

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:



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 cm³ of a total of 1 cm³) was incubated with [³H]acetate, ⁸⁶Rb⁺, 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 ³H and ⁸⁶Rb radioactivity. It was found that $1/11^{\text{th}}$ of the total amount (not concentration!) of ³H added and $1/6^{\text{th}}$ of the total amount (not concentration!) ⁸⁶Rb 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.
 $T = 300 \text{ K}$, $F = 96.5 \text{ kJ V}^{-1} \text{ mol}^{-1}$, $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ (not $\text{kJ K}^{-1} \text{ mol}^{-1}$). ΔG° for the reaction $\text{ADP} + \text{P}_i = \text{ATP}$ is 30.5 kJ mol^{-1} .

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

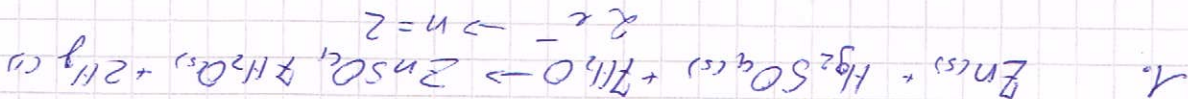
$$\Delta G' = -nFE'$$

$$\rightarrow \Delta\text{pH} \rightarrow -\log \rightarrow -2.303$$

$$\Delta\text{p} \sim K_b + A_c$$

$$A_c \frac{1}{1714}$$

$$K_b \frac{1}{14}$$



$$E_{MF} = 1,4151 - 1,2 \times 10^{-3} (T - 298) - 7 \times 10^{-6} (T - 298)^2$$

$$S_o \Delta G, \Delta H, \Delta S \text{ bei } 45^\circ C$$

$$45^\circ C = 318,15 K$$

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

$$F = 96500 \text{ C/mol}\cdot K$$

$$E^\circ = 1,4151 V (\text{at } 298 K)$$

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

$$E = 1,3381 V$$

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

$$\Delta G = -2 \cdot 96500 \cdot 1,3381 V$$

$$\Delta G = -267903,13 \text{ J/mol}$$

$$\Delta G = -267,9 \text{ kJ/mol}$$

$$\Delta S = +n \cdot F \cdot (dE/dT)$$

$$\Delta S = +2 \cdot 96500 \cdot \left(\frac{-0,007}{29,15} \right)$$

$$\Delta S = -2581,6 \text{ J/mol}\cdot K$$

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

$$\Delta H = -267,9 \text{ kJ/mol} + 318,15 K \cdot 0,25816 \text{ kJ/mol}\cdot K$$

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

$$= 20,15 K$$

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

$$= -9027 V$$

$$\Delta E = 1,4151 - 1,3381$$

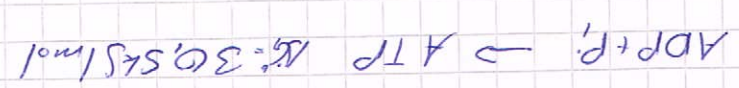
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Problem 2

interior 0,002 cm³
exterior 1,000 cm³
outer: 0,998 m³

3 H 1/11 } interior
86 Rb 1/6

outer: 1 mM ATP, 902 mM ADP
1 mM P_i



n = 1

F = 96 500 (mol/V)
R = 8,314 (J/molK)
T = 300 K
ΔG° = 30 500 J/mol

$$K = \frac{[ATP]}{[ADP][P_i]} = \frac{1 \times 10^{-3} M}{5 \times 10^{-4} \times 1 \times 10^{-3}} = 5 \times 10^4$$

$k_{in} = 10,8197$

| | |
|-----------|-------|
| out | in |
| 3 H 1/11 | 45455 |
| 86 Rb 1/6 | 83333 |
| | 910,9 |
| | 99,9 |

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

$\Delta G_H = 1,698$

$\Delta G = \Delta \psi - (2,3RT) \ln \Delta p_H$

$\Delta G = -0,279$

$n = -\frac{\Delta G}{F \Delta \psi}$
 $n = 2,17$

$\Delta G' = 57 478,7 \text{ J/mol}$

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

$\Delta \psi = -0,179$

$\Delta \psi = -(RT/2F) \cdot \ln ([Rb^{86}] / [H^3])$