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Chapter 18

Electrochemistry

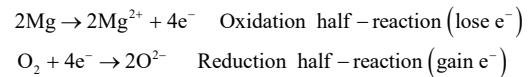
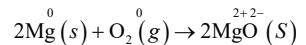
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Electrochemical Processes

Electrochemical processes are oxidation-reduction reactions in which:

- the energy released by a spontaneous reaction is converted to electricity or
- electrical energy is used to cause a nonspontaneous reaction to occur



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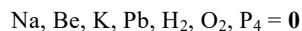
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Oxidation Number 1

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.

1. Free elements (uncombined state) have an oxidation number of zero



2. In monatomic ions, the oxidation number is equal to the charge on the ion.



3. The oxidation number of oxygen is **usually** -2 . In H_2O_2 and O_2^{2-} it is -1 .

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Oxidation Number 2

4. The oxidation number of hydrogen is **+1** *except* when it is bonded to metals in binary compounds. In these cases, its oxidation number is **-1**.
5. Group IA metals are **+1**, IIA metals are **+2** and fluorine is always **-1**.
6. The sum of the oxidation numbers of all the atoms in a molecule or ion is equal to the charge on the molecule or ion.

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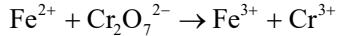
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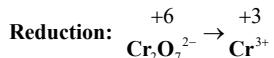
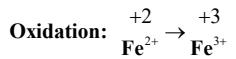
Balancing Redox Equations 1

The oxidation of Fe^{2+} to Fe^{3+} by $\text{Cr}_2\text{O}_7^{2-}$ in acid solution ?

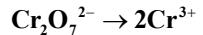
1. Write the unbalanced equation for the reaction in ionic form.



2. Separate the equation into two half-reactions.



3. Balance the atoms other than O and H in each half-reaction.

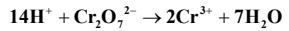
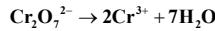


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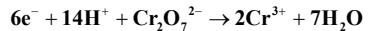
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Balancing Redox Equations 2

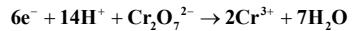
4. For reactions in acid, add H_2O to balance O atoms and H^+ to balance H atoms.



5. Add electrons to one side of each half-reaction to balance the charges on the half-reaction.



6. If necessary, equalize the number of electrons in the two half-reactions by multiplying the half-reactions by appropriate coefficients.



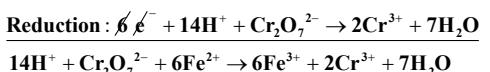
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Balancing Redox Equations 3

7. Add the two half-reactions together and balance the final equation by inspection. **The number of electrons on both sides must cancel.**



8. Verify that the number of atoms and the charges are balanced.

$$14 \times 1 - 2 + 6 \times 2 = 24 = 6 \times 3 + 2 \times 3$$

9. For reactions in basic solutions, add OH^- to **both sides** of the equation for every H^+ that appears in the final equation.

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Example 18.1 1

Write a balanced ionic equation to represent the oxidation of iodide ion (I^-) by permanganate ion (MnO_4^-) in basic solution to yield molecular iodine (I_2) and manganese(IV) oxide (MnO_2).

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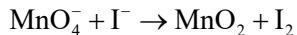
Example 18.1₂

Strategy

We follow the preceding procedure for balancing redox equations. Note that the reaction takes place in a basic medium.

Solution

Step 1: The unbalanced equation is

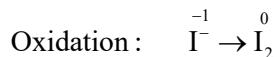


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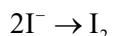
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Example 18.1₃

Step 2: The two half-reactions are



Step 3: We balance each half-reaction for number and type of atoms and charges. Oxidation half-reaction: We first balance the I atoms:



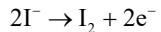
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Example 18.1₄

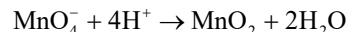
To balance charges, we add two electrons to the right-hand side of the equation:



Reduction half-reaction: To balance the O atoms, we add two H₂O molecules on the right:



To balance the H atoms, we add four H⁺ ions on the left:



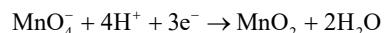
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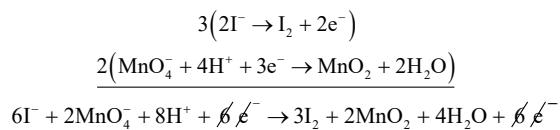
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Example 18.1₅

There are three net positive charges on the left, so we add three electrons to the same side to balance the charges:



Step 4: We now add the oxidation and reduction half reactions to give the overall reaction. In order to equalize the number of electrons, we need to multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2 as follows:



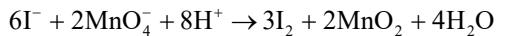
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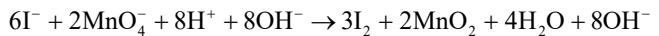
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Example 18.1₆

The electrons on both sides cancel, and we are left with the balanced net ionic equation:



This is the balanced equation in an acidic medium. However, because the reaction is carried out in a basic medium, for every H⁺ ion we need to add equal number of OH⁻ ions to both sides of the equation:



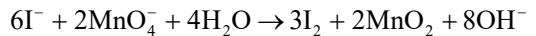
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Example 18.1₇

Finally, combining the H⁺ and OH⁻ ions to form water, we obtain

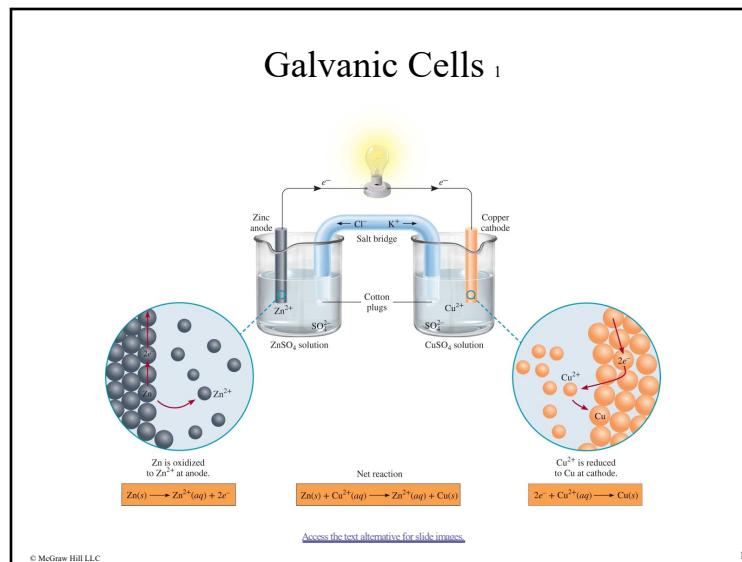


Step 5: A final check shows that the equation is balanced in terms of both atoms and charges.

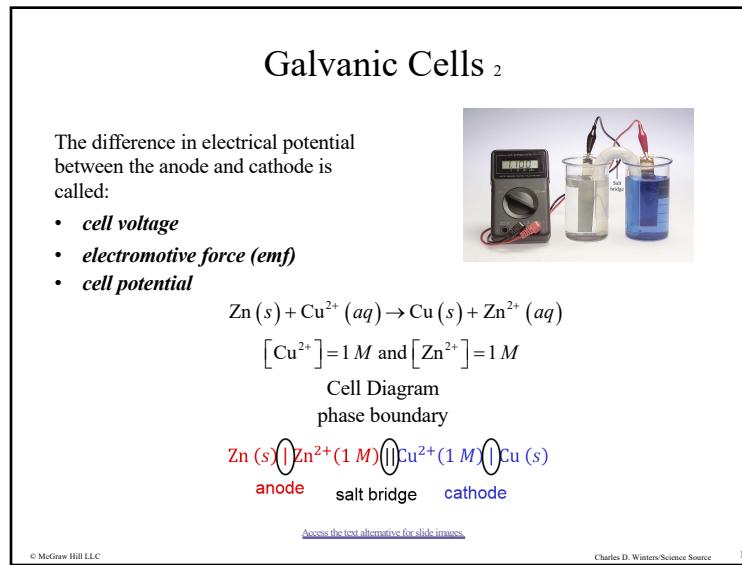
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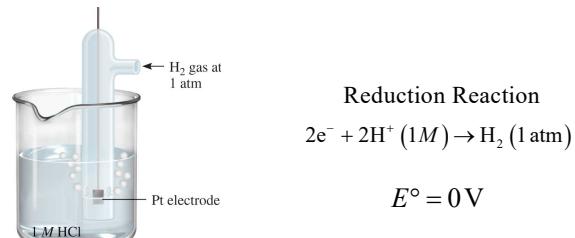
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Standard Reduction Potentials 1

Standard reduction potential (E°) is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 M and all gases are at 1 atm.

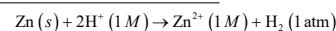
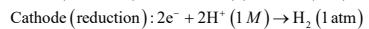
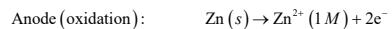
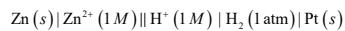
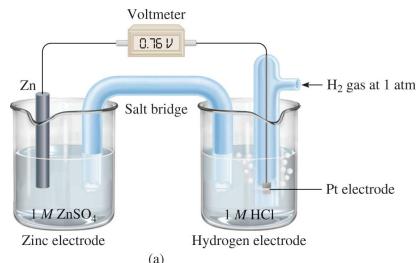


Standard hydrogen electrode (SHE)

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Standard Reduction Potentials 2



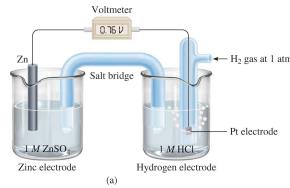
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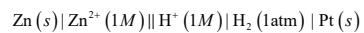
Standard Reduction Potentials 3

$$E_{\text{cell}}^{\circ} = 0.76 \text{ V}$$



Standard emf (E_{cell}°)

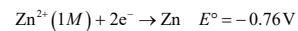
$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$



$$E_{\text{cell}}^{\circ} = E_{\text{H}^+/\text{H}_2}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

$$0.76 \text{ V} = 0 - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$$

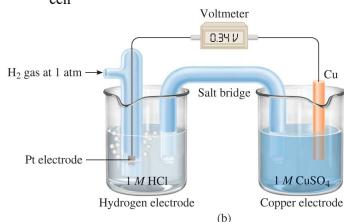


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Standard Reduction Potentials 4

$$E_{\text{cell}}^{\circ} = 0.34 \text{ V}$$

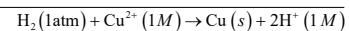
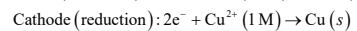
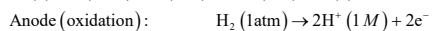
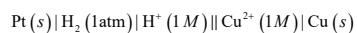


$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{H}^+/\text{H}_2}^{\circ}$$

$$0.34 \text{ V} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - 0$$

$$E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.34 \text{ V}$$



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Standard Reduction Potentials (E°)

Half-Reaction	Standard Reduction Potentials at 25°C*
$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}^{\text{red}}$	+0.44
$\text{Fe}^{2+} + 2e^- + 2\text{H}^+ \rightarrow \text{Fe} + 2\text{H}_2\text{O}$	+0.48
$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}^{\text{red}}$	+0.82
$\text{Cr}^{3+} + 3e^- + 3\text{H}^+ \rightarrow \text{Cr} + 3\text{H}_2\text{O}$	+0.77
$\text{PtO}_4 + 4\text{H}^+ + 4\text{e}^- + \text{Sb}^{3+} + 2\text{Cl}^- \rightarrow \text{Pt} + \text{Sb}(\text{OH})_3 + 2\text{H}_2\text{O}$	+1.70
$\text{MnO}_4 + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.51
$\text{MnO}_4 + 8\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_4^{\text{red}} + 4\text{H}_2\text{O}$	+1.51
$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	+1.36
$\text{Cl}_2 + 2e^- + 2\text{H}_2\text{O} \rightarrow \text{ClO}_3^- + 4\text{H}^+$	+1.23
$\text{MnO}_4 + 4\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.23
$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$	+1.07
$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	+0.76
$\text{Ag}^{+} + e^- \rightarrow \text{Ag}^{\text{red}}$	+0.80
$\text{Ag}^{+} + 2\text{H}^+ + 2e^- \rightarrow \text{Ag} + \text{H}_2$	+0.75
$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$	+0.88
$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	+0.53
$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}^{\text{red}}$	+0.24
$\text{MnO}_4 + 4\text{H}^+ + 3e^- \rightarrow \text{MnO}_4^{\text{red}} + 2\text{H}_2\text{O}$	+0.20
$\text{H}_2 + 2e^- \rightarrow 2\text{H}^-$	+0.13
$\text{D}_2 + 2e^- \rightarrow 2\text{D}^-$	-0.13
$\text{N}_2 + 2e^- \rightarrow \text{N}_2^{\text{red}}$	-0.14
$\text{N}_2^{\text{red}} + 2e^- \rightarrow \text{N}_2$	-0.25
$\text{PbO}_2 + 2e^- + 4\text{H}^+ + \text{Sb}^{3+} \rightarrow \text{Pb} + \text{Sb}(\text{OH})_3 + 2\text{H}_2\text{O}$	-0.31
$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}^{\text{red}}$	-0.40
$\text{O}_2 + 2e^- \rightarrow \text{O}_2^{\text{red}}$	-0.44
$\text{O}_2^{\text{red}} + 2e^- \rightarrow \text{O}_2$	-0.74
$\text{SO}_4^{2-} + 2e^- \rightarrow \text{S}^{2-}$	-0.96
$\text{H}_2\text{O}_2 + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-1.03
$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}^{\text{red}}$	-1.66
$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}^{\text{red}}$	-2.37
$\text{Cl}^- + 2e^- \rightarrow \text{Cl}^{\text{red}}$	-2.71
$\text{O}_2^{\text{red}} + 2e^- \rightarrow \text{O}_2$	-2.71
$\text{Br}^- + 2e^- \rightarrow \text{Br}^{\text{red}}$	-2.90
$\text{I}^- + 2e^- \rightarrow \text{I}^{\text{red}}$	-3.03
$\text{F}^- + 2e^- \rightarrow \text{F}^{\text{red}}$	-3.05

*The half-cell reduction potentials are for the standard species and the oxidation is 1 for the given reaction. Please note that oxidation strength increases as the value of E° decreases.

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- E° is for the reaction as written
- The more positive E° the greater the tendency for the substance to be reduced
- The half-cell reactions are reversible
- The sign of E° changes when the reaction is reversed
- Changing the stoichiometric coefficients of a half-cell reaction **does not** change the value of E°

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Example 18.2

Predict what will happen if molecular bromine (Br_2) is added to a solution containing NaCl and NaI at 25°C . Assume all species are in their standard states.

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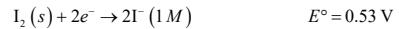
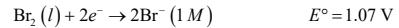
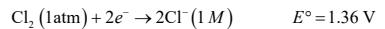
Example 18.2₂

Strategy

To predict what redox reaction(s) will take place, we need to compare the standard reduction potentials of Cl₂, Br₂, and I₂ and apply the diagonal rule.

Solution

From Table 18.1, we write the standard reduction potentials as follows:



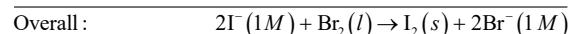
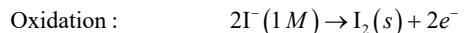
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Example 18.2₃

Applying the diagonal rule we see that Br₂ will oxidize I⁻ but will not oxidize Cl⁻. Therefore, the only redox reaction that will occur appreciably under standard-state conditions is



Check

We can confirm our conclusion by calculating E_{cell}° . Try it. Note that the Na⁺ ions are inert and do not enter into the redox reaction.

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Example 18.3₁

A galvanic cell consists of a Mg electrode in a 1.0 M $\text{Mg}(\text{NO}_3)_2$ solution and an Ag electrode in a 1.0 M AgNO_3 solution. Calculate the standard emf of this cell at 25°C.

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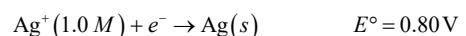
Example 18.3₂

Strategy

At first it may not be clear how to assign the electrodes in the galvanic cell. From Table 18.1 we write the standard reduction potentials of Ag and Mg and apply the diagonal rule to determine which is the anode and which is the cathode.

Solution

The standard reduction potentials are



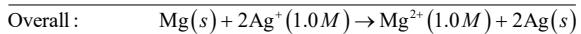
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Example 18.3₃

Applying the diagonal rule, we see that Ag⁺ will oxidize Mg:



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Example 18.3₄

Note that in order to balance the overall equation we multiplied the reduction of Ag⁺ by 2. We can do so because, as an intensive property, E° is not affected by this procedure. We find the emf of the cell by using Equation (18.1) and Table 18.1:

$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ &= E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Mg}^{2+}/\text{Mg}}^\circ \\ &= 0.80\text{V} - (-2.37\text{V}) \\ &= 3.17\text{V} \end{aligned}$$

Check

The positive value of E° shows that the forward reaction is favored.

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Spontaneity of Redox Reactions 1

$$\Delta G = -nFE_{\text{cell}} \quad n = \text{number of moles of electrons in reaction}$$

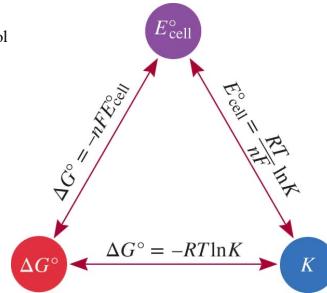
$$\Delta G^\circ = -nFE_{\text{cell}}^\circ \quad F = 96,500 \frac{\text{J}}{\text{V} \cdot \text{mol}} = 96,500 \text{C/mol}$$

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

$$E_{\text{cell}}^\circ = \frac{RT}{nF} \ln K = \frac{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{n(96,500 \text{ J/V} \cdot \text{mol})} \ln K$$

$$E_{\text{cell}}^\circ = \frac{0.0257 \text{ V}}{n} \ln K$$

$$E_{\text{cell}}^\circ = \frac{0.0592 \text{ V}}{n} \log K$$



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Spontaneity of Redox Reactions 2

Table 18.2 Relationships Among ΔG° , K , and E_{cell}°

ΔG°	K	E_{cell}°	Reaction Under Standard – State Conditions
Negative	> 1	Positive	Favors formation of products.
0	$= 1$	0	Reactants and products are equally favored.
Positive	< 1	Negative	Favors formation of reactants.

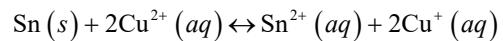
$$\Delta G^\circ = -RT \ln K = -nFE_{\text{cell}}^\circ$$

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Example 18.4₁

Calculate the equilibrium constant for the following reaction at 25°C:



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Example 18.4₂

Strategy

The relationship between the equilibrium constant K and the standard emf is given by Equation (18.5):

$$E_{\text{cell}}^\circ = (0.0257 \text{ V}/n) \ln K$$

Thus, if we can determine the standard emf, we can calculate the equilibrium constant. We can determine the E_{cell}° of a hypothetical galvanic cell made up of two couples (Sn^{2+}/Sn and Cu^{2+}/Cu) from the standard reduction potentials in Table 18.1.

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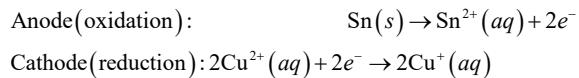
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Example 18.4 ₃

Solution

The half-cell reactions are



$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ &= E_{\text{Cu}^{2+}/\text{Cu}^+}^\circ - E_{\text{Sn}^{2+}/\text{Sn}}^\circ \\ &= 0.15\text{ V} - (-0.14\text{ V}) \\ &= 0.29\text{ V} \end{aligned}$$

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Example 18.4 ₄

Equation (18.5) can be written

$$\ln K = \frac{nE^\circ}{0.0257\text{ V}}$$

In the overall reaction we find $n = 2$. Therefore,

$$\ln K = \frac{(2)(0.29\text{ V})}{0.0257\text{ V}} = 22.6$$

$$K = e^{22.6} = 7 \times 10^9$$

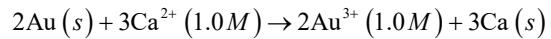
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Example 18.5₁

Calculate the standard free-energy change for the following reaction at 25°C:



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Example 18.5₂

Strategy

The relationship between the standard free energy change and the standard emf of the cell is given by Equation (18.3): $\Delta G^\circ = -nFE_\text{cell}^\circ$.

Thus, if we can determine E_cell° we can calculate ΔG° . We can determine the E_cell° of a hypothetical galvanic cell made up of two couples (Au^{3+}/Au and Ca^{2+}/Ca) from the standard reduction potentials in Table 18.1.

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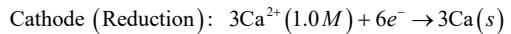
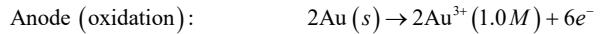
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Example 18.5₃

Solution

The half-cell reactions are



$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \\ &= E_{\text{Ca}^{2+}/\text{Ca}}^{\circ} - E_{\text{Au}^{3+}/\text{Au}}^{\circ} \\ &= -2.87\text{ V} - 1.50\text{ V} \\ &= -4.37\text{ V} \end{aligned}$$

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Example 18.5₄

Now we use Equation (18.3):

$$\Delta G^{\circ} = -nFE^{\circ}$$

The overall reaction shows that $n = 6$, so

$$\begin{aligned} G^{\circ} &= -(6)(96,500\text{ J/V}\cdot\text{mol})(-4.37\text{ V}) \\ &= 2.53 \times 10^6 \text{ J/mol} \\ &= 2.53 \times 10^3 \text{ kJ/mol} \end{aligned}$$

Check

The large positive value of ΔG° tells us that the reaction favors the reactants at equilibrium. The result is consistent with the fact that E° for the galvanic cell is negative.

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The Effect of Concentration on Cell Emf

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \Delta G = -nFE \quad \Delta G^\circ = -nFE^\circ$$

$$-nFE = -nFE^\circ + RT \ln Q$$

Nernst equation

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

At 298 K

$$E = E^\circ - \frac{0.0257 \text{ V}}{n} \ln Q \quad E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q$$

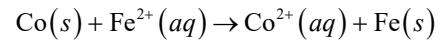
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Example 18.6

Predict whether the following reaction would proceed spontaneously as written at 298 K:



given that $[\text{Co}^{2+}] = 0.15 M$ and $[\text{Fe}^{2+}] = 0.68 M$.

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Example 18.6₂

Strategy

Because the reaction is not run under standard-state conditions (concentrations are not 1 M), we need Nernst's equation [Equation (18.8)] to calculate the emf (E) of a hypothetical galvanic cell and determine the spontaneity of the reaction. The standard emf (E°) can be calculated using the standard reduction potentials in Table 18.1. Remember that solids do not appear in the reaction quotient (Q) term in the Nernst equation. Note that 2 moles of electrons are transferred per mole of reaction, that is, $n = 2$.

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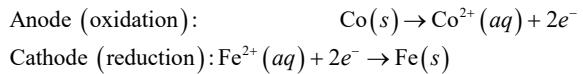
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Example 18.6₃

Solution

The half-cell reactions are



$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ &= E_{\text{Fe}^{2+}/\text{Fe}}^\circ - E_{\text{Co}^{2+}/\text{Co}}^\circ \\ &= -0.44 \text{ V} - (-0.28 \text{ V}) \\ &= -0.16 \text{ V} \end{aligned}$$

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Example 18.6₄

From Equation (18.8) we write

$$\begin{aligned} E &= E^\circ - \frac{0.0257\text{V}}{n} \ln Q \\ &= E^\circ - \frac{0.0257\text{V}}{n} \ln \left[\frac{[\text{Co}^{2+}]}{[\text{Fe}^{2+}]} \right] \\ &= -0.16\text{V} - \frac{0.0257\text{V}}{2} \ln \frac{0.15}{0.68} \\ &= -0.16\text{V} + 0.019\text{V} \\ &= -0.14\text{V} \end{aligned}$$

Because E is negative, the reaction is not spontaneous in the direction written.

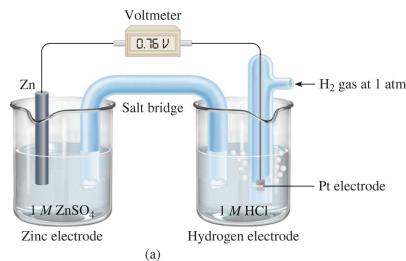
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Example 18.7₁

Consider the galvanic cell shown in Figure 18.4(a). In a certain experiment, the emf (E) of the cell is found to be 0.54 V at 25°C. Suppose that $[\text{Zn}^{2+}] = 1.0\text{ M}$ and $P_{\text{H}_2} = 1.0\text{ atm}$. Calculate the molar concentration of H^+ .



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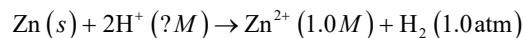
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Example 18.7₂

Strategy

The equation that relates standard emf and nonstandard emf is the Nernst equation. The overall cell reaction is



Given the emf of the cell (E), we apply the Nernst equation to solve for $[\text{H}^+]$. Note that 2 moles of electrons are transferred per mole of reaction; that is, $n = 2$.

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Example 18.7₃

Solution

As we saw earlier, the standard emf (E°) for the cell is 0.76 V. From Equation (18.8) we write

$$\begin{aligned} E &= E^\circ - \frac{0.0257\text{V}}{n} \ln Q \\ &= E^\circ - \frac{0.0257\text{V}}{n} \ln \frac{[\text{Zn}^{2+}]P_{\text{H}_2}}{[\text{H}^+]^2} \\ 0.54\text{V} &= 0.76\text{V} - \frac{0.0257\text{V}}{2} \ln \frac{(1.0)(1.0)}{[\text{H}^+]^2} \\ -0.22\text{V} &= -\frac{0.0257\text{V}}{2} \ln \frac{1}{[\text{H}^+]^2} \\ 17.1 &= \ln \frac{1}{[\text{H}^+]^2} \\ e^{17.1} &= \frac{1}{[\text{H}^+]^2} \\ [\text{H}^+] &= \sqrt{\frac{1}{3 \times 10^7}} = 2 \times 10^{-4}\text{M} \end{aligned}$$

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Example 18.7 ₄

Check

The fact that the nonstandard-state emf (E) is given in the problem means that not all the reacting species are in their standard-state concentrations. Thus, because both Zn^{2+} ions and H_2 gas are in their standard states, $[\text{H}^+]$ is not 1 M .

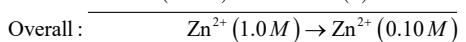
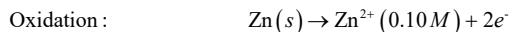
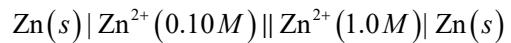
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Concentration Cells

Galvanic cell from two half-cells composed of the *same* material but differing in ion concentrations.



$$E = E^\circ - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{Zn}^{2+}]_{\text{dil}}}{[\text{Zn}^{2+}]_{\text{conc}}}$$

$$E = 0 - \frac{0.0257 \text{ V}}{2} \ln \frac{0.10}{1.0} = 0.0296 \text{ V}$$

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Batteries 1

Dry cell

Leclanché cell

Anode: $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-$
Cathode: $2\text{NH}_4^+(aq) + 2\text{MnO}_2(s) + 2e^- \rightarrow \text{Mn}_2\text{O}_3(s) + 2\text{NH}_3(aq) + \text{H}_2\text{O}(l)$
 $\text{Zn}(s) + 2\text{NH}_4^+(aq) + 2\text{MnO}_2(s) \rightarrow \text{Zn}^{2+}(aq) + 2\text{NH}_3(aq) + \text{H}_2\text{O}(l) + \text{Mn}_2\text{O}_3(s)$

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Batteries 2

Mercury Battery

Anode: $\text{Zn}(\text{Hg}) + 2\text{OH}^-(aq) \rightarrow \text{ZnO}(s) + \text{H}_2\text{O}(l) + 2e^-$
Cathode: $\text{HgO}(s) + \text{H}_2\text{O}(l) + 2e^- \rightarrow \text{Hg}(l) + 2\text{OH}^-(aq)$
 $\text{Zn}(\text{Hg}) + \text{HgO}(s) \rightarrow \text{ZnO}(s) + \text{Hg}(l)$

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Batteries 3

Lead storage battery

Anode : $\text{Pb}(s) + \text{SO}_4^{2-}(aq) \rightarrow \text{PbSO}_4(s) + 2e^-$
Cathode : $\text{PbO}_2(s) + 4\text{H}^+(aq) + \text{SO}_4^{2-}(aq) + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$

$$\text{Pb}(s) + \text{PbO}_2(s) + 4\text{H}^+(aq) + 2\text{SO}_4^{2-}(aq) \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$$

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Batteries 4

$\text{Li} \rightarrow \text{Li}^+ + e^-$

$\text{Li}^+ + \text{CoO}_2 + e^- \rightarrow \text{LiCoO}_2$

Solid State Lithium Battery

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Batteries 5

A fuel cell is an electrochemical cell that requires a continuous supply of reactants to keep functioning.

Anode : $2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq}) \rightarrow 4\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$

Cathode : $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$

$$\underline{\hspace{10em}}$$

$$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$$

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Chemistry In Action: Bacteria Power

$$\text{CH}_3\text{COO}^- + 2\text{O}_2 + \text{H}^+ \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$$

$$\text{CH}_3\text{COO}^- + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 7\text{H}^+ + 8\text{e}^-$$

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$$

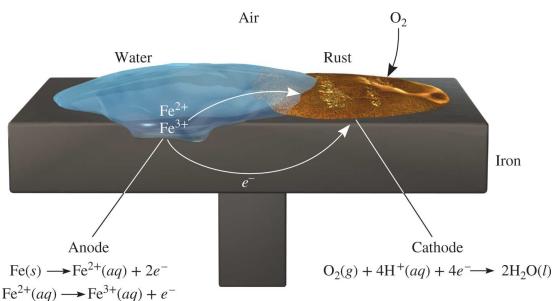
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Courtesy of Derek R. Lovley/Environmental Biotechnology, Univ. of Massachusetts 54

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Corrosion

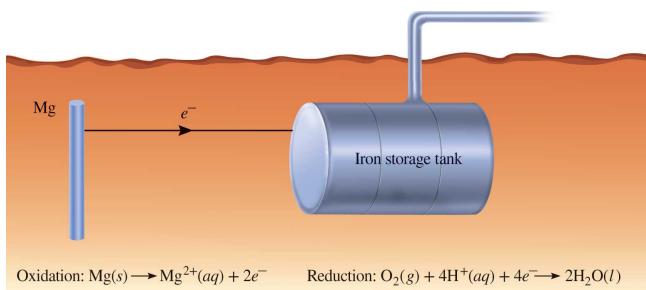
Corrosion is the term usually applied to the deterioration of metals by an electrochemical process.



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Cathodic Protection of an Iron Storage Tank



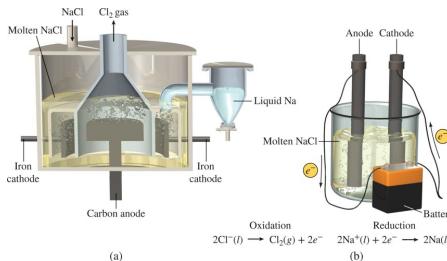
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Electrolysis

Electrolysis is the process in which electrical energy is used to cause a **nonspontaneous** chemical reaction to occur.

Electrolysis of molten NaCl

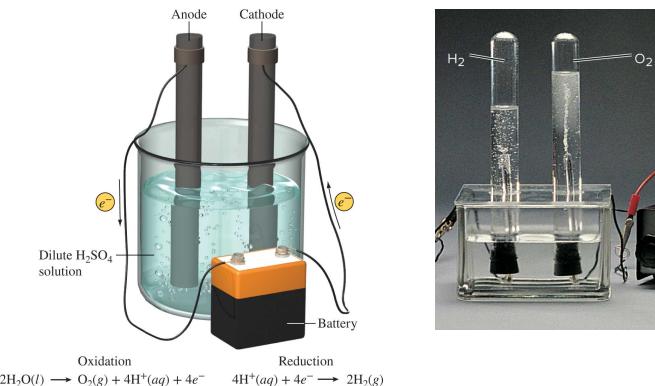


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Electrolysis of Water



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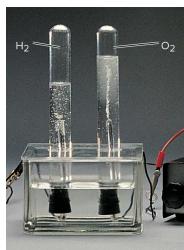
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Example 18.8₁

An aqueous Na_2SO_4 solution is electrolyzed, using the apparatus shown in Figure 18.18. If the products formed at the anode and cathode are oxygen gas and hydrogen gas, respectively, describe the electrolysis in terms of the reactions at the electrodes.



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Example 18.8₂

Strategy

Before we look at the electrode reactions, we should consider the following facts: (1) Because NaSO_4 does not hydrolyze, the pH of the solution is close to 7. (2) The Na^+ ions are not reduced at the cathode and the SO_4^{2-} ions are not oxidized at the anode. These conclusions are drawn from the electrolysis of water in the presence of sulfuric acid and in aqueous sodium chloride solution, as discussed earlier. Therefore, both the oxidation and reduction reactions involve only water molecules.

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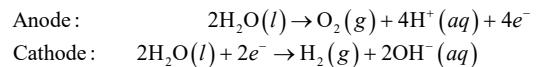
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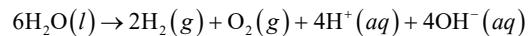
Example 18.8₃

Solution

The electrode reactions are



The overall reaction, obtained by doubling the cathode reaction coefficients and adding the result to the anode reaction, is



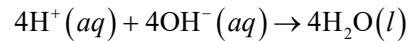
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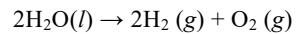
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Example 18.8₄

If the H⁺ and OH⁻ ions are allowed to mix, then



and the overall reaction becomes

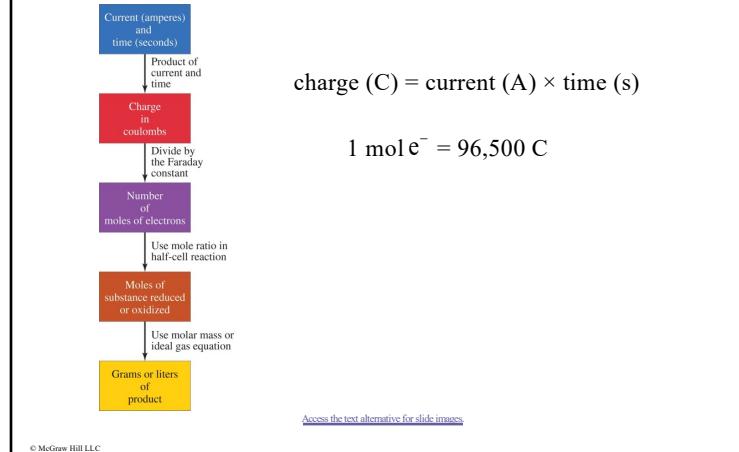


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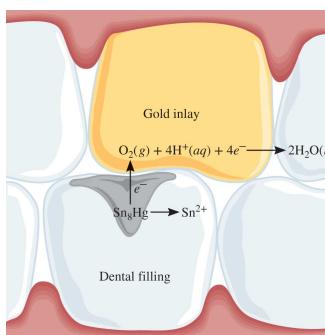
Electrolysis and Mass Changes



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Chemistry In Action: Dental Filling Discomfort

$\text{Hg}_2^{2+}/\text{Ag}_2\text{Hg}_3$	0.85 V
$\text{Sn}^{2+}/\text{Ag}_3\text{Sn}$	-0.05 V
$\text{Sn}^{2+}/\text{Sn}_8\text{Hg}$	-0.13 V

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Example 18.9₁

A current of 1.26 A is passed through an electrolytic cell containing a dilute sulfuric acid solution for 7.44 h. Write the half-cell reactions and calculate the volume of gases generated at STP.

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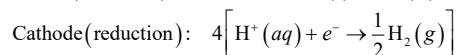
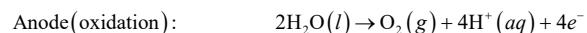
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Example 18.9₂

Strategy

Earlier we saw that the half-cell reactions for the process are



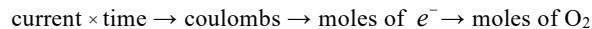
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Example 18.9₃

According to Figure 18.20, we carry out the following conversion steps to calculate the quantity of O₂ in moles:



Then, using the ideal gas equation we can calculate the volume of O₂ in liters at STP. A similar procedure can be used for H₂.

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Example 18.9₄

Solution

First we calculate the number of coulombs of electricity that pass through the cell:

$$?C = 1.26 \text{ A} \times 7.44 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} = 3.37 \times 10^4 \text{ C}$$

Next, we convert number of coulombs to number of moles of electrons

$$3.37 \times 10^4 \text{ C} \times \frac{1 \text{ mol } e^-}{96,500 \text{ C}} = 0.349 \text{ mol } e^-$$

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Example 18.9₅

From the oxidation half-reaction we see that 1 mol O₂ = 4 mol e⁻. Therefore, the number of moles of O₂ generated is

$$0.349 \text{ } \mu\text{mol} e^- \times \frac{1 \text{ mol O}_2}{4 \text{ } \mu\text{mol} e^-} = 0.0873 \text{ mol O}_2$$

The volume of 0.0873 mol O₂ at STP is given by

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{(0.0873 \text{ mol})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(273 \text{ K})}{1 \text{ atm}} = 1.96 \text{ L} \end{aligned}$$

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Example 18.9₆

The procedure for hydrogen is similar. To simplify, we combine the first two steps to calculate the number of moles of H₂ generated:

$$3.37 \times 10^4 \cancel{\text{C}} \times \frac{1 \text{ mol } e^-}{96,500 \cancel{\text{C}}} \times \frac{1 \text{ mol H}_2}{2 \cancel{\text{mol } e^-}} = 0.175 \text{ mol H}_2$$

The volume of 0.175 mol H₂ at STP is given by

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{(0.175 \text{ mol})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(273 \text{ K})}{1 \text{ atm}} = 3.92 \text{ L} \end{aligned}$$

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Example 18.9

Check

Note that the volume of H₂ is twice that of O₂ (see Figure 18.18), which is what we would expect based on Avogadro's law (at the same temperature and pressure, volume is directly proportional to the number of moles of gases).

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