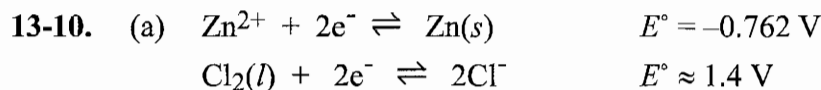


**CHAPTER 13**  
**FUNDAMENTALS OF ELECTROCHEMISTRY**

- 13-1.** Electric charge (coulombs) refers to the quantity of positive or negative particles. Current (amperes) is the quantity of charge moving past a point in a circuit each second. Electric potential (volts) measures the work that can be done by (or must be done to) each coulomb of charge as it moves from one point to another.
- 13-2.** (a)  $1/1.602\ 176\ 53 \times 10^{-19}\ \text{C/electron} = 6.241\ 509\ 48 \times 10^{18}\ \text{electrons/C}$   
 (b)  $F = 96\ 485.338\ 3\ \text{C/mol}$
- 13-3.** (a)  $I = \text{coulombs/s}$ . Every mol of  $\text{O}_2$  accepts 4 mol of  $e^-$ .  $16\ \text{mol O}_2/\text{day} = 64\ \text{mol } e^-/\text{day} = 7.41 \times 10^{-4}\ \text{mol } e^-/\text{s} = 71.5\ \text{C/s} = 71.5\ \text{A}$   
 (b)  $I = \text{Power}/E = 500\ \text{W}/115\ \text{V} = 4.35\ \text{A}$ . The resting human uses 16 times as much current as the refrigerator.  
 (c)  $\text{Power} = E \cdot I = (1.1\ \text{V})(71.5\ \text{A}) = 79\ \text{W}$
- 13-4.** (a)  $I = \frac{6.00\ \text{V}}{2.0 \times 10^3\ \text{W}} = 3.00\ \text{mA} = 3.00 \times 10^{-3}\ \text{C/s}$   
 $\left( \frac{3.00 \times 10^{-3}\ \text{C/s}}{9.649 \times 10^4\ \text{C/mol}} \right) (6.022 \times 10^{23}\ e^-/\text{mole}) = 1.87 \times 10^{16}\ e^-/\text{s}$   
 (b)  $P = E \cdot I = (6.00\ \text{V})(3.00 \times 10^{-3}\ \text{A}) = 1.80 \times 10^{-2}\ \text{W}$   
 $\Rightarrow \frac{1.80 \times 10^{-2}\ \text{J/s}}{1.87 \times 10^{16}\ e^-/\text{s}} = 9.63 \times 10^{-19}\ \text{J}/e^-$   
 (c)  $(1.87 \times 10^{16}\ e^-/\text{s})(1\ 800\ \text{s}) = 3.37 \times 10^{19}\ \text{electrons} = 5.60 \times 10^{-5}\ \text{mol}$   
 (d)  $P = EI = E(E/R) = E^2/R \Rightarrow E = \sqrt{PR} = \sqrt{(100\ \text{W})(2.00 \times 10^3\ \text{W})} = 447\ \text{V}$
- 13-5.** (a)  $\text{I}_2 + 2e^- \rightleftharpoons 2\text{I}^-$  ( $\text{I}_2$  is the oxidant)  
 (b)  $2\text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{S}_4\text{O}_6^{2-} + 2e^-$  ( $\text{S}_2\text{O}_3^{2-}$  is the reductant)  
 (c)  $1.00\ \text{g S}_2\text{O}_3^{2-} / (112.13\ \text{g/mol}) = 8.92\ \text{mmol S}_2\text{O}_3^{2-} = 8.92\ \text{mmol } e^-$   
 $(8.92 \times 10^{-3}\ \text{mol})(9.649 \times 10^4\ \text{C/mol}) = 861\ \text{C}$   
 (d)  $\text{Current (A)} = \text{coulombs/s} = 861\ \text{C}/60\ \text{s} = 14.3\ \text{A}$



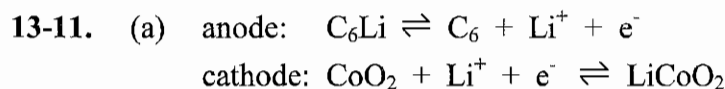


The Appendix lists standard reduction potentials for  $\text{Cl}_2(g)$  and  $\text{Cl}_2(aq)$ , but not for  $\text{Cl}_2(l)$ . Both listed potentials are close to 1.4 V, so the potential for  $\text{Cl}_2(l)$  is probably also close to 1.4 V. Electrons flow from the more negative electrode (Zn) through the circuit to the more positive electrode (C).

(b) One mol of  $\text{Cl}_2$  requires 2 mol of  $\text{e}^-$ .

$$\text{Moles of } \text{Cl}_2 \text{ consumed in 1.00 hr} = \frac{1}{2} (\text{mol of } \text{e}^-/\text{hr}) =$$

$$\left[ \frac{1}{2} \left( 1.00 \times 10^3 \frac{\text{C}}{\text{s}} \right) / (9.64 \times 10^4 \text{ C/mol}) \right] (3600 \text{ s/hr}) = 18.7 \text{ mol of } \text{Cl}_2 = 1.32 \text{ kg.}$$



(b)  $1 \text{ mA} = 1 \times 10^{-3} \frac{\text{C}}{\text{s}}$ .  $1 \text{ h} = 3600 \text{ s}$

$$1 \text{ mA}\cdot\text{h} = \left( 1 \times 10^{-3} \frac{\text{C}}{\text{s}} \right) (3600 \text{ s}) = 3.6 \text{ C}$$

(c)  $\frac{1 \text{ g LiCoO}_2}{97.87 \text{ g/mol}} = 1.02_{17} \times 10^{-2} \text{ mol LiCoO}_2$  which holds  $1.02_{17} \times 10^{-2} \text{ mol Li}^+$   
and  $1.02_{17} \times 10^{-2} \text{ mol e}^-$ .  $(1.02_{17} \times 10^{-2} \text{ mol e}^-) \left( 9.649 \times 10^5 \frac{\text{C}}{\text{mol e}^-} \right) = 985.8 \text{ C}$

$$\text{Charge capacity} = \left( 985.8 \frac{\text{C}}{\text{g LiCoO}_2} \right) \left( \frac{1 \text{ mA}\cdot\text{h}}{3.6 \text{ C}} \right) = 273.8 \frac{\text{mA}\cdot\text{h}}{\text{g LiCoO}_2}$$

(d) Fraction of Li available =  $\frac{140 \text{ mA}\cdot\text{h/g}}{273.8 \text{ mA}\cdot\text{h/g}} = 0.51$

(e) Energy stored per unit mass = work that can be done / mass =  $E \cdot q$  / mass  
=  $(3.7 \text{ V}) \left( 140 \frac{\text{mA}\cdot\text{h}}{\text{g LiCoO}_2} \right) = (3.7 \text{ V}) \left( 0.140 \frac{\text{A}\cdot\text{h}}{\text{g LiCoO}_2} \right) = 0.52 \frac{\text{W}\cdot\text{h}}{\text{g LiCoO}_2}$

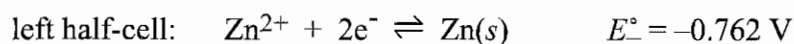
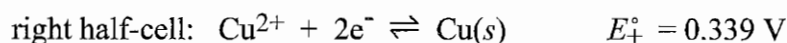
**13-12.**  $\text{Cl}_2$  is strongest because it has the most positive reduction potential.

**13-13.** (a) Since it becomes harder to reduce Fe(III) to Fe(II) in the presence of  $\text{CN}^-$ , Fe(III) is stabilized more than Fe(II).

(b) Since it becomes easier to reduce Fe(III) to Fe(II) in the presence of phenanthroline, Fe(II) is stabilized more than Fe(III).

**13-14.**  $E^\circ$  applies when activities of reactants and products are unity.  $E$  applies to whatever activities exist. At equilibrium,  $E$  goes to zero.  $E^\circ$  is constant.

**13-15.** (a)  $\text{Zn}(s) \mid \text{Zn}^{2+}(0.1 \text{ M}) \parallel \text{Cu}^{2+}(0.1 \text{ M}) \mid \text{Cu}(s)$



$$E = \left\{ 0.339 - \frac{0.05916}{2} \log \frac{1}{0.1} \right\} - \left\{ -0.762 - \frac{0.05916}{2} \log \frac{1}{0.1} \right\} = 1.101 \text{ V}$$

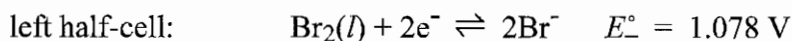
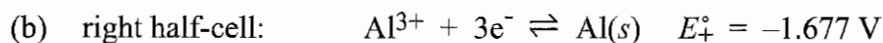
Since the voltage is positive, electrons are transferred from Zn to Cu. The net reaction is  $\text{Cu}^{2+} + \text{Zn}(s) \rightleftharpoons \text{Cu}(s) + \text{Zn}^{2+}$ .

(b) Since  $\text{Cu}^{2+}$  ions are consumed in the right half-cell,  $\text{Zn}^{2+}$  ions must migrate from the left half-cell into the salt bridge to help balance charge. I hope you like  $\text{Zn}^{2+}$ , because that is what your body will take up.

**13-16.** (a)  $E = -0.238 - \frac{0.05916}{3} \log \frac{P_{\text{AsH}_3}}{[\text{H}^+]^3}$

(b)  $E = -0.238 - \frac{0.05916}{3} \log \frac{1.0 \times 10^{-3}}{(10^{-3.00})^3} = -0.356 \text{ V}$

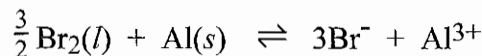
**13-17.** (a)  $\text{Pt}(s) \mid \text{Br}_2(l) \mid \text{HBr}(aq, 0.10 \text{ M}) \parallel \text{Al}(\text{NO}_3)_3(aq, 0.010 \text{ M}) \mid \text{Al}(s)$



right half-cell:  $E_+ = \left\{ -1.677 - \frac{0.05916}{3} \log \frac{1}{[0.010]} \right\} = -1.7164 \text{ V}$

left half-cell:  $E_- = \left\{ 1.078 - \frac{0.05916}{2} \log [0.10]^2 \right\} = 1.1372 \text{ V}$

$E = E_+ - E_- = -1.7164 - 1.1372 = -2.854 \text{ V}$ . The right electrode is more negative, so electrons flow from Al to Pt. Reduction occurs at the left-hand electrode. The spontaneous reaction is



(c) 14.3 mL of  $\text{Br}_2 = 44.6 \text{ g} = 0.279 \text{ mol}$  of  $\text{Br}_2$ . 12.0 g of Al = 0.445 mol of Al. The reaction requires  $3/2$  mol of  $\text{Br}_2$  for every mol of Al. The  $\text{Br}_2$  will be used up first.

(d) 0.231 mL of  $\text{Br}_2 = 0.721 \text{ g}$  of  $\text{Br}_2 = 4.51 \times 10^{-3} \text{ mol}$   $\text{Br}_2 = 9.02 \times 10^{-3} \text{ mol } e^- = 870 \text{ C}$ .  $\text{Work} = E \cdot q = (1.50)(870) = 1.31 \text{ kJ}$ .

$$(c) \quad I = \sqrt{P/R} = \sqrt{(1.00 \times 10^{-4})/(1.20 \times 10^3)} = 2.89 \times 10^{-4} \text{ A}$$

$$= 2.99 \times 10^{-9} \text{ mol e}^-/\text{s} = 9.97 \times 10^{-10} \text{ mol Al/s} = 2.69 \times 10^{-8} \text{ g/s}$$

**13-18.** The activities of the solid reagents do not change until they are used up. The only aqueous species,  $\text{OH}^-$ , is created at the cathode and consumed in equal amounts at the anode, so its concentration remains constant in the cell. Therefore, none of the activities change during the life cycle of the cell until something is used up.

**13-19.** (a) right half-cell:  $E_+ = \left\{ 0.222 - \frac{0.05916}{2} \log [\text{Cl}^-]^2 \right\} = 0.2812 \text{ V}$

left half-cell:  $E_- = \left\{ -0.350 - \frac{0.05916}{2} \log [\text{F}^-]^2 \right\} = -0.2908 \text{ V}$

$$E = E_+ - E_- = 0.2812 - (-0.2908) = 0.572 \text{ V}$$

(b) Electrons flow from the left half-cell ( $E = -0.2908 \text{ V}$ ) to the right half-cell ( $E = 0.2812 \text{ V}$ ).

(c)  $[\text{Pb}^{2+}] = K_{\text{sp}} (\text{for PbF}_2) / [\text{F}^-]^2 = (3.6 \times 10^{-8}) / (0.10)^2 = 3.6 \times 10^{-6} \text{ M}$

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

right half-cell:  $E_+ = \left\{ 0.799 - \frac{0.05916}{2} \log \frac{1}{[\text{Ag}^+]^2} \right\} = 0.2812 \text{ V}$

left half-cell:  $E_- = \left\{ -0.126 - \frac{0.05916}{2} \log \frac{1}{[\text{Pb}^{2+}]} \right\} = -0.2870 \text{ V}$

$$E = E_+ - E_- = 0.2812 - (-0.2870) = 0.568 \text{ V}$$

The agreement between the two calculations is reasonable.

**13-20.** A hydrogen pressure of 727.2 Torr corresponds to  $(727.2 \text{ Torr})/(760 \text{ Torr/atm}) = 0.9568 \text{ atm}$ .

$$(0.9568 \text{ atm})(1.01325 \text{ bar/atm}) = 0.9695 \text{ bar.}$$

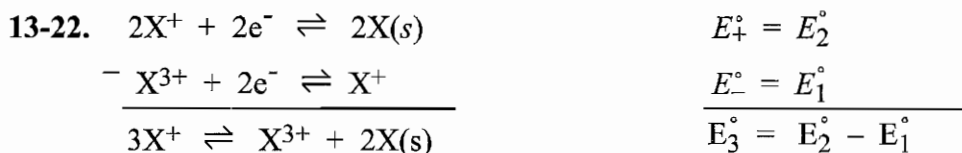
$$0.7983 = E^\circ_{\text{Ag}^+|\text{Ag}} - 0.05916 \log \frac{[0.01000](0.914)}{(0.9695)^{1/2} [0.01000](0.898)}$$

$$\Rightarrow E^\circ_{\text{Ag}^+|\text{Ag}} = 0.7992 \text{ V}$$

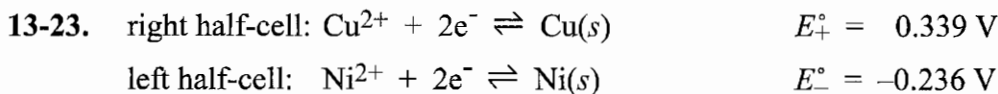
**13-21.** Balanced reaction:  $\text{HOBr} + 2\text{e}^- + \text{H}^+ \rightleftharpoons \text{Br}^- + \text{H}_2\text{O}$



$$E_3^\circ = \frac{-1F(1.584) - 1F(1.098)}{-2F} = 1.341 \text{ V}$$



If  $E_2^\circ > E_1^\circ$ , then  $E_3^\circ \geq 0$  and disproportionation is spontaneous.



The ionic strength of the right half-cell is 0.009 0 M, and the ionic strength of the left half-cell is 0.008 0 M. At  $\mu = 0.009$  0 M,  $\gamma_{Cu^{2+}} = 0.690$ .

At  $\mu = 0.008$  0 M,  $\gamma_{Ni^{2+}} = 0.705$ .

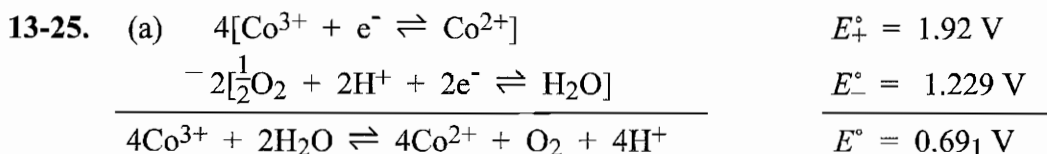
$$\begin{aligned}
 E_+ &= E_+^\circ - \frac{0.05916}{2} \log \frac{1}{[Cu^{2+}]\gamma_{Cu^{2+}}} \\
 &= 0.339 - \frac{0.05916}{2} \log \frac{1}{(0.0030)(0.690)} = 0.259_6 \text{ V} \\
 E_- &= E_-^\circ - \frac{0.05916}{2} \log \frac{1}{[Ni^{2+}]\gamma_{Ni^{2+}}} \\
 &= -0.236 - \frac{0.05916}{2} \log \frac{1}{(0.0020)(0.705)} = -0.320_3 \text{ V}
 \end{aligned}$$

$$E = E_+ - E_- = 0.580 \text{ V}$$

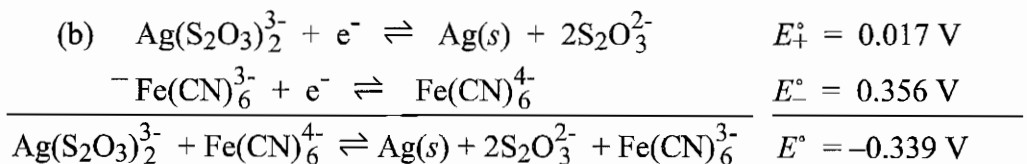
Electrons flow from Ni ( $E = -0.320_3$  V) to Cu ( $E = 0.259_6$  V).

$$\text{13-24. (a) } E^\circ = \frac{-\Delta G^\circ}{nF} = \frac{(+257 \times 10^3 \text{ J/mol})}{(2)(9.6485 \times 10^4 \text{ C/mol})} = 1.33 \text{ V}$$

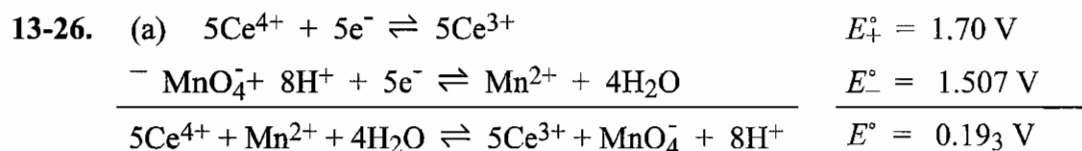
$$\text{(b) } K = 10^{nE^\circ/0.05916} = 1 \times 10^{45}$$



$$\Delta G^\circ = -4FE^\circ = -2.7 \times 10^5 \text{ J} \qquad K = 10^{4E^\circ/0.05916} = 10^{47}$$



$$\Delta G^\circ = -1FE^\circ = 32.7 \text{ kJ} \qquad K = 10^{1E^\circ/0.05916} = 1.9 \times 10^{-6}$$

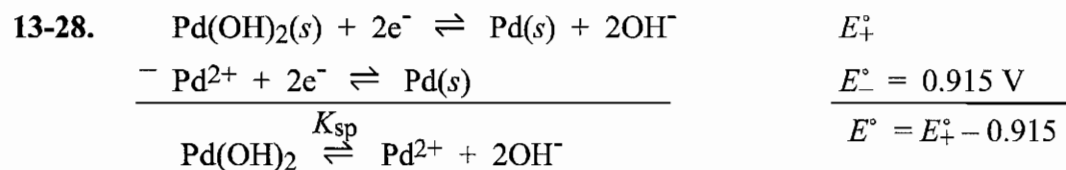
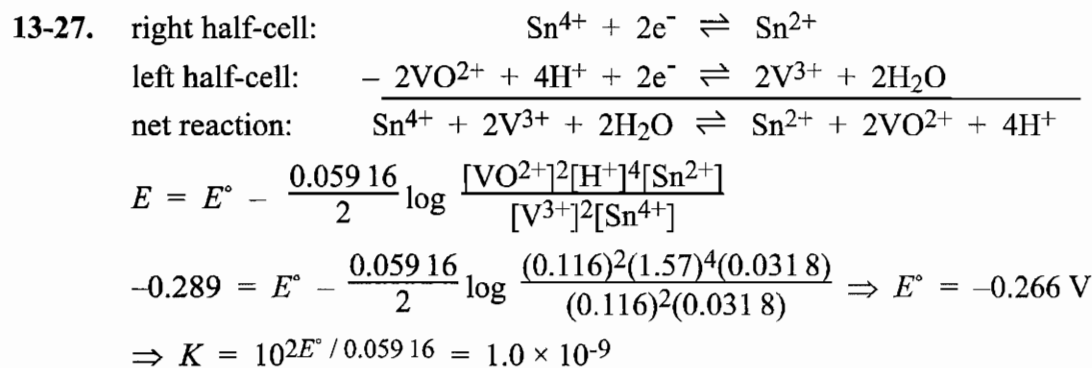


$$(b) \quad \Delta G^\circ = -5FE^\circ = -93.1 \text{ kJ} \quad K = 10^{5E^\circ/0.05916} = 2 \times 10^{16}$$

$$\begin{aligned}
 (c) \quad E &= \left\{ 1.70 - \frac{0.05916}{5} \log \frac{[\text{Ce}^{3+}]^5}{[\text{Ce}^{4+}]^5} \right\} - \left\{ 1.507 - \frac{0.05916}{5} \log \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8} \right\} \\
 &= 1.52_{23} - 1.54_{25} = -0.02_0 \text{ V}
 \end{aligned}$$

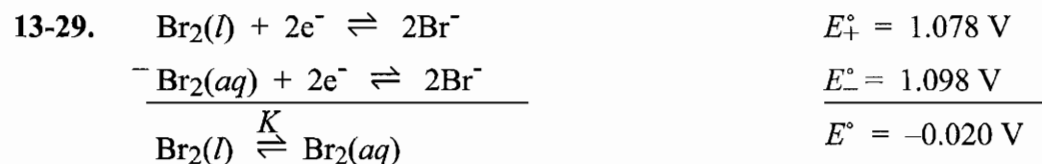
$$(d) \quad \Delta G = -5FE = +10 \text{ kJ}$$

$$\begin{aligned}
 (e) \quad \text{At equilibrium, } E = 0 &\Rightarrow E^\circ = \frac{0.05916}{5} \log \frac{[\text{Ce}^{3+}]^5[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Ce}^{4+}]^5[\text{Mn}^{2+}]} \\
 &\Rightarrow [\text{H}^+] = 0.62 \Rightarrow \text{pH} = 0.21
 \end{aligned}$$



$$\text{But } K_{\text{sp}} = 3 \times 10^{-28} \Rightarrow E^\circ = \frac{0.05916}{2} \log K_{\text{sp}} = -0.814$$

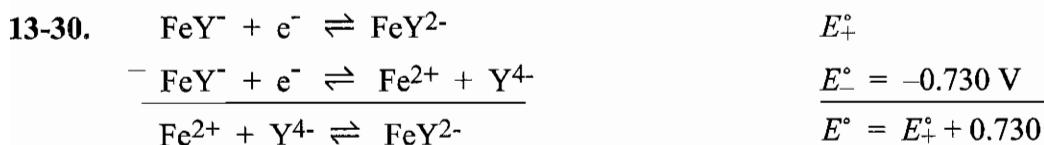
$$-0.814 = E_1^\circ - 0.915 \Rightarrow E_1^\circ = 0.101 \text{ V}$$



$$\text{At equilibrium, } E = 0. \text{ Therefore, } 0 = -0.020 - \frac{0.05916}{2} \log \frac{[\text{Br}_2(\text{aq})]}{[\text{Br}_2(\text{l})]}$$

$$\Rightarrow K = \frac{[\text{Br}_2(\text{aq})]}{[\text{Br}_2(\text{l})]} = 0.21_1 \text{ M.}$$

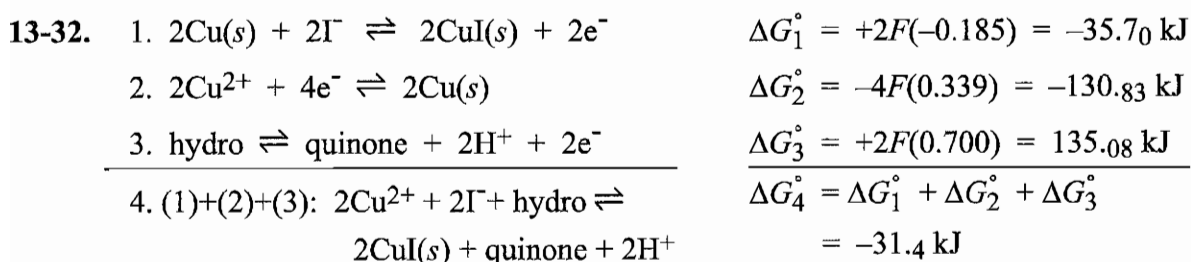
That is, the solubility of  $\text{Br}_2$  in water is  $0.21_1 \text{ M} = 34 \text{ g/L}$ .



But  $E^\circ = 0.05916 \log [K_f \text{ (for FeY}^{2-})] = 0.846 \text{ V} \Rightarrow E_+^\circ = E^\circ - E_-^\circ = 0.116 \text{ V}$ .

$$\text{13-31.} \quad E^\circ(T) = E^\circ + \frac{dE^\circ}{dT} \Delta T$$

$$E^\circ(50^\circ \text{ C}) = -1.677 \text{ V} + (0.533 \times 10^{-3} \text{ V/K})(25 \text{ K}) = -1.664 \text{ V}$$



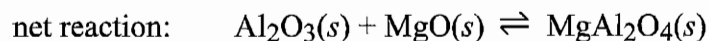
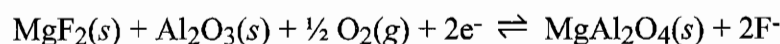
Since  $2\text{e}^-$  are transferred in the net reaction,  $E_4^\circ = \frac{-\Delta G_4^\circ}{2F} = +0.163 \text{ V}$

$$K = 10^{(2)(0.163)/0.05916} = 3.2 \times 10^5.$$

$$\text{13-33. (a)} \quad E(\text{right}) = E^\circ(\text{right}) - \frac{RT}{2F} \ln \frac{\mathcal{A}_{\text{F}^-}^2(\text{right})}{P_{\text{O}_2}^{1/2}(\text{right})}$$

$$E(\text{left}) = E^\circ(\text{left}) - \frac{RT}{2F} \ln \frac{\mathcal{A}_{\text{F}^-}^2(\text{left})}{P_{\text{O}_2}^{1/2}(\text{left})}$$

Net reaction: reverse left half-reaction and add it to right half-reaction:



Nernst equation for net reaction:

$$E(\text{right}) - E(\text{left}) = E^\circ(\text{right}) - E^\circ(\text{left}) - \frac{RT}{2F} \ln \frac{\mathcal{A}_{\text{F}^-}^2(\text{right})}{P_{\text{O}_2}^{1/2}(\text{right})} + \frac{RT}{2F} \ln \frac{\mathcal{A}_{\text{F}^-}^2(\text{left})}{P_{\text{O}_2}^{1/2}(\text{left})}$$



The activities of  $F^-$  are the same on both sides and the activities of  $O_2$  are also the same on both sides, so the  $\ln$  terms cancel, leaving  $E(\text{cell}) = E^\circ(\text{right}) - E^\circ(\text{left}) = E^\circ(\text{cell})$ .

(b)  $\Delta G^\circ = -nFE^\circ = -(2)(9.6485 \times 10^4 \text{ C/mol})(0.1529 \text{ J/C}) = -29.51 \text{ kJ/mol}$ ,  
where we made use of the fact that a volt is equivalent to one joule/coulomb.

(c)  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$   
 $-nFE^\circ = \Delta H^\circ - T\Delta S^\circ = -nF(0.1223 + 3.06 \times 10^{-5} T)$   
 $= -nF(0.1223 \text{ V}) - nF(3.06 \times 10^{-5} T)$   
 $= \underbrace{-nF(0.1223 \text{ V})}_{\Delta H^\circ} - T \underbrace{\{nF(3.06 \times 10^{-5} \text{ V/K})\}}_{\Delta S^\circ}$

$$\Delta H^\circ = -nF(0.1223 \text{ V}) = -(2)(9.6485 \times 10^4 \text{ C/mol})(0.1223 \text{ J/C})$$

$$= -23.60 \text{ kJ/mol}$$

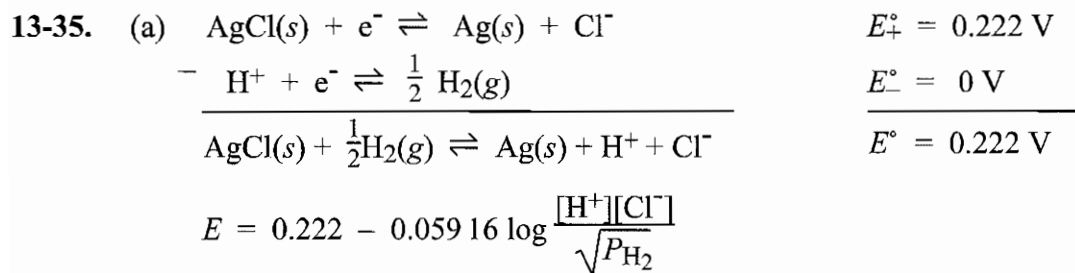
$$\Delta S^\circ = nF(3.06 \times 10^{-5} \text{ V/K})$$

$$= (2)(9.6485 \times 10^4 \text{ C/mol})(3.06 \times 10^{-5} \text{ V/K})$$

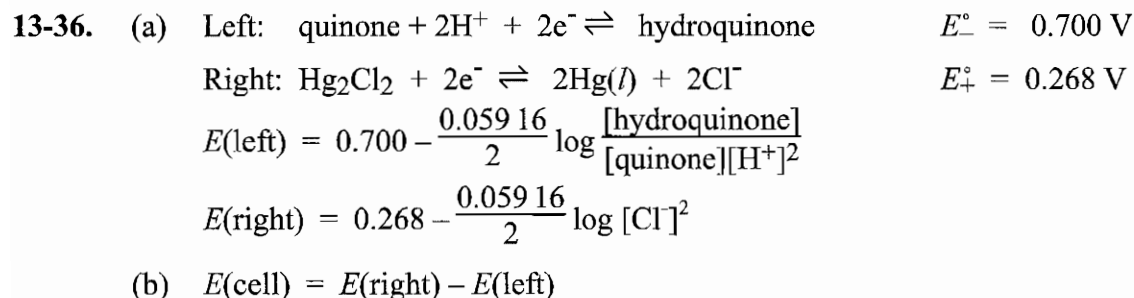
$$= 5.90 \text{ C}\cdot\text{V}/(\text{K}\cdot\text{mol}) = 5.90 \text{ J}/(\text{K}\cdot\text{mol}), \text{ where we made use of the}$$

conversion coulomb-volt = joule.

**13-34.** In the right half-cell, the reaction  $\text{Hg}^{2+} + \text{Y}^{4-} \rightleftharpoons \text{HgY}^{2-}$  is at equilibrium, even though the net cell reaction  $\text{Hg}^{2+} + \text{H}_2 \rightleftharpoons \text{Hg}(l) + 2\text{H}^+$  is not at equilibrium.



(b)  $0.485 = 0.222 - 0.05916 \log \frac{(10^{-3.60})[\text{Cl}^-]}{\sqrt{1.00}} \Rightarrow [\text{Cl}^-] = 0.143 \text{ M}$



$$= \left\{ 0.268 - \frac{0.05916}{2} \log [\text{Cl}^-]^2 \right\} - \left\{ 0.700 - \frac{0.05916}{2} \log \frac{[\text{hydroquinone}]}{[\text{quinone}][\text{H}^+]^2} \right\}$$

$$E(\text{cell}) = -0.432 - \frac{0.05916}{2} \log \frac{[\text{quinone}][\text{H}^+]^2[\text{Cl}^-]^2}{[\text{hydroquinone}]}$$

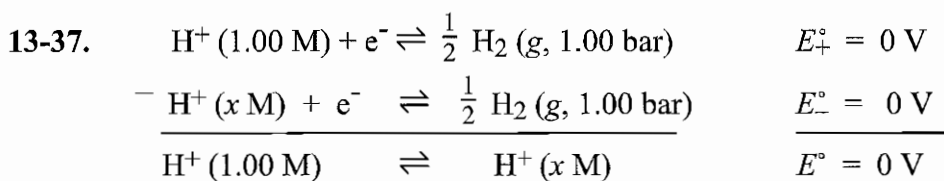
Setting  $[\text{Cl}^-] = 0.50 \text{ M}$  and noting  $[\text{quinone}] = [\text{hydroquinone}]$ , we find

$$E(\text{cell}) = -0.432 - 0.05916 \log (0.50) - 0.05916 \log [\text{H}^+]$$

$$E(\text{cell}) = -0.414 + 0.05916 \text{ pH} \quad (A = -0.414, B = 0.05916 \text{ V per pH unit})$$

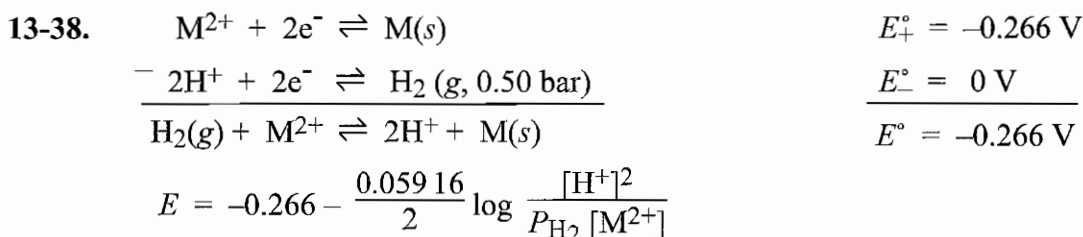
(c)  $E(\text{cell}) = -0.414 + 0.05916 (4.50) = -0.148$

Since  $E < 0$ , electrons flow from right to left ( $\text{Hg} \rightarrow \text{Pt}$ ) through the meter.



$$E = 0.490 = 0 - 0.05916 \log [\text{H}^+] \Rightarrow [\text{H}^+] = 5.2 \times 10^{-9} \text{ M}$$

$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]} = \frac{(0.050)(K_w/[\text{H}^+])}{0.10} = 9.6 \times 10^{-7}$$

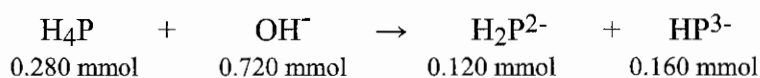


$[\text{H}^+]$  in the left half-cell is found by considering the titration of 28.0 mL of the tetraprotic pyrophosphoric acid (abbreviated  $\text{H}_4\text{P}$ ) with 72.0 mL of  $\text{KOH}$ .

$$28.0 \text{ mL of } 0.0100 \text{ M } \text{H}_4\text{P} = 0.280 \text{ mmol}$$

$$72.0 \text{ mL of } 0.0100 \text{ M } \text{KOH} = 0.720 \text{ mmol}$$

First, 0.280 mmol  $\text{OH}^-$  consumes 0.280 mmol of  $\text{H}_4\text{P}$ , giving 0.280 mmol of  $\text{H}_3\text{P}^-$  and  $(0.720 - 0.280 =) 0.440$  mmol of  $\text{OH}^-$ . Then 0.280 mmol  $\text{OH}^-$  consumes 0.280 mmol of  $\text{H}_3\text{P}^-$ , giving 0.280 mmol of  $\text{H}_2\text{P}^{2-}$  and  $(0.440 - 0.280 =) 0.160$  mmol of  $\text{OH}^-$ . Finally, 0.160 mmol of  $\text{OH}^-$  reacts with 0.280 mmol of  $\text{H}_2\text{P}^{2-}$  to create 0.160 mmol of  $\text{HP}^{3-}$ , leaving 0.120 mmol of unreacted  $\text{H}_2\text{P}^{2-}$ .



$$\text{pH} = \text{p}K_3 + \log \frac{[\text{HP}^{3-}]}{[\text{H}_2\text{P}^{2-}]} = 6.70 + \log \frac{0.160}{0.120} = 6.82 \Rightarrow [\text{H}^+] = 1.5_0 \times 10^{-7} \text{ M}$$

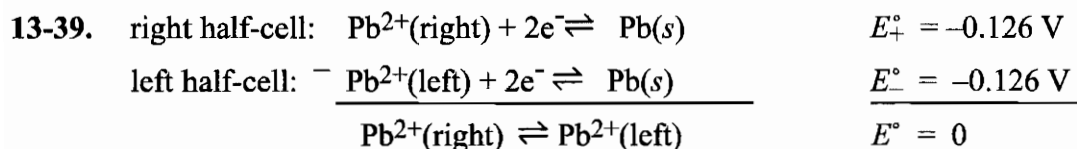
Putting the known values of  $[H^+]$  and  $P_{H_2}$  into the Nernst equation gives

$$\begin{aligned} -0.246 &= -0.266 - \frac{0.05916}{2} \log \frac{[H^+]^2}{P_{H_2} [M^{2+}]} \\ &= -0.266 - \frac{0.05916}{2} \log \frac{[1.50 \times 10^{-7}]^2}{0.50 [M^{2+}]} \Rightarrow [M^{2+}] = 2.13 \times 10^{-13} \text{ M} \end{aligned}$$

In the right half-cell we have the equilibrium

	$M^{2+}$	+	$F_{EDTA}$	$\rightleftharpoons$	$MY^{2-}$
initial mmol/mL	$\frac{0.280}{100}$		$\frac{0.720}{100}$		—
final mmol/mL	small		$\frac{0.440}{100}$		$\frac{0.280}{100}$

$$K_f = \frac{[MY^{2-}]}{[M^{2+}] \alpha_{Y^{4-}} F_{EDTA}} = \frac{0.280/100}{(2.13 \times 10^{-13})(0.0042)(0.440/100)} = 7.1 \times 10^{14}$$



Nernst equation for net cell reaction:

$$-0.0018 = -\frac{0.05916}{2} \log \frac{[Pb^{2+}(\text{left})]}{[Pb^{2+}(\text{right})]} \Rightarrow \frac{[Pb^{2+}(\text{left})]}{[Pb^{2+}(\text{right})]} = 1.15$$

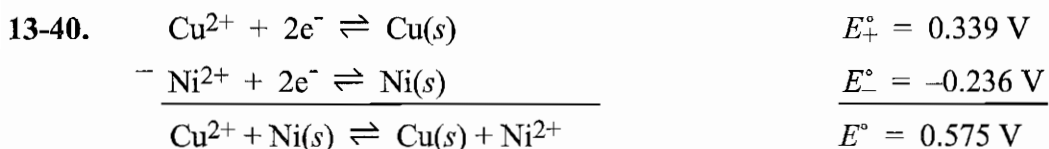
For each half-cell, we can write  $[CO_3^{2-}] = K_{sp}(\text{for } PbCO_3) / [Pb^{2+}]$

$$\frac{[CO_3^{2-}(\text{left})]}{[CO_3^{2-}(\text{right})]} = \frac{K_{sp}(\text{for } PbCO_3) / [Pb^{2+}(\text{left})]}{K_{sp}(\text{for } PbCO_3) / [Pb^{2+}(\text{right})]} = \frac{1}{1.15} = 0.87$$

In each compartment the  $Ca^{2+}$  concentration is equal to the total concentration of all carbonate species (since  $PbCO_3$  is much less soluble than  $CaCO_3$ ). Let the fraction of all carbonate species in the form  $CO_3^{2-}$  be  $\alpha_{CO_3^{2-}}$

(i.e.,  $[CO_3^{2-}] = \alpha_{CO_3^{2-}} [\text{total carbonate}]$ ). We can say that  $[Ca^{2+}] = [\text{total carbonate}] = [CO_3^{2-}] / \alpha_{CO_3^{2-}}$ . The value of  $\alpha_{CO_3^{2-}}$  is the same in both compartments, since the pH is the same. Now we can write

$$\begin{aligned} \frac{K_{sp}(\text{calcite})}{K_{sp}(\text{aragonite})} &= \frac{[Ca^{2+}(\text{left})][CO_3^{2-}(\text{left})]}{[Ca^{2+}(\text{right})][CO_3^{2-}(\text{right})]} = \frac{[CO_3^{2-}(\text{left})]^2 / \alpha_{CO_3^{2-}}}{[CO_3^{2-}(\text{right})]^2 / \alpha_{CO_3^{2-}}} \\ &= (0.87)^2 = 0.76. \end{aligned}$$



The ionic strength of the right half-cell is 0.10 M and  $\gamma_{\text{Cu}^{2+}} = 0.405$ .

The ionic strength of the left half-cell is 0.010 M and  $\gamma_{\text{Ni}^{2+}} = 0.675$ .

$$0.512 = 0.575 - \frac{0.05916}{2} \log \frac{(0.0025)(0.675)}{[\text{Cu}^{2+}](0.405)} \Rightarrow [\text{Cu}^{2+}] = 3.09 \times 10^{-5} \text{ M}$$

$$K_{\text{sp}} = [\text{Cu}^{2+}]\gamma_{\text{Cu}^{2+}}[\text{IO}_3^-]^2\gamma_{\text{IO}_3^-}^2 = (3.09 \times 10^{-5})(0.405)(0.10)^2(0.775)^2 = 7.5 \times 10^{-8}$$

**13-41.**  $E^\circ'$  is the effective reduction potential for a half-reaction at pH 7, instead of pH 0. Since living systems tend to have a pH much closer to 7 than to 0,  $E^\circ'$  provides a better indication of redox behavior in an organism.

$$\text{13-42. (a)} \quad E = 0.731 - \frac{0.05916}{2} \log \frac{P_{\text{C}_2\text{H}_4}}{P_{\text{C}_2\text{H}_2}[\text{H}^+]^2}$$

$$\text{(b)} \quad E = \underbrace{0.731 + 0.05916 \log [\text{H}^+]^2}_{\text{This is } E^\circ' \text{ when pH} = 7} - \frac{0.05916}{2} \log \frac{P_{\text{C}_2\text{H}_4}}{P_{\text{C}_2\text{H}_2}}$$

$$\text{(c)} \quad E^\circ' = 0.731 + 0.05916 \log (10^{-7.00}) = 0.317 \text{ V}$$

$$\text{13-43.} \quad E = E^\circ - \frac{0.05916}{2} \log \frac{[\text{HCN}]^2}{P_{(\text{CN})_2}[\text{H}^+]^2}$$

Substituting  $[\text{HCN}] = \frac{[\text{H}^+] F_{\text{HCN}}}{[\text{H}^+] + K_a}$  into the Nernst equation gives

$$E = 0.373 - \frac{0.05916}{2} \log \frac{[\text{H}^+]^2 F_{\text{HCN}}^2}{([\text{H}^+] + K_a)^2 P_{(\text{CN})_2} [\text{H}^+]^2}$$

$$E = 0.373 + \underbrace{0.05916 \log ([\text{H}^+] + K_a)}_{\text{This is } E^\circ' \text{ when pH} = 7} - \frac{0.05916}{2} \log \frac{F_{\text{HCN}}^2}{P_{(\text{CN})_2}}$$

Inserting  $K_a = 6.2 \times 10^{-10}$  for HCN and  $[\text{H}^+] = 10^{-7.00}$  gives

$$E^\circ' = 0.373 + 0.05916 \log (10^{-7.00} + 6.2 \times 10^{-10}) = -0.041 \text{ V.}$$



$$E = 0.204 - \frac{0.05916}{2} \log \frac{[\text{HCO}_2\text{H}]^2}{[\text{H}_2\text{C}_2\text{O}_4][\text{H}^+]^2}$$

$$\text{But } [\text{HCO}_2\text{H}] = \frac{[\text{H}^+] F_{\text{HCO}_2\text{H}}}{[\text{H}^+] + K_a} \text{ and } [\text{H}_2\text{C}_2\text{O}_4] = \frac{[\text{H}^+]^2 F_{\text{H}_2\text{C}_2\text{O}_4}}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}$$

Putting these expressions into the Nernst equation gives

$$E = 0.204 - \frac{0.05916}{2} \log \frac{[\text{H}^+]^2 F_{\text{HCO}_2\text{H}}^2 ([\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2)}{([\text{H}^+] + K_a)^2 [\text{H}^+]^2 F_{\text{H}_2\text{C}_2\text{O}_4} [\text{H}^+]^2}$$

$$E = 0.204 - \frac{0.05916}{2} \log \frac{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}{([\text{H}^+] + K_a)^2 [\text{H}^+]^2} - \frac{0.05916}{2} \log \frac{F_{\text{HCO}_2\text{H}}^2}{F_{\text{H}_2\text{C}_2\text{O}_4}}$$

This is  $E^{\circ'}$  when pH = 7

Putting in  $[\text{H}^+] = 10^{-7.00}$  M,  $K_a = 1.80 \times 10^{-4}$ ,  $K_1 = 5.62 \times 10^{-2}$ , and  $K_2 = 5.42 \times 10^{-5}$  gives  $E^{\circ'} = -0.268$  V.

13-45.  $E = E^{\circ} - 0.05916 \log \frac{[\text{H}_2\text{Red}^-]}{[\text{HOx}]}$

$$\text{But } [\text{HOx}] = \frac{[\text{H}^+] F_{\text{HOx}}}{[\text{H}^+] + K_a} \text{ and } [\text{H}_2\text{Red}^-] = \frac{[\text{H}^+]^2 F_{\text{H}_2\text{Red}^-}}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}$$

Putting these values into the Nernst equation gives

$$E = E^{\circ} - 0.05916 \log \frac{[\text{H}^+]^2 F_{\text{H}_2\text{Red}^-} ([\text{H}^+] + K_a)}{[\text{H}^+] F_{\text{HOx}} ([\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2)}$$

$$E = E^{\circ} - \underbrace{0.05916 \log \frac{[\text{H}^+] ([\text{H}^+] + K_a)}{[\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2}}_{E^{\circ'}} - 0.05916 \log \frac{F_{\text{H}_2\text{Red}^-}}{F_{\text{HOx}}}$$

Since  $E^{\circ'} = 0.062$  V, we find  $E^{\circ} = -0.036$  V.

13-46.  $E = E^{\circ} - \frac{0.05916}{2} \log \frac{[\text{HNO}_2]}{[\text{NO}_3^-][\text{H}^+]^3}$

$$\text{But } [\text{HNO}_2] = \frac{[\text{H}^+] F_{\text{HNO}_2}}{[\text{H}^+] + K_a} \text{ and } [\text{NO}_3^-] = F_{\text{NO}_3^-}$$

Putting these values into the Nernst equation gives

$$E = E^{\circ} - \underbrace{\frac{0.05916}{2} \log \frac{1}{([\text{H}^+] + K_a)[\text{H}^+]^2}}_{E^{\circ'}} - \frac{0.05916}{2} \log \frac{F_{\text{HNO}_2}}{F_{\text{NO}_3^-}}$$

$$E^{\circ'} = 0.433 = 0.940 - \frac{0.05916}{2} \log \frac{1}{(10^{-7} + K_a)(10^{-7})^2} \Rightarrow K_a = 7.2 \times 10^{-4}.$$

