## Calculations in Bioenergetics

## Basic Relationships:

## Redox potential and standard redox potential (Nernst-Peters equation):

$$
E_{h}{ }^{\prime}=E_{0}{ }^{\prime}+\frac{R T}{n F} \ln \frac{\text { [oxid.] }}{[\text { red. }]}
$$

$\mathrm{E}_{\mathrm{h}}{ }^{\prime} \quad$ redox potential at $\mathrm{pH} 7(\mathrm{~V})$
$\mathrm{E}_{0}{ }^{\prime} \quad$ standard redox potential (both [oxid.] \& [red.] are $1 \mathrm{~mol} / \mathrm{l}$ ), at $\mathrm{pH} 7(\mathrm{~V})$
$\mathrm{R} \quad$ universal gas constant, $\mathrm{R}=8.3143 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$
T temperature ( K )
n number of electrons transferred
F Faraday (Faraday‘s charge), $\mathrm{F}=96487 \mathrm{JV}^{-1} \mathrm{~mol}^{-1}=96487 \mathrm{C} \mathrm{mol}^{-1}$
ln natural logarithm, $\ln =2.303 \log$
[oxid.] concentration of the substance in oxidised form ( $\mathrm{mol} / \mathrm{l}$ )
[red.] concentration of the substance in reduced form ( $\mathrm{mol} / \mathrm{l}$ )

## Free enthalpy change and equilibrium constant:

$$
\begin{aligned}
& \mathrm{A}+\mathrm{B} \leftrightarrow \mathrm{C}+\mathrm{D} \\
& \mathrm{~K}_{\mathrm{eq}}=\frac{[\mathrm{C}]_{\mathrm{eq}}[\mathrm{D}]_{\mathrm{eq}}}{[\mathrm{~A}]_{\mathrm{eq}}[\mathrm{~B}]_{\mathrm{eq}}}
\end{aligned}
$$

$$
\Delta G=-R T \ln K_{e q}+R T \ln \frac{[C][D]}{[A][B]}
$$



$$
\Delta G=\Delta G^{0}+R T \ln \frac{[C][D]}{[A][B]}
$$

$\Delta \mathrm{G} \quad$ free enthalpy change $\left(\mathrm{J} \mathrm{mol}^{-1}\right)$
$\Delta \mathrm{G}^{0} \quad$ standard free enthalpy change (concentrations of all reactants \& products are $\left.1 \mathrm{~mol} / \mathrm{l}\right)\left(\mathrm{J} \mathrm{mol}^{-1}\right)$
$\mathrm{R} \quad$ universal gas constant, $\mathrm{R}=8.3143 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$
T temperature in (K)
$\mathrm{K}_{\mathrm{eq}} \quad$ equilibrium constant
$\ln \quad$ natural logarithm, $\ln =2.303 \mathrm{log}$
$[\mathrm{A}],[\mathrm{B}]$, and $[\mathrm{C}],[\mathrm{D}] \quad \ldots$ actual concentrations of the reactants and products, respectively $(\mathrm{mol} / \mathrm{l})$
$[\mathrm{A}]_{\mathrm{eq}},[\mathrm{B}]_{\mathrm{eq}}$, and $[\mathrm{C}]_{\mathrm{eq}},[\mathrm{D}]_{\mathrm{eq}} \ldots$ equilibrium concentrations of the reactants and products, respectively $(\mathrm{mol} / \mathrm{l})$

## Free enthalpy change and redox potential:

$$
\begin{aligned}
& \Delta G^{\prime}=-n F \Delta E_{h}{ }^{\prime} \\
& \Delta G^{\prime \prime}=-n F \Delta E_{0}^{\prime}
\end{aligned}
$$

$\Delta \mathrm{G}^{\prime} \quad$ free enthalpy change at $\mathrm{pH} 7\left(\mathrm{~J} \mathrm{~mol}^{-1}\right)$
$\Delta \mathrm{G}^{0,} \quad$ standard free enthalpy change (concentrations of all reactants are $\left.1 \mathrm{~mol} / \mathrm{l}\right)$ at $\mathrm{pH} 7\left(\mathrm{~J} \mathrm{~mol}^{-1}\right)$
$\Delta \mathrm{E}_{\mathrm{h}}{ }^{\prime} \quad$ difference in redox potentials between two redox systems, at $\mathrm{pH} 7(\mathrm{~V})$
$\Delta \mathrm{E}_{0}{ }^{\prime}$ difference in standard redox potentials (all reactants are at conc. $1 \mathrm{~mol} / \mathrm{l}$ ) between two redox systems, at pH 7 (V)
n number of electrons transferred
F Faraday (Faraday‘s charge), $\mathrm{F}=96487 \mathrm{JVV}^{-1} \mathrm{~mol}^{-1}=96487 \mathrm{C} \mathrm{mol}^{-1}$

Osmotic work:


A osmotic work $\left(\mathrm{J} \mathrm{mol}^{-1}\right)$
n amount of protons transported against the concentration gradient (numerically equivalent to number of moles)
$\mathrm{R} \quad$ universal gas constant, $\mathrm{R}=8.3143 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$
T temperature (K)
$\ln \quad$ natural logarithm, $\ln =2.303 \log$
$c_{1} \quad$ concentration of the particles at the original side of the membrane
$\mathrm{c}_{2} \quad$ concentration of the particles at the other side of the membrane
E membrane potential difference resulting from uneven distribution of protons (V)
F Faraday (Faraday‘s charge), $\mathrm{F}=96487 \mathrm{JV}^{-1} \mathrm{~mol}^{-1}=96487 \mathrm{C} \mathrm{mol}^{-1}$

## Examples:

## TASK 1

What is the redox potential $\boldsymbol{E}_{\boldsymbol{h}}{ }^{\prime}$ of the system $\mathrm{NAD}^{+} / \mathrm{NADH}$ against hydrogen electrode, if the standard redox potential $\boldsymbol{E}_{0}{ }^{\prime}$ is -0.32 V and ratio $\mathrm{NAD}^{+} / \mathrm{NADH}$ is $10: 1$ ? (temperature $25^{\circ} \mathrm{C}, \mathrm{R}=8.3143 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}, \mathrm{~F}=96487 \mathrm{~J} \mathrm{~V}^{-1} \mathrm{~mol}^{-1}$ )

## Solution:

Use the Nernst-Peters equation

$$
E_{h}^{\prime}=E_{0}{ }^{\prime}+\frac{R T}{n F} \ln \frac{\left[N A D^{+}\right]}{[N A D H]}
$$

and take into account that $\mathrm{NAD}^{+}$transfers two electrons.

$$
\begin{aligned}
\mathrm{E}_{\mathrm{h}}^{\prime} \quad & =-0.32+\frac{8.3143 \times 298.15}{2 \times 96487} \times \ln 10= \\
& =-0.32+0.0128458 \times 2.3026= \\
& =-0.32+0.0296= \\
& \cong-\mathbf{0 . 2 9 \mathbf { V }}
\end{aligned}
$$

## TASK 2

What is the value of the equilibrium constant of ATP hydrolysis at $37^{\circ} \mathrm{C}$

$$
K_{e q}=\frac{[\mathrm{ADP}]\left[\mathrm{P}_{\mathrm{i}}\right]}{[\mathrm{ATP}]\left[\mathrm{H}_{2} \mathrm{O}\right]}
$$

$$
\text { if } \Delta \mathrm{G}^{0 \prime}=-35{\mathrm{~kJ} . \mathrm{mol}^{-1} ? \quad\left(\mathrm{R}=8.3143 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right), ~}_{\text {a }}
$$

Solution:

$$
\Delta G^{0}=-R T \ln K_{e q}
$$

From this equation $\ln \mathrm{K}_{\mathrm{eq}}=\Delta \mathrm{G}^{0} /-\mathrm{RT}=-35000 /(-8.3143 \times 310.15)=13.5732$

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{eq}}=\mathrm{e}^{13.5732} \cong \mathbf{7 . 8 \times 1 \mathbf { 1 0 } ^ { \mathbf { 5 } }} \\
\text { Or: } & \ln \mathrm{K}_{\mathrm{eq}}=13.5732 \\
& \log \mathrm{~K}_{\mathrm{eq}}=13.5732 / 2.303=5.893 \\
& \mathrm{~K}_{\mathrm{eq}}=10^{5.893} \cong \underline{\mathbf{7 . 8} \times 10^{5}}
\end{aligned}
$$

## TASK 3

For the hydrolysis of 1 mole of ATP to ADP at $37{ }^{\circ} \mathrm{C}$, the standard free enthalpy change $\boldsymbol{\Delta} \boldsymbol{G}^{\boldsymbol{0}}=-35 \mathrm{~kJ} . \mathrm{mol}^{-1}$. Calculate the free enthalpy change $\boldsymbol{\Delta} \boldsymbol{G}$ at the ratio ATP $/ \mathrm{ADP}=100: 1$.
(Temperature $37{ }^{0} \mathrm{C}, \mathrm{R}=8.3143 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$. Concentrations of water and inorganic phosphate are to be omitted from the equilibrium equation, assuming that they do not change significantly)

Solution:
$\underset{100}{\mathrm{ATP}+\mathrm{H}_{2} \mathrm{O}} \longleftrightarrow \underset{1}{\mathrm{ADP}}+\mathrm{P}_{\mathrm{i}} \quad \Delta \boldsymbol{G}=\Delta \boldsymbol{G}^{0}+\boldsymbol{R} \boldsymbol{T} \ln \frac{[A D P]}{[\boldsymbol{A T P}]}$
$\Delta \mathrm{G}=-35000+8.3143 \times 310.15 \times \ln \frac{1}{100}=$

$$
=-35000-11875.26=
$$

$$
=-46875.26=
$$

$$
\cong-46.9 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

## TASK 4

In the mitochondrial respiratory chain, reduced NAD (NADH) is reoxidised by flavin dehydrogenases:
$\mathrm{NADH}+\mathrm{H}^{+}+\mathrm{FAD} \rightarrow \mathrm{NAD}^{+}+\mathrm{FADH}_{2}$
The difference in the standard redox potentials $\boldsymbol{\Delta} \boldsymbol{E}_{0}{ }^{\prime}$ for the oxidation of NADH by FAD is +0.2 V . Calculate the standard free enthalpy change $\Delta G^{\boldsymbol{\theta}}\left(\right.$ in $\left.\mathrm{kJ} \mathrm{mol}^{-1}\right)$. $\left(\mathrm{F}=96487 \mathrm{~J} \mathrm{~V}^{-1} \mathrm{~mol}^{-1}\right)$

Solution:

$$
\Delta G^{0 \prime}=-n F \Delta E_{0}^{\prime}
$$

Take into account that the reaction involves transfer of two electrons.
$\Delta \mathrm{G}^{0 \boldsymbol{}}=\quad-2 \times 96487 \times 0.2=-38594.8 \cong-\mathbf{3 8 . 6} \mathbf{~ k J ~ m o l}{ }^{-1}$

## TASK 5

What is the osmotic work $\boldsymbol{A}$ for transfer of 1 mole of protons by respiratory chain complexes through the inner mitochondrial membrane, from matrix side $(\mathrm{pH}=7)$ to the inter-membrane space $(\mathrm{pH}=6)$ at $37^{\circ} \mathrm{C}$ ? What is the corresponding difference in membrane potential $\boldsymbol{\Delta} \boldsymbol{E}$ (expressed in V) ?
$\left(\mathrm{R}=8.3143 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}, \mathrm{~F}=96487 \mathrm{JV}^{-1} \mathrm{~mol}^{-1}\right)$

Solution:

$\mathrm{n}=1$
$\mathrm{R}=8.3143 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$
$\mathrm{T}=310.15 \mathrm{~K}$
$\mathrm{c}_{1}=10^{-7} \mathrm{~mol} / 1$
$\mathrm{c}_{2}=10^{-6} \mathrm{~mol} / 1$

$$
\begin{aligned}
\mathrm{A} & =1 \times 8.3143 \times 310.15 \times 2.303 \times \log 10= \\
& =5937.6 \mathrm{~J} \mathrm{~mol}^{-1}= \\
& \cong \underline{\mathbf{5 . 9} \mathbf{~ k J ~ m o l}}{ }^{-1}
\end{aligned}
$$

$\Delta \mathrm{E}=\mathrm{A} / \mathrm{F}=5937.6 / 96487 \cong \underline{\mathbf{0 . 0 6 1 ~ V}}$

MUDr. Jan Pláteník, PhD \& Prof. MUDr. Jiří Kraml, DrSc, 2004

