12.4 (a) $6[Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-]$

$1[Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)]$

$$6\ Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightarrow 6\ Fe^{3+}(aq) + 6\ e^- + 2\ Cr^{3+}(aq) + 7\ H_2O(l)$$

$$6\ Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14\ H^+(aq) \rightarrow 6\ Fe^{3+}(aq) + 2\ Cr^{3+}(aq) + 7\ H_2O(l)$$

Fe^{2+} is the reducing agent and $Cr_2O_7^{2-}$ is the oxidizing agent.

(b) $5\ [C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4\ H^+(aq) + 4\ e^-]$

$4\ [MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)]$

$$5\ C_2H_5OH(aq) + 5\ H_2O(l) + 4\ MnO_4^-(aq) + 32\ H^+(aq) + 20\ e^- \rightarrow 5\ CH_3COOH(aq) + 20\ H^+(aq) + 20\ e^- + 4\ Mn^{2+}(aq) + 16\ H_2O(l)$$

$$5\ C_2H_5OH(aq) + 4\ MnO_4^-(aq) + 12\ H^+(aq) \rightarrow 5\ CH_3COOH(aq) + 4\ Mn^{2+}(aq) + 11\ H_2O(l)$$

C_2H_5OH is the reducing agent and MnO_4^- is the oxidizing agent.

(c) The reaction is $I^-(aq) + NO_3^-(aq) \rightarrow I_2(aq) + NO(g)$.

$3[2\ I^-(aq) \rightarrow I_2(aq) + 2\ e^-]$

$2\ [NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \rightarrow NO(g) + 2\ H_2O(l)]$

$$6\ I^-(aq) + 2\ NO_3^-(aq) + 8\ H^+(aq) + 6\ e^- \rightarrow 3\ I_2(aq) + 6\ e^- + 2\ NO(g) + 4\ H_2O(l)$$

$$6\ I^-(aq) + 2\ NO_3^-(aq) + 8\ H^+(aq) \rightarrow 3\ I_2(aq) + 2\ NO(g) + 4\ H_2O(l)$$

I^- is the reducing agent and NO_3^- is the oxidizing agent.

(d) $3[As_2S_3(s) + 8\ H_2O(l) \rightarrow 2\ H_3AsO_4(aq) + 3\ S(s) + 10\ H^+(aq) + 10\ e^-]$

$10\ [NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \rightarrow NO(g) + 2\ H_2O(l)]$

$$3\ As_2S_3(s) + 10\ NO_3^-(aq) + 24\ H_2O(l) + 40\ H^+(aq) + 30\ e^- \rightarrow 6\ H_3AsO_4(aq) + 9\ S(s) + 10\ NO(g) + 20\ H_2O(l) + 30\ H^+(aq) + 30\ e^-$$

$$3\ As_2S_3(s) + 10\ NO_3^-(aq) + 4\ H_2O(l) + 10\ H^+(aq) \rightarrow 6\ H_3AsO_4(aq) + 9\ S(s) + 10\ NO(g)$$

As_2S_3 is the reducing agent (both As and S are oxidized) and NO_3^- is the oxidizing agent.

12.6 (a) $Cl_2O_7(g) \rightarrow 2\ ClO_2^-(aq) + 3\ H_2O(l)$ (O's balanced)

$Cl_2O_7(g) + 6\ H_2O(l)$
$\rightarrow 2\ ClO_2^-(aq) + 3\ H_2O(l) + 6\ OH^-(aq)$ (H's balanced)

$Cl_2O_7(g) + 3\ H_2O(l) + 8\ e^-$
$\rightarrow 2\ ClO_2^-(aq) + 6\ OH^-(aq)$ (charge balanced)

$H_2O_2(aq) \rightarrow O_2(g)$ (O's balanced)

$H_2O_2(aq) + 2\ OH^-(aq) \rightarrow O_2(g) + 2\ H_2O(l)$ (H's balanced)

$H_2O_2(aq) + 2\ OH^-(aq) \rightarrow O_2(g) + 2\ H_2O(l) + 2e^-$ (charge balanced)

Combining the two half-reactions:

$1[Cl_2O_7(g) + 3\ H_2O(l) + 8\ e^- \rightarrow 2\ ClO_2^-(aq) + 6\ OH^-(aq)]$

$4[H_2O_2(aq) + 2\ OH^-(aq) \rightarrow O_2(g) + 2\ H_2O(l) + 2\ e^-]$

$Cl_2O_7(g) + 3\ H_2O(l) + 8\ e^- + 4\ H_2O_2(aq) + 8\ OH^-(aq) \rightarrow$
$2\ ClO_2^-(aq) + 6\ OH^-(aq) + 4\ O_2(g) + 8\ H_2O(l) + 8\ e^-$

$Cl_2O_7(g) + 4\ H_2O_2 + 2\ OH^-(aq) \rightarrow 2\ ClO_2^-(aq) + 4\ O_2(g) + 5\ H_2O(l)$

Cl_2O_7 is the oxidizing agent and H_2O_2 is the reducing agent.

(b) $MnO_4^-(aq) \rightarrow MnO_2(s) + 2\ H_2O(l)$ (O's balanced)

$MnO_4^-(aq) + 4\ H_2O(l)$
$\rightarrow MnO_2(s) + 2\ H_2O(l) + 4\ OH^-(aq)$ (H's balanced)

$MnO_4^-(aq) + 2\ H_2O(l) + 3\ e^- \rightarrow$
$MnO_2(s) + 4\ OH^-(aq)$ (charge balanced)

$S^{2-}(aq) \rightarrow S(s) + 2\ e^-$

Combining the two half-reactions:

$2[MnO_4^-(aq) + 2\ H_2O(l) + 3\ e^- \rightarrow MnO_2(s) + 4\ OH^-(aq)]$

$3[S^{2-}(aq) \rightarrow S(s) + 2\ e^-]$

$2\ MnO_4^-(aq) + 4\ H_2O(l) + 6\ e^- + 3\ S^{2-}(aq) \rightarrow$
$2\ MnO_2(s) + 8\ OH^-(aq) + 3\ S(s) + 6\ e^-$

$2\ MnO_4^-(aq) + 4\ H_2O(l) + 3\ S^{2-}(aq) \rightarrow 2\ MnO_2(s) + 8\ OH^-(aq) + 3\ S(s)$

MnO_4^- is the oxidizing agent and S^{2-} is the reducing agent.

(c) $N_2H_4(g) + 2\ H_2O(l) \rightarrow 2\ NO(g)$ (O's balanced)

$N_2H_4(g) + 2\ H_2O(l) + 8\ OH^-(aq) \rightarrow 2\ NO(g) + 8\ H_2O(l)$ (H's balanced)

$N_2H_4(g) + 8\ OH^-(aq) \rightarrow 2\ NO(g) + 6\ H_2O(l) + 8\ e^-$ (charge balanced)

$ClO_3^-(aq) \rightarrow Cl^-(aq) + 3\ H_2O(l)$ (O's balanced)

$ClO_3^-(aq) + 6\ H_2O(l) \rightarrow Cl^-(aq) + 3\ H_2O(l) + 6\ OH^-(aq)$ (H's balanced)

$ClO_3^-(aq) + 3\ H_2O(l) + 6\ e^- \rightarrow Cl^-(aq) + 6\ OH^-(aq)$ (charge balanced)

Combining the two half-reactions:

$3[N_2H_4(g) + 8\ OH^-(aq) \rightarrow 2\ NO(g) + 6\ H_2O(l) + 8\ e^-]$

$4[ClO_3^-(aq) + 3\ H_2O(l) + 6\ e^- \rightarrow Cl^-(aq) + 6\ OH^-(aq)]$

$3\ N_2H_4(g) + 24\ OH^-(aq) + 4\ ClO_3^-(aq) + 12\ H_2O(l) + 24\ e^- \rightarrow$

$6\ NO(g) + 18\ H_2O(l) + 24\ e^- + 4\ Cl^-(aq) + 24\ OH^-(aq)$

$3\ N_2H_4(g) + 4\ ClO_3^-(aq) \rightarrow 6\ NO(g) + 6\ H_2O(l) + 4\ Cl^-(aq)$

N_2H_4 is the reducing agent and ClO_3^- is the oxidizing agent.

(d) $Pb(OH)_4^{2-}(aq) \rightarrow PbO_2(s) + 2\ H_2O(l) + 2\ e^-$

$ClO^-(aq) + H_2O(l) + 2\ e^- \rightarrow Cl^-(aq) + 2\ OH^-(aq)$

$Pb(OH)_4^{2-}(aq) + ClO^-(aq) + H_2O(l) + 2\ e^- \rightarrow$

$PbO_2(s) + Cl^-(aq) + 2\ H_2O(l) + 2\ OH^-(aq) + 2\ e^-$

or

$Pb(OH)_4^{2-}(aq) + ClO^-(aq) \rightarrow PbO_2(s) + Cl^-(aq) + H_2O(l) + 2\ OH^-(aq)$

$Pb(OH)_4^{2-}$ is the reducing agent and ClO^- is the oxidizing agent.

12.22 The unknown metal ions are reduced, increasing the weight of the unknown metal electrode. The cell can be written as $Fe(s)|Fe^{2+}(aq)||M^+(aq)|M(s)$ showing that the M^+/M electrode is the cathode, because this is where reduction is occuring.

$Fe^{2+} + 2e \rightarrow Fe(s)$

$E° = -0.44\ V$

$E°\ (cathode) = +1.24\ V + E°\ (anode)$

$E°\ (cathode) = +1.24\ V + (-0.44\ V) = +0.80\ V$

12.60 (a) $Au^{3+}(aq) + 3\,e^- \rightarrow Au(s)$

$$\text{current} = (6.66\ \mu\text{g Au})\left(\frac{10^{-6}\text{ g}}{1\ \mu\text{g}}\right)\left(\frac{1\text{ mol Au}}{196.97\text{ g Au}}\right)\left(\frac{3\text{ mol e}^-}{1\text{ mol Au}}\right)$$

$$\left(\frac{9.6485\times10^4\text{ C}}{1\text{ mol e}^-}\right)\left(\frac{1\text{ A}}{1\text{ C}\cdot\text{s}^{-1}}\right)\left(\frac{1}{1800\text{ s}}\right) = 5.44\times10^{-6}\text{ A}$$

(b) $Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 12\,e^- \rightarrow 2\,Cr(s) + 7\,H_2O(l)$

$$\text{time} = (6.66\ \mu\text{g Cr})\left(\frac{10^{-6}}{1\ \mu\text{g}}\right)\left(\frac{1\text{ mol Cr}}{52.00\text{ g Cr}}\right)\left(\frac{6\text{ mol e}^-}{1\text{ mol Cr}}\right)$$

$$\left(\frac{9.6485\times10^4\text{ C}}{1\text{ mol e}^-}\right)\left(\frac{1\text{ A}}{1\text{ C}\cdot\text{s}^{-1}}\right)\left(\frac{1}{0.100\text{ A}}\right) = 0.741\text{ s}$$

12.90 Consider $Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$ $(E° = -1.66)$. With this half-reaction as the anode reaction and one or both of the given reduction reactions, a cell with a positive potential can be constructed. Two adjacent filled teeth, simultaneously in contact with the aluminum, could behave as two independent cells at different potentials, corresponding to the two possible reduction half-reactions. Current will then flow between them, stimulating the pain sensors.

The two possible cell reactions are

$$3\,Hg_2^{2+}(aq) + 4\,Ag(s) + 2\,Al(s) \rightarrow 2\,Ag_2Hg_3(s) + 2\,Al^{3+}(aq) \qquad E°_{cell} = +2.51\text{ V}$$

$$3\,Sn^{2+}(aq) + 9\,Ag(s) + 2\,Al(s) \rightarrow 3\,Ag_3Sn(s) + 2\,Al^{3+}(aq) \qquad E°_{cell} = +1.61\text{ V}$$