

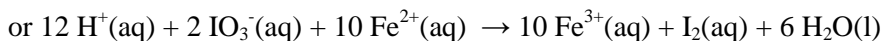
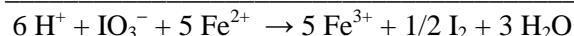
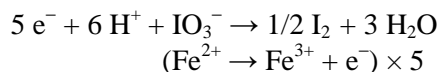
14. See Table 4.2 in Chapter 4 of the text for rules for assigning oxidation numbers.

- a. H (+1), O (!2), N (+5)
- b. Cl (!1), Cu (+2)
- c. O (0)
- d. H (+1), O (!1)
- e. H(+1), O (!2), C (0)
- f. Ag (0)
- g. Pb (+2), O (!2), S (+6)
- h. O (!2), Pb (+4)
- i. Na (+1), O (!2), C (+3)
- j. O (!2), C (+4)
- k. $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_3$ contains NH_4^+ ions and SO_4^{2-} ions. Thus, cerium exists as the Ce^{4+} ion.
H (+1), N (!3), Ce (+4), S (+6), O (!2)
- l. O (!2), Cr (+3)

18. Galvanic cells use spontaneous redox reactions to produce a voltage. The key is to have an overall positive E_{cell}° value when manipulating the half-reactions. For any two half-reactions, the half-reaction with the most positive reduction potential will always be the cathode reaction. For negative potentials, this will be the half-reaction with the standard reduction potential closest to zero. The remaining half-reaction (the one with the most negative E_{red}°) will be reversed and become the anode half-reaction ($E_{\text{ox}} = -E_{\text{red}}^{\circ}$). This combination will always yield a positive overall standard cell potential which can be used to run a galvanic cell.

26. Reference Exercise 17.25 for a typical galvanic cell diagram. The contents of each half-cell compartment are identified below with all solute concentrations at 1.0 M and all gases at 1.0 atm.

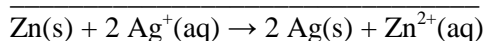
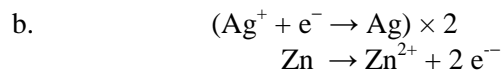
a. Reference Table 17.1 for the balanced half-reactions.



Cathode: Pt electrode; IO_3^- , I_2 and H_2SO_4 (H^+ source) in solution.

Note: $\text{I}_2(\text{s})$ would make a poor electrode since it sublimes.

Anode: Pt electrode; Fe^{2+} and Fe^{3+} in solution



Cathode: Ag electrode; Ag⁺ in solution; Anode: Zn electrode; Zn²⁺ in solution

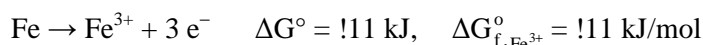
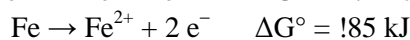


$$\Delta G^\circ = -nFE^\circ = -(2 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(+0.44 \text{ J/C})(1 \text{ kJ}/1000 \text{ J}) = 85 \text{ kJ}$$

$$85 \text{ kJ} = 0 + [\Delta G_{\text{f, Fe}^{2+}}^\circ + 0], \Delta G_{\text{f, Fe}^{2+}}^\circ = +85 \text{ kJ}$$

We can get $\Delta G_{\text{f, Fe}^{3+}}^\circ$ two ways. Consider: $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+} \quad E^\circ = 0.77 \text{ V}$

$$\Delta G^\circ = -(1 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(0.77 \text{ J/C}) = -74,300 \text{ J} = -74 \text{ kJ}$$



or consider: $\text{Fe}^{3+} + 3 \text{e}^- \rightarrow \text{Fe} \quad E^\circ = +0.036 \text{ V}$

$$\Delta G^\circ = -(3 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(+0.036 \text{ J/C}) = -10,400 \text{ J} \approx -10. \text{ kJ}$$

$-10. \text{ kJ} = 0 + [\Delta G_{\text{f, Fe}^{3+}}^\circ + 0], \Delta G_{\text{f, Fe}^{3+}}^\circ = -10. \text{ kJ/mol}$; Round-off error explains the 1 kJ discrepancy.

48. a. $\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu} \quad E^\circ = 0.34 \text{ V}$; $\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+ \quad E^\circ = 0.16 \text{ V}$; To reduce Cu^{2+} to Cu but not reduce Cu^{2+} to Cu^+ , the reducing agent must have a standard oxidation potential $E_{\text{ox}}^\circ = -E^\circ$ between -0.34 V and -0.16 V (so E_{cell}° is positive only for the Cu^{2+} to Cu reduction). The reducing agents (species oxidized) are on the right side of the half-reactions in Table 17.1. The reagents at standard conditions which have E_{ox}° ($=-E^\circ$) between -0.34 V and -0.16 V are Ag (in 1.0 M Cl^-) and H_2SO_3 .

b. $\text{Br}_2 + 2 \text{e}^- \rightarrow 2 \text{Br}^- \quad E^\circ = 1.09 \text{ V}$; $\text{I}_2 + 2 \text{e}^- \rightarrow 2 \text{I}^- \quad E^\circ = 0.54 \text{ V}$; From Table 17.1, VO^{2+} , Au (in 1.0 M Cl^-), NO, ClO_2^- , Hg_2^{2+} , Ag, Hg, Fe^{2+} , H_2O_2 and MnO_4^- are all capable at standard conditions of reducing Br_2 to Br^- but not reducing I_2 to I^- . When these reagents are coupled with Br_2 , $E_{\text{cell}}^\circ > 0$, and when coupled with I_2 , $E_{\text{cell}}^\circ < 0$.

54. As is the case for all concentration cells, $E_{\text{cell}}^\circ = 0$, and the smaller ion concentration is always in the anode compartment. The general Nernst equation for the $\text{Ni} | \text{Ni}^{2+}(x \text{ M}) || \text{Ni}^{2+}(y \text{ M}) | \text{Ni}$ concentration cell is:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log Q = -\frac{0.0591}{2} \log \frac{[\text{Ni}^{2+}]_{\text{anode}}}{[\text{Ni}^{2+}]_{\text{cathode}}}$$

- a. Both compartments are at standard conditions ($[\text{Ni}^{2+}] = 1.0 \text{ M}$), and $E_{\text{cell}} = E_{\text{cell}}^{\circ} = 0 \text{ V}$. No electron flow occurs.
- b. Cathode = 2.0 M Ni^{2+} ; Anode = 1.0 M Ni^{2+} ; Electron flow is always from the anode to the cathode, so electrons flow to the right in the diagram.

$$E_{\text{cell}} = \frac{-0.0591}{2} \log \frac{[\text{Ni}^{2+}]_{\text{anode}}}{[\text{Ni}^{2+}]_{\text{cathode}}} = \frac{-0.0591}{2} \log \frac{1.0}{2.0} = 8.9 \times 10^{-3} \text{ V}$$

- c. Cathode = 1.0 M Ni^{2+} ; Anode = 0.10 M Ni^{2+} ; Electrons flow to the left in the diagram.

$$E_{\text{cell}} = \frac{-0.0591}{2} \log \frac{0.10}{1.0} = 0.030 \text{ V}$$

- d. Cathode = 1.0 M Ni^{2+} ; Anode = $4.0 \times 10^{-5} \text{ M Ni}^{2+}$; Electrons flow to the left in the diagram.

$$E_{\text{cell}} = \frac{-0.0591}{2} \log \frac{4.0 \times 10^{-5}}{1.0} = 0.13 \text{ V}$$

- e. Because both concentrations are equal, $\log (2.5/2.5) = \log 1.0 = 0$ and $E_{\text{cell}} = 0$. No electron flow occurs.

62. $3 \text{ Ni}^{2+}(\text{aq}) + 2 \text{ Al}(\text{s}) \rightarrow 2 \text{ Al}^{3+}(\text{aq}) + 3 \text{ Ni}(\text{s})$ $E_{\text{cell}}^{\circ} = -0.23 \text{ V} + 1.66 \text{ V} = 1.43 \text{ V}$; $n = 6$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3}, \quad 1.82 \text{ V} = 1.43 \text{ V} - \frac{0.0591}{6} \log \frac{[\text{Al}^{3+}]^2}{(1.0)^3}$$

$$\log [\text{Al}^{3+}]^2 = -39.59, \quad [\text{Al}^{3+}]^2 = 10^{-39.59}, \quad [\text{Al}^{3+}] = 1.6 \times 10^{-20} \text{ M}$$

$$\text{Al}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Al}^{3+}(\text{aq}) + 3 \text{ OH}^{-}(\text{aq}) \quad K_{\text{sp}} = [\text{Al}^{3+}] [\text{OH}^{-}]^3; \text{ From the problem, } [\text{OH}^{-}] = 1.0 \times 10^{-4} \text{ M.}$$

$$K_{\text{sp}} = (1.6 \times 10^{-20}) (1.0 \times 10^{-4})^3 = 1.6 \times 10^{-32}$$