

22-2. (a)

$$E = 0.000 - \frac{0.0592}{2} \log \frac{P_{\text{H}_2}}{[\text{H}^+]^2} = - \frac{0.0592}{2} \log \frac{0.987}{(1.76)^2} = 0.015 \text{ V}$$

(b)

$$E = 1.178 - \frac{0.0592}{5} \log \frac{(2 \times 10^{-4})^{1/2}}{(0.194)(3.5 \times 10^{-3})^6} = 1.017 \text{ V}$$

(c)

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

22-3. (a)  $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$   $E^0 = 0.000 \text{ V}$ 

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

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

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

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

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

$$(1) \quad E = 0.771 - 0.0592 \log (0.0111/0.0111) = 0.771 \text{ V}$$

$$(2) \quad \mu = \frac{1}{2}[0.0111 \times 2^2 + 0.0111 \times 3^2 + 2 \times 0.0111 \times 1^2 + 3 \times 0.0111 \times 1^2] \\ = 0.100$$

From Table a2-1,

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

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

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

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

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

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

$$(b) \quad E_{\text{right}} = 0.36 - 0.0592 \log \frac{4.50 \times 10^{-2}}{(7.00 \times 10^{-2})^2} = 0.37 \text{ V}$$

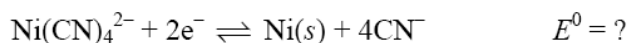
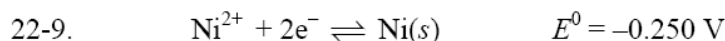
$$E_{\text{left}} = -0.763 - \frac{0.0592}{2} \log \frac{1}{(7.50 \times 10^{-4})^2} = -0.855$$

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

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

$$E_{\text{left}} = 0.000 - \frac{0.0592}{2} \log \frac{0.200}{(7.50 \times 10^{-4})^2} = -0.164 \text{ V}$$

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



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

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

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

For the 2nd reaction,

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

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

$$E^0 = -0.250 - \frac{0.0592}{2} \log 1 \times 10^{22} = -0.90 \text{ V}$$