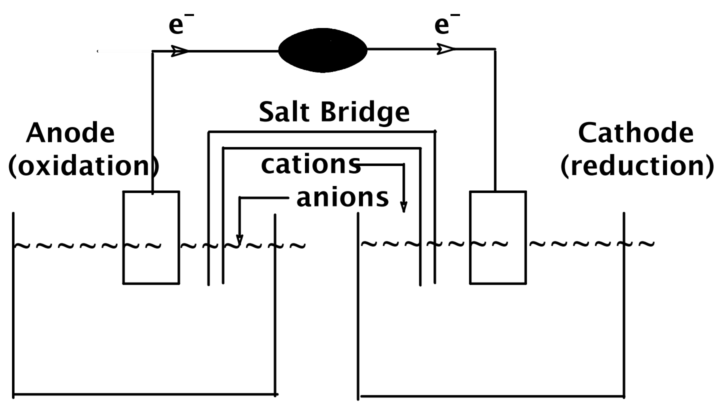
Unit VI(6)-III: Electrochemistry Chapter 17 Assigned Problems Answers

Exercises

Galvanic Cells, Cell Potentials, Standard Reduction Potentials, and Free Energy

25. A typical galvanic cell diagram is:



The diagram for all cells will look like this. The contents of each half-cell compartment will be identified for each reaction, with all solute concentrations at 1.0 *M* and all gases at 1.0 atm. For Exercises 17.25 and 17.26, the flow of ions through the salt bridge was not asked for in the questions. If asked, however, cations always flow into the cathode compartment, and anions always flow into the anode compartment. This is required to keep each compartment electrically neutral.

a. Table 17.1 of the text lists balanced reduction half-reactions for many substances. For this overall reaction, we need the Cl_2 to Cl^- reduction half-reaction and the Cr^{3+} to $Cr_2O_7^{2-}$ oxidation half-reaction. Manipulating these two half-reactions gives the overall balanced equation.

$$(Cl_2 + 2\ e^- \rightarrow 2\ Cl^-) \times 3$$
$$7\ H_2O + 2\ Cr^{3+} \rightarrow Cr_2O_7^{2-} + 14\ H^+ + 6\ e^-$$

$$7\ H_2O(l) + 2\ Cr^{3+}(aq) + 3\ Cl_2(g) \rightarrow Cr_2O_7^{2-}(aq) + 6\ Cl^-(aq) + 14\ H^+(aq)$$

The contents of each compartment are:

Cathode: Pt electrode; Cl_2 bubbled into solution, Cl^- in solution

Anode: Pt electrode; Cr^{3+}, H^+, and $Cr_2O_7^{2-}$ in solution

We need a nonreactive metal to use as the electrode in each case, since all the reactants and products are in solution. Pt is a common choice. Another possibility is graphite.

b. $Cu^{2+} + 2e^- \rightarrow Cu$

$Mg \rightarrow Mg^{2+} + 2e^-$

$Cu^{2+}(aq) + Mg(s) \rightarrow Cu(s) + Mg^{2+}(aq)$

Cathode: Cu electrode; Cu^{2+} in solution; Anode: Mg electrode; Mg^{2+} in solution

27. To determine E° for the overall cell reaction, we must add the standard reduction potential to the standard oxidation potential ($E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$). Reference Table 17.1 for values of standard reduction potentials. Remember that $E^\circ_{ox} = -E^\circ_{red}$ and that standard potentials are <u>not</u> multiplied by the integer used to obtain the overall balanced equation.

25a. $E^\circ_{cell} = E^\circ_{Cl_2 \rightarrow Cl^-} + E^\circ_{Cr^{3+} \rightarrow Cr_2O_7^{2-}} = 1.36\ V + (-1.33\ V) = 0.03\ V$

25b. $E^\circ_{cell} = E^\circ_{Cu^{2+} \rightarrow Cu} + E^\circ_{Mg \rightarrow Mg^{2+}} = 0.34\ V + 2.37\ V = 2.71\ V$

29. Reference Exercise 17.25 for a typical galvanic cell design. 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. For each pair of half-reactions, the half-reaction with the largest (most positive) standard reduction potential will be the cathode reaction, and the half-reaction with the smallest (most negative) reduction potential will be reversed to become the anode reaction. Only this combination gives a spontaneous overall reaction, i.e., a reaction with a positive overall standard cell potential. Note that in a galvanic cell as illustrated in Exercise 17.25, the cations in the salt bridge migrate to the cathode, and the anions migrate to the anode.

a. $Cl_2 + 2e^- \rightarrow 2Cl^-$ $\quad E^\circ = 1.36\ V$

$2Br^- \rightarrow Br_2 + 2e^-$ $\quad -E^\circ = -1.09\ V$

$Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$ $\quad E^\circ_{cell} = 0.27\ V$

The contents of each compartment are:

Cathode: Pt electrode; $Cl_2(g)$ bubbled in, Cl^- in solution

Anode: Pt electrode; Br_2 and Br^- in solution

b. $(2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O) \times 5$ $\quad E^\circ = 1.60\ V$

$(4H_2O + Mn^{2+} \rightarrow MnO_4^- + 8H^+ + 5e^-) \times 2$ $\quad -E^\circ = -1.51$

V

$10H^+ + 5IO_4^- + 8H_2O + 2Mn^{2+} \rightarrow 5IO_3^- + 5H_2O + 2MnO_4^- + 16H^+$ $\quad E^\circ_{cell} = 0.09\ V$

This simplifies to:

$H_2O(l) + 5IO_4^-(aq) + 2Mn^{2+}(aq) \rightarrow 5IO_3^-(aq) + 2MnO_4^-(aq) + 6H^+(aq)$ $\quad E^\circ_{cell} = 0.09\ V$

Cathode: Pt electrode; IO_4^-, IO_3^-, and H_2SO_4 (as a source of H^+) in solution

Anode: Pt electrode; Mn^{2+}, MnO_4^- and H_2SO_4 in solution

31. In standard line notation, the anode is listed first and the cathode is listed last. A double line separates the two compartments. By convention, the electrodes are on the ends with all solutes and gases towards the middle. A single line is used to indicate a phase change. We also included all concentrations.

25a. Pt | Cr^{3+} (1.0 *M*), $Cr_2O_7^{2-}$ (1.0 *M*), H^+ (1.0 *M*) || Cl_2 (1.0 atm) | Cl^- (1.0 *M*) | Pt

25b. Mg | Mg^{2+} (1.0 *M*) || Cu^{2+} (1.0 *M*) | Cu

29a. Pt | Br^- (1.0 *M*), Br_2 (1.0 *M*) || Cl_2 (1.0 atm) | Cl^- (1.0 *M*) | Pt

29b. Pt | Mn^{2+} (1.0 *M*), MnO_4^- (1.0 *M*), H^+ (1.0 *M*) || IO_4^- (1.0 *M*), H^+ (1.0 *M*), IO_3^- (1.0 *M*) | Pt

33. Locate the pertinent half-reactions in Table 17.1, and then figure which combination will give a positive standard cell potential. In all cases, the anode compartment contains the species with the smallest standard reduction potential. For part a, the copper compartment is the anode, and in part b, the cadmium compartment is the anode.

a.

$$Au^{3+} + 3\,e^- \rightarrow Au \qquad E° = 1.50\ V$$
$$(Cu^+ \rightarrow Cu^{2+} + e^-) \times 3 \qquad -E° = -0.16\ V$$

$$Au^{3+}(aq) + 3\,Cu^+(aq) \rightarrow Au(s) + 3\,Cu^{2+}(aq) \qquad E^o_{cell} = 1.34\ V$$

b.

$$(VO_2^+ + 2\,H^+ + e^- \rightarrow VO^{2+} + H_2O) \times 2 \qquad E° = 1.00\ V$$
$$Cd \rightarrow Cd^{2+} + 2e^- \qquad -E° = 0.40\ V$$

$$2\,VO_2^+(aq) + 4\,H^+(aq) + Cd(s) \rightarrow 2\,VO^{2+}(aq) + 2\,H_2O(l) + Cd^{2+}(aq) \qquad E^o_{cell} = 1.40\ V$$

35. a.

$$(5\,e^- + 8\,H^+ + MnO_4^- \rightarrow Mn^{2+} + 4\,H_2O) \times 2 \qquad E° = 1.51\ V$$
$$(2\,I^- \rightarrow I_2 + 2\,e^-) \times 5 \qquad -E° = -0.54\ V$$

$$16\,H^+(aq) + 2\,MnO_4^-(aq) + 10\,I^-(aq) \rightarrow 5\,I_2(aq) + 2\,Mn^{2+}(aq) + 8\,H_2O(l) \qquad E^o_{cell} = 0.97\ V$$

This reaction is spontaneous at standard conditions because $E^o_{cell} > 0$.

b.

$$(5\,e^- + 8\,H^+ + MnO_4^- \rightarrow Mn^{2+} + 4\,H_2O) \times 2 \qquad E° = 1.51\ V$$
$$(2\,F^- \rightarrow F_2 + 2\,e^-) \times 5 \qquad -E° = -2.87\ V$$

$$16\,H^+(aq) + 2\,MnO_4^-(aq) + 10\,F^-(aq) \rightarrow 5\,F_2(aq) + 2\,Mn^{2+}(aq) + 8\,H_2O(l) \qquad E^o_{cell} = -1.36\ V$$

This reaction is not spontaneous at standard conditions because $E^o_{cell} < 0$.

37. $Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$ $E° = 1.36$ V

$(ClO_2^- \rightarrow ClO_2 + e^-) \times 2$ $-E° = -0.954$ V

$2\ ClO_2^-(aq) + Cl_2(g) \rightarrow 2\ ClO_2(aq) + 2\ Cl^-(aq)$ $E^o_{cell} = 0.41$ V = 0.41 J/C

$\Delta G° = -nFE^o_{cell} = -(2 \text{ mol } e^-)(96{,}485 \text{ C/mol } e^-)(0.41 \text{ J/C}) = -7.9 \times 10^4 \text{ J} = -79$ kJ

39. Because the cells are at standard conditions, $w_{max} = \Delta G = \Delta G° = -nFE^o_{cell}$. See Exercise 17.33 for the balanced overall equations and for E^o_{cell}.

33a. $w_{max} = -(3 \text{ mol } e^-)(96{,}485 \text{ C/mol } e^-)(1.34 \text{ J/C}) = -3.88 \times 10^5 \text{ J} = -388$ kJ

33b. $w_{max} = -(2 \text{ mol } e^-)(96{,}485 \text{ C/mol } e^-)(1.40 \text{ J/C}) = -2.70 \times 10^5 \text{ J} = -270.$ kJ

41. $CH_3OH(l) + 3/2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ $\Delta G° = 2(-237) + (-394) - [-166] = -702$ kJ

The balanced half-reactions are:

$H_2O + CH_3OH \rightarrow CO_2 + 6\ H^+ + 6\ e^-$ and $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$

For 3/2 mol O_2, 6 moles of electrons will be transferred (n = 6).

$$\Delta G° = -nFE°,\ E° = \frac{-\Delta G°}{nF} = \frac{-(-702{,}000 \text{ J})}{(6 \text{ mole } e^-)(96{,}485 \text{ C/mol } e^-)} = 1.21 \text{ J/C} = 1.21 \text{ V}$$

43. Good oxidizing agents are easily reduced. Oxidizing agents are on the left side of the reduc-tion half-reactions listed in Table 17.1. We look for the largest, most positive standard reduction potentials to correspond to the best oxidizing agents. The ordering from worst to best oxidizing agents is:

	K^+	<	H_2O	<	Cd^{2+}	<	I_2	<	$AuCl_4^-$	<	IO_3^-
E°(V)	-2.87		–0.83		–0.40		0.54		0.99		1.20

44. Good reducing agents are easily oxidized. The reducing agents are on the right side of the reduction half-reactions listed in Table 17.1. The best reducing agents have the most nega-tive standard reduction potentials (E°) or the most positive standard oxidation potentials, E^o_{ox} (= -E°). The ordering from worst to best reducing agents is:

	F^-	<	H_2O	<	I_2	<	Cu^+	<	H^-	<	K
-E°(V)	-2.92		–1.23		–1.20		–0.16		2.23		2.92

45. a. $2\ H^+ + 2\ e^- \rightarrow H_2$ $E° = 0.00$ V; $Cu \rightarrow Cu^{2+} + 2\ e^-$ $-E° = -0.34$ V

$E^o_{cell} = -0.34$ V; No, H^+ cannot oxidize Cu to Cu^{2+} at standard conditions ($E^o_{cell} < 0$).

b. $Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E° = 0.77$ V; $2\ I^- \rightarrow I_2 + 2\ e^-$ $-E° = -0.54$ V

$E^o_{cell} = 0.77 - 0.54 = 0.23$ V; Yes, Fe^{3+} can oxidize I^- to I_2.

c. $H_2 \rightarrow 2\ H^+ + 2\ e^-$ $-E° = 0.00$ V; $Ag^+ + e^- \rightarrow Ag$ $E° = 0.80$ V

$E^o_{cell} = 0.80$ V; Yes, H_2 can reduce Ag^+ to Ag at standard conditions ($E^o_{cell} > 0$).

d. $Fe^{2+} \rightarrow Fe^{3+} + e^-$ $-E° = -0.77$ V; $Cr^{3+} + e^- \rightarrow Cr^{2+}$ $E° = -0.50$ V

$E^o_{cell} = -0.50 - 0.77 = -1.27$ V; No, Fe^{2+} cannot reduce Cr^{3+} to Cr^{2+} at standard conditions.

46.

$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$	$E° = 1.36$ V	$Ag^+ + e^- \rightarrow Ag$	$E° = 0.80$ V
$Pb^{2+} + 2\ e^- \rightarrow Pb$	$E° = -0.13$ V	$Zn^{2+} + 2\ e^- \rightarrow Zn$	$E° = -0.76$ V
$Na^+ + e^- \rightarrow Na$	$E° = -2.71$ V		

a. Oxidizing agents (species reduced) are on the left side of the above reduction half-reactions. Of the species available, Ag^+ would be the best oxidizing agent since it has the largest E° value. Note that Cl_2 is a better oxidizing agent than Ag^+, but it is not one of the choices listed.

b. Reducing agents (species oxidized) are on the right side of the reduction half-reactions. Of the species available, Zn would be the best reducing agent since it has the largest -E° value.

c. $SO_4^{2-} + 4\ H^+ + 2\ e^- \rightarrow H_2SO_3 + H_2O$ $E° = 0.20$ V; SO_4^{2-} can oxidize Pb and Zn at standard conditions. When SO_4^{2-} is coupled with these reagents, E^o_{cell} is positive.

d. $Al \rightarrow Al^{3+} + 3\ e^-$ $-E° = 1.66$ V; Al can reduce Ag^+ and Zn^{2+} at standard conditions since $E^o_{cell} > 0$.

47. a. $2\ Br^- \rightarrow Br_2 + 2\ e^-$ $-E° = -1.09$ V; $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$ $-E° = -1.36$ V; $E° > 1.09$ V to oxidize Br^-; $E° < 1.36$ V to not oxidize Cl^-; $Cr_2O_7^{2-}$, O_2, MnO_2, and IO_3^- are all possible since when all of these oxidizing agents are coupled with Br^-, $E^o_{cell} > 0$, and when coupled with Cl^-, $E^o_{cell} < 0$ (assuming standard conditions).

b. $Mn \rightarrow Mn^{2+} + 2\ e^-$ $-E° = 1.18$; $Ni \rightarrow Ni^{2+} + 2\ e^-$ $-E° = 0.23$ V; Any oxidizing agent with $-0.23\ V > E° > -1.18$ V will work. $PbSO_4$, Cd^{2+}, Fe^{2+}, Cr^{3+}, Zn^{2+} and H_2O will be able to oxidize Mn but not Ni (assuming standard conditions).

49.

$$ClO^- + H_2O + 2\ e^- \rightarrow 2\ OH^- + Cl^- \qquad E° = 0.90\ V$$
$$2\ NH_3 + 2\ OH^- \rightarrow N_2H_4 + 2\ H_2O + 2\ e^- \qquad -E° = 0.10\ V$$

$$ClO^-(aq) + 2\ NH_3(aq) \rightarrow Cl^-(aq) + N_2H_4(aq) + H_2O(l) \qquad E^o_{cell} = 1.00\ V$$

Because E°_{cell} is positive for this reaction, at standard conditions ClO^- can spontaneously oxidize NH_3 to the somewhat toxic N_2H_4.

The Nernst Equation

57. $$\begin{array}{lr} Cu^{2+} + 2\,e^- \rightarrow Cu & E^\circ = 0.34\ V \\ Zn \rightarrow Zn^{2+} + 2\,e^- & -E^\circ = 0.76\ V \\ \hline Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s) & E^\circ_{cell} = 1.10\ V \end{array}$$

Because Zn^{2+} is a product in the reaction, the Zn^{2+} concentration increases from 1.00 *M* to 1.20 *M*. This means that the reactant concentration of Cu^{2+} must decrease from 1.00 *M* to 0.80 *M* (from the 1:1 mol ratio in the balanced reaction).

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log Q = 1.10\ V - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 1.10\ V - \frac{0.0591}{2}\log\frac{1.20}{0.80} = 1.10\ V - 0.0052\ V = 1.09\ V$$

65. See Exercises 17.25, 17.27, and 17.29 for balanced reactions and standard cell potentials. Balanced reactions are necessary to determine n, the moles of electrons transferred.

25a. $7\ H_2O + 2\ Cr^{3+} + 3\ Cl_2 \rightarrow Cr_2O_7^{2-} + 6\ Cl^- + 14\ H^+ \qquad E^\circ_{cell} = 0.03\ V = 0.03\ J/C$

$\Delta G^\circ = -nFE^\circ_{cell} = -(6\ mol\ e^-)(96{,}485\ C/mol\ e^-)(0.03\ J/C) = -1.7 \times 10^4\ J = -20\ kJ$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log Q\text{: At equilibrium, } E_{cell} = 0 \text{ and } Q = K\text{, so:}$$

$$E^\circ_{cell} = \frac{0.0591}{n}\log K,\ \log K = \frac{nE^\circ}{0.0591} = \frac{6(0.03)}{0.0591} = 3.05,\ K = 10^{3.05} = 1 \times 10^3$$

Note: When determining exponents, we will round off to the correct number of significant figures after the calculation is complete in order to help eliminate excessive round-off error.

25b. $\Delta G^\circ = -(2\ mol\ e^-)(96{,}485\ C/mol\ e^-)(2.71\ J/C) = -5.23 \times 10^5\ J = -523\ kJ$

$$\log K = \frac{2(2.71)}{0.0591} = 91.709,\ K = 5.12 \times 10^{91}$$

29a. $\Delta G^\circ = -(2\ mol\ e^-)(96{,}485\ C/mol\ ^-)(0.27\ J/C) = -5.21 \times 10^4\ J = -52\ kJ$

$$\log K = \frac{2(0.27)}{0.0591} = 9.14, \; K = 1.4 \times 10^{9}$$

29b. $\Delta G° = -(10 \text{ mol } e^-)(96{,}485 \text{ C/mol } e^-)(0.09 \text{ J/C}) = -8.7 \times 10^4 \text{ J} = -90 \text{ kJ}$

$$\log K = \frac{10(0.09)}{0.0591} = 15.23, \; K = 2 \times 10^{15}$$

Electrolysis

77. a. $Al^{3+} + 3\,e^- \rightarrow Al$; 3 mol e^- are needed to produce 1 mol Al from Al^{3+}.

$$1.0 \times 10^3 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{3 \text{ mol } e^-}{\text{mol Al}} \times \frac{96{,}485 \text{ C}}{\text{mol } e^-} \times \frac{1 \text{ s}}{100.0 \text{ C}} = 1.07 \times 10^5 \text{ s}$$

$$= 30. \text{ hours}$$

b. $1.0 \text{ g Ni} \times \frac{1 \text{ mol Ni}}{58.69 \text{ g Ni}} \times \frac{2 \text{ mol } e^-}{\text{mol Ni}} \times \frac{96{,}485 \text{ C}}{\text{mol } e^-} \times \frac{1 \text{ s}}{100.0 \text{ C}} = 33 \text{ s}$

c. $5.0 \text{ mol Ag} \times \frac{1 \text{ mol } e^-}{\text{mol Ag}} \times \frac{96{,}485 \text{ C}}{\text{mol } e^-} \times \frac{1 \text{ s}}{100.0 \text{ C}} = 4.8 \times 10^3 \text{ s} = 1.3 \text{ hours}$

79. $15 \text{ A} = \frac{15 \text{ C}}{\text{s}} \times \frac{60 \text{ s}}{\text{min}} \times \frac{60 \text{ min}}{\text{h}} = 5.4 \times 10^4$ C of charge passed in 1 hour

a. $5.4 \times 10^4 \text{ C} \times \frac{1 \text{ mol } e^-}{96{,}485 \text{ C}} \times \frac{1 \text{ mol Co}}{2 \text{ mol } e^-} \times \frac{58.93 \text{ g Co}}{\text{mol Co}} = 16 \text{ g Co}$

b. $5.4 \times 10^4 \text{ C} \times \frac{1 \text{ mol } e^-}{96{,}485 \text{ C}} \times \frac{1 \text{ mol Hf}}{4 \text{ mol } e^-} \times \frac{178.5 \text{ g Hf}}{\text{mol Hf}} = 25 \text{ g Hf}$

c. $2\,I^- \rightarrow I_2 + 2\,e^-$; $5.4 \times 10^4 \text{ C} \times \frac{1 \text{ mol } e^-}{96{,}485 \text{ C}} \times \frac{1 \text{ mol } I_2}{2 \text{ mol } e^-} \times \frac{253.8 \text{ g } I_2}{\text{mol } I_2} = 71 \text{ g } I_2$

d. $CrO_3(l) \rightarrow Cr^{6+} + 3\,O^{2-}$; 6 mol e^- are needed to produce 1 mol Cr from molten CrO_3.

$$5.4 \times 10^4 \text{ C} \times \frac{1 \text{ mol } e^-}{96{,}485 \text{ C}} \times \frac{1 \text{ mol Cr}}{6 \text{ mol } e^-} \times \frac{52.00 \text{ g Cr}}{\text{mol Cr}} = 4.9 \text{ g Cr}$$

89. $Au^{3+} + 3\,e^- \rightarrow Au$ $E° = 1.50$ V $Ni^{2+} + 2\,e^- \rightarrow Ni$ $E° = -0.23$ V
$Ag^+ + e^- \rightarrow Ag$ $E° = 0.80$ V $Cd^{2+} + 2\,e^- \rightarrow Cd$ $E° = -0.40$ V

$2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$ $E° = -0.83$ V

Au(s) will plate out first since it has the most positive reduction potential, followed by Ag(s), which is followed by Ni(s), and finally Cd(s) will plate out last since it has the most negative reduction potential of the metals listed. Water will not interfere with the plating process.