CHEM1109 Answers to Problem Sheet 9

1. **The reaction quotient is given by** $Q = \dfrac{[\mathrm{NAD^+}][\mathrm{H^+}]^2}{[\mathrm{NADH}][\mathrm{H^+}]} = [\mathrm{H^+}]$

as NADH and NAD$^+$ are at standard, 1 M concentrations.

As pH = -log$_{10}$([H$^+$]), the biological standard state corresponds to [H$^+$] = $10^{-7.0}$ M.

The cell potential for this 2e$^-$ process with [H$^+$] = $10^{-7.0}$ M can be calculated using the Nernst equation,

$$E^{\circ\prime} = E^o - \frac{RT}{nF}\ln Q = (0.527) - \frac{(8.314)\times(298)}{(2)\times(96485)}\ln(10^{-7.0}) = \ 0.73\ \mathrm{V}$$

2. (a) **Combining the half cell for oxidation of NADH with the half cell for reduction of the Pv$^-$ ion gives the overall cell reaction as:**

$$\mathrm{NADH + Py^- + 3H^+ \rightleftharpoons NAD^+ + PyH_2^- + 2H^+}$$

or

$$\mathrm{NADH + Py^- + H^+ \rightleftharpoons NAD^+ + PyH_2^-}$$

(b) $E^{\circ\prime}$ **= -0.185 + 0.73 = 0.55 V**

(c) **The equilibrium constant for this 2e$^-$ process can be calculated using** $E^{\mathrm{o}}_{\mathrm{cell}} = \dfrac{RT}{nF}\ln K$ **:**

$$\ln K = \frac{(2)\times(96485\,\mathrm{C\,mol^{-1}})}{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})} \times (0.55) = 42.8$$

$$K = e^{42.8} = 3.7 \times 10^{18}$$

(d) **Using** $\Delta G^\circ = -nFE^\circ$ **or** $\Delta G^\circ = -RT\ln K$**:**

$$\Delta G^\circ = -\mathrm{nFE}^\circ = -(2) \times (96485\ \mathrm{C\ mol^{-1}}) \times (0.55\ \mathrm{V})$$
$$= -110000\ \mathrm{J\ mol^{-1}} = -110\ \mathrm{kJ\ mol^{-1}}$$

or

$$\Delta G^\circ = -RT\ln K = -(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (298\ \mathrm{K}) \times \ln(3.7 \times 10^{18})$$
$$= -110\ \mathrm{kJ\ mol^{-1}}$$

(e) (i) **If the pH is reduced to 6.0, [H$^+$] = $10^{-6.0}$. This will decrease *E* for the oxidation of NADH and hence increase the overall cell potential:**

$$E(\mathrm{NADH/NAD^+}) = E^o - \frac{RT}{nF}\ln Q$$

$$= (0.527\ \mathrm{V}) - \frac{(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})}{(2) \times (96485\,\mathrm{C\,mol^{-1}})} \ln(10^{-6.0})$$

$$= 0.70\ \mathrm{V}$$

Hence, $E_{\mathrm{overall}} = (-0.185 + 0.70)\ \mathrm{V} = 0.52\ \mathrm{V}$

(ii) **If NADH is at the non-standard concentration of 0.1 M, the reaction quotient for the NADH/NAD$^+$ cell becomes**

$$Q = \frac{[\mathrm{NAD^+}][\mathrm{H^+}]^2}{[\mathrm{NADH}][\mathrm{H^+}]} = \frac{[\mathrm{H^+}]}{[\mathrm{NADH}]} = \frac{(10^{-7.0})}{(0.1)} = 10^{-6}$$

As in part (i), this decreases E(NADH/NAD$^+$) to 0.70 V and hence decreases E_{overall} to 0.52 V.

3. **Assuming that the cell membrane has a much higher permeability to K$^+$ than for all other ions, the intracellular → extracellular process corresponds to the reaction and reaction quotient below:**

$$\mathrm{K^+}_{\mathrm{intracellular}} \rightarrow \mathrm{K^+}_{\mathrm{extracellular}}$$

$$Q = [\mathrm{K^+}]_{\mathrm{extracellular}}/[[\mathrm{K^+}]_{\mathrm{intracellular}} = 4/140 = 0.029$$

The temperature of healthy human is around 37 °C, or (37 + 273) K = 310 K.

The *standard* cell potential, $E°$, is zero as if all concentrations are 1 M, there is no overall process. Hence, the potential difference arises from the concentration difference only and is given by the Nernst equation (z is the valence of the ion diffusing, i.e. +1 for K$^+$):

$$E = \frac{RT}{zF} \ln Q$$

$$= [(8.314 \times 310)/96500]\ln(0.029) = -0.095\ \mathrm{V}$$

4. (a) **Between experiments (1) and (2), [NO] is constant. Doubling [O$_2$] leads to the initial reaction rate doubling:**

the reaction is first order with respect to O$_2$.

Between experiments (1) and (3), [O$_2$] is constant. Doubling [NO] leads to the initial reaction rate increases by a factor of four:

the reaction is second order with respect to NO.

Thus,

$$\text{rate} \propto [\mathrm{O_2}][\mathrm{NO}]^2 = k[\mathrm{O_2}][\mathrm{NO}]^2$$

Using experiment (1), rate = 3.20×10^{-3} mol L^{-1} s^{-1} when $[O_2] = 1.10 \times 10^{-2}$ mol L^{-1} and [NO] = 1.30×10^{-2} mol L^{-1}. Hence, for *k* and its units:

$$3.20 \times 10^{-3} \text{ mol L}^{-1} = k \times (1.10 \times 10^{-2} \text{ mol L}^{1}) \times (1.30 \times 10^{-2} \text{ mol L}^{1})^{2}$$

$$(\text{mol L}^{-1}\text{ s}^{-1}) = (\text{units of } k) \times (\text{mol L}^{-1}) \times (\text{mol L}^{-1})^{2}$$

$$k = 1.7 \times 10^{3} \text{ mol}^{-2}\text{ L}^{2}\text{ s}^{-1}$$

(b) **According to the reaction equation:**

$$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$

Two moles of NO_2 are produced for every mole of O_2 which reacts. The react of formation of NO_2 is thus twice the rate of consumption of oxygen. If the initial rate of consumption of oxygen is 1×10^{3} mol L^{-1} s^{-1}, the initial rate of formation of $NO_2(g)$ is 2×10^{3} mol L^{-1} s^{-1}.