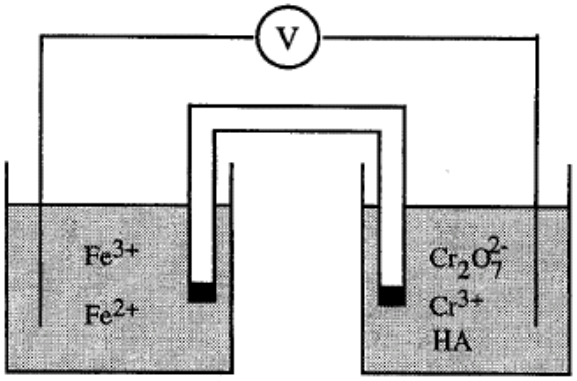
14-9. (a)



(b) oxidation: $Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$

reduction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$

(c) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightleftharpoons 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

14-12 Cl2 is the strongest since it has the most positive reduction potential.

14-15 E^0 is the potential measured when all concentrations are at unity. E is the potential measured for arbitrary concentrations. At equilibrium, E will go down in value. E^0 is a constant.

14-20. (a) right half-cell: $E_+ = \left\{ 0.222 - \frac{0.059\,16}{2} \log [Cl^-]^2 \right\} = 0.281_2$ V

left half-cell: $E_- = \left\{ -0.350 - \frac{0.059\,16}{2} \log [F^-]^2 \right\} = -0.290_8$ V

$E = E_+ - E_- = 0.281_2 - (-0.290_8) = 0.572$ V

(b) $[Pb^{2+}] = K_{sp}$ (for PbF_2) / $[F^-]^2 = (3.6 \times 10^{-8}) / (0.10)^2 = 3.6 \times 10^{-6}$ M

$[Ag^+] = K_{sp}$ (for AgCl) / $[Cl^-] = (1.8 \times 10^{-10}) / (0.10) = 1.8 \times 10^{-9}$ M

right half-cell: $E_+ = \left\{ 0.799 - \frac{0.059\,16}{2} \log \frac{1}{[Ag^+]^2} \right\} = 0.281_2$ V

left half-cell: $E_- = \left\{ -0.126 - \frac{0.059\,16}{2} \log \frac{1}{[Pb^{2+}]} \right\} = -0.287_0$ V

$E = E_+ - E_- = 0.281_2 - (-0.287_0) = 0.568$ V

The agreement is good.

14-25. (a) $E^\circ = \frac{-\Delta G^\circ}{nF} = \frac{(+257 \times 10^3 \text{ J/mol})}{(2)(9.648\,5 \times 10^4 \text{ C/mol})} = 1.33$ V

(b) $K = 10^{nE^\circ/0.059\,16} = 1 \times 10^{45}$

14-29.

$$\begin{array}{rl} \mathrm{Pd(OH)_2}(s) + 2e^- \rightleftharpoons \mathrm{Pd}(s) + 2\mathrm{OH^-} & E^\circ_+ \\ \underline{- \ \mathrm{Pd^{2+}} + 2e^- \rightleftharpoons \mathrm{Pd}(s)} & \underline{E^\circ_- = 0.915\ \mathrm{V}} \\ \mathrm{Pd(OH)_2} \overset{K_{sp}}{\rightleftharpoons} \mathrm{Pd^{2+}} + 2\mathrm{OH^-} & E^\circ = E^\circ_+ - 0.915 \end{array}$$

But $K_{sp} = 3 \times 10^{-28} \Rightarrow E^\circ = \dfrac{0.059\,16}{2} \log K_{sp} = -0.814$

$-0.814 = E_1^\circ - 0.915 \Rightarrow E_1^\circ = 0.101\ \mathrm{V}$

14-31.

$$\begin{array}{rl} \mathrm{FeY^-} + e^- \rightleftharpoons \mathrm{FeY^{2-}} & E^\circ_+ \\ \underline{- \ \mathrm{FeY^-} + e^- \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{Y^{4-}}} & \underline{E^\circ_- = -0.730\ \mathrm{V}} \\ \mathrm{Fe^{2+}} + \mathrm{Y^{4-}} \rightleftharpoons \mathrm{FeY^{2-}} & E^\circ = E^\circ_+ + 0.730 \end{array}$$

But $E^\circ = 0.059\,16 \log [K_f \text{ (for } \mathrm{FeY^{2-}})] = 0.847\ \mathrm{V} \Rightarrow E^\circ_+ = E^\circ - E^\circ_- = 0.117\ \mathrm{V}$