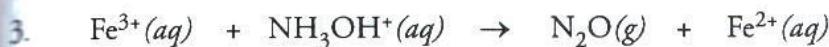


Answers to Study Questions and Problems

1. a. oxidation: $\text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq) + 2e^-$
reduction: $\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$
- b. the half-cell reactions are already balanced; the reduction reaction must be multiplied by two so that the number of electrons lost equals the number of electrons gained:
 $\text{Fe}(s) + 2\text{Ag}^+(aq) \rightarrow 2\text{Ag}(s) + \text{Fe}^{2+}(aq)$
- c. $\text{Fe}(s)|\text{Fe}^{2+}(aq)||\text{Ag}^+(aq)|\text{Ag}(s)$
 $+0.44\text{V} \quad +0.80\text{V} \quad E^\circ = +1.24\text{V}$ (E° is positive)

2. a. reduction: $\text{ClO}^-(aq) \rightarrow \text{Cl}^-(aq)$
 $\text{ClO}^-(aq) + 2\text{H}^+(aq) + 2e^- \rightarrow \text{Cl}^-(aq) + \text{H}_2\text{O}$
- oxidation: $\text{MnO}_2(s) \rightarrow \text{MnO}_4^-(aq)$
 $\text{MnO}_2(s) + 2\text{H}_2\text{O} \rightarrow \text{MnO}_4^-(aq) + 4\text{H}^+(aq) + 3e^-$
- b. the half-cell reactions are already balanced (for acidic solution); the reduction reaction must be multiplied by three and the oxidation reaction by two so that the number of electrons lost equals the number gained; then the acidic conditions must be changed to basic conditions by adding hydroxide (2OH^-) to both sides:
- $$2\text{MnO}_2(s) + 3\text{ClO}^- + \text{H}_2\text{O} \rightarrow 3\text{Cl}^- + 2\text{MnO}_4^- + 2\text{H}^+$$
- $$2\text{MnO}_2(s) + 3\text{ClO}^- + 2\text{OH}^- \rightarrow 3\text{Cl}^- + 2\text{MnO}_4^- + \text{H}_2\text{O} \quad (\text{aq}) \text{ notation omitted.}$$
- c. $\text{MnO}_2(s)/\text{MnO}_4^-(aq) \parallel \text{ClO}^-, \text{Cl}^-(aq)$
 $-0.588\text{V} \quad +0.89\text{V} \quad E^\circ = +0.30\text{V}$ (E° is positive)

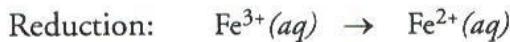


Step 1: Recognize the reaction:

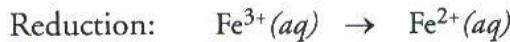
There is an obvious change in the oxidation number of iron, from +3 to +2. Sometimes a change in oxidation number isn't quite so clear.

Step 2: Separate into half-reactions:

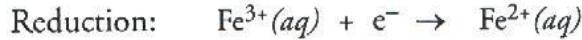
The $\text{Fe}^{3+}(aq)$ is reduced to $\text{Fe}^{2+}(aq)$; this means that the other component in the reaction must be oxidized.



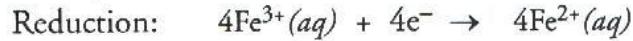
Step 3: Balance the half-reactions for mass:



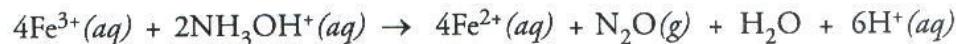
Step 4: Balance the half-reactions for charge:



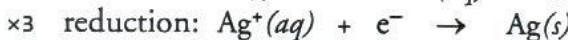
Step 5: Balance the electrons lost and gained:



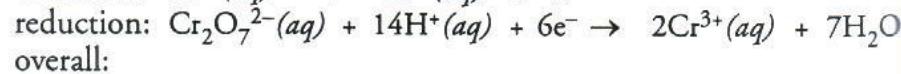
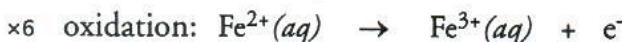
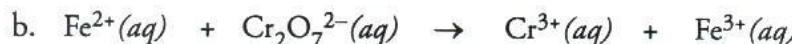
Step 6: Combine the two half-reactions:



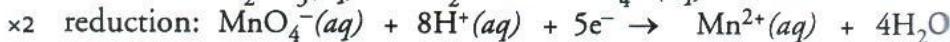
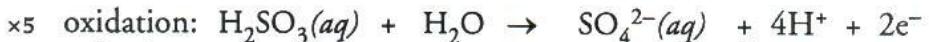
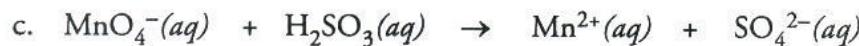
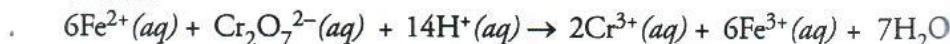
4. In acidic solution:



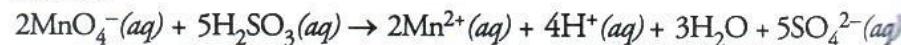
overall:



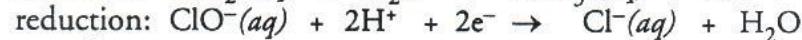
overall:



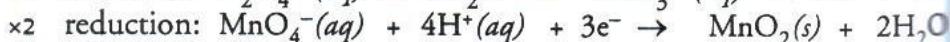
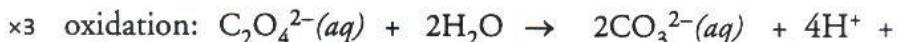
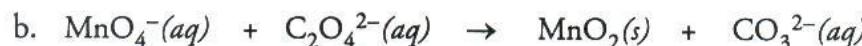
overall:



5. In basic solution:



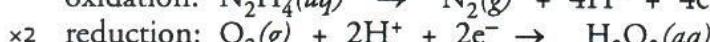
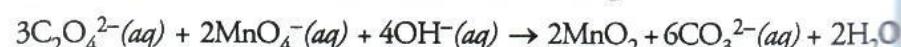
overall:



overall:



convert (add 4 OH⁻ to both sides and cancel H₂O):



overall:



If you look at this equation carefully, you'll notice that it is already balanced.

You will probably find it easier to balance the equations assuming acidic conditions, and then convert to basic conditions at the end—even though the half-reactions are unrealistic.

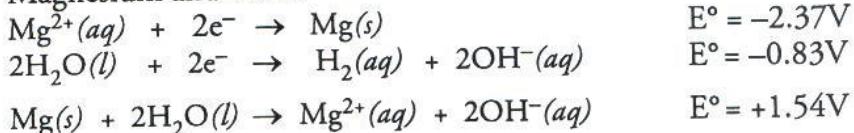
6. Look up the half-cell standard reduction potentials:

- a. $\text{Co}^{2+}(aq) + 2e^- \rightarrow \text{Co}(s)$ $E^\circ = -0.28\text{V}$ anode
 $\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$ $E^\circ = +0.80\text{V}$
 $\text{Co}(s)|\text{Co}^{2+}(aq) \parallel \text{Ag}^+(aq)|\text{Ag}(s)$ $E^\circ = +0.28 + 0.80 = +1.08\text{V}$
- b. $\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)$ $E^\circ = -0.25\text{V}$ anode
 $\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$ $E^\circ = +0.337\text{V}$
 $\text{Ni}(s)|\text{Ni}^{2+}(aq) \parallel \text{Cu}^{2+}(aq)|\text{Cu}(s)$ $E^\circ = +0.25 + 0.337 = +0.59\text{V}$
- c. $\text{Sn}^{2+}(aq) + 2e^- \rightarrow \text{Sn}(s)$ $E^\circ = -0.14\text{V}$
 $\text{Mg}^{2+}(aq) + 2e^- \rightarrow \text{Mg}(s)$ $E^\circ = -2.37\text{V}$ anode
 $\text{Mg}(s)|\text{Mg}^{2+}(aq) \parallel \text{Sn}^{2+}(aq)|\text{Sn}(s)$ $E^\circ = -0.14 + 2.37 = +2.23\text{V}$

The half-cell with the more negative potential will be the anode.

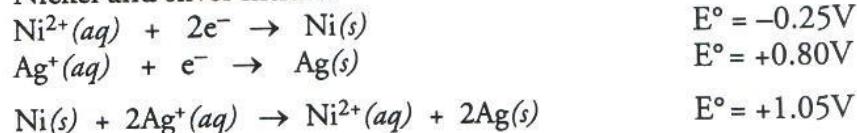
Change the sign of the reduction potential for oxidation at the anode.

7. a. Magnesium and water:



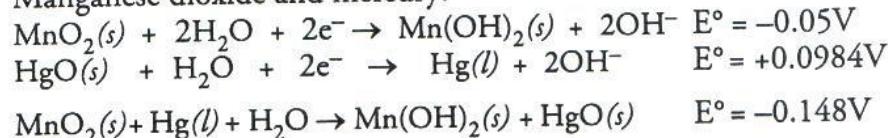
The reaction is spontaneous.

b. Nickel and silver nitrate:



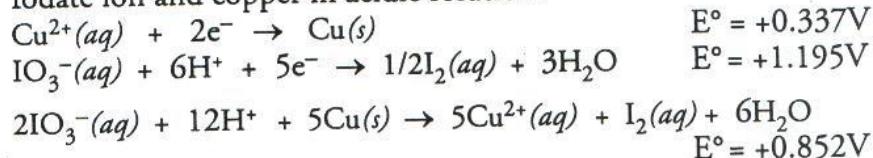
The reaction is spontaneous.

c. Manganese dioxide and mercury:

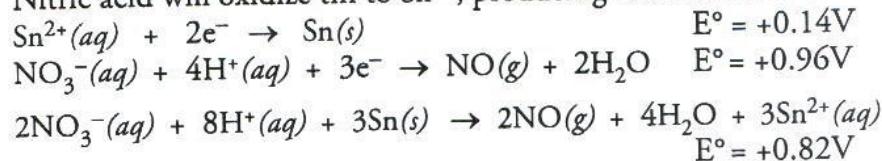


This reaction is *not* spontaneous; it will not happen.

d. Iodate ion and copper in acidic solution:



The reaction is spontaneous.

e. Nitric acid will oxidize tin to Sn^{2+} , producing nitric oxide NO?

The reaction is spontaneous.

All three quantities E_{cell}° , $\Delta G_{\text{rxn}}^{\circ}$, and K , are related:

$$\Delta G_{\text{rxn}}^{\circ} = -nFE_{\text{cell}}^{\circ} = -RT\ln K$$

8. The standard cell potential is
 $E_{\text{cell}}^{\circ} = E_{\text{oxid}}^{\circ} + E_{\text{red}}^{\circ} = -0.337 + 0.7994 = +0.46\text{V}$.
The reaction is spontaneous.

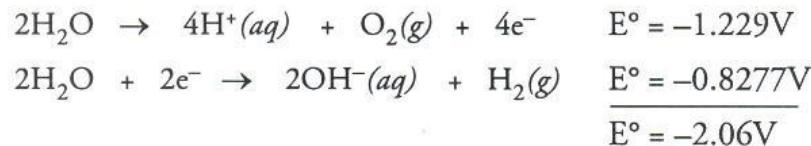
At equilibrium at 25°C, $E^{\circ} = (RT/nF)\ln K$, and $\ln K = nE^{\circ}/0.0257$
 $K = 3.52 \times 10^{15}$

$$\Delta G_{\text{rxn}}^{\circ} = -nFE^{\circ} = -2 \times 96485 \times 0.46 = -88.8 \text{ kJ}$$

and $\Delta G_{\text{rxn}}^{\circ} = -RT\ln K = -8.314 \times 298.15\text{K} \times 35.8 = -88.8 \text{ kJ}$

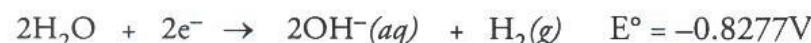
9. $\text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq) \quad E^{\circ} = +1.100\text{V}$
- The initial potential $E_{\text{cell}}^{\circ} = E_{\text{oxid}}^{\circ} + E_{\text{red}}^{\circ} = +0.763 + 0.337 = 1.100\text{V}$
 - The cell potential at time t :
Use the Nernst equation:

$$E = E^{\circ} - (0.0257/n)\ln Q = +1.100 - (0.0257/2)\ln(1.50/0.50)$$
 $= +1.100 - 0.014 = 1.086\text{V}$
 - Quantity of copper deposited = $0.50 \text{ M} \times 0.100\text{L} = 0.05 \text{ mol Cu}$
Quantity of electrons = 0.10 mol
Charge = 0.10 faraday = 9648.5 C
 - Approximate energy provided = average potential × charge
 $= 1.093\text{V} \times 9648.5\text{C}$
 $= 10.5 \text{ kJ}$
10. In general choose the lowest combination of half-cell potentials (the lowest sum) but be aware that the relative concentrations do matter.



11. $2\text{Cl}^{-}(aq) \rightarrow \text{Cl}_2(g) + 2e^{-} \quad E^{\circ} = -1.36\text{V}$
- $1000 \text{ kg} = 1,000,000 \text{ g} = 1,000,000 / 70.905 = 14103 \text{ moles Cl}_2$
number of electrons = 28,207 moles (2 electrons for each Cl_2)
= 28,207 faradays
 $= 28,207 \times 96,485 \text{ C} = 2.72 \times 10^9 \text{ C}$

$$2.72 \times 10^9 \text{ C} / 2.5 \times 10^5\text{A} = 1.09 \times 10^4 \text{ seconds}$$
 $= 3.02 \text{ hours}$



- number of OH^{-} = 28,207 moles (1 electron for each)
mass of sodium hydroxide = 1.13 million grams

- Energy = Potential × Charge = $5.0\text{V} \times 2.72 \times 10^9 \text{ C} = 1.36 \times 10^{10}\text{J}$
= 3780 kWh