

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

as NADH and  $\text{NAD}^+$  are at standard, 1 M concentrations.

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

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

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

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



or



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

- (c) The equilibrium constant for this  $2e^-$  process can be calculated using  $E^{\circ}_{\text{cell}}$

$$= \frac{RT}{nF} \ln K :$$

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

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

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

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

or

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

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

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

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

$$= 0.70 \text{ V}$$

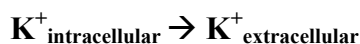
Hence,  $E_{\text{overall}} = (-0.185 + 0.70) \text{ V} = 0.52 \text{ V}$

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

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

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

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



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

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

The *standard* cell potential,  $E^\circ$ , 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<sup>+</sup>):

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

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

4. (a) Between experiments (1) and (2), [NO] is constant. Doubling [O<sub>2</sub>] leads to the initial reaction rate doubling:

the reaction is first order with respect to O<sub>2</sub>.

Between experiments (1) and (3), [O<sub>2</sub>] 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,

$$\text{rate} \propto [\text{O}_2][\text{NO}]^2 = k[\text{O}_2][\text{NO}]^2$$

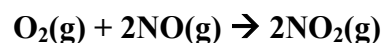
Using experiment (1), rate =  $3.20 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$  when  $[\text{O}_2] = 1.10 \times 10^{-2} \text{ mol L}^{-1}$  and  $[\text{NO}] = 1.30 \times 10^{-2} \text{ mol L}^{-1}$ . Hence, for  $k$  and its units:

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

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

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

(b) According to the reaction equation:



Two moles of  $\text{NO}_2$  are produced for every mole of  $\text{O}_2$  which reacts. The rate of formation of  $\text{NO}_2$  is thus twice the rate of consumption of oxygen. If the initial rate of consumption of oxygen is  $1 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$ , the initial rate of formation of  $\text{NO}_2(\text{g})$  is  $2 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$ .