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

(c) 
\[ E = 0.446 - \frac{0.0592}{2} \log 0.0520 = 0.446 + 0.038 = 0.484 \text{ V} \]

22.3. (a) \[ 2H^+ + 2e^- \rightleftharpoons H_2 \quad E^0 = 0.000 \text{ V} \]

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

(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 \( a_{H^+} = 0.86 \times 0.02 = 0.0172 \)

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

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

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

(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,
\[ \gamma_{Fe^{2+}} = 0.40 \quad \text{and} \quad a_{Fe^{2+}} = 0.40 \times 0.0111 = 0.00444 \]

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

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

22.8. (a) \[ E_{\text{right}} = -0.151 - 0.0592 \log 0.100 = -0.092 \text{ V} \]
23.2. The source of alkaline errors in pH measurements with a glass electrode arises from the exchange of singly charged ions, such as Na or K ions in the surface of the glass membrane with

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

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

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

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

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

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

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

22.9. \[ \text{Ni}^{2+} + 2e^- \rightleftharpoons \text{Ni(s)} \quad E^0 = -0.250 \text{ V} \]

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

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

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

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

For the 2nd reaction,

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

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

\[ E^0 = -0.250 - \frac{0.0592}{2} \log 1 \times 10^{21} = -0.90 \text{ V} \]
protons from the water. The potential of the system then responds to the alkali ion activity as well as the hydrogen ion activity.

23.4. Hydration of the surface of the glass takes place in which singly charged metal ions in the glass are exchanged with protons of the water.

23-7. (a) The asymmetry potential in a membrane arises from differences in the composition or structure of the inner and outer surfaces. These differences may arise from contamination of one of the surfaces, wear and abrasion and/or strains set up during manufacturing.

(b) The boundary potential for a membrane electrode is a potential that develops when the membrane separates two solutions that have different concentrations of a cation or an anion that the membrane binds selectively.

(c) The junction potential in a glass/reference electrode system develops at the interface between the saturated KCl solution in the salt bridge and the sample solution. It is caused by charge separation created by the differences in the rates at which ions migrate across the interface.

(d) The membrane in a solid-state electrode for F⁻ is crystalline LaF₃, which when immersed in aqueous solution, dissociates according to the equation

\[
\text{LaF}_3(s) \rightarrow \text{La}^{3+} + 3\text{F}^-
\]

Thus, the boundary potential develops across this membrane when it separates two solutions of F⁻ ion concentration.
23-13. (a) \[ E_{\text{right}} = 0.771 - 0.0592 \log \frac{0.0150}{0.0250} = 0.784 \text{ V} \]

\[ E_{\text{left}} = E_{\text{SCE}} = 0.244 \text{ V} \]

\[ E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.784 - 0.244 = 0.540 \text{ V} \]

(b) \[ E_{\text{right}} = -0.763 - \frac{0.0592}{2} \log \frac{1}{0.00228} = -0.841 \text{ V} \]

\[ E_{\text{left}} = E_{\text{SCE}} = 0.244 \text{ V} \]

\[ E_{\text{cell}} = -0.841 - 0.244 = -1.085 \text{ V} \]

(c) \[ E_{\text{right}} = -0.369 - 0.0592 \log \frac{0.0450}{0.0250} = -0.384 \text{ V} \]

\[ E_{\text{left}} = E_{\text{Ag}/\text{AgCl}} = 0.199 \text{ V} \]

\[ E_{\text{cell}} = -0.384 - 0.199 = -0.583 \text{ V} \]

(d) \[ E_{\text{right}} = 0.536 - \frac{0.0592}{2} \log \frac{(0.00433)^3}{0.00667} = 0.681 \text{ V} \]

\[ E_{\text{left}} = 0.199 \text{ V} \]

\[ E_{\text{cell}} = 0.482 \text{ V} \]

23-14. (a) \[ \text{Cu}^+ + e^- \rightleftharpoons \text{Cu} (s) \]

\[ E^0 = 0.521 \text{ V} \]

\[ E = 0.521 - 0.0592 \log \frac{1}{[\text{Cu}^+]} = 0.521 - 0.0592 \log \frac{[\text{Br}^-]}{K_{sp}} \]

When \([\text{Br}^-] = 1.00, E = E^0_{\text{CuBr}}\)
$$E_{\text{CuBr}}^0 = 0.521 - 0.0592 \log \frac{1.00}{5.2 \times 10^{-9}} = 0.031 \text{ V}$$

(b) \( \text{SCE}||\text{CuBr(sat'd)}, \text{Br}^-|\text{M}|\text{Cu} \)

(c) \[ E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.031 - 0.0592 \log [\text{Br}^-] - E_{\text{SCE}} \]

\[ = 0.031 + 0.0592 \text{pBr} - 0.244 \]

\[ \text{pBr} = (E_{\text{cell}} - 0.031 + 0.244)/0.0592 = (E_{\text{cell}} + 0.213)/0.0592 \]

(d) \[ \text{pBr} = (-0.095 + 0.213)/0.0592 = 1.99 \]

24.5. Most organic electrode processes involve hydrogen ions. Unless buffered solutions are used, marked pH changes can occur at the electrode surface as the reaction proceeds.

24.9. A plot of \( E_{\text{appl}} \) versus \( \log \frac{i}{i_j - i} \) should yield a straight line having a slope of \( \frac{-0.0592}{n} \).

Thus, \( n \) is readily obtained from the slope.

24.10. For the reduction of quinone (Q) to hydroquinone (H_2Q), Equation 25-3 takes the form

\[ E_{\text{appl}} = E_Q^0 - \frac{0.0592}{n} \log \left( \frac{c_{\text{H}_2\text{Q}}^0}{c_Q^0 (c_{\text{H}^+}^0)^2} \right) - E_{\text{ref}} \]

where \( c_{\text{H}^+}^0 \) is the concentration of H^+ at the electrode surface. Substituting Equations 25-7 and 25-10 into this equation gives

\[ E_{\text{appl}} = E_Q^0 - \frac{0.0592}{n} \log \left( \frac{k_Q}{k_{\text{H}_2\text{Q}} (c_{\text{H}^+}^0)^2} \right) - \frac{0.0592}{n} \log \left( \frac{i}{i_j - i} \right) - E_{\text{ref}} \]

When \( i = i_j/2 \), \( E_{\text{appl}} \) is the half-wave potential. With the added assumption that \( k_Q \approx k_{\text{H}_2\text{Q}} \), the foregoing equation becomes
\[ E_{1/2} = E^\circ_Q - E^\circ_{\text{ref}} - \frac{0.0592}{n} \log \left( \frac{1}{(c_{H^+}^\circ)^n} \right) \]  

\[ = 0.599 - 0.244 \times 0.0592 \text{pH} \]

\[ = 0.355 - 0.0592 \text{pH} \]

(a) At pH 7.00,

\[ E_{1/2} = 0.355 - 0.0592 \times 7.00 = -0.059 \text{ V} \]

(b) At pH 5.00

\[ E_{1/2} = 0.355 - 0.0592 \times 5.00 = +0.059 \text{ V} \]