eq}=[H3CCOO^-]*[H_3O^+]/[H3CCOOH]/[H_2O]=K_a/[H_2O]=10^{\wedge(-4{,}76)}/55{,}3=3{,}1425*10^{\wedge(-7)}=10^{\wedge(-6{,}5)}$;

$\Delta G_{eqH3CCOO}=-R\bullet T\bullet\ln(K_{aeq})=-8{,}3144*298{,}15*\ln(10^{\wedge(-6{,}5)})/1000$=**37,1** $^{kJ}/_{mol}$ .

$\Delta G_{eqOHCCOOH}=G_{OHCCOO}+G_{H3O+}-(G_{OHCCOOH}+G_{H2O})=G_{OHCCOO}$**+22,44-(296,032+0)=37,1** $^{kJ}/_{mol}$;
$G_{OHCCOO}=\Delta G_{eqOHCCOOH}-G_{H3O+}+(G_{OHCCOOH}+G_{H2O})$=**37,1-22,44+(415,8+0)=430,46** $^{kJ}/_{mol}$;

Oks: $H_2COHCOO^-+H^-(H^++2e^-)+H_3O^+$=>$H_3CCOO^-+2H_2O$; $E°_{OxH2COHCOO}$=-0,033 V absolute; [23]

$\Delta G_{eq}=E°_{OxH2COHCOO}*F*n$=(0,033)*96485*2==**6,368** $^{kJ}/_{mol}$;
$\Delta G_{eq}=G_{H3CCOO}+2G_{H2O}–(G_{OHCCOO}+G_{H3O+}+G_{H-})$=**430,46**+2***0-(414,3+22,44)=-6,28** $^{kJ}/_{mol}$;
$\Delta G_{eq}=G_{H3CCOO}+2G_{H2O}–(G_{OHCCOO}+G_{H3O+}+G_{H-})$=**430,46**+2***85,6-(414,3+22,44)=164,92** $^{kJ}/_{mol}$;
$G_{H-}=G_{H3CCOO}+2G_{H2O}–(G_{OHCCOO}+G_{H3O+}+\Delta G_{eq})$=**430,46**+2***0-(414,3+22,44+6,368)=-12,648** $^{kJ}/_{mol}$;
$G_{H-}=G_{H3CCOO}+2G_{H2O}–(G_{OHCCOO}+G_{H3O+}+\Delta G_{eq})$=**430,46**+2***85,6-(414,3+22,44+6,368)=158,55** $^{kJ}/_{mol}$;

Glycolate $H_2COHCOO^-$+ NADH + $H_3O^+$ => acetate $H_3CCOO^-+2H_2O$ + $NAD^+$

$\Delta G_{Hess}=\Delta G°_{CH3COO}+\Delta G°_{NAD+}+2\Delta G°_{H2O}-\Delta G°_{H2COHCOO}-\Delta G°_{NADH}-\Delta G°_{H3O}$=**-161,8** $^{kJ}/_{mol}$;
=**-240,963+1112,534**-2*237,191-(**-403,2968+1175,5732**-213,2746)=**-161,8** $^{kJ}/_{mol}$ **exoergic**...........
$\Delta G_{eq}=(E°_{Red}-E°_{OxH2COHCOO})*F*n$=(-0,4095--0,033)*96485*2=(-0,38)*96485*2=**-72,65** $^{kJ}/_{mol}$;

Red: **NADH = $NAD^+$ + $H^-(H^++2e^-)$**; $E°_{Red}$= -0,4095 V David Harris absolute

Glyoxylate Oks: $OHCCOO^-$+ $H^-(H^++2e^-)+H_3O^+$=> Glycolate $H_2COHCOO^-+H_2O$ ; $E°_{Ox}$=0,1305 V absolute

Glyoxylate $OHCCOO^-+NADH+H_3O^+$=>$H_2COHCOO^-+NAD^++H_2O$ Glycolate

$\Delta G_{eq}=(E°_{Red}-E_{oH2O})*F*n$=(-0,4095-0,1305)*96485*2=(-0,54)*96485*2=**-104,2** $^{kJ}/_{mol}$;
$\Delta G_{Hess}=\Delta G°_{H2COHCOOH}+\Delta G°_{NAD+}+\Delta G°_{H2O}-\Delta G°_{H2COHCOO}-\Delta G°_{NADH}-\Delta G°_{H3O}$= **-63,66** $^{kJ}/_{mol}$;
=**-403,2968+1112,534-151,549-(-426,588+1175,5732**-213,2746)= **21,98** $^{kJ}/_{mol}$ **;**
=**-403,2968+1112,534**-237,191-(**-426,588+1175,5732**-213,2746)=**-63,66** $^{kJ}/_{mol}$ **exoergic**..............;
=**-403,2968+1112,534**+0-(**-426,588+1175,5732+22,44**)=**-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!

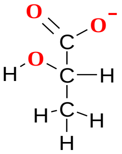
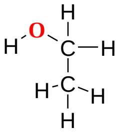
Reactants Pyruvic acid+**Q** => products acetaldehyde bicarbonate + $H_3O^+$

| *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**:

$$\Delta G_{eq}Aerobic=\Delta E°\bullet F\bullet n=(E°_{Red}-E°_{Ox})*F*n=(-0{,}0159-0{,}4095)*96485*2=(0{,}3936)*F*n=75{,}95 \text{ kJ/mol}$$

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

$$K_{eq}Aerobic=\frac{[NADH]\cdot[pyruvate^-]\cdot[H_3O^+]}{[NAD^+]\cdot[lactate^-]\cdot[H_2O]}=e^{-\frac{\Delta G_{eqAerobic}}{R\bullet T}}=e^{-\frac{75955}{8.314\bullet 298.15}}=10^{-13{,}3};$$

$\Delta G_{Hess}=\Delta G°_{NADH}+\Delta G°_{H3CC=OCOO}+\Delta G°_{H3O}-\Delta G°_{NAD+}-\Delta G°_{H3CCH2OHCOO}-\Delta G°_{H2O}=45{,}764$ 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 $\Delta G_{min}=\Delta G_{eqAnaerobic}=-76$.......kJ/mol reduction reaching equilibrium mixture constant $4{,}9336\bullet 10^{-14}=K_{eq}Aerobic$ value.

Prigogine attractor is free energy change absolute minimum $\Delta G_{min}$ 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 $\mathbf{H_3CCHO+HCO_3^-}$ (25 C) 298.15 K, using the data table!

Reactants Lactate+**Q** => products ethanol bicarbonate

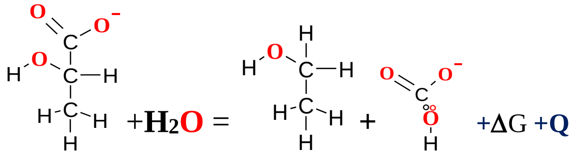
| *Substance* | $\Delta H°_H$ kJ/mol | $\Delta S°_H$ J/mol/K | $\Delta G°_H$ kJ/mol |
|---|---|---|---|
| $\mathbf{H_3CCH(OH)COO^-}$ | **-688,29** | **-1290,852** | **-303,4256** |
| $\mathbf{H_3CCH(OH)COO^-}$ | -686,2 | -557,71 | -313.70 |
| $\mathbf{H_3CCH_2OH_{aq}}$ | **-290,77** | **-1227,764** | **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** |

$\mathbf{H_3CCH(OH)COO^-+H_2O{=}{>}H_3CCH_2OH_l+HCO_3+Q}+\Delta G$

**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............**

$\Delta G_{Hess}=\Delta G°_{H3CCH2OH}+\Delta G°_{HCO3}-\Delta G°_{H2O}-\Delta G°_{H3CCH2OHCOO-}=\mathbf{75{,}2864-544{,}9688-(-151{,}549-303{,}4256)}=\mathbf{-14{,}71}$ kJ/mol

$\Delta H_{Hess}=\Delta H°_{H3CCH2OH}+\Delta H°_{HCO3}-\Delta H°_{H2O}-\Delta H°_{H3CCH2OHCOO-}=\mathbf{-290{,}77-692{,}4948-(-286{,}65-688{,}29)}=\mathbf{-8{,}325}$ kJ/mol

$\Delta S_{dispersed}=-\Delta H_{Hess}/T=\mathbf{8{,}325}/298{,}15=\mathbf{27{,}9}$ J/K/mol;

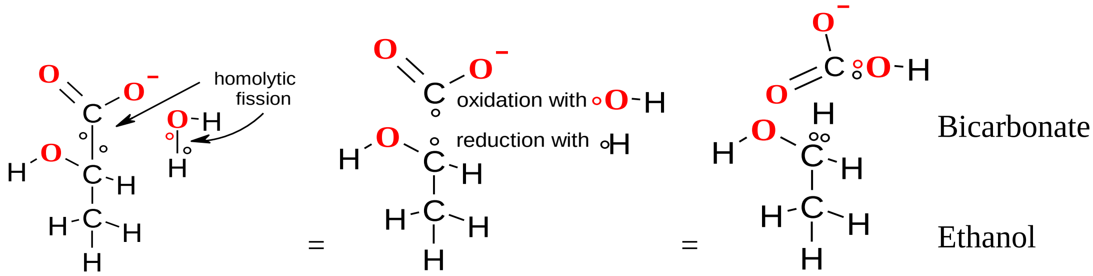
**BioThermodynam06** $\Delta S_{Hess}=\Delta S°_{H3CCH2OH}+\Delta S°_{HCO3-}-\Delta S°_{H2O}-\Delta S°_{H3CCH2OHCOO-}=\mathbf{21{,}51}$ J/mol/K;

$=\mathbf{-1227{,}764-494{,}768-(-453{,}188-1290{,}852)=21{,}51}$ 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 ;<u>dispersed-lost energy</u> **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!

Reactants Alanine $++O_{2aqua}+H_2O$ => products 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 $NH_4^+{}_{(aq)} + H_2O + \Delta G + Q \Rightarrow H_3O^+ + NH_{3(aq)}$

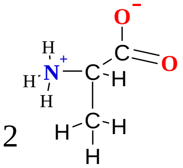
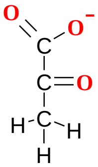
**BioThermodynamics 2006;** MassachusettsTinstitute

$pKa=9,245$ ; $\Delta G_H = -RT\ln(10^{-pKa}) = 52,77$ 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  $+O_{2aqua}+H_2O \Rightarrow$ 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•298,15 K= **144,7.** kJ/mol;bound TΔSn dispersed energy $\Delta G_{reversereaction}$ **spontaneous** $\Delta G_{Hess}$

# THERMODYNAMICS Exercise XXIII succinate $^-OOCCH_2CH_2COO^-$ malate $^-OOCHCOHCH_2COO^-$

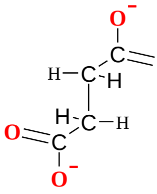
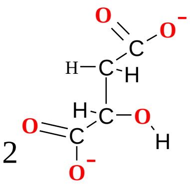
Physiologic conditions pH=7,36 T=310,15 K (37° C)

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* | ΔH°,$^{kJ}/_{mol}$ | ΔS°,$^{J}/_{mol/K}$ | $ΔG_h$,$^{kJ}/_{mol}$ | $ΔH_h$,$^{kJ}/_{mol}$ | $ΔS_h$,$^{J}/_{mol/K}$ | 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.$ΔH_h=2ΔH°_{-OOCHCOHCH2COO-}-2ΔH°_{-OOCCH2CH2COO-}-_ΔH°_{O2}$=………………………………………………………………………$^{kJ}/_{mol}$….
=2*-1079,8-2*-908,7-(-11,715)= -2159,6+1829,115= -330,485 **exothermic**……………………………………$^{……..kJ}/_{mol}$…..
2.$ΔS_{dispersed}$= -$ΔH_h$/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. **Δ**$S_H$=2ΔS°$_{-OOCHCOHCH2COO-}$-2ΔS°$_{-OOCCH2CH2COO-}$-$_Δ$S°$_{O2}$ =……………………………………………………………………$^{J}/_{mol/K}$….
……………….=2*-1,3314-2*-1,268110,876=-2,6628-108,34= -111,0…………………………………………………$^{J}/_{mol/K}$….
3. Δ$S_{total}$= Δ$S_H$+ Δ$S_{dispersed}$ =1065,565-111 = 954,565 ……………………………………………………………… $^{J}/_{mol/K}$
4. **Δ**$G_H$ = **Δ**$H_H$ – T***Δ**$S_H$ = -330,485-310,15*0,111= -296,06………………………………………………**exoegic**.$^{kJ}/_{mol}$……
T•Δ$S_{total}$=954,565 $^{J}$/K/$_{mol}$•310,15 K= **296,06**…………………………………………………………………$^{kJ}/_{mol}$…..
bound TΔSn← dispersed energy Δ$G_{reversereaction}$ Q=330,485 $^{kJ}/_{mol}$ **spontaneous** Δ$G_{Hess}$ = -296 $^{kJ}/_{mol}$…

$pK_{eq}$=-log($K_{eq}$)=-ln(10)*(-**Δ**$G_{eq}$/R/T)=-ln(10)*(296,06*1000/8,3144/310,15)= -ln(10)*79,9081= **-**4,38088…..

$K_{eq}$ =EXP(-**Δ**$G_{eq}$/R/T)= $10^{-pKeq}$=$10^{4,38088}$=2,4*$10^4$ temperature 310,15 K (37° C)

| *CRC Substance* | ΔH°,$^{kJ}/_{mol}$ | ΔS°,$^{J}/_{mol/K}$ | $ΔG_H$,$^{kJ}/_{mol}$ | $ΔH_H$,$^{kJ}/_{mol}$ | $ΔC_H$,$^{J}/_{mol/K}$ | 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)

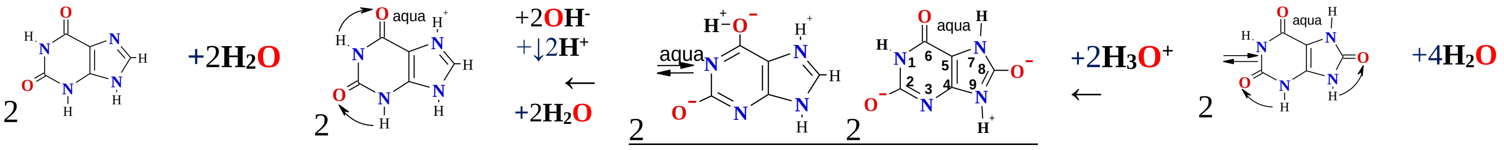
Xanthine $^-$ $C_5H_4N_4O_{2(s)}$ to ureate $^-$ $C_5H_4N_4O_3^-{}_{(s)}{}^-$ (37 C) 310.15 K, using the data table!
Reactants xanthine +$O_{2\,aqua}$=> products ureate ionic force **I**=0,25 .
pK$_a$ Alberty, Robert A.Q 2006.

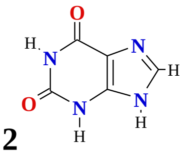
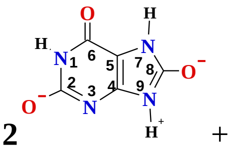
| CRC 2010 *Substance* | ΔH°, kJ/mol | ΔS°, J/mol/K | ΔG$_H$, kJ/mol | ΔH$_H$, kJ/mol | ΔC$_H$, J/mol/K | pK | pK |
|---|---|---|---|---|---|---|---|
| Uric acid $C_5H_5N_4O_3^+{}_{(aq)}$ | - | - | -193,84 | 3.0 | -121 | pK2= | 4,207 |
| ureate $C_5H_4N_4O_{3(aq)}$ | - | - | - | -0,5 | -217 | pK1= | 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 |
| **$O_{2\,aqua}$** | -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)



 **2** +**2 $H_2O$**+**$O_{2\,aqua}$**=>disoluted in water=> **2**  + **2 $H_3O^+$**+ΔG+**Q**

Reactants **2** $C_5H_4N_4O_{2(aqua)}$ +**2 $H_2O$** + **$O_{2\,aqua}$** => **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•$\Delta S_{total}$=1270,145 J/K/mol•310,15 K= **393,94**...................................................................................kJ/mol;

bound TΔSn← dispersed energy Q=466,605 kJ/mol **spontaneous** $\Delta G_{Hess}$ = -393,936 kJ/mol...

pK$_{eq}$=-log(K$_{eq}$)=-ln(10)*(-**Δ**G$_{eq}$/R/T)=-ln(10)*(466,605*1000/8,3144/310,15)= -ln(10)*180,945= -5,19819............
K$_{eq}$ =EXP(-**Δ**G$_{eq}$/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 $CH_3CH_2\text{-}O\text{-}OCCH_3$ hydrolysis to $CH_3CH_2OH+HOOCCH_3$

$$CH_3CH_2\text{-}O\text{-}OCCH_3+H_2O\Rightarrow CH_3CH_2OH+{}^-O\text{-}OCCH_3;\Delta G_{Lehninger}=-19{,}6\ {}^{kJ}/_{mol}$$

$$\Delta G_{Hess}=\Delta G°_{CH3CH2OH}+\Delta G°_{CH3COO}-\Delta G°_{CH3CH2\text{-}O\text{-}OCCH3}-\Delta G_{H2O}=\mathbf{75{,}2864\text{-}241{,}663\text{-}(4{,}9176\text{-}151{,}549)=\text{-}19{,}745}\ {}^{kJ}/_{mol};$$

$$\mathbf{K}_{Lehninger}=\exp(19600/8{,}3144/298{,}15)=\frac{[CH_3COO^-]\cdot[CH_3CH_2OH]}{[H_2O]\cdot[CH_3CH_2OOCCH_3]}=2715{,}172$$

I=0,25 M, **BioTherm06**, pH=7,36, $\Delta G_{Hess}=\Delta G°_{CH3CH2OH}+\Delta G°_{CH3COO}+\Delta G°_{H3O+}-\Delta G°_{CH3CH2\text{-}O\text{-}OCCH3}-2*\Delta G_{H2O}=89{,}8\,{}^{kJ}/_{mol};$

| $\Delta H°,{}^{kJ}/_{mol}$ | $\Delta H°,{}^{J}/_{mol/K}$ | $\Delta S_H,{}^{kJ}/_{mol}$ | $\Delta G°,{}^{kJ}/_{mol}$ |
|---|---|---|---|
| **$H_3CCOO^-$** | -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** |

$=\mathbf{75{,}2864\text{-}241{,}663}\text{-}213{,}275\text{-}(\mathbf{4{,}9176+}2\mathbf{*}\text{-}237{,}191)=89{,}8\ {}^{kJ}/_{mol}$; pH=7,36

$$CH_3CH_2\text{-}O\text{-}OCCH_3+2H_2O\Rightarrow CH_3CH_2\text{-}OH+{}^-O\text{-}OCCH_3+H_3O^+;$$

$\Delta H_H=\Delta H°_{CH3CH2OH}+\Delta H°_{CH3COO}+\Delta H°_{H3O}-\Delta H°_{CH3CH2OOCCH3}-2*\Delta H_{H2O}=\mathbf{-6{,}42}\,{}^{kJ}/_{mol}$

$=\mathbf{-290{,}77\text{-}486{,}836}\text{-}285{,}81\text{-}(\mathbf{-485{,}3+}2\mathbf{*}\text{-}285{,}85)=\mathbf{-6{,}42}\ {}^{kJ}/_{mol}$

$\Delta S_H=\Delta S°_{CH3CH2OH}+\Delta S°_{CH3COO}+\Delta S°_{H3O+}-\Delta S°_{CH3CH2\text{-}O\text{-}OCCH3}-2*\Delta S_{H2O}=\mathbf{-540{,}4}\ {}^{J}/_{mol/K}$

$=\mathbf{-1227{,}76\text{-}813{,}043}\text{-}3{,}854\text{-}(\mathbf{-1644{,}15+}2\mathbf{*}69{,}9565)=\mathbf{-540{,}4}\ {}^{J}/_{mol/K}$

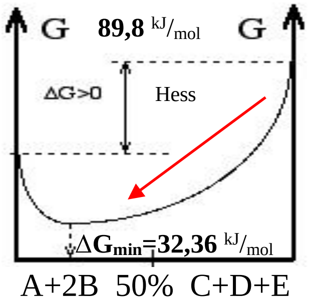
$\Delta G_H=\Delta H_H-T*\Delta S_H=\mathbf{-6{,}42}\text{-}298{,}15*\text{-}0{,}\mathbf{5404=154{,}7}.{}^{kJ}/_{mol}$ **endoergic**;

$$\mathbf{K}_{eqLehninger}=\mathbf{K}_{Lehninger}[H_3O^+]/[\mathbf{H_2O}]=2715{,}172/55{,}34573*10^{\wedge(-7,36)}=\frac{[CH_3COO^-]\cdot[CH_3CH_2OH]\cdot[H_3O^+]}{[H_2O]^2\cdot[CH_3CH_2OOCCH_3]}=10^{\wedge(-5,67)}$$ At pH=7,36

$\mathbf{\Delta G_{eq}=-R\bullet T\bullet ln(K_{eq})=-R\bullet T\bullet ln}(10^{\wedge(-5,67)})=-8{,}3144*298{,}15*\ \mathbf{ln}(10^{\wedge(-5,67)})=32{,}36\ \ {}^{kJ}/_{mol};$

Endoergic exothermic $CH_3CH_2\text{-}O\text{-}OCCH_3$ hydrolizeHess free energy change positive $\mathbf{\Delta G_{hydrolise}}=89{,}8\ {}^{kJ}/_{mol}$ , but minimizes $\Delta\mathbf{G_{min}}=\Delta\mathbf{G_{eq}}=32{,}36\ {}^{kJ}/_{mol}$ reaching

equilibrium mixture $\mathbf{K_{eq}}=10^{\wedge(-5,67)}=\frac{[CH_3COO^-]\cdot[CH_3CH_2OH]\cdot[H_3O^+]}{[H_2O]^2\cdot[CH_3CH_2OOCCH_3]}$ .



**$CH_3CH_2$-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

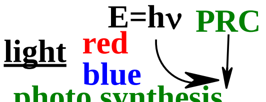
Calculate $\Delta H_H$, $\Delta S_H$, $\Delta G_H$ and the amount of heat **exothermic**, **athermic** or **endothermic** reaction at standard conditions 298.15 K. **PRC** Photo Synthetic Reaction Center ENZYME complex drive green plants products $\mathbf{C_6H_{12}O_6}$ and oxygen $6O_{2aqua}$. by photon **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:

$$6HCO_3^-+6H_3O^++Q\overset{PRC+hv}{=\!=\!>}C_6H_{12}O_6+6O_{2aqua}+6H_2O$$

against **osmolar** concentration gradient 12/1. Oxygen $\mathbf{6O_2}$ and water $\mathbf{6H_2O}$ pushed out

$$\text{out of cell } 6H_2O+6O_{2aqua}\overset{\underline{\textbf{Aquaporins}}}{<\!=\!=}6O_{2aqua}+6H_2O \text{ inside cell}$$

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 — photo synthesis — glucose + **oxygen** water

$$6HCO_3^-+6H_3O^+ + Q + \Delta G_{Hess} \xrightleftharpoons[\text{reverse reaction}]{\text{photo synthesis}} C_6H_{12}O_6+ 6\ O_2+6H_2O$$

Mention whether the reaction will be **exoergic** or **endoergic**! Universal gas constant $R=8{,}3144\ ^{J}/_{mol}/_{K}$;

$$\Delta G_{channel}=-\mathbf{RTln}(C_{osm}[6O_{2aqua}+6H_2O]_{left}/C_{osm}[6O_{2aqua}+6H_2O]_{righ})=-12\mathbf{RTln}(12/1)= -36.96\ ^{kJ}/_{mol}\text{..........}$$

| *Substance* | before | after |
|---|---|---|
| $O_{2aqua}$ | $[O_2]=6\cdot10^{-5}$ M | $[O_2]=6\cdot10^{-5}$ 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 $\mathbf{6O_{2aqua}}$ $\Delta G_{6O_2}= -6.1599*6= -36.9596$ ........................................................................................................$^{kJ}/_{mol}$

$\Delta G_{6H_2O}=-6\mathbf{RTln}([H_2O]_{right}/[H_2O]_{left})=6*8{,}3144*310{,}15*\mathbf{ln}(1/12)= -36.9596$...............................................$^{kJ}/_{mol}$...

For **6 $H_2O$** $\Delta G_{6H_2O} = -6.1599*6= -36.9596$ ......................................................................................................$^{kJ}/_{mol}$

.**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.......................................................................

......

$T\bullet\Delta S_{6O_2}= -0{,}12396\bullet298{,}15=\mathbf{36.9596}$................kJ/mol <u>used energy of **PRC** </u>bound $T\Delta Sn=3040{,}1\ ^{kJ}/_{mol}$ <u>out</u> off $\mathbf{O_2}$...

$T\bullet\Delta S_{6H_2O} = -0{,}12396\bullet298{,}15=\mathbf{36.9596}$.............kJ/mol <u>used energy of **PRC** </u>bound $T\Delta Sn=3040{,}1\ ^{kJ}/_{mol}$ <u>out</u> off $\mathbf{H_2O}$

......

For $\mathbf{6O_{2aqua}+6H_2O}$ $T\bullet\Delta S_{6H_2O+6O_2}=\mathbf{36.9596+36.9596=73.919}$............kJ/mol <u>of **PRC** </u>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 $\mathbf{6O_{2aqua}+6H_2O}$ consuming bicarbonate end hydrogen ions $\mathbf{6HCO_3^-+6H_3O^+}$ drive spontaneous flow of $\mathbf{6O_{2aqua}+6H_2O}$ through aquaporins out of **PRC** cells against membrane concentration gradient 12/1 with standard free energy $\Delta G_{6H_2O+6O_2}$= **-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$_2$O**+ΔG**+Q**=>**RetinalCH=O**+NAD**H+H$_3$O$^+$**

| *Substance* | ΔH°$_H$ $^{kJ}/_{mol}$ | ΔS°$_H$ $^{J}/_{mol/K}$ | ΔG°$_H$ $^{kJ}/_{mol}$ |
|---|---|---|---|
| **RetinalCH=O** | | | **1141,45** |
| **RetinalCH=O** | **-** | **-** | **1198,9852** |
| Retinol**CH$_2$OH** | | | **1195,07** |
| Retinol**CH$_2$OH** | - | - | **1256,7164** |
| NAD**H** | **-41,41** | **-4465,708** | **1175,5732** |
| NAD**H** | -1036,66 | -140,50 | 1120,09 |
| **H$_3$O$^+$** | -285.81 | -3.854 | -213,275 |
| NAD$^+$ | **-10,30** | **-3766,008** | **1112,534** |
| NAD$^+$ | -1007,48 | -183 | 1059,11 |
| **H$_2$O** | -285.85 | 69.9565 | -237,191 |
| **H$_2$O** | **-286,65** | **-453,188** | **-151,549** |

I=0 M; I=0,1 M

1118,78;1135,91;

Thermodynamic **E°$^2$**$_{Retinol}$=**0,2415+0,10166=0,34316 V**;

1170,78;1189,14;

Absolute **E°$^2$**$_{Retinol}$=**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$_2$O**=**RetinalCH=O+2H$_3$O$^+$+H$^-$(2e$^-$)** ;

**E°$^2$$_{H2O}$ =0,190**+0,0591/2*log([**H$_2$O**]$^2$)=**0,2415 V**;

**Ox NAD$^+$+H$^-$(2e$^-$)**=**NADH** ; **E°$^1$=**-0,4095 **V;**

Standard potential **E° voltos** David Harris; KortlyShucha data

ΔG$_{Hess}$=ΔG°$_{\mathbf{RetinalCHO}}$+ΔH°$_{\mathbf{NADH}}$ +ΔG°$_{\mathbf{H3O}}$ -ΔG°$_{\mathbf{RetinnnolOH}}$-ΔH°$_{\mathbf{NAD+}}$-ΔH°$_{\mathbf{H2O}}$=

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$_2$O**+ΔG**+Q**=>**RetinalCH=O**+NAD**H+H$_3$O$^+$;**

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

Absolute **E°$^2$**$_{Retinol}$=**0,34316**-0,3982=-0,05504 **V**

ΔE°=**E°$^2$$_{H2O}$-E°$^1$**=-0,05504–(-0,4095)=**0,3545 V**, **n** is **2**;

**ΔG$_{eq}$**Aerobic=**ΔE°•F•n=(**-0,05504-(-0,4095)**)*2*96485=(0,3545)*2*96485=-R•T•ln(K$_{eq}$)= 68,4** $^{kJ}/_{mol}$

$$\mathbf{K_{eq}}\mathrm{Aerobic}=\frac{[\mathrm{NADH}]\cdot[\mathrm{RetinalCHO}]\cdot[\mathrm{H_3O^+}]}{[\mathrm{NAD^+}]\cdot[\mathrm{Retinol\,OH}]\cdot[\mathrm{H_2O}]}=e^{-\frac{\Delta G_{eqAerobic}}{R\bullet T}}=e^{-\frac{68408}{8.314\bullet 298.15}}=\mathbf{1{,}036\bullet 10^{-12}=10^{-11{,}985}}$$

; Homeostasis joined

**O$_{2aqua}$** NADH oxidase with alcochol dehydrogenase ratio [**NADH**]/[**NAD$^+$**]=10$^{-6}$ favored **ΔG**$_{aerobic}$**=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$_{min}$**=Δ**G$_{eq}$**Aerobic=68,4......$^{kJ}/_{mol}$ and anaerobic **ΔG$_{min}$**=Δ**G**$_{eqAnaerobic}$= -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$_{eq}$**$_{Anaerobic}$.

Prigogine attractor is free energy change absolute minimum at Equilibrium

**ΔG**$_{min}$=68,4.......$^{kJ}/_{mol}$= $|$ΔG$_{eq}|$ < $|$ΔG$_{Hess}|$ **=144,4**........$^{kJ}/_{mol}$.

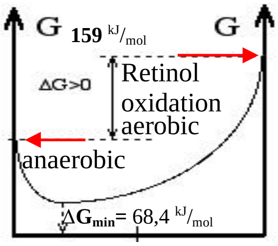
Anaerobic **ΔG**$_{eq}$=**ΔE°•F•n**=-0.3545 V•2 mol•96485 $^C/_{mol}$= -68,4........$^{kJ}/_{mol}$ favored.

Insufficient low **O$_{2aqua}$** 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

**ΔG**$_{anaerobic}$= -27,86........$^{kJ}/_{mol}$

Anaeirobic homeostasis ratio [**NAD$^+$**]/[**NADH**]=1/10 over [**NADH**] favore reduction:

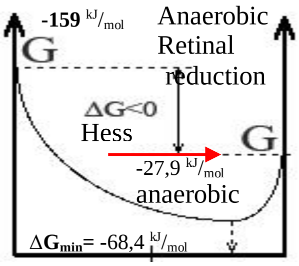
$$\mathbf{\Delta G}_{anaerobic}\mathbf{=-68{,}4}+8{,}3144*298{,}15*\mathbf{ln}\left(\frac{1}{10}\,\frac{1}{10}\,\frac{55.333}{10^{-7.36}}\right)=\mathbf{-27{,}86}\ ^{\mathbf{kJ}}/_{\mathbf{mol}}\ ;$$



A+B+C50%D+E+F

NAD$^+$+H$_3$CCH$_2$OH+ H$_2$O

NADH+H$_3$CCHO+H$_3$O$^+$



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

NADH+H$_3$CCHO+H$_3$O$^+$

NAD$^+$+H$_3$CCH$_2$OH+ H$_2$O

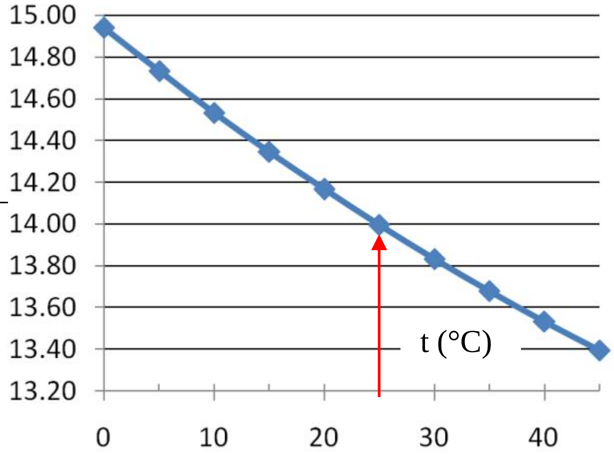
$$\mathbf{K_{eq}}\mathrm{Anaerobic}=\frac{[\mathrm{NAD^+}]\cdot[\mathrm{Retinol\,OH}]\cdot[\mathrm{H_2O}]}{[\mathrm{NADH}]\cdot[\mathrm{RetinalCHO}]\cdot[\mathrm{H_3O^+}]}\ ;\ \mathbf{K}_{eq}\ \mathrm{Weak\ Aerobic}=\frac{[\mathrm{NADH}]\cdot[\mathrm{RetinalCHO}]\cdot[\mathrm{H_3O^+}]}{[\mathrm{NAD^+}]\cdot[\mathrm{Retinol\,OH}]\cdot[\mathrm{H_2O}]}\ ;[\mathbf{NADH}]/[\mathbf{NAD^+}]=770/1;$$

**ΔG**$_{aerobic}$=**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



$$K_{eq1}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=3.26\cdot10^{-18}\ ;$$

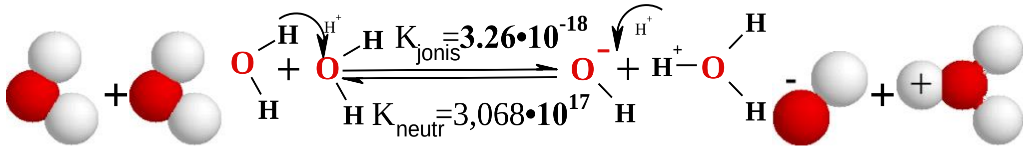
=10^(-13,9965)/55,34573^2=3,291*10^(-18);

$\Delta G_{Hess}=\Delta H_{Hess}-T*\Delta S_{Hess}$=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•T•ln($K_{H3O^++OH^-}$)+2*0=99.8 kJ/mol hydroxonium and hydroxide ions. [1,8,14]

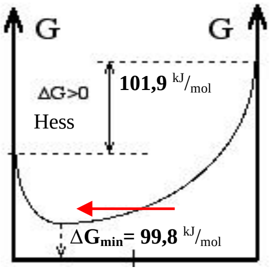


$$K_{eq1}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=\mathbf{3,26\cdot10^{-18}}$$

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

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

$$K_{eq1}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=\mathbf{3.26\cdot10^{-18}}\ ;\ \text{up to } \Delta G_{min} = \Delta G_{eq} = 99{,}8\ \text{kJ/mol}$$



A+B 50% C+D

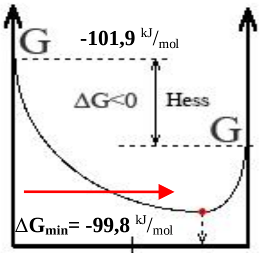
$H_2O+H_2O$ reactants products $H_3O^++OH^-$

Free energy change $\Delta G_{Hess}$ 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:

$$3.26\cdot10^{-18}=\frac{[OH^-]\cdot[H_3O^+]}{[H_2O]\cdot[H_2O]}=K_{eq1}=\frac{1}{K_{eq2}}=\frac{1}{\frac{[H_2O]\cdot[H_2O]}{[OH^-]\cdot[H_3O^+]}}=\frac{1}{3{,}068*10^{17}}\ .$$

Le Chatelier principle is Prigogine attractor for Free energy change minimum $\Delta G_{min}$ reaching at equilibrium. Free energy change minimum reaching establishes equilibrium.



C+D 50% A+B

$H_3O^++OH^-$ reactants products $H_2O+H_2O$.

Water factorial constant and concentration square $K_w$ water constant.

$K_{eq1}*[H_2O]^2$ =3.26•10$^{-18}$*55,33$^2$=10$^{-14}$=$K_w$ ,

one calculates water ions factorial constant $K_w$ = $[H_3O^+][OH^-]$ =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 6th page $C+6H_{2gas}+3O_{2gas}$=>$C_6H_{12}O_6$ ; $\Delta G^\circ_{Alberty}$=**-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 $G_{C6H12O6}$=**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 $G_{C6H12O6}$=<u>2840</u>-6***78.08**-6***85.64**+6*(**22.44**+**46.08**)=2268.8 $^{kJ}/_{mol}$ ,

Free energy of glucose__$G_{C6H12O6}$=<u>2840</u>-6***330**-6***0**+6*(**22.44**+**46.08**)=**1271** $^{kJ}/_{mol}$ ,

Free energy of glucose_$G_{C6H12O6}$ =2840-6***330**-6***85,64**+6*(**22,44**+**46,08**)=**757** $^{kJ}/_{mol}$ ,

Free energy of glucose $G_{C6H12O6}$=<u>2840</u>-6***78.08**-6*0+6*(**22.44**+**46.08**)<u>=2782.6</u> $^{kJ}/_{mol}$ .

Glucose free energy by Alberty $G_{C6H12O6}$=**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, $[HCO_3^-]$=**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 $E^\circ_{H(Pt)}$=**-0.2965** V.
Note: Classic potential scale is assumed for hydrogen classic reference zero $E^\circ_{H(Pt)classic}$=**0** V.

Nernst's half reaction: $6H_2O$<=> $O_{2aqua}+4H_3O^++4e^-$ ; $E^\circ_{O2}$=1.0868 V; $\Delta G_{eqO2}=E^\circ_{O2aq}\bullet F\bullet n_{\underline{e-}}$=**419,3** $^{kJ}/_{mol}$ .

$\Delta G_{O2aqAlberty}=G_{O2aq}+4G_{H3O+}-6G_{H2O}$=**330-4*22,44-6*0=419,76** $^{kJ}/_{mol}$ $\Delta G_{eqO2}$=1,0865*96485*4=**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 Volts .

Oxygen homeostasis energy change $\Delta G_{eqHomeostasisO2}=E^\circ_{O2}\bullet F\bullet 1\bullet 4$=0,4346*96485*4=**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 :

$\Delta G_{AlbertyAbsoluteC6H12O6}=E^\circ_{C6H12O6}\bullet F\bullet 1\bullet 24$=**-0,**1392 *96485*24=**-322** $^{kJ}/_{mol}$ calculated is exoergic free energy change: $\Delta G_{AlbertyC6H12O6}=30*G_{H3O+}+6*G_{HCO3-}\ (G_{C6H12O6}+6*G_{O2Homeostasis\_arterial}+42*G_{H2O\_Biochem})$=**- 1086,8** $^{kJ}/_{mol}$

negative $\Delta G_{AlbertyHessC6H12O6}$=30***22,44**+6***46,08-(1568**+6***78,08**+42***0**)=**-1086,8** $^{kJ}/_{mol}$.

Homeostasis potential **is** $E_{C6H12O6}=E^\circ_{C6H12O6}+{}^{0.0591}/_{24}\bullet\log([HCO_3^-]^6\bullet[H_3O^+]^{30}/_{[C6H12O6]}/_{[H2O]^{42}})$=
=$-0,1392+{}^{0,0591}/_{24}*\log(\mathbf{0,0154^{\wedge 6}}*10^{\wedge(-7,36*30)}/5/10^{\wedge(-3)}/_{55,346^{\wedge 42}})$=**-0,8843** Volts and free energy change of homeostasis is exoergic, negative $\Delta G_{HomeostasisC6H12O6}=E^\circ_{C6H12O6}\bullet F\bullet 1\bullet 24$=**-0,88427***96485*24=**-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)•**F•n**=-1,226*96485*24=**-2840** $^{kJ}/_{mol}$.

$\Delta G_{Homeostasis}=\Delta E\bullet F\bullet n=(E^\circ_{C6H12O6}-E^\circ_{O2})\bullet F\bullet n$=(**-0,88427**-0,4349)•**F•n**=-1,31917*96485*24=**-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=**-322,34** $^{kJ}/_{mol}$

<u>on Alberty data Hess calculated</u> $\Delta G_{AlbertyC6H12O6}$=30***22,44**+6***46,08-(1271**+6***78.1**+42***0**)=**-789,9** $^{kJ}/_{mol}$ and Biochemistry conditions Hes s value $\Delta G_{HessC6H12O6}$=30***22,44**+6***46,08**-(2268,8+6***78.1**+42***0**)=**-1787,7** $^{kJ}/_{mol}$ .

The oxygen reduction: 6*($O_{2aqua}+4H_3O^++4e^-\Leftrightarrow 6H_2O$;) standard potential $E^\circ_{O2}$=**1.0868** Volts and Glucose Homeostasis constant with values $[H_3O^+]=10^{-7,36}$ M, $[HCO_3^-]$=**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:

$6H_3O^++6HCO_3$=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 $H_3CHC(OH)COO^-$.

$H_3CHC(OH)COO^- + H_2O \Rightarrow H_3CC=OCOO^- + H_3O^+ + H^-(H^+ + 2e^-)$; $E°_{H3CHC(OH)COO}=-0,0159$ V;

$\Delta G_{eqH3CHC(OH)COO}=E°_{eqH3CHC(OH)COO}\bullet F\bullet 2=-0,0159*96485*2=-3,068$ $^{kJ}/_{mol}$;

$\Delta G_{HessCH3CH2OH}=G_{H3CC=OCOO}+G_{H3O+}+G_{H-}-(G_{H3CHC(OH)COO}+G_{H2O})=534,2+22,44+G_{H-}-(668,8+0)=-3,068$ $^{kJ}/_{mol}$.

$\Delta G_{HessCH3CH2OH}=G_{H3CC=OCOO}+G_{H3O+}+G_{H-}-(G_{H3CHC(OH)COO}+G_{H2O\_Biochem})=534,2+22,44+G_{H-}-(668,8+85,64)=-3,068$ $^{kJ}/_{mol}$.

$\Delta G_{HessCH3CH2OH}-G_{H3CC=OCOO}-G_{H3O+}+(G_{H3CHC(OH)COO}+G_{H2O})=G_{H-}=-3,068-534,2-22,44+(668,8+0)=109,092$ $^{kJ}/_{mol}$.

$\Delta G_{HessCH3CH2OH}-G_{H3CC=OCOO}-G_{H3O+}+(G_{H3CHC(OH)COO}+G_{H2O\_Biochem})=G_{H-}=-3,068-534,2-22,44+(668,8+85,64)=194,7$ $^{kJ}/_{mol}$.

I=0,25 M, **BioTherm06**, pH=7,36, $\Delta G_H=G°_{H3CC=OCOO-}+G°_{H3O+}+G_{H-}-G_{H3CHC(OH)COO-}-G_{H2O}=$ $^{kJ}/_{mol}$;

| *Viela* | $\Delta H°_H$ $^{kJ}/_{mol}$ | $\Delta S°_H$ $^{J}/_{mol/K}$ | $\Delta G°_H$ , $^{kJ}/_{mol}$ ; |
|---|---|---|---|
| **$PyruvEnolP^{3-}$** | -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** |
| $H_3CHC(OH)COO^-$ | **-688,29** | **-1290,9** | **-303,4** |
| $H_3CHC(OH)COOH$ | | | |

$G_{H2O}=0$ $^{kJ}/_{mol}$; $G_{H-}=-3,068-534,2-22,44+(668,8+0)=109,092$ $^{kJ}/_{mol}$

$G_{H2O\_Biochem}=85,64$ $^{kJ}/_{mol}$;$G_H=-3,068-534,2-22,44+(668,8+85,64)=194,7$ $^{kJ}/_{mol}$

$G_{H3CHC(OH)COO}=534,2$ $^{kJ}/_{mol}$;

$G_{H3CHC(OH)COO}=668,8$ $^{kJ}/_{mol}$;

$G_{H3CHC(OH)COOH+}=3G_{CO2gas}+3G_{H2O}-(3G_{O2gas})=2271$ $^{kJ}/_{mol}$;

$pK_a=3,86$; $\Delta H_c°=1361,9$ $^{kJ}/_{mol}$; $G_{H3CHC(OH)COOH}=2271$ $^{kJ}/_{mol}$;$H_3CHC(OH)COOH+3O_{2gas}=3CO_{2gas}+3H_2O$;

$\Delta H_c°=3G_{CO2gas}+3G_{H2O}-(G_{H3CHC(OH)COOH}+3G_{O2gas})=3*0+3*0-(G_{H3CHC(OH)COOH}+3*303)=1361,9$ $^{kJ}/_{mol}$;

$G_{H3CHC(OH)COOH+}=3G_{CO2gas}+3G_{H2O}-(3G_{O2gas})=3*0+3*0-(+3*303)-1361,9=G_{H3CHC(OH)COOH}=2271$ $^{kJ}/_{mol}$;

**Lactic acid** Formation 71st page $3C+3H_{2gas}+1,5O_{2gas}\Rightarrow H_3CHC(OH)COOH$; $G_{H3CHC(OH)COOH}=-303,4$ $^{kJ}/_{mol}$ [8];

$\Delta G_{H3CHC(OH)COOH}=G_{H3CHC(OH)COOH}-(3G_{Cgraph}+3*G_{H2gas}+1,5*G_{O2gas})=-303,4$ $^{kJ}/_{mol}$;

$G_{H3CHC(OH)COOH}=-303,4+(3*91,26+3*85,6+1,5*303)=681,7$ $^{kJ}/_{mol}$;

Lactic acid $H_3CHC(OH)COOH+H_2O\Leftrightarrow H_3CHC(OH)COO^-+H_3O^+$; $pK_{a1}=3,86$;

$K_{eq}=[H_3CHC(OH)COO^-]*[H_3O^+]/[H_3CHC(OH)COOH]/[H_2O]=K_a/[H_2O]=10^{\wedge(-3,86)}/55,3=2,5*10^{\wedge(-6)}=10^{\wedge(-5,603)}$;

$\Delta G_{eqH3CHC(OH)COOH}=-R\bullet T\bullet \ln(K_{aeq})=-8,3144*298,15*\ln(10^{\wedge(-5,603)})/1000=31,98$ $^{kJ}/_{mol}$ .

$\Delta G_{H3CHC(OH)COO}=G_{H3CHC(OH)COO}+2G_{H3O+}-(G_{LacticAc}+2G_{H2O})=G_{Succinat}+2*22,44-(681,7+2*0)=31,98$ $^{kJ}/_{mol}$;

$G_{H3CHC(OH)COO}=\Delta G_{H3CHC(OH)COO}-2G_{H3O+}+(G_{LacticAc}+2G_{H2O})=31,98-2*22,44+(681,7+2*0)=668,8$ $^{kJ}/_{mol}$;

**Pyruvic acid**$^-$ Formation 71st page $3C+2H_{2gas}+1,5O_{2gas}\Rightarrow H_3CC=OCOOH$; $\Delta G_{Succinat}=-344,62$ $^{kJ}/_{mol}$ [8];

$\Delta G_{Fumarat}=G_{Fumarat}-(3G_{Cgraph}+2G_{H2gas}+1,5*G_{O2gas})=-344,62$ $^{kJ}/_{mol}$;

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

**Pyruvic acid** $H_3CC=OCOOH+H_2O\Leftrightarrow H_3CHC(OH)COO^-+H_3O^+$; $pK_{a1}=2,5$;

$K_{eq}=[H_3CHC(OH)COO^-]*[H_3O^+]/[H_3CC=OCOOH]/[H_2O]=K_a/[H_2O]=10^{\wedge(-2,5)}/55,3=2,5*10^{\wedge(-6)}=10^{\wedge(-4,243)}$;

$\Delta G_{eqH3CC=OCOOH}=-R\bullet T\bullet \ln(K_{aeq})=-8,3144*298,15*\ln(10^{\wedge(-4,243)})/1000=24,22$ $^{kJ}/_{mol}$ .

$\Delta G_{H3CHC(OH)COO}=G_{H3CHC(OH)COO}+2G_{H3O+}-(G_{LacticAc}+2G_{H2O})=G_{Succinat}+2*22,44-(554,86+2*0)=24,22$ $^{kJ}/_{mol}$;

$G_{H3CHC(OH)COO}=\Delta G_{H3CHC(OH)COO}-2G_{H3O+}+(G_{LacticAc}+2G_{H2O})=24,22-2*22,44+(554,86+2*0)=534,2$ $^{kJ}/_{mol}$;

**$NADPH = NADP^+ + H^-(H^+ + 2e^-)$**; $E°_{NADH}=-0,41135$ V; absolute Lehninger; [6]$^-$

$\mathbf{H_2O_2}$ veidošanās 41st page $\mathbf{H_{2gas}}+\mathbf{O_{2}}_{gas}\Rightarrow \mathbf{H_2O_2}$ ; $\Delta\mathbf{G}^\circ_{\mathrm{UnivAlberta}}=-134,03\ ^{kJ}/_{mol}$ ; $\Delta\mathbf{G}^\circ_{\mathrm{Alberty}}=\mathbf{-48,39}\ ^{kJ}/_{mol}$ ;

$\Delta G_{\mathrm{Alberty}}=G_{\mathbf{H2O2}}-(G_{\mathbf{O2}\mathrm{gas}}+G_{\mathbf{H2gas}})=\underline{\mathbf{274,5-(85,64+303}}\mathbf{)=-114,14}\ ^{kJ}/_{mol}(-134,03\ ^{kJ}/_{mol};)(=\mathbf{-48,39}\ ^{kJ}/_{mol})$

| *Viela* | $\Delta H^\circ_H\ ^{kJ}/_{mol}$ | $\Delta S^\circ_H\ ^{J}/_{mol/K}$ | $\Delta G^\circ_H\ ^{kJ}/_{mol}$ |
|---|---|---|---|
| $\mathbf{H_2O_2}_{aqua}$ | **-191,99** | **-481,688** | **-48,39** |
| $\mathbf{H_2O_2}_{aqua}$ | -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 $\underline{G_{\mathbf{H2O2}}=\mathbf{274,5}}\ ^{kJ}/_{mo}$

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

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

**Succinat**$^{2-}$ Formation 41st page $4\mathbf{C}+2\mathbf{H_{2gas}}+2\mathbf{O_2}_{gas}\Rightarrow(CH_2)_2(C\mathbf{O_2}^-)(C\mathbf{O_2}^-)$ ; $\Delta G_{\mathbf{Succinat}}=\mathbf{-522,4}\ ^{kJ}/_{mol}$ Alberty;

$\Delta G_{\mathbf{SuccinatFor}}=G_{\mathbf{SuccinatFor}}-(\mathbf{4G}_{\mathrm{Cgraph}}+\mathbf{2*}G_{\mathbf{H2}\mathrm{gas}}+\mathbf{2*}G_{\mathrm{O2gas}})=\mathbf{-522,4}\ ^{kJ}/_{mol}$;

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

**Fumarate** $^{2-}$ Formation 41st page $4\mathbf{C}+\mathbf{H_{2gas}}+2\mathbf{O_2}_{gas}\Rightarrow(CH)_2(C\mathbf{O_2}^-)(C\mathbf{O_2}^-)$ ; $\Delta G_{\mathbf{Fumarat}}=\mathbf{-519,5}\ ^{kJ}/_{mol}$ Alberty;

$\Delta G_{\mathbf{Fumarat}}=G_{\mathbf{FumaratFor}}-(\mathbf{4G}_{\mathrm{Cgraph}}+G_{\mathbf{H2}\mathrm{gas}}+\mathbf{2*}G_{\mathrm{O2gas}})=\mathbf{-519,5}\ ^{kJ}/_{mol}$;

$G_{\mathbf{FumaratFor}}=\mathbf{-519,5+(4*91,26+85,6+2*303)=537,1}\ ^{kJ}/_{mol}$; ;

Succinic acid $(CH_2)_2(C\mathbf{O_2}H)_2+\mathbf{H_2O}\rightleftharpoons(CH_2)_2(C\mathbf{O_2}H)(C\mathbf{O_2})^-+H_3O^+$; $pK_{a1}=4,2$;

$K_{a1eq}=[(CH_2)_2(C\mathbf{O_2}H)(C\mathbf{O_2})^-]*[H_3O^+]/[(CH_2)_2(C\mathbf{O_2}H)_2]/[\mathbf{H_2O}]=K_{a1}/[\mathbf{H_2O}]=10^{\wedge(-4,2)}/55,3=1,14*10^{\wedge(-6)}=10^{\wedge(-5,94)}$;

**Succinat**$^{2-}$ $(CH_2)_2(C\mathbf{O_2}H)(C\mathbf{O_2})^-+\mathbf{H_2O}\rightleftharpoons(CH_2)_2(C\mathbf{O_2}^-)(C\mathbf{O_2}^-)+H_3O^+$; $pK_{a2}=5,6$;

$K_{a2eq}=[(CH_2)_2(C\mathbf{O_2}^-)(C\mathbf{O_2}^-)]*[H_3O^+]/[(CH_2)_2(C\mathbf{O_2}H)(C\mathbf{O_2})^-]/[\mathbf{H_2O}]=K_{a2}/[\mathbf{H_2O}]=10^{\wedge(-5,6)}/55,3=4,54*10^{\wedge(-8)}=10^{\wedge(-7,34)}$;

$(CH_2)_2(C\mathbf{O_2}H)_2+2\mathbf{H_2O}\rightleftharpoons(CH_2)_2(C\mathbf{O_2}^-)(C\mathbf{O_2}^-)+2H_3O^+$; $K_{aeq}=K_{a1eq}*K_{a2eq}=1,14*10^{\wedge(-6)}*4,54*10^{\wedge(-8)}=10^{\wedge(-13,3)}$;

$\Delta G_{\mathbf{eqSuccinat}}=-R\bullet T\bullet\ln(K_{\mathbf{aeq}})=-8,3144*298,15*\ln(10^{\wedge(-13,3)})/1000=\mathbf{75,9}\ ^{kJ}/_{mol}$ .

$\Delta G_{\mathbf{Succinat}}=G_{\mathbf{Succinat}}+2G_{H3O+}-(G_{\mathbf{SuccinicAc}}+2G_{H2O})=G_{\mathbf{Succinat}}+\mathbf{2*22,44-(619,8+2*0)=75,9}\ ^{kJ}/_{mol}$;

$G_{\mathbf{Succinat}}=\Delta G_{\mathbf{Succinat}}-2G_{H3O+}+(G_{\mathbf{SuccinicAc}}+2G_{H2O})=\mathbf{75,9-2*22,44+(619,8+2*0)=650,8}\ ^{kJ}/_{mol}$;

Fumaric acid $(CH)_2(C\mathbf{O_2}H)_2+\mathbf{H_2O}\rightleftharpoons(CH)_2(C\mathbf{O_2}H)(C\mathbf{O_2})^-+H_3O^+$; $pk_{a1}=3,03$ ;

$K_{a1eq}=[(CH)_2(C\mathbf{O_2}H)(C\mathbf{O_2})^-]*[H_3O^+]/[(CH)_2(C\mathbf{O_2}H)_2]/[\mathbf{H_2O}]=K_{a1}/[\mathbf{H_2O}]=10^{\wedge(-3,03)}/55,3=1,69*10^{\wedge(-5)}=10^{\wedge(-4,77)}$;

**Fumarate** $^{2-}\rightleftharpoons(CH)_2(C\mathbf{O_2}H)(C\mathbf{O_2})^-+\mathbf{H_2O}\rightleftharpoons(CH)_2(C\mathbf{O_2}^-)(C\mathbf{O_2}^-)+H_3O^+$; $pK_{a2}=4,44$;

$K_{a2eq}=[(CH)_2(C\mathbf{O_2}^-)(C\mathbf{O_2}^-)]*[H_3O^+]/[(CH)_2(C\mathbf{O_2}H)(C\mathbf{O_2})^-]/[\mathbf{H_2O}]=K_{a2}/[\mathbf{H_2O}]=10^{\wedge(-4,44)}/55,3=6,57*10^{\wedge(-7)}=10^{\wedge(-6,18)}$;

$(CH)_2(C\mathbf{O_2}H)_2+2\mathbf{H_2O}\rightleftharpoons(CH)_2(C\mathbf{O_2}^-)(C\mathbf{O_2}^-)+2H_3O^+$; $K_{aeq}=K_{a1eq}*K_{a2eq}=1,69*10^{\wedge(-5)}*6,57*10^{\wedge(-7)}=10^{\wedge(-10,955)}$;

$\Delta G_{\mathbf{eqFumarat}}=-R\bullet T\bullet\ln(K_{\mathbf{aeq}})=-8,3144*298,15*\ln(10^{\wedge(-10,955)})/1000=\mathbf{62,53}\ ^{kJ}/_{mol}$ .

$\Delta G_{\mathbf{Fumarat}}=G_{\mathbf{Fumarat}}+2G_{H3O+}-(G_{\mathbf{FumaricAc}}+2G_{H2O})=G_{\mathbf{Fumarat}}+\mathbf{2*22,44-(537,1+2*0)=62,53}\ ^{kJ}/_{mol}$;

$G_{\mathbf{Fumarat}}=\Delta G_{\mathbf{Fumarat}}-2G_{H3O+}+(G_{\mathbf{FumaricAc}}+2G_{H2O})=\mathbf{62,53-2*22,44+(537,1+2*0)=554,75}\ ^{kJ}/_{mol}$;

Ox $\mathbf{O_2}_{aqua}\mathbf{+2H_3O^++2e^-=H_2O_2}_{aqua}\mathbf{+2H_2O}$; $\mathbf{E}^\circ_{\mathbf{OxO2\_H2O2}}=-0,4495$ V absolute University Alberta ;

$\underline{\Delta G_{\mathrm{Alberty}\mathbf{OxO2\_H2O2}}=G_{\mathbf{H2O2}}+2*G_{\mathbf{H2O}}-(G_{\mathbf{O2}\mathrm{aqua}}+2*G_{\mathbf{H3O+}})=\mathbf{274,5+2*0-(330+2*22,44)=-100,4}}\ ^{kJ}/_{mol}$ ;

$\Delta\mathbf{G}_{\mathbf{eq}\mathrm{AlbertyAbsolute}\mathbf{OxO2\_H2O2}}=\mathbf{E}^\circ_{\mathbf{eqOxO2\_H2O2}}\bullet F\bullet1\bullet2=\mathbf{-0,}4495*96485*2=\mathbf{-86,7}\ ^{kJ}/_{mol}$;

Nernst’s half Red $\mathbf{Succinate^{2-}+2H_2O=Fumarate^{2-}+2H_3O^++2e^-}$ ; $\mathbf{E}^\circ_{\mathbf{RedSuccinate}}=0,2512$ V; absolute potential ;

Alberty $\Delta G_{\mathbf{eqSuccinat}\_\mathrm{Fumarat}}=G_{\mathbf{Fumarat}}+2G_{H3O+}-(G_{\mathbf{Succinat}}+2G_{\mathbf{H2O}})=\mathbf{554,75}+2*\mathbf{22,44-(650,8}+2*0)=\mathbf{-51,2}\ ^{kJ}/_{mol}$;

$\Delta\mathbf{G}_{\mathbf{eq}\mathrm{AlbertyNernst}\mathbf{RedSuccinatFumarat}}=\mathbf{E}^\circ_{\mathbf{eqNernstHalfSuccinat}\_\mathrm{Fumarat}}\bullet F\bullet1\bullet2=\mathbf{0,}2512*96485*2=\mathbf{48,47}\ ^{kJ}/_{mol}$;

Standard equilibrium state attractor for non equilibrium states

$\mathbf{Succinat^{2-}+O_2}_{aqua}\Rightarrow\mathbf{fumarate^{2-}+H_2O_2}_{aqua}\mathbf{+Q+\Delta G}$; $\mathbf{\Delta G_{min}=\Delta G_{eqSuccinat\_}}{}_{H2O2}\mathbf{=-38,3}\ ^{kJ}/_{mol}$;

Alberty $\underline{\text{Hess }\Delta G_{\mathbf{Succinat\_}\mathrm{H2O2}}=G_{\mathbf{Fumarat}}+G_{H2O2}-(G_{\mathbf{Succinat}}+G_{\mathrm{O2aqua}})=\mathbf{554,75+274,5-(650,8+330)=-151,55}}\ ^{kJ}/_{mol}$;

$\mathbf{\Delta G_{min}=\Delta G_{eq}}=(\mathbf{E^\circ_{RedSuccinate}-E^\circ_{OxO2}})\mathbf{*F*n}=(0,2512-0,4495)*96485*2=(-0,1983)*96485*2=\mathbf{-38,3}\ ^{kJ}/_{mol}$;

Nernst’s half Red $\mathbf{Succinate^{2-}+2H_2O=Fumarate^{2-}+2H_3O^++2e^-}$ ; $\mathbf{E}^\circ_{\mathbf{RedSuccinate}}=0,2512$ V; absolute potential ;

$\Delta G_{\mathbf{eqSuccinat}\_\mathrm{Fumarat}}=G_{\mathbf{FumaratFor}}+2G_{H3O+}-(G_{\mathbf{SuccinatFor}}+2G_{\mathbf{H2O}})=\mathbf{537,1}+2*\mathbf{22,44-(619,8}+2*0)=\mathbf{-37,82}\ ^{kJ}/_{mol}$;

$\Delta G_{\mathbf{eqSuccinat}\_\mathrm{Fumarat}}=G_{\mathbf{FumaratFor}}+2G_{H3O+}-(G_{\mathbf{SuccinatFor}}+2G_{\mathbf{H2O}})=\mathbf{537,1}+2*\mathbf{22,44-(619,8}+2*85,64)=\mathbf{-209,1}\ ^{kJ}/_{mol}$;

$\Delta\mathbf{G}_{\mathbf{eq}\mathrm{AlbertyNernst}\mathbf{RedSuccinatFumarat}}=\mathbf{E}^\circ_{\mathbf{eqNernstHalfSuccinat}\_\mathrm{Fumarat}}\bullet F\bullet1\bullet2=\mathbf{0,}2512*96485*2=\mathbf{48,47}\ ^{kJ}/_{mol}$;

Standard equilibrium state attractor for non equilibrium states

$\mathbf{Succinat^{2-}+O_2}_{aqua}\Rightarrow\mathbf{fumarate^{2-}+H_2O_2}_{aqua}\mathbf{+Q+\Delta G}$; $\mathbf{\Delta G_{min}=\Delta G_{eqSuccinat\_}}{}_{H2O2}\mathbf{=-38,3}\ ^{kJ}/_{mol}$;

Alberty Hess $\underline{\Delta G_{\mathbf{Succinat\_}\mathrm{H2O2}}=G_{\mathbf{Fumarat}}+G_{H2O2}-(G_{\mathbf{Succinat}}+G_{\mathrm{O2aqua}})=\mathbf{537,1+274,5-(619,8+330)=-151,55}}\ ^{kJ}/_{mol}$;

$\mathbf{\Delta G_{min}=\Delta G_{eq}}=(\mathbf{E^\circ_{RedSuccinate}-E^\circ_{OxO2}})\mathbf{*F*n}=(0,2512-0,4495)*96485*2=(-0,1983)*96485*2=\mathbf{-38,3}\ ^{kJ}/_{mol}$;

**$CH_3CH_2OH$** ethanol formation from elements:

$2C+3H_{2gas}+1/2O_{2gas}=>CH_3CH_2OH$ ; $\Delta G^\circ_{Alberty}=75,2864\ ^{kJ}/_{mol}$ ; $\Delta G^\circ_{HessCRC}=-181\ ^{kJ}/_{mol}$ ;

$\Delta G^\circ_{Alberty}=G_{CH3CH2OH}-(2G_{Cgraph}+3*G_{H2gas}+1/2*G_{O2gas})=75,2864\ ^{kJ}/_{mol}$ ;

$\Delta G^\circ_{CRC}=G_{CH3CH2OH}-(2G_{Cgraph}+3*G_{H2gas}+1/2*G_{O2gas})=-181\ ^{kJ}/_{mol}$ ;

$\Delta G^\circ_{Alberty}+(2G_{Cgraph}+3*G_{H2gas}+1/2*G_{O2gas})= 75,2864+(2*91,26+3*85,6+1/2*303)=G_{CH3CH2OH}=666,106\ ^{kJ}/_{mol}$ ;

$\Delta G^\circ_{CRC}+(2G_{Cgraph}+3*G_{H2gas}+1/2*G_{O2gas})=-181+(2*91,26+3*85,6+1/2*303)=G_{CH3CH2OH}=409,82\ ^{kJ}/_{mol}$ ;

**$CH_3CHO$** acetaldehyde formation from elements: $2C+2H_{2gas}+1/2O_{2gas}=>CH_3CHO$ ;

$\Delta G^\circ_{Alberty}=G_{CH3CHO}-(2G_{Cgraph}+2*G_{H2gas}+1/2*G_{O2gas})=32,282\ ^{kJ}/_{mol}$ ;

$\Delta G^\circ_{CRC}=G_{CH3CHO}-(2G_{Cgraph}+2*G_{H2gas}+1/2*G_{O2gas})= 24,06\ ^{kJ}/_{mol}$ ;

$\Delta G^\circ_{Alberty}+(2G_{Cgraph}+2*G_{H2gas}+1/2*G_{O2gas})=32,282+(2*91,26+2*85,6+1/2*303)=G_{CH3CHO}=537,5\ ^{kJ}/_{mol}$ ;

$\Delta G^\circ_{CRC}+(2G_{Cgraph}+2*G_{H2gas}+1/2*G_{O2gas})=24,06+(2*91,26+2*85,6+1/2*303)=G_{CH3CHO}=529,28\ ^{kJ}/_{mol}$ ;

$CH_3CH_2OH+H_2O=CH_3CHO+H_3O^++H^-(H^++2e^-)$; 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* | $\Delta H^\circ_H\ ^{kJ}/_{mol}$ | $\Delta S^\circ_H\ ^{J}/_{mol/K}$ | $\Delta G^\circ_H\ ^{kJ}/_{mol}$ | CRC Handbook of Chemistry and Physics 2010 90th David R. Lide |
|---|---|---|---|---|
| **$H_3C-CH=O$** | -212,23 | -281,84 | 24,06 | $G_{CH3CHO}=529,28\ ^{kJ}/_{mol}$ ; |
| **$H_3C-CH=O$** | **-213,88** | **-825,64** | **32,2824** | $G_{CH3CHO}=537,5\ ^{kJ}/_{mol}$ ; |
| **NADH** | **-41,41** | **-4465,708** | **1175,5732** | BioThermodynam06; |
| NAD**H** | -1036,66 | -140,50 | 1120,09 | |
| **$H_3O^+$** | -285.81 | -3.854 | -213,275 | |
| $NAD^+$ | **-10,30** | **-3766,008** | **1112,534** | BioThermodynamic,2006,Massachusetts Tecnology Institute,Alberty |
| $NAD^+$ | -1007,48 | -183 | 1059,11 | |
| **$H_3CCH_2OH$** | **-290,77** | **-1227,764** | **75,2864** | Alberty $G_{CH3CH2OH}=666,106\ ^{kJ}/_{mol}$ ; |
| $H_3CCH_2OH_{aq}$ | -288,3 | -357,7394 | -181,64 | CRC $G_{CH3CH2OH}=409,82\ ^{kJ}/_{mol}$ ; |
| **$H_2O$** | -285.85 | 69.9565 | -237,191 | $G_{H2O}=0\ ^{kJ}/_{mol}$; $G_{H-}=-10,6-537,5-22,44+(409,82+0)=-160,7\ ^{kJ}/_{mol}$. |
| **$H_2O$** | **-286,65** | **-453,188** | **-151,549** | $G_{H2O\_Biochem}=85,64\ ^{kJ}/_{mol}$. $G_{H-}=-10,6-537,5-22,44+(409,82+85,64)=-75,08\ ^{kJ}/_{mol}$ |

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

$NAD^++\cancel{H^-(H^++2e^-)}+CH_3CH_2OH+H_2O=NADH+CH_3CHO+H_3O^++\cancel{H^-(H^++2e}^-)$;

$NAD^++CH_3CH_2OH+H_2O=NADH+CH_3CHO+H_3O^+$;

$\Delta G_{min}=\Delta G_{eq}=(E^\circ_{eqNernsCH3CH2OH}-E^\circ_{NAD+})*F*n=(-0,055+0,4095)*96485*2=(0,4562)*96485*2=68,408\ ^{kJ}/_{mol}$;

$\Delta G_{HessAlbertyCH3CH2OH}=G_{NADH}+G_{H3O+}+G_{CH3CHO}-(G_{NAD+}+G_{CH3CH2OH}+G_{H2O})=\underline{68,02\ ^{kJ}/_{mol}}.$

$=1112,534+22,44+537,5-(1175,5+666,106+0)=-169,1\ ^{kJ}/_{mol}$.

$=1112,534+22,44+32,282-(1175,5+75,2864+0)=-83,53\ ^{kJ}/_{mol}$.

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

$=1112,534+22,44+32,282-(1175,5+75,2864+85,64)=-169,2\ ^{kJ}/_{mol}$.

$H_3CHC(OH)COO^- + \mathbf{H_2O} \Rightarrow H_3CC{=}OCOO^- + \mathbf{H_3O^+} + \mathbf{H^-(H^+ + 2e^-)}$; $\mathbf{E°}_{H3CHC(OH)COO} = -0{,}0159$ V;

$\Delta\mathbf{G}_{\mathbf{eq}H3CHC(OH)COO} = \mathbf{E°}_{\mathbf{eq}H3CHC(OH)COO} \bullet F \bullet 2 = \mathbf{-0{,}}0159 * 96485 * 2 = \mathbf{-3{,}068}\ ^{kJ}/_{mol}$;

$\Delta\mathbf{G}_{\mathbf{HessCH3CH2OH}} = \mathbf{G}_{H3CC=OCOO} + G_{H3O+} + G_{H-} - (\mathbf{G}_{H3CHC(OH)COO} + G_{\mathbf{H2O}}) = \mathbf{534{,}2} + \mathbf{22{,}44} + G_{H-} - (\mathbf{668{,}8} + 0) = \mathbf{-3{,}068}\ ^{kJ}/_{mol}$.

$\Delta\mathbf{G}_{\mathbf{HessCH3CH2OH}} = \mathbf{G}_{H3CC=OCOO} + G_{H3O+} + G_{H-} - (\mathbf{G}_{H3CHC(OH)COO} + G_{\mathbf{H2O}\_Biochem}) = \mathbf{534{,}2} + \mathbf{22{,}44} + G_{H-} - (\mathbf{668{,}8} + \mathbf{85{,}64}) = \mathbf{-3{,}068}\ ^{kJ}/_{mol}$.

$\Delta\mathbf{G}_{\mathbf{HessCH3CH2OH}} - \mathbf{G}_{H3CC=OCOO} - G_{H3O+} + (\mathbf{G}_{H3CHC(OH)COO} + G_{\mathbf{H2O}}) = G_{H-} = \mathbf{-3{,}068 - 534{,}2 - 22{,}44 + (668{,}8} + 0\mathbf{) = 109{,}092}\ ^{kJ}/_{mol}$.

$\Delta\mathbf{G}_{\mathbf{HessCH3CH2OH}} - \mathbf{G}_{H3CC=OCOO} - G_{H3O+} + (\mathbf{G}_{H3CHC(OH)COO} + G_{\mathbf{H2O}\_Biochem}) = G_{H-} = \mathbf{-3{,}068 - 534{,}2 - 22{,}44 + (668{,}8} + \mathbf{85{,}64) = 194{,}7}\ ^{kJ}/_{mol}$.

I=0,25 M, **BioTherm06**, pH=7,36, $\Delta G_H = G°_{H3CC=OCOO-} + G°_{\mathbf{H3O+}} + G_{H-} - G_{H3CHC(OH)COO-} - G_{\mathbf{H2O}} =\ ^{kJ}/_{mol}$;

| *Viela* | $\Delta H°_H\ ^{kJ}/_{mol}$ | $\Delta S°_H\ ^{J}/_{mol/K}$ | $\Delta G°_H$ , $^{kJ}/_{mol}$ ; |
|---|---|---|---|
| **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** |
| $H_3CHC(OH)COO^-$ | **-688,29** | **-1290,9** | **-303,4** |

$G_{\mathbf{H2O}} = \mathbf{0}\ ^{kJ}/_{mol}$; $G_{H-} = \mathbf{-3{,}068 - 534{,}2 - 22{,}44 + (668{,}8} + 0\mathbf{) = 109{,}092}\ ^{kJ}/_{mol}$

$G_{\mathbf{H2O}\_Biochem} = \mathbf{85{,}64}\ ^{kJ}/_{mol}$; $G_H = \mathbf{-3{,}068 - 534{,}2 - 22{,}44 + (668{,}8} + \mathbf{85{,}64) = 194{,}7}\ ^{kJ}/_{mol}$

$G_{H3CHC(OH)COO} = \mathbf{534{,}2}\ ^{kJ}/_{mol}$; p$K_a$=2,5;

$G_{H3CHC(OH)COO} = \mathbf{668{,}8}\ ^{kJ}/_{mol}$; p$K_a$=3,86;

**p$K_a$**=3,86; $\Delta H_c° = 1361{,}9\ ^{kJ}/_{mol}$; $G_{H3CHC(OH)COOH} = \mathbf{2271}\ ^{kJ}/_{mol}$;$H_3CHC(OH)COOH + 3\mathbf{O_2}_{gas} = 3C\mathbf{O_2}_{gas} + 3\mathbf{H_2O}$;

$\Delta H_c° = 3G_{C\mathbf{O2}gas} + 3G_{H2O} - (G_{H3CHC(OH)COOH} + 3G_{\mathbf{O2}gas}) = 3*\mathbf{0} + 3*\mathbf{0} - (G_{H3CHC(OH)COOH} + 3\mathbf{*303}) = 1361{,}9\ ^{kJ}/_{mol}$;

$G_{H3CHC(OH)COOH} + = 3G_{C\mathbf{O2}gas} + 3G_{H2O} - (\ 3G_{\mathbf{O2}gas}) = 3*\mathbf{0} + 3*\mathbf{0} - (+3\mathbf{*303})\ -1361{,}9 = G_{H3CHC(OH)COOH} = \mathbf{2271}\ ^{kJ}/_{mol}$;

**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];

$\Delta G_{H3CHC(OH)COOH} = G_{H3CHC(OH)COOH} - (\mathbf{3G}_{Cgraph} + \mathbf{3*}G_{\mathbf{H2}gas} + \mathbf{1{,}5*}G_{O2gas}) = \mathbf{-303{,}4}\ ^{kJ}/_{mol}$;

$G_{H3CHC(OH)COOH} = \mathbf{-303{,}4 + (3*91{,}26 + 3*85{,}6 + 1{,}5*303) = 681{,}7}\ ^{kJ}/_{mol}$;

Lactic acid $H_3CHC(OH)COOH + \mathbf{H_2O} \Leftrightarrow H_3CHC(OH)COO^- + H_3O^+$; p$K_a$=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=**31,98** $^{kJ}/_{mol}$ .

$\Delta G_{H3CHC(OH)COO} = G_{H3CHC(OH)COO} + 2G_{H3O+} - (G_{\mathbf{LacticAc}} + 2G_{H2O}) = G_{\mathbf{Succinat}} + \mathbf{2*22{,}44 - (681{,}7 + 2*0) = 31{,}98}\ ^{kJ}/_{mol}$;

$G_{H3CHC(OH)COO} = \Delta G_{H3CHC(OH)COO} - 2G_{H3O+} + (G_{\mathbf{LacticAc}} + 2G_{H2O}) = \mathbf{31{,}98 - 2*22{,}44 + (681{,}7 + 2*0) = 668{,}8}\ ^{kJ}/_{mol}$;

**Pyruvic acid$^-$** Formation 71st page $3\mathbf{C} + 2\mathbf{H_{2gas}} + 1{,}5\mathbf{O_2}_{gas} \Rightarrow H_3CC{=}OCOOH$; $\Delta G_{\mathbf{Succinat}} = \mathbf{-344{,}62}\ ^{kJ}/_{mol}$ Alberty;

$\Delta G_{\mathbf{Fumarat}} = G_{\mathbf{Fumarat}} - (\mathbf{3G}_{Cgraph} + 2G_{\mathbf{H2}gas} + \mathbf{1{,}5*}G_{O2gas}) = \mathbf{-344{,}62}\ ^{kJ}/_{mol}$;

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

**Pyruvic acid** $H_3CC{=}OCOOH + \mathbf{H_2O} \Leftrightarrow H_3CHC(OH)COO^- + H_3O^+$; p$K_a$=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=**24,22** $^{kJ}/_{mol}$ .

$\Delta G_{H3CHC(OH)COO} = G_{H3CHC(OH)COO} + 2G_{H3O+} - (G_{\mathbf{LacticAc}} + 2G_{H2O}) = G_{\mathbf{Succinat}} + \mathbf{2*22{,}44 - (554{,}86 + 2*0) = 24{,}22}\ ^{kJ}/_{mol}$;

$G_{H3CHC(OH)COO} = \Delta G_{H3CHC(OH)COO} - 2G_{H3O+} + (G_{\mathbf{LacticAc}} + 2G_{H2O}) = \mathbf{24{,}22 - 2*22{,}44 + (554{,}86 + 2*0) = 534{,}2}\ ^{kJ}/_{mol}$;

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

**Red lactate$^-$+H$_2$O<=>pyruvate$^-$+H$_3$O$^+$+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$_2$O=NADH+ pyruvate$^-$+H$_3$O$^+$**;

Balanced **n=2=m** with **2e$^-$** electrons ΔE° **NAD$^+$ accept** electrons from **lactate**:

$$\Delta\mathbf{G}_{\mathbf{eq}Aerobic} = \mathbf{\Delta E° \bullet F \bullet n = (E°_{Red} - E°_{Ox}) * F * n =} (-0{,}0159 — \mathbf{0{,}4095}) * 96485\mathbf{*2=}(0{,}3936)\mathbf{*2}=\mathbf{75{,}95}\ ^{kJ}/_{mol}$$

$$\mathbf{K}_{\mathbf{eq}Aerobic} = EXP(-\Delta\mathbf{G}_{\mathbf{eq}Aerobic}/R/T) = EXP(-75950/8{,}3144/298{,}15) = 10^{-13{,}3};$$

$$\mathbf{K}_{\mathbf{eq}Aerobic} = \frac{[NADH] \cdot [pyruvate^-] \cdot [H_3O^+]}{[NAD^+] \cdot [lactate^-]\ \cdot [H_2O]} = e^{-\frac{\Delta G_{eqAerobic}}{R \bullet T}} = \mathbf{e}^{-\frac{759500}{8.314 \bullet 298.15}} = \mathbf{10^{-13,3}};$$

$\Delta G_{Hess} = \Delta H_{Hess} - T * \Delta S_{Hess} = \mathbf{45{,}764} - 298{,}15 * \mathbf{-0{,}5479605} = \mathbf{209{,}14}$.......$^{kJ}/_{mol}$ **endoergic**; formation 62nd page