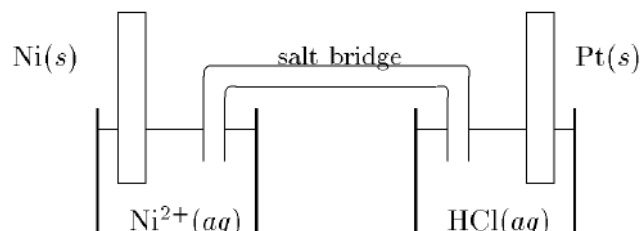# Answers to HW 7#

**17.2** When the two electrodes in the following diagram are connected by a wire, electrons flow from the left electrode as metallic nickel is oxidized to Ni^{2+} at the left-hand electrode; the electrons are taken up by H^+ ions at the right-hand electrode. In the salt bridge, negative ions flow from right to left and positive ions from left to right.

Bubbles of gaseous hydrogen are released to rise through the solution in the right-hand cell compartment. The overall reaction is

$$Ni(s) + 2\ HCl(aq) \rightarrow H_2(g) + NiCl_2(aq)$$
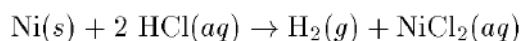
17.5 At the anode, $Zn(s)$ is being oxidized to $Zn^{2+}(aq)$; at the cathode, $Cl_2(g)$ is being reduced to $Cl^-(aq)$.

a) $\boxed{Zn(s) + Cl_2(g) \longrightarrow Zn^{2+}(aq) + 2\,Cl^-(aq)}$.
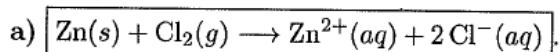
b) An ampere is a coulomb per second. Hence

$$Q = \left(\frac{0.800\ C}{1\ s}\right) \times 25.0\ min\left(\frac{60\ s}{1\ min}\right) = \boxed{1.20 \times 10^3\ C}$$

In moles

$$n_{e^-} = \left(\frac{0.800\ C}{1\ s}\right) \times 25.0\ min\left(\frac{60\ s}{1\ min}\right)\left(\frac{1\ mol\ e^-}{96\,485.3\ C}\right) = \boxed{0.0124\ mol\ e^-}$$

c) The oxidation half-reaction is $Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$. Therefore

$$m_{Zn} = 0.0124\ mol\ e^- \times \left(\frac{1\ mol\ Zn}{2\ mol\ e^-}\right)\left(\frac{65.39\ g\ Zn}{1\ mol\ Zn}\right) = \boxed{0.407\ g}$$

The calculation assumes that no side-reactions occur that divert electrons.

d) The reduction half-reaction is $Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$. Therefore the passage of 0.0124 mol of electrons reduces 0.00622 mol of $Cl_2(g)$ (if no side-reactions occur). Use the ideal-gas law to calculate the volume of this amount of chlorine at 25°C (298 K) and a pressure of 1 atm

$$V_{Cl_2} = \frac{n_{Cl_2}RT}{P} = \frac{(0.00622\ mol)(0.08206\ L\ atm\ mol^{-1}K^{-1})(298\ K)}{1\ atm} = \boxed{0.152\ L}$$

17.11 Represent the reduction half-reaction as $Ag^+(aq) + e^- \longrightarrow Ag(s)$. Use the molar mass of Ag and molar ratios from the balanced half-equation to compute the chemical amount of electrons transferred in the production of 1.00 g of metallic silver

$$n_{e^-} = 1.00 \text{ g Ag} \times \left(\frac{1 \text{ mol Ag}}{107.9 \text{ g Ag}} \right) \left(\frac{1 \text{ mol } e^-}{1 \text{ mol Ag}} \right) = 0.00927 \text{ mol } e^-$$

The free energy change of the cell during the production of the 1.00 g of Ag at 298 K equals the standard free energy change of the reaction at that temperature. This is the case because all of the reactants and products stay in their standard states

$$\Delta G = \Delta G^\circ = -n\mathcal{F}\mathcal{E}_{cell}^\circ = -(0.00927 \text{ mol})(96\,485 \text{ C mol}^{-1})(1.03 \text{ V}) = \boxed{-921 \text{ J}}$$

The negative sign in the answer means that the reaction is spontaneous. The maximum electrical work *produced* by the cell equals $-w_{elec,max}$ because positive work is work that is absorbed. This maximum is attained if the cell is operated reversibly

$$-w_{elec,max} = -w_{elec,rev} = -\Delta G = \boxed{921 \text{ J}}$$

17.25 **a)** The disproportionation of $Br_2(l)$ in acid is represented

$$6\,Br_2(l) + 18\,H_2O(l) \longrightarrow 2\,BrO_3^-(aq) + 10\,Br^-(aq) + 12\,H_3O^+(aq)$$
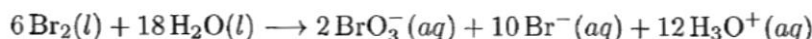
for which the standard potential difference is

$$\mathcal{E}_{cell}^\circ = \mathcal{E}_{reduction}^\circ - \mathcal{E}_{oxidation}^\circ$$
$$= \mathcal{E}^\circ(Br_2|Br^-) - \mathcal{E}^\circ(BrO_3^-|Br_2) = 1.065 - 1.52 = -0.46 \text{ V}$$

The negative $\mathcal{E}_{cell}^\circ$ means $Br_2(l)$ $\boxed{\text{will not disproportionate}}$ to $Br^-(aq)$ and $BrO_3^-(aq)$ in water under standard acidic conditions.

b) The reduction giving Br_2 has a larger reduction potential than the one giving Br^- ion. Hence $\boxed{Br^-}$ is more easily oxidized than Br_2 and must be a stronger reducing agent under standard acidic conditions

17.26 **a)** ClO^- tends to disproportionate spontaneously at pH 14 to give Cl^- and ClO_2^-. The $\Delta\mathcal{E}^\circ$ of the reaction is $0.90 - 0.59 = 0.31$ V.

b) According to the reduction potentials given in the problem ClO^- is oxidized to ClO_2^- more readily than Cl^- is oxidized to ClO^- at pH 14; the ClO^- is the stronger reducing agent under these conditions. However, neither of these is a very good reducing agent.