22-2. (a)

$$E = 0.000 - \frac{0.0592}{2}\log\frac{p_{H_2}}{[H^+]^2} = -\frac{0.0592}{2}\log\frac{0.987}{(1.76)^2} = 0.015\ \text{V}$$

(b)

$$E = 1.178 - \frac{0.0592}{5}\log\frac{\left(2\times10^{-4}\right)^{1/2}}{(0.194)(3.5\times10^{-3})^6} = 1.017\ \text{V}$$

(c)

$$E = 0.446 - \frac{0.0592}{2}\log 0.0520 = 0.446 + 0.038 = 0.484\ \text{V}$$

22-3. (a) $2H^+ + 2e^- \rightleftharpoons H_2$ $\qquad E^0 = 0.000$ V

(1) $E = 0.000 - (0.0592/2)\log[1/(0.020)^2] = -0.101$ V

(2) ionic strength $\mu = \frac{1}{2}[0.02 \times 1^2 + 0.03 \times 1^2 + 0.05 \times 1^2] = 0.050$

From Table a2-1, $\gamma_{H^+} = 0.86$ and $a_{H^+} = 0.86 \times 0.02 = 0.0172$

$E = 0.000 - (0.0592/2)\log[1.00/(0.0172)^2] = -0.104$ V

(b) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\qquad E^0 = 0.771$ V

(1) $E = 0.771 - 0.0592\log(0.0111/0.0111) = 0.771$ V

(2) $\mu = \frac{1}{2}[0.0111 \times 2^2 + 0.0111 \times 3^2 + 2 \times 0.0111 \times 1^2 + 3 \times 0.0111 \times 1^2]$

$= 0.100$

From Table a2-1,

$\gamma_{Fe^{2+}} = 0.40$ and $a_{Fe^{2+}} = 0.40 \times 0.0111 = 0.00444$

$\gamma_{Fe^{3+}} = 0.18$ and $a_{Fe^{3+}} = 0.18 \times 0.0111 = 0.00200$

$E = 0.771 - 0.0592\log[0.00444/0.00200] = 0.750$ V

22.8. (a) $E_{right} = -0.151 - 0.0592\log 0.100 = -0.092$ V

$$E_{\text{left}} = 0.320 - \frac{0.0592}{3}\log\frac{1}{(0.0400)(0.200)^2} = 0.265 \text{ V}$$

$E_{\text{cell}} = -0.092 - 0.265 = -0.357$ V  Not spontaneous as written

(b) $$E_{\text{right}} = 0.36 - 0.0592 \log\frac{4.50\times10^{-2}}{(7.00\times10^{-2})} = 0.37 \text{ V}$$

$$E_{\text{left}} = -0.763 - \frac{0.0592}{2}\log\frac{1}{(7.50\times10^{-4})} = -0.855$$

$E_{\text{cell}} = 0.37 - (-0.86) = 1.23$ V  Spontaneous as written (oxidation on left)

(c) $E_{\text{right}} = 0.222 - 0.592 \log (7.50 \times 10^{-4}) = 0.407$ V

$$E_{\text{left}} = 0.000 - \frac{0.0592}{2}\log\frac{0.200}{(7.50\times10^{-4})^2} = -0.164 \text{ V}$$

$E_{\text{cell}} = 0.407 - (-0.164) = 0.571$ V  Spontaneous as written (oxidation on left)

22-9. $Ni^{2+} + 2e^- \rightleftharpoons Ni(s)$  $E^0 = -0.250$ V

$Ni(CN)_4^{2-} + 2e^- \rightleftharpoons Ni(s) + 4CN^-$  $E^0 = ?$

$$E_{Ni^{2+}/Ni} = -0.250 - \frac{0.0592}{2}\log\frac{1}{[Ni^{2+}]}$$

$$K_f = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$$

$$E = -0.250 - \frac{0.0592}{2}\log\frac{K_f[CN^-]^4}{[Ni(CN)_4^{2-}]}$$

For the 2nd reaction,

$$E = E^0 - \frac{0.0592}{2}\log\frac{[CN^-]^4}{[Ni(CN)_4^{2-}]}$$

When $[CN^-]^4/[Ni(CN)_4^{2-}] = 1.00$, $E = E^0 = -0.250 - \frac{0.0592}{2}\log K_f$

$$E^0 = -0.250 - \frac{0.0592}{2}\log 1\times10^{22} = -0.90 \text{ V}$$