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Biophysical Chemistry

Week 5 Problems

To be handed in by Thursday 3rd April 2014, 17:00
(either at my office 01/05 under the door or at the secretary's office 3rd floor or in exceptional circumstances as a *single pdf file* via e-mail)

1. The overall reaction of a cell is:

$Zn_{(s)} + Hg_2SO_{4(s)} + 7H_2O \rightarrow ZnSO_4.7H_2O_{(s)} + 2Hg_{(l)}$

The e.m.f. (in volts) is given by:
$1.4151 - 1.2 \times 10^{-3}\ (T-298) - 7 \times 10^{-6}\ (T-298)^2$, where T is the thermodynamic temperature. Calculate ΔG, ΔH and ΔS for the above cell at 45 °C.

2. A suspension of mitochondria (internal volume 0.002 cm^3 of a total of 1 cm^3) (= 1 mL) was incubated with [^{3}H]acetate, $^{86}Rb^+$, valinomycin (ionophore which makes the membrane permeable to Rb^+), ADP, P_i and succinate, for a period to permit the ATP level to reach a constant value. At the end of this incubation the mitochondria were rapidly filtered from a part of the incubation and counted for ^{3}H and ^{86}Rb radioactivity. It was found that 1/11th of the total amount (not concentration!) of ^{3}H added and 1/6th of the total amount (not concentration!) ^{86}Rb added was also found in the mitochondria. The remaining mitochondrial suspension was analysed for ATP, ADP and P_i. These concentrations were 1 mM, 0.02 mM and 1 mM respectively. Are these data compatible with the view that 2 protons must pass across the mitochondrial membrane for each ATP molecule synthesised.
T = 300 K, F = 96.5 kJ V^{-1} mol^{-1}, R = 8.31 J K^{-1} mol^{-1} (not kJ K^{-1} mol^{-1}!). ΔG°′ for the reaction ADP + P_i = ATP is 30.5 kJ mol^{-1}.

(i): ΔG′= -n.F.Δp (a form of -nFE′); compare the result calculated from the equilibrium constant with that calculated from the acetate and Rb^+ data.
(ii): ΔpH can be related to the ratio of $[acetate]_{inside}$ over that of $[acetate]_{outside}$.
(iii): $\Delta\psi = -(RT/zF).\ln([Rb^+]_{in}/[Rb^+]_{out})$
(iv): $\Delta p = \Delta\psi - (2.3RT/F)\Delta pH$

ΔG′ = -nFE′ ⇝ Δp

Ac 1/11th → ΔpH → -log → -2,303

Rb 1/6th Δp ~ Rb + Ac

Week 5 Problems

1. $Zn_{(s)} + Hg_2SO_{4(s)} + 7H_2O \rightarrow ZnSO_4 \cdot 7H_2O_{(s)} + 2Hg_{(l)}$
$2e^- \rightarrow n = 2$

$EMF: 1{,}4151 - 1{,}2 \times 10^{-3}(T-298) - 7 \cdot 10^{-6}(T-298)^2$

ges $\Delta G, \Delta H, \Delta S$ bei 45°C

$45°C = 318{,}15K$

$R = 8{,}314\ J/mol \cdot K$

$F = 96\,500\ J/mol\,K$

$E° = 1{,}4151\ V$ (at 298K)

$E = 1{,}4151 - 1{,}2 \times 10^{-3} \cdot (318{,}15 - 298) - 7 \times 10^{-6}(318{,}15-298)$

$= 1{,}3881\ V$

$\Delta G = -n \cdot F \cdot E$

$\Delta G = -2 \cdot 96\,500 \cdot 1{,}3881 V$

$\Delta G = 267\ 903{,}3\ J/mol$

$= 267{,}9\ kJ/mol$

$\Delta E = 1{,}4151 - 1{,}3881$

$= -0{,}027\ V$

$\Delta T = 318{,}15 - 298$

$= 20{,}15K$

$\Delta S = +n \cdot F \cdot (\Delta E / \Delta T)$

$\Delta S = +2 \cdot 96500 \cdot \left(\frac{-0{,}027}{20{,}15}\right)$

$\Delta S = 258{,}6\ J/mol \cdot K$

$\Delta H = \Delta G + T\Delta S$

$\Delta H = 267{,}9\ kJ/mol + 318{,}15K \cdot 0{,}2586\ kJ/mol \cdot K$

$\Delta H = 350{,}2\ kJ/mol$

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Problem 2

internal $0{,}002\ cm^3$ outer: $0{,}998\ m^3$

outer $1{,}000\ cm^3$

^3H 1/11 } internal

^{86}Rb 1/6

outer: 1mM ATP, 0,02mM ADP

1mM P_i

$ADP + P_i \rightarrow ATP$ $\Delta G^{\circ\prime} = 30{,}5\ kJ/mol$

$n = 1$

$F = 96\,500\ C/mol\ V$
$R = 8{,}314\ J/mol\ K$
$T = 300\ K$
$\Delta G^\circ = 30\,500\ J/mol$

$$K = \frac{[ATP]}{[ADP][P_i]} = \frac{1\times10^{-3}M}{2\times10^{-5}\cdot 1\times10^{-3}} = 5\times10^{4}$$

$\ln K = 10{,}8197$

			in	out	
^3H	1/11	10/11	45455	910,9	49,9
^{86}Rb	1/6	5/6	83333	835,0	99,8

$\Delta pH = \log\left(\frac{45455}{910{,}9}\right)$

$\Delta pH = 1{,}698$

$\Delta\psi = -(RT/zF)\cdot\ln([Rb^+]_{in}/[Rb^+]_{out})$

$\Delta\psi = -0{,}119$

$\Delta p = \Delta\psi - (2{,}3RT/F)\Delta pH$

$\Delta p = -0{,}219$

$\Delta G' = \Delta G^\circ + RT\cdot\ln K$

$\Delta G' = 57\,473{,}7\ J/mol$

$$n = -\frac{\Delta G'}{F\Delta p}$$

$n = 2{,}7$