

Chapter 17 Review Questions and Text Homework Solutions

Review Questions

2. Before we answer the question, here are four important terms relating to redox reactions and galvanic cells.
- Cathode: The electrode at which reduction occurs.
 - Anode: The electrode at which oxidation occurs.
 - Oxidation half-reaction: The half-reaction in which electrons are products. In a galvanic cell, the oxidation half-reaction always occurs at the anode.
 - Reduction half-reaction: The half-reaction in which electrons are reactants. In a galvanic cell, the reduction half-reaction always occurs at the cathode.

See Figures 17.2 and 17.3 for designs of galvanic cells. The electrode compartment in which reduction occurs is called the cathode and the electrode compartment in which oxidation occurs is called the anode. These compartments have electrodes (a solid surface) immersed in a solution. For a standard cell, the solution contains the reactant and product solutes and gases that are in the balanced half-reactions. The solute concentrations are all 1 *M* and gas partial pressures are all 1 atm for a standard cell. The electrodes are connected via a wire and a salt-bridge connects the two solutions.

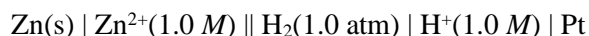
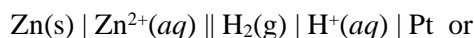
The purpose of the electrodes is to provide a solid surface for electron transfer to occur in the two compartments. Electrons always flow from the anode (where they are produced) to the cathode (where they are reactants). The salt bridge allows counter ions to flow into the two cell compartments to maintain electrical neutrality. Without a salt bridge, no sustained electron flow can occur. In the salt bridge, anions flow into the anode to replenish the loss of negative charge as electrons are lost; cations flow into the cathode to balance the negative charge as electrons are transferred into the cathode. The “pull” or driving force on the electrons is called the cell potential ($\mathcal{E}_{\text{cell}}$) or the electromotive force. The unit of electrical potential is the volt (V) which is defined as 1 joule of work per coulomb of charge transferred. It is the cell potential that can be used to do useful work. We harness the spontaneous redox reaction to produce a cell potential which can do useful work.

3. The zero point for standard reduction potentials (\mathcal{E}°) is the standard hydrogen electrode. The half-reaction is: $2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$. This half-reaction is assigned a standard potential of zero, and all other reduction half-reactions are measured relative to this zero point. Substances less easily reduced than H^+ have negative standard reduction potentials ($\mathcal{E}^\circ < 0$), while substances more easily reduced than H^+ have positive standard reduction potentials ($\mathcal{E}^\circ > 0$). The species most easily reduced has the most positive \mathcal{E}° value; this is F_2 . The least easily reduced species is Li^+ with the most negative \mathcal{E}° value.

When a reduction half-reaction is reversed to obtain an oxidation half-reaction, the sign of the reduction potential is reversed to give the potential for the oxidation half-reaction ($\mathcal{E}_{\text{ox}}^{\circ} = -\mathcal{E}_{\text{red}}^{\circ}$). The species oxidized are on the product side of the reduction half-reactions listed in Table 17.1. Li will have the most positive oxidation potential [$\mathcal{E}_{\text{ox}}^{\circ} = -\mathcal{E}_{\text{red}}^{\circ} = -(-3.05 \text{ V}) = 3.05 \text{ V}$], so Li is the most easily oxidized of the species. The species most easily oxidized is the best reducing agent. The worst reducing agent is F^{-} because it has the most negative oxidation potential ($\mathcal{E}_{\text{ox}}^{\circ} = -2.87 \text{ V}$).

For a spontaneous reaction at standard conditions, $\mathcal{E}_{\text{cell}}^{\circ}$ must be positive ($\mathcal{E}_{\text{cell}}^{\circ} = \mathcal{E}_{\text{red}}^{\circ} + \mathcal{E}_{\text{ox}}^{\circ} > 0$). For any two half-reactions, there is only one way to manipulate them to come up with a positive $\mathcal{E}_{\text{cell}}^{\circ}$ (a spontaneous reaction). Because the half-reactions do not depend on how many times the reaction occurs, half-reactions are an intensive property. This means that the value of $\mathcal{E}_{\text{red}}^{\circ}$ or $\mathcal{E}_{\text{ox}}^{\circ}$ is not changed when the half-reactions are multiplied by integers to get the electrons to cross off.

The line notation of the standard galvanic cell illustrated in Figure 17.5 of the text would be:



The double line represents the salt-bridge separating the anode and cathode compartments. To the left of the double line are the pertinent anode compartment contents, and to the right are the pertinent cathode compartment contents. At each end, the electrodes are listed; to the inside, the solution contents are listed. A single line is used to separate the contents of each compartment whenever there is a phase change. Here in the cathode compartment, a single line is used to separate $\text{H}_2(\text{g})$ from $\text{H}^{+}(\text{aq})$ and to separate $\text{H}^{+}(\text{aq})$ from Pt (the electrode). When concentrations and partial pressures are not listed, they are assumed to be standard (1.0 *M* for solutes and 1.0 atm for gases). For cells having nonstandard concentrations and pressures, we always include the actual concentrations and pressures in the line notation instead of the phases.

4. $\Delta G^{\circ} = -nF\mathcal{E}^{\circ}$; ΔG° is the standard free energy change for the overall balanced reaction, n is the number of electrons transferred in the overall balanced reaction, F is called the Faraday constant (1 $F = 96,485$ coulombs of charge transferred per mole of electrons), and \mathcal{E}° is the standard cell potential for the reaction. For a spontaneous redox reaction, $\mathcal{E}_{\text{cell}}^{\circ}$ is positive while $\Delta G_{\text{rxn}}^{\circ}$ is negative. The negative sign is necessary to convert the positive $\mathcal{E}_{\text{cell}}^{\circ}$ value for a spontaneous reaction into a negative $\Delta G_{\text{rxn}}^{\circ}$. The superscript $^{\circ}$ indicates standard conditions. These are $T = 25^{\circ}\text{C}$, solute concentrations of 1.0 *M*, and gas partial pressures of 1.0 atm. Note that n is necessary in order to convert the intensive property \mathcal{E}° into the extensive property ΔG° .
5. $\mathcal{E} = \mathcal{E}^{\circ} - \frac{RT}{nF} \ln Q$; at 25°C , the Nernst equation is: $\mathcal{E} = \mathcal{E}^{\circ} - \frac{0.0591}{n} \log Q$

Nonstandard conditions are when solutes are not all 1.0 M and/or partial pressures of gases are not all 1.0 atm. Nonstandard conditions also occur when $T \neq 25^\circ\text{C}$. For most problem solving, $T = 25^\circ\text{C}$ is usually assumed, hence the second version of the Nernst equation is most often used.

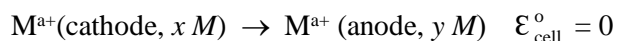
\mathcal{E} = cell potential at the conditions of the cell; \mathcal{E}° = standard cell potential; n = number of electrons transferred in the overall reaction, and Q is the reaction quotient determined at the concentrations and partial pressures of the cell contents.

At equilibrium, $\mathcal{E} = 0$ and $Q = K$. At 25°C , $\mathcal{E}^\circ = (0.0591/n)\log K$. The standard cell potential allows calculation of the equilibrium constant for a reaction. When $K < 1$, the $\log K$ term is negative, so $\mathcal{E}_{\text{cell}}^\circ$ is negative and ΔG° is positive. When $K > 1$, the $\log K$ term is positive, so $\mathcal{E}_{\text{cell}}^\circ$ is positive and ΔG° is negative.

From the equation $\mathcal{E}^\circ = (0.0591/n)\log K$, the value of \mathcal{E}° allows calculation of the equilibrium constant K . We say that \mathcal{E}° gives the equilibrium position for a reaction. \mathcal{E} is the actual cell potential at the conditions of the cell reaction. The sign of \mathcal{E} determines the spontaneity of the cell reaction. If \mathcal{E} is positive, then the cell reaction is spontaneous as written (the forward reaction can be used to make a galvanic cell to produce a voltage). If \mathcal{E} is negative, the forward reaction is not spontaneous at the conditions of cell, but the reverse reaction is spontaneous. The reverse reaction can be used to form a galvanic cell. \mathcal{E}° can only be used to determine spontaneity when all reactants and products are at standard conditions ($T = 25^\circ\text{C}$, $[] = 1.0 M$, $P = 1.0 \text{ atm}$).

6. Concentration cell: A galvanic cell in which both compartments contain the same components, but at different concentrations. All concentration cells have $\mathcal{E}_{\text{cell}}^\circ = 0$ because both compartments contain the same contents. The driving force for the cell is the different ion concentrations between the anode and cathode. The cell produces a voltage as long as the ion concentrations are different. Equilibrium for a concentration cell is reached ($\mathcal{E} = 0$) when the ion concentrations in the two compartments are equal.

The net reaction in a concentration cell is:



and the Nernst equation is:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \log Q = -\frac{0.0591}{a} \log \frac{[\text{M}^{\text{a+}}(\text{anode})]}{[\text{M}^{\text{a+}}(\text{cathode})]}$$

where a is the number of electrons transferred.

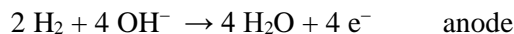
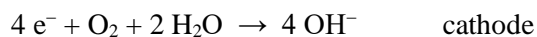
To register a potential ($\mathcal{E} > 0$), the $\log Q$ term must be a negative value. This occurs when $\text{M}^{\text{a+}}(\text{cathode}) > \text{M}^{\text{a+}}(\text{anode})$. The higher ion concentration is always at the cathode and the lower ion concentration is always at the anode. The magnitude of the cell potential depends on the magnitude of the differences in ion concentrations between the anode and cathode. The larger the difference in ion concentrations, the more negative the $\log Q$ term and the more positive the cell potential. Thus, as the difference in ion concentrations between the anode and cathode compartments increase, the cell potential increases. This can be accomplished by decreasing the ion concentration at the anode and/or by increasing the ion concentration at the cathode.

When NaCl is added to the anode compartment, Ag^+ reacts with Cl^- to form $\text{AgCl}(s)$. Adding Cl^- lowers the Ag^+ concentration which causes an increase in the cell potential. To determine K_{sp} for AgCl ($K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$), we must know the equilibrium Ag^+ and Cl^- concentrations. Here, $[\text{Cl}^-]$ is given and we use the Nernst equation to calculate the $[\text{Ag}^+]$ at the anode.

7. As a battery discharges, $\mathcal{E}_{\text{cell}}$ decreases, eventually reaching zero. A charged battery is not at equilibrium. At equilibrium, $\mathcal{E}_{\text{cell}} = 0$ and $\Delta G = 0$. We get no work out of an equilibrium system. A battery is useful to us because it can do work as it approaches equilibrium.

Both fuel cells and batteries are galvanic cells that produce cell potentials to do useful work. However, fuel cells, unlike batteries, have the reactants continuously supplied and can produce a current indefinitely.

The overall reaction in the hydrogen-oxygen fuel cell is $2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(l)$. The half-reactions are:



Utilizing the standard potentials in Table 17.1, $\mathcal{E}_{\text{cell}}^{\circ} = 0.40 \text{ V} + 0.83 \text{ V} = 1.23 \text{ V}$ for the hydrogen-oxygen fuel cell. As with all fuel cells, the $\text{H}_2(g)$ and $\text{O}_2(g)$ reactants are continuously supplied. See Figure 17.16 of the text for a schematic of this fuel cell.

8. The corrosion of a metal can be viewed as the process of returning metals to their natural state. The natural state of metals is to have positive oxidation numbers. This corrosion is the oxidation of a pure metal (oxidation number = 0) into its ions. For corrosion of iron to take place, you must have:
- exposed iron surface – a reactant
 - $\text{O}_2(g)$ – a reactant
 - $\text{H}_2\text{O}(l)$ – a reactant, but also provides a medium for ion flow (it provides the salt bridge)
 - ions – to complete the salt bridge

Because water is a reactant and acts as a salt bridge for corrosion, cars do not rust in dry air climates, while corrosion is a big problem in humid climates. Salting roads in the winter also increases the severity of corrosion. The dissolution of the salt into ions on the surface of a metal increases the conductivity of the aqueous solution and accelerates the corrosion process.

Some of the ways metals (iron) are protected from corrosion are listed below.

- Paint: Covers the metal surface so no contact occurs between the metal and air. This only works as long as the painted surface is not scratched.

- b. Durable oxide coatings: Covers the metal surface so no contact occurs between the metal and air.
 - c. Galvanizing: Coating steel with zinc; Zn forms an effective oxide coating over steel; also, zinc is more easily oxidized than the iron in the steel.
 - d. Sacrificial metal: Attaching a more easily oxidized metal to an iron surface; the more active metal is preferentially oxidized instead of iron.
 - e. Alloying: Adding chromium and nickel to steel; the added Cr and Ni form oxide coatings on the steel surface.
 - f. Cathodic protection: A more easily oxidized metal is placed in electrical contact with the metal we are trying to protect. It is oxidized in preference to the protected metal. The protected metal becomes the cathode electrode, thus, cathodic protection.
9. An electrolytic cell uses electrical energy to produce a chemical change. The process of electrolysis involves forcing a current through a cell to produce a chemical change for which the cell potential is negative. Electrical work is used to force a nonspontaneous reaction to occur.

The units for current are amperes (A) which equal 1 coulomb of charge per second.

current (A) \times time (s) = coulombs of charge passed

We use Faraday's constant ($F = 96,485$ coulombs of charge per mole) to convert coulombs of charge passed into moles of electrons passed. The half-reaction gives the mole ratio between moles of electrons and moles of metal produced (or plated out). Plating means depositing the neutral metal on the electrode by reducing the metal ions in solution.

In electrolysis, as with any redox reaction, the reaction that occurs first is the one most favored thermodynamically. The reduction reaction most favored thermodynamically has the largest, most positive $\mathcal{E}_{\text{red}}^{\circ}$ value. The oxidation reaction most likely to occur is the one with the largest, most positive $\mathcal{E}_{\text{ox}}^{\circ}$ value. Note that for electrolytic cells, $\mathcal{E}_{\text{cell}}^{\circ} < 0$, so the $\mathcal{E}_{\text{red}}^{\circ}$ and $\mathcal{E}_{\text{ox}}^{\circ}$ values are commonly negative. The half-reactions that occur first as a current is applied are the ones with the least negative potentials (which are the most positive potentials). To predict the cathode half-reaction, write down the half-reaction and $\mathcal{E}_{\text{red}}^{\circ}$ value for all species present that can be reduced. The cathode reaction that occurs has the least negative (most positive) $\mathcal{E}_{\text{red}}^{\circ}$ value. The same thing is done for the anode; write down everything present that can be oxidized; the species oxidized has the least negative (most positive) $\mathcal{E}_{\text{ox}}^{\circ}$ value. Note that we commonly assume standard conditions when predicting which half-reactions occur, so we can use the standard potentials in Table 17.1.

When molten salts are electrolyzed, there is only one species present that can be oxidized (the anion in simple salts) and there is only one species that can be reduced (the cation in simple salts). When H_2O is present as is the case when aqueous solutions are electrolyzed, we must consider the oxidation and reduction of water as potential reactions that can occur. When water is present, more reactions can take place, making predictions more difficult.

When the voltage required to force a chemical reaction to occur is larger than expected, this is called overvoltage. The amount of overvoltage necessary to force a reaction to occur varies with the type of substance present. Because of this, \mathcal{E}° values must be used cautiously when predicting the half-reactions that occur.

10. Electrolysis is used to produce many pure metals and pure elements for commercial use. It also is used to purify metals as well as to plate out thin coatings on substances to provide protection from corrosion and to beautify objects. Another application of electrolysis is the charging of batteries.

When aqueous NaCl is electrolyzed, water, with its less negative reduction potential is preferentially reduced over Na^+ ions. Thus, the presence of water doesn't allow Na^+ ions to be reduced to Na. In molten NaCl, water is not present, so Na^+ can be reduced to Na.

Purification by electrolysis is called electrorefining. See the text for a discussion of the electrorefining of copper. Electrorefining is possible because of the selectivity of electrode reactions. The anode is made up of the impure metal. A potential is applied so just the metal of interest and all more easily oxidized metals are oxidized at the anode. The metal of interest is the only metal plated at the cathode due to the careful control of the potential applied. The metal ions that could plate out at the cathode in preference to the metal we are purifying will not be in solution, because these metals were not oxidized at the anode.

Text Homework

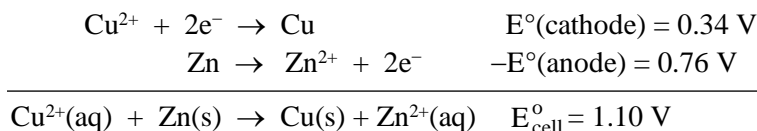
22. Galvanic cells use spontaneous redox reactions to produce a voltage. For a spontaneous redox reaction, the key is to have an overall positive E_{cell}° value when manipulating the half-reactions. For any two half-reactions, the half-reaction with the most positive reduction potential will always be the cathode reaction. The remaining half-reaction (the one with the most negative E_{red}°) will be reversed and become the anode half-reaction. This combination will always yield an overall reaction having a positive standard cell potential that can be used to run a galvanic cell.

24.
$$E = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log Q$$

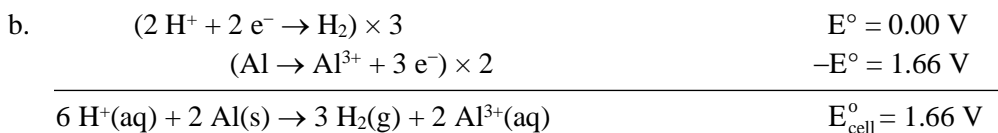
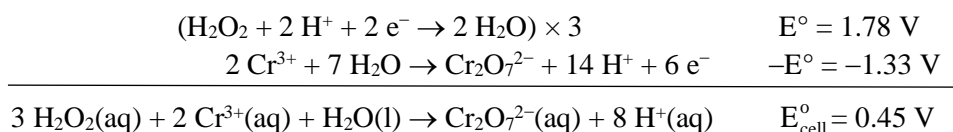
A concentration cell has the same anode and cathode contents; thus $E_{\text{cell}}^\circ = 0$ for a concentration cell. No matter which half-reaction you choose, the opposite half-reaction is occurring in the other cell. The driving force to produce a voltage is the $-\log Q$ term in the Nernst equation. Q is determined by the concentration of ions in the anode and cathode compartments. The larger the difference in concentrations, the larger is the $-\log Q$ term, and the larger is the voltage produced. Therefore, the driving force for concentration cells is the difference in ion concentrations between the cathode and anode compartments. When the ion concentrations are equal, $Q = 1$ and $\log Q = 0$, and no voltage is produced.

28. Aluminum has the ability to form a durable oxide coating over its surface. Once the HCl dissolves this oxide coating, Al is exposed to H^+ and is easily oxidized to Al^{3+} , i.e., the Al foil disappears after the oxide coating is dissolved.

38. A galvanic cell at standard conditions must have a positive overall standard cell potential ($E_{\text{cell}}^{\circ} > 0$). The only combination of the half-reactions that gives a positive cell potential is:



- a. The reducing agent causes reduction to occur since it always contains the species which is oxidized. Zn is oxidized in the galvanic cell, so Zn is the reducing agent. The oxidizing agent causes oxidation to occur since it always contains the species which is reduced. Cu^{2+} is reduced in the galvanic cell, so Cu^{2+} is the oxidizing agent. Electrons will flow from the zinc compartment (the anode) to the copper compartment (the cathode).
- b. From the work above, $E_{\text{cell}}^{\circ} = 1.10 \text{ V}$.
- c. The pure metal that is a product in the spontaneous reaction is copper. So the copper electrode will increase in mass as $\text{Cu}^{2+}(\text{aq})$ is reduced to $\text{Cu}(\text{s})$. The zinc electrode will decrease in mass for this galvanic cell as $\text{Zn}(\text{s})$ is oxidized to $\text{Zn}^{2+}(\text{aq})$.
48. a.



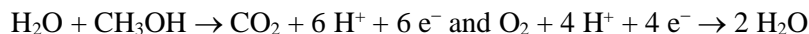
54. Because the cells are at standard conditions, $w_{\text{max}} = \Delta G = \Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$. See Exercise 48 for the balanced overall equations and for E_{cell}° .

48a. $w_{\text{max}} = -(6 \text{ mol e}^{-})(96,485 \text{ C/mol e}^{-})(0.45 \text{ J/C}) = -2.6 \times 10^5 \text{ J} = -260 \text{ kJ}$

48b. $w_{\text{max}} = -(6 \text{ mol e}^{-})(96,485 \text{ C/mol e}^{-})(1.66 \text{ J/C}) = -9.61 \times 10^5 \text{ J} = -961 \text{ kJ}$

58. $\text{CH}_3\text{OH}(\text{l}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \quad \Delta G^{\circ} = 2(-237) + (-394) - [-166] = -702 \text{ kJ}$

The balanced half-reactions are:

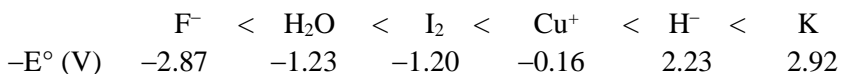


For $3/2 \text{ mol O}_2$, 6 mol of electrons will be transferred ($n = 6$).

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

60. 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 negative standard

reduction potentials (E°) or the most positive standard oxidation potentials $E^\circ_{\text{ox}} (= -E^\circ)$. The ordering from worst to best reducing agents is:



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

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

- a. Both compartments are at standard conditions ($[\text{Ni}^{2+}] = 1.0 \text{ M}$), and $E_{\text{cell}} = E^\circ_{\text{cell}} = 0 \text{ V}$. 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.

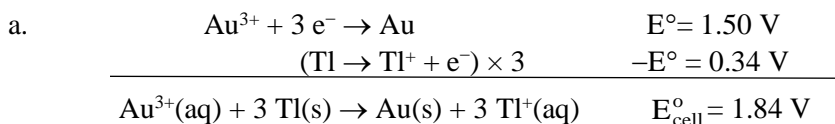
$$E_{\text{cell}} = \frac{-0.0591}{2} \log \frac{0.10}{1.0} = 0.030 \text{ V}$$

- 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.

80.



- b. $\Delta G^\circ = -nFE^\circ_{\text{cell}} = -(3 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(1.84 \text{ J/C}) = -5.33 \times 10^5 \text{ J} = -533 \text{ kJ}$

$$\log K = \frac{nE^\circ}{0.0591} = \frac{3(1.84)}{0.0591} = 93.401, \quad K = 10^{93.401} = 2.52 \times 10^{93}$$

- c. At 25°C , $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log Q$, where $Q = \frac{[\text{Tl}^+]^3}{[\text{Au}^{3+}]}$.

$$E_{\text{cell}} = 1.84 \text{ V} - \frac{0.0591}{3} \log \frac{[\text{Tl}^+]^3}{[\text{Au}^{3+}]} = 1.84 - \frac{0.0591}{3} \log \frac{(1.0 \times 10^{-4})^3}{1.0 \times 10^{-2}}$$

$$E_{\text{cell}} = 1.84 - (-0.20) = 2.04 \text{ V}$$

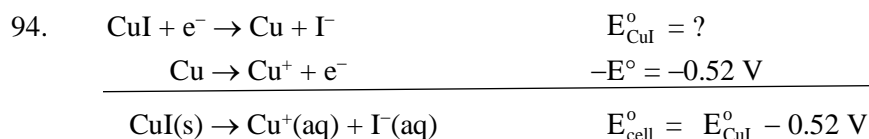


$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3}, \quad 1.82 \text{ V} = 1.43 \text{ V} - \frac{0.0591}{6} \log \frac{[\text{Al}^{3+}]^2}{(1.0)^3}$$

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

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

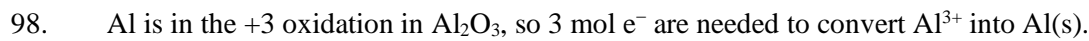
$$K_{\text{sp}} = (1.6 \times 10^{-20})(1.0 \times 10^{-4})^3 = 1.6 \times 10^{-32}$$



For this overall reaction, $K = K_{\text{sp}} = 1.1 \times 10^{-12}$:

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_{\text{sp}} = \frac{0.0591}{1} \log(1.1 \times 10^{-12}) = -0.71 \text{ V}$$

$$E_{\text{cell}}^{\circ} = -0.71 \text{ V} = E_{\text{CuI}}^{\circ} - 0.52, \quad E_{\text{CuI}}^{\circ} = -0.19 \text{ V}$$



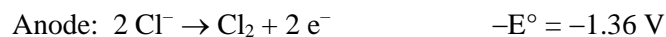
$$2.00 \text{ h} \times \frac{60 \text{ min}}{\text{h}} \times \frac{60 \text{ s}}{\text{min}} \times \frac{1.00 \times 10^6 \text{ C}}{\text{s}} \times \frac{1 \text{ mol e}^{-}}{96,485 \text{ C}} \times \frac{1 \text{ mol Al}}{3 \text{ mol e}^{-}} \times \frac{26.98 \text{ g Al}}{\text{mol Al}} = 6.71 \times 10^5 \text{ g}$$

112. Reduction occurs at the cathode, and oxidation occurs at the anode. First, determine all the species present; then look up pertinent reduction and/or oxidation potentials in Table 17-1 for all these species. The cathode reaction will be the reaction with the most positive reduction potential, and the anode reaction will be the reaction with the most positive oxidation potential.

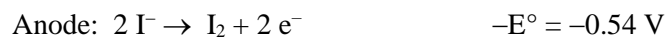
a. Species present: K^{+} and F^{-} ; K^{+} can be reduced to K, and F^{-} can be oxidized to F_2 (from Table 17.1). The reactions are:



b. Species present: Cu^{2+} and Cl^{-} ; Cu^{2+} can be reduced, and Cl^{-} can be oxidized. The reactions are:



c. Species present: Mg^{2+} and I^{-} ; Mg^{2+} can be reduced, and I^{-} can be oxidized. The reactions are:



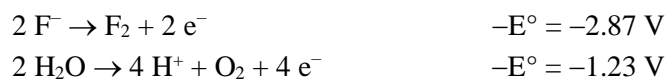
114. These are all in aqueous solutions, so we must also consider the reduction and oxidation of H₂O in addition to the potential redox reactions of the ions present. For the cathode reaction, the species with the most positive reduction potential will be reduced, and for the anode reaction, the species with the most positive oxidation potential will be oxidized.

a. Species present: K⁺, F⁻, and H₂O. Possible cathode reactions are:



Because it is easier to reduce H₂O than K⁺ (assuming standard conditions), H₂O will be reduced by the preceding cathode reaction.

Possible anode reactions are:



Because H₂O is easier to oxidize than F⁻ (assuming standard conditions), H₂O will be oxidized by the preceding anode reaction.

b. Species present: Cu²⁺, Cl⁻, and H₂O; Cu²⁺ and H₂O can be reduced. The reduction potentials are E[°] = 0.34 V for Cu²⁺ and E[°] = -0.83 V for H₂O (assuming standard conditions). Cu²⁺ will be reduced to Cu at the cathode (Cu²⁺ + 2 e⁻ → Cu).

Cl⁻ and H₂O can be oxidized. The oxidation potentials are -E[°] = -1.36 V for Cl⁻ and -E[°] = -1.23 V for H₂O (assuming standard conditions). From the potentials, we would predict H₂O to be oxidized at the anode (2 H₂O → 4 H⁺ + O₂ + 4 e⁻). *Note:* In real life, Cl⁻ is oxidized to Cl₂ when water is present due to a phenomenon called overvoltage (see Section 17.8 of the text). Because overvoltage is difficult to predict, we will generally ignore it.

c. Species present: Mg²⁺, I⁻, and H₂O: The only possible cathode reactions are:



Reduction of H₂O will occur at the cathode since E_{H₂O}[°] is more positive.

The only possible anode reactions are:



Oxidation of I⁻ will occur at the anode because -E_{H₂O}[°] is more positive.

120. $\text{Ag}^+(\text{aq}) + \text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2 \text{Ag}(\text{s})$ $E_{\text{cell}}^{\circ} = 0.80 - 0.34 \text{ V} = 0.46 \text{ V}$; a galvanic cell produces a voltage as the forward reaction occurs. Any stress that increases the tendency of the forward reaction to occur will increase the cell potential, whereas a stress that decreases the tendency of the forward reaction to occur will decrease the cell potential.

- Added Cu^{2+} (a product ion) will decrease the tendency of the forward reaction to occur, which will decrease the cell potential.
- Added NH_3 removes Cu^{2+} in the form of $\text{Cu}(\text{NH}_3)_4^{2+}$. Because a product ion is removed, this will increase the tendency of the forward reaction to occur, which will increase the cell potential.
- Added Cl^- removes Ag^+ in the form of $\text{AgCl}(\text{s})$. Because a reactant ion is removed, this will decrease the tendency of the forward reaction to occur, which will decrease the cell potential.

d. $Q_1 = \frac{[\text{Cu}^{2+}]_0}{[\text{Ag}^+]_0^2}$; as the volume of solution is doubled, each concentration is halved.

$$Q_2 = \frac{1/2 [\text{Cu}^{2+}]_0}{(1/2 [\text{Ag}^+]_0)^2} = \frac{2[\text{Cu}^{2+}]_0}{[\text{Ag}^+]_0^2} = 2Q_1$$

The reaction quotient is doubled because the concentrations are halved. Because reactions are spontaneous when $Q < K$, and because Q increases when the solution volume doubles, the reaction is closer to equilibrium, which will decrease the cell potential.

- Because $\text{Ag}(\text{s})$ is not a reactant in this spontaneous reaction, and because solids do not appear in the reaction quotient expressions, replacing the silver electrode with a platinum electrode will have no effect on the cell potential.

130. For $\text{C}_2\text{H}_5\text{OH}$, H has a +1 oxidation state, and O has a -2 oxidation state. This dictates a -2 oxidation state for C. For CO_2 , O has a -2 oxidation state, so carbon has a +4 oxidation state. Six moles of electrons are transferred per mole of carbon oxidized (C goes from -2 \rightarrow +4). Two moles of carbon are in the balanced reaction, so $n = 12$.

$$w_{\text{max}} = -1320 \text{ kJ} = \Delta G = -nFE, \quad -1320 \times 10^3 \text{ J} = -nFE = -(12 \text{ mol } e^-)(96,485 \text{ C/mol } e^-)E$$

$$E = 1.14 \text{ J/C} = 1.14 \text{ V}$$

142. Moles of $e^- = 50.0 \text{ min} \times \frac{60 \text{ s}}{\text{min}} \times \frac{2.50 \text{ C}}{\text{s}} \times \frac{1 \text{ mol } e^-}{96,485 \text{ C}} = 7.77 \times 10^{-2} \text{ mol } e^-$

$$\text{Moles of Ru} = 2.618 \text{ g Ru} \times \frac{1 \text{ mol Ru}}{101.1 \text{ g Ru}} = 2.590 \times 10^{-2} \text{ mol Ru}$$

$$\frac{\text{Moles of } e^-}{\text{Moles of Ru}} = \frac{7.77 \times 10^{-2} \text{ mol } e^-}{2.590 \times 10^{-2} \text{ mol Ru}} = 3.00; \text{ the charge on the ruthenium ions is } +3.$$

