**Assignment 23 – Worked Answers**

1. Nicotinamide adenine dinucleotide (NADH), a cofactor in many biochemical reactions, is a strong reducing agent in water solution:

   \[
   \text{NADH} + \text{H}^+ \quad \text{NAD}^+ + 2\text{H}^+ + 2e^- \quad E^\circ = 0.113 \text{ V}
   \]

   Calculate the value of \( E^\circ \) (reduction potential at the biological standard state of pH = 7.0) for this half cell at 298 K.

   First, turn the reaction around so that it is written as a reduction, which will change \( E^\circ \) to -0.113 V. Next use the Nernst Equation, with 1 M the concentration for everything but H\(^+\), which is \( 1 \times 10^{-7} \).

   \[
   E^\circ' = E^\circ - \frac{RT}{nF} \ln Q = -0.113 - \frac{(8.314 \times 298 \div 2 \times 96485)}{2 \times 10^{-7}} = -0.320 \text{ V}
   \]

2. The pyruvate ion (Pv\(^-\)) is reduced to the lactate ion (PvH\(_2\)^-) at pH 7 in the following half cell.

   \[
   \text{Pv}^- + 2\text{H}^+ + 2e^- \quad \text{PvH}_2^- \quad E^\circ = -0.185 \text{ V}
   \]

   Assume this half cell is combined with the NADH half cell of Q1 at pH 7

   a) Write the overall cell reaction

   \[
   \text{NADH} + 3\text{H}^+ + \text{Pv}^- \quad \text{NAD}^+ + 2\text{H}^+ + \text{PvH}_2^- \]

   b) What is the voltage of this cell at pH 7?

   \[
   E^\circ' = -0.185 - (-0.320) = 0.135 \text{ V}
   \]

   c) What is the equilibrium constant for this reaction at 298 K and pH 7?

   \[
   E^\circ' = \frac{(RT/nF)\ln K}{\ln K = nFE^\circ' \div RT = (2 \times 96485 \times 0.135) \div (8.314 \times 298) = 10.51} \quad K = 3.69 \times 10^4
   \]

   d) What is the value of \( \Delta G^\circ \) for this reaction at 298 K?

   \[
   \Delta G^\circ = -nFE^\circ' = (2 \times 96485 \times 0.135) = -2.61 \times 10^4 \text{ J (or –26.1 kJ)}
   \]
e) Would the emf of the cell *increase*, *decrease* or *remain unchanged* if (i) the pH were reduced to 6.0, (ii) [NADH] were reduced to 0.1 M, (iii), T was increased to 37°C?

You need to write out the Nernst Equations for each half cell and calculate the changes.

i) The emf would **increase**
(0.165 V – this change decreases the magnitude of the concentration-dependent term for both half cells, but makes a larger difference to the pyruvate half cell since it is dependent on \([H^+]^2\) rather than \([H^+]\))

ii) The emf would **decrease**
(0.105 V – this decreases the magnitude of the concentration-dependent term for the NADH half cell only)

iii) You could be lazy and say there is not enough information to answer the question, since we are only given \(E^\circ\) values at 25°C, but it is better to say that the emf would **decrease**.
(0.097 V - The magnitude of the concentration-dependent terms in both half-cells will increase, since these are directly dependent on temperature, but since the LnQ term is much larger for the pyruvate half cell, this will push the two values closer together.)

3. Typical concentrations of Na\(^+\) and K\(^+\) in the intracellular and extracellular fluid are given below.

\[
\begin{align*}
\text{Na}^+ &= 142 \text{ mM extracellular, 10 mM intracellular} \\
\text{K}^+ &= 4 \text{ mM extracellular, 140 mM intracellular}
\end{align*}
\]

Estimate the potential difference between the inside and outside of a cell.

This is taken directly from the lecture notes. Calling the outside of the cell the products and the inside the reactants,

\[
E = E^\circ - \frac{(RT/nF)(\ln Q)}{}
\]

\[
E = 0 - \left\{ \frac{(8.314 \times 310)}{96485} \ln \left\{ \frac{(4 \times 142)}{(140 \times 10)} \right\} \right\} = 0.024 \text{ V}
\]

(Meaning that the flow of an electron from the inside to the outside of the cell is a spontaneous process)