

Calculations in Bioenergetics

Basic Relationships:

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

$$E_h' = E_0' + \frac{RT}{nF} \ln \frac{[\text{oxid.}]}{[\text{red.}]}$$

E_h' redox potential at pH 7 (V)

E_0' standard redox potential (both [oxid.] & [red.] are 1 mol/l), at pH 7 (V)

R universal gas constant, $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$

T temperature (K)

n number of electrons transferred

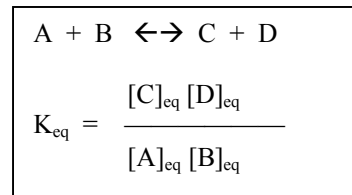
F Faraday (Faraday's charge), $F = 96\,487 \text{ J V}^{-1} \text{ mol}^{-1} = 96\,487 \text{ C mol}^{-1}$

ln natural logarithm, $\ln = 2.303 \log$

[oxid.] concentration of the substance in oxidised form (mol/l)

[red.] concentration of the substance in reduced form (mol/l)

Free enthalpy change and equilibrium constant:



$$\Delta G = -RT \ln K_{\text{eq}} + RT \ln \frac{[C] [D]}{[A] [B]}$$

$$\Delta G^0 = -RT \ln K_{\text{eq}}$$

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

ΔG free enthalpy change (J mol^{-1})

ΔG^0 standard free enthalpy change (concentrations of all reactants & products are 1 mol/l) (J mol^{-1})

R universal gas constant, $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$

T temperature in (K)

K_{eq} equilibrium constant

ln natural logarithm, $\ln = 2.303 \log$

[A], [B], and [C],[D] ...actual concentrations of the reactants and products, respectively (mol/l)

$[A]_{\text{eq}}$, $[B]_{\text{eq}}$, and $[C]_{\text{eq}}$, $[D]_{\text{eq}}$...equilibrium concentrations of the reactants and products, respectively (mol/l)

Free enthalpy change and redox potential:

$$\Delta G' = -n F \Delta E_h'$$

$$\Delta G^{0'} = -n F \Delta E_0'$$

$\Delta G'$ free enthalpy change at pH 7 (J mol^{-1})

$\Delta G^{0'}$ standard free enthalpy change (concentrations of all reactants are 1 mol/l) at pH 7 (J mol^{-1})

$\Delta E_h'$ difference in redox potentials between two redox systems, at pH 7 (V)

$\Delta E_0'$ difference in standard redox potentials (all reactants are at conc. 1 mol/l) between two redox systems, at pH 7 (V)

n number of electrons transferred

F Faraday (Faraday's charge), $F = 96\,487 \text{ J V}^{-1} \text{ mol}^{-1} = 96\,487 \text{ C mol}^{-1}$

Osmotic work:

$$A = n R T \ln \frac{c_2}{c_1}$$

$$E = \frac{A}{F}$$

A osmotic work (J mol^{-1})

n amount of protons transported against the concentration gradient (numerically equivalent to number of moles)

R universal gas constant, $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$

T temperature (K)

ln natural logarithm, $\ln = 2.303 \log$

c_1 concentration of the particles at the original side of the membrane

c_2 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), $F = 96\,487 \text{ J V}^{-1} \text{ mol}^{-1} = 96\,487 \text{ C mol}^{-1}$

Examples:

TASK 1

What is the redox potential E_h' of the system $\text{NAD}^+ / \text{NADH}$ against hydrogen electrode, if the standard redox potential E_0' is -0.32 V and ratio $\text{NAD}^+ / \text{NADH}$ is 10:1? (temperature 25°C , $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$, $F = 96\,487 \text{ J V}^{-1} \text{ mol}^{-1}$)

Solution:

Use the Nernst-Peters equation

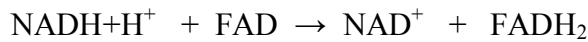
$$E_h' = E_0' + \frac{R T}{n F} \ln \frac{[\text{NAD}^+]}{[\text{NADH}]}$$

and take into account that NAD^+ transfers two electrons.

$$\begin{aligned} E_h' &= -0.32 + \frac{8.3143 \times 298.15}{2 \times 96\,487} \times \ln 10 = \\ &= -0.32 + 0.0128458 \times 2.3026 = \\ &= -0.32 + 0.0296 = \\ &\cong \underline{\underline{-0.29 \text{ V}}} \end{aligned}$$

TASK 4

In the mitochondrial respiratory chain, reduced NAD (NADH) is reoxidised by flavin dehydrogenases:



The difference in the standard redox potentials $\Delta E_0'$ for the oxidation of NADH by FAD is +0.2 V. Calculate the standard free enthalpy change $\Delta G^{0'}$ (in kJ mol^{-1}).
($F = 96\,487 \text{ J V}^{-1} \text{ mol}^{-1}$)

Solution:

$$\Delta G^{0'} = -n F \Delta E_0'$$

Take into account that the reaction involves transfer of two electrons.

$$\Delta G^{0'} = -2 \times 96487 \times 0.2 = -38\,594.8 \cong \underline{\underline{-38.6 \text{ kJ mol}^{-1}}}$$

TASK 5

What is the osmotic work A for transfer of 1 mole of protons by respiratory chain complexes through the inner mitochondrial membrane, from matrix side (pH = 7) to the inter-membrane space (pH = 6) at 37°C ? What is the corresponding difference in membrane potential ΔE (expressed in V)?

($R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$, $F = 96\,487 \text{ J V}^{-1} \text{ mol}^{-1}$)

Solution:

$$A = n RT \ln \frac{c_2}{c_1}$$

$$\begin{aligned} n &= 1 \\ R &= 8.3143 \text{ J K}^{-1} \text{ mol}^{-1} \\ T &= 310.15 \text{ K} \\ c_1 &= 10^{-7} \text{ mol/l} \\ c_2 &= 10^{-6} \text{ mol/l} \end{aligned}$$

$$\begin{aligned} A &= 1 \times 8.3143 \times 310.15 \times 2.303 \times \log_{10} = \\ &= 5\,937.6 \text{ J mol}^{-1} = \\ &\cong \underline{\underline{5.9 \text{ kJ mol}^{-1}}} \end{aligned}$$

$$\Delta E = A / F = 5\,937.6 / 96\,487 \cong \underline{\underline{0.061 \text{ V}}}$$