

## CHAPTER 10 ELECTROLYTIC CELLS

### Reflect on Your Learning

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1. *[Likely initial answer]* If the cell potential is a negative value, this might mean that the reaction goes in reverse or maybe does not happen at all.  
*[More complete answer]* A negative cell potential indicates that the predicted cell reaction is nonspontaneous and requires an external power supply to force the reaction to occur.
2. *[Likely initial answer]* Elements are produced by decomposing naturally occurring substances using heat or electricity or using a single displacement reaction.  
*[More complete answer]* Most elements are produced or refined in industrial processes using aqueous, nonaqueous, or molten salt electrolysis.
3. *[Likely initial answer]* There is probably some relationship but it is not clear what that might be.  
*[More complete answer]* The coefficients in the half-reaction equation provide the mole ratio of electrons to the product at the electrode.
4. *[Likely initial answer]* All of these are interrelated with science and technology producing useful products and processes for society.  
*[More complete answer]* The technology of electrolytic cells preceded any scientific understanding of the processes. Eventually, atomic and redox theories developed to explain known electrolytic cells. Further scientific investigation of electrolytic cells led to new technologies that were very useful to society, which in turn encouraged more research. Today, the continuing cycle of scientific understanding and technological development continues.

### Try This Activity: A Nonspontaneous Reaction

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- (a) There is no initial evidence of reaction.
- (b) Near the positive terminal of the battery, the colourless solution changes to a yellow-brown solution (with some black precipitate). Near the negative terminal of the battery, bubbles of gas form.
- (c) The evidence for chemical reaction is both the colour change and gas formation. (A precipitate may also be observed.)
- (d) The battery supplies energy to cause the reaction.
- (e) The colour change means at least one new substance (and probably two substances) is/are formed at the negative battery terminal.
- (f) The two substances might be hydrogen or oxygen (the gas) and iodine (the brown colour). Diagnostic tests for hydrogen and oxygen can be done with a lit or glowing splint. A diagnostic test for iodine can be done by dissolving it in a nonpolar liquid like a hydrocarbon. (Appendix A6)
- (g) To improve this design, the gas produced should be collected by downward displacement of water.
- (h) Forcing a nonspontaneous reaction to occur is a way of producing new substances.

## 10.1 ELECTROLYSIS

### PRACTICE

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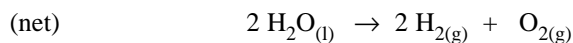
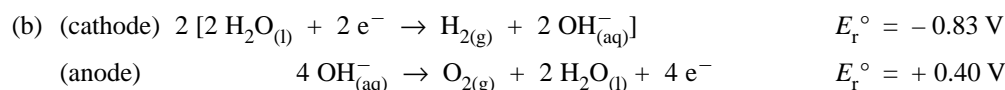
#### Understanding Concepts

1. (a) (cathode)  $\text{Ni}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightarrow \text{Ni}_{(\text{s})}$   $E_r^\circ = -0.26 \text{ V}$   
(anode)  $2 \text{I}_{(\text{aq})}^- \rightarrow \text{I}_{2(\text{s})} + 2 \text{e}^-$   $E_r^\circ = +0.54 \text{ V}$   

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(net)  $\text{Ni}_{(\text{aq})}^{2+} + 2 \text{I}_{(\text{aq})}^- \rightarrow \text{Ni}_{(\text{s})} + \text{I}_{2(\text{s})}$   
 $\Delta E^\circ = E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode})$   
 $= -0.26 \text{ V} - (+0.54 \text{ V})$   
 $\Delta E^\circ = -0.80 \text{ V}$

The minimum applied potential difference required to make this cell operate at standard conditions is 0.80 V.

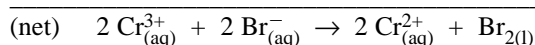
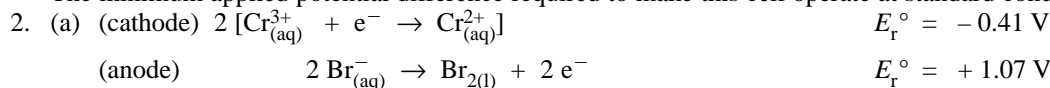


$$\Delta E^{\circ} = E_{\text{r}}^{\circ} (\text{cathode}) - E_{\text{r}}^{\circ} (\text{anode})$$

$$= -0.83 \text{ V} - (+0.40 \text{ V})$$

$$\Delta E^{\circ} = -1.23 \text{ V}$$

The minimum applied potential difference required to make this cell operate at standard conditions is 1.23 V.

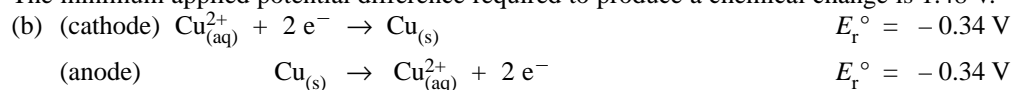


$$\Delta E^{\circ} = E_{\text{r}}^{\circ} (\text{cathode}) - E_{\text{r}}^{\circ} (\text{anode})$$

$$= -0.41 \text{ V} - (+1.07 \text{ V})$$

$$\Delta E^{\circ} = -1.48 \text{ V}$$

The minimum applied potential difference required to produce a chemical change is 1.48 V.

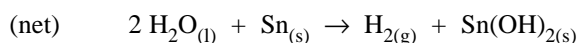
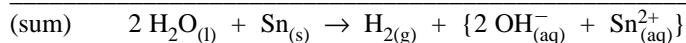
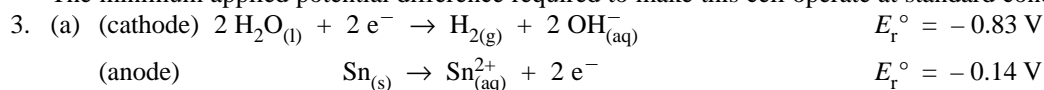


$$\Delta E^{\circ} = E_{\text{r}}^{\circ} (\text{cathode}) - E_{\text{r}}^{\circ} (\text{anode})$$

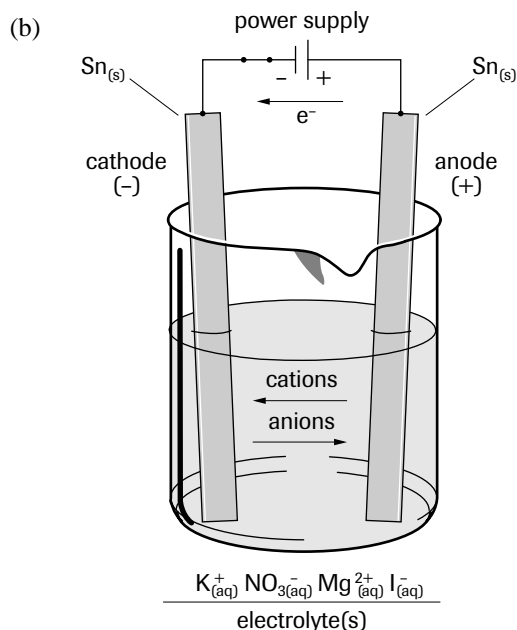
$$= -0.34 \text{ V} - (-0.34 \text{ V})$$

$$\Delta E^{\circ} = 0.00 \text{ V}$$

The minimum applied potential difference required to make this cell operate at standard conditions is 0.00 V.



**Note:** Simultaneous production of  $\text{Sn}^{2+}$  and  $\text{OH}^-$  aqueous ions forms (low-soluble) solid tin(II) hydroxide,  $\text{Sn}(\text{OH})_2$ .



- (c) A 1.5-V cell should be more than enough potential difference to power this reaction, since calculation indicates the minimum required is only 0.69 V at standard conditions.

$$\begin{aligned}\Delta E^\circ &= E^\circ_{r(\text{cathode})} - E^\circ_{r(\text{anode})} \\ &= -0.83 \text{ V} - (-0.14 \text{ V})\end{aligned}$$

$$\Delta E^\circ = -0.69 \text{ V}$$

The minimum applied potential difference required to produce a chemical change is 0.69 V.

4. The cell would not have a spontaneous reaction. The strongest oxidizing agent present in this cell is water; and it has an  $E^\circ_r$  well below that of the strongest reducing agent present, sulfate and lead. The calculated  $\Delta E^\circ$  value at standard conditions is  $-0.47 \text{ V}$ .

### Making Connections

5. A specific consumer product that is used sometimes as an electric cell and sometimes as an electrolytic cell is a rechargeable battery of any type.

## SECTION 10.1 QUESTIONS

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### Understanding Concepts

- At the cathode of an electrolytic cell, the oxidizing agent reacts by gaining electrons. At the anode of an electrolytic cell, the reducing agent reacts by losing electrons.
- The cathode and anode of an electrolytic cell are labelled with signs opposite to those in a galvanic cell. (The common convention (used in this text) labels the anode of a galvanic cell “negative” because it is a source of electrons and the cell is an electrical power supply. The anode of an electrolytic cell is labelled “negative” because it is not a power source, rather it is an electrical load. For electrical loads, the electrode sign is assigned using the sign of the electrode of a power supply to which it is attached.)
- In an electrolytic cell, electrons move through the external circuit from the anode to the cathode. Within the cell, cations move toward the cathode and anions move toward the anode.
- A power supply is required for an electrolytic cell because the reaction is nonspontaneous, which means that the oxidizing agent cannot attract or remove electrons from the reducing agent. A potential difference must be supplied to move electrons from one to the other.
- (a)  $\Delta E^\circ = E^\circ_{r(\text{Cr}^{2+}/\text{Cr})} - E^\circ_{r(\text{Cr}^{3+}/\text{Cr}^{2+})}$   
 $= -0.91 \text{ V} - (-0.41 \text{ V})$   
 $\Delta E^\circ = -0.50 \text{ V}$

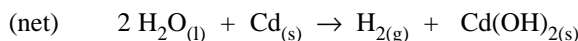
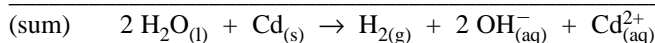
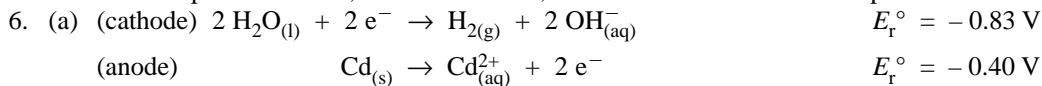
The cell potential value,  $\Delta E^\circ = -0.50 \text{ V}$ , indicates this reaction is nonspontaneous.

$$\begin{aligned}
 \text{(b)} \quad \Delta E^\circ &= E_r^\circ (\text{Fe}^{3+}/\text{Fe}^{2+}) - E_r^\circ (\text{Ag}^+/\text{Ag}) \\
 &= +0.77 \text{ V} - (+0.80 \text{ V}) \\
 \Delta E^\circ &= -0.03 \text{ V}
 \end{aligned}$$

The cell potential value,  $\Delta E^\circ = -0.03 \text{ V}$ , indicates this reaction is nonspontaneous.

$$\begin{aligned}
 \text{(c)} \quad \Delta E^\circ &= E_r^\circ (\text{Pb}^{2+}/\text{Pb}) - E_r^\circ (\text{Cu}^{2+}/\text{Cu}) \\
 &= -0.13 \text{ V} - (+0.34 \text{ V}) \\
 \Delta E^\circ &= -0.47 \text{ V}
 \end{aligned}$$

The cell potential value,  $\Delta E^\circ = -0.47 \text{ V}$ , indicates this reaction is nonspontaneous.

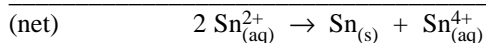
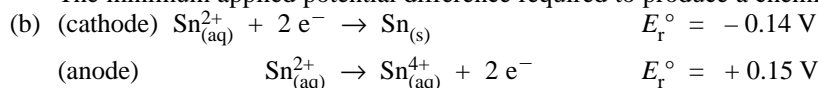


**Note:**  $\text{Cd}^{2+}$  and  $\text{OH}^-$  aqueous ions form (low-soluble) solid cadmium(II) hydroxide,  $\text{Cd}(\text{OH})_2$ .

$$\begin{aligned}
 \Delta E^\circ &= E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode}) \\
 &= -0.83 \text{ V} - (-0.40 \text{ V})
 \end{aligned}$$

$$\Delta E^\circ = -0.43 \text{ V}$$

The minimum applied potential difference required to produce a chemical change is 0.43 V.

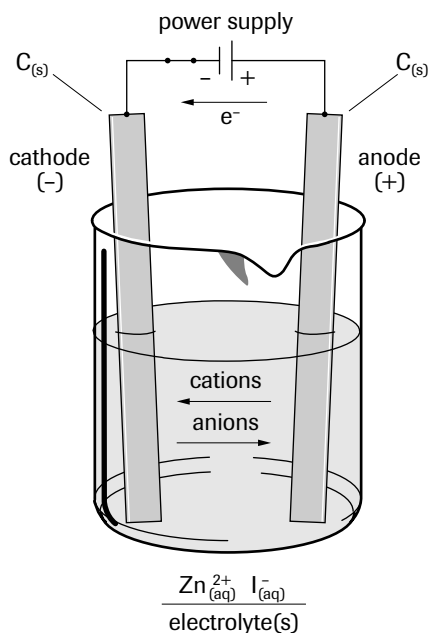


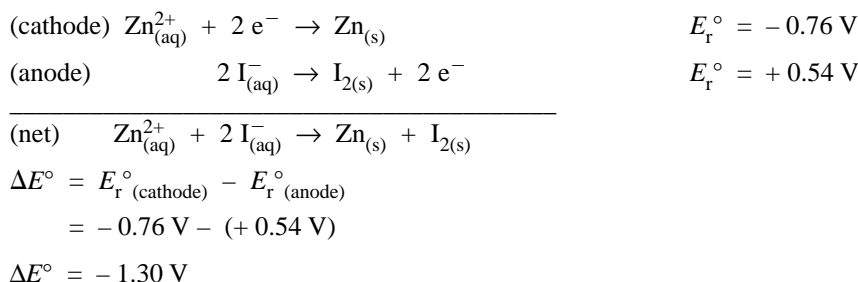
$$\begin{aligned}
 \Delta E^\circ &= E_r^\circ (\text{cathode}) - E_r^\circ (\text{anode}) \\
 &= -0.14 \text{ V} - (+0.15 \text{ V})
 \end{aligned}$$

$$\Delta E^\circ = -0.29 \text{ V}$$

The minimum applied potential difference required to produce a chemical change is 0.29 V.

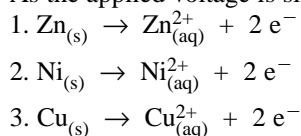
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The cell potential is  $-1.30 \text{ V}$ .

8. (a) As the applied voltage is slowly increased, half-reactions occur at the anode in the following order:



(Whether copper oxidizes to copper(I) ion or to copper(II) ion can be controlled by the potential applied.)

- (b) At the platinum cathode, the following half-reaction occurs:  $2 \text{H}_2\text{O}_{(\text{l})} + 2 \text{e}^{-} \rightarrow \text{H}_{2(\text{g})} + 2 \text{OH}_{(\text{aq})}^{-}$ .
9. No spontaneous reaction should occur in the cell, because theoretically, the  $E_{\text{r}}^{\circ}$  values at both electrodes are the same, giving a cell potential of zero. Thus, a potential difference *greater* than zero must be applied to cause any reaction.

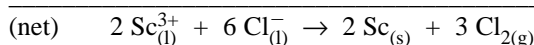
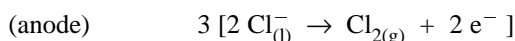
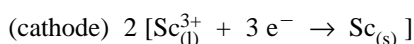
## 10.2 SCIENCE AND TECHNOLOGY OF ELECTROLYSIS

### PRACTICE

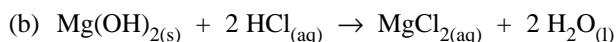
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#### Understanding Concepts

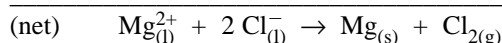
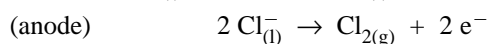
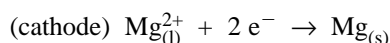
1. (a) Producing active metals by electrolysis of their aqueous compounds is a problem because water will react at the cathode before the metal ions will. As well, many ionic compounds of these metals have low solubility.  
 (b) These problems can be overcome by performing the electrolysis in the absence of water (e.g., using molten ionic compounds) or sometimes by using high potential to “overpower” the slower reaction of water.
2. The ions present in the electrolysis cell are  $\text{Sc}_{(\text{l})}^{3+}$  and  $\text{Cl}_{(\text{l})}^{-}$ .



3. (a)  $\text{Ca}(\text{OH})_{2(\text{s})} + \text{MgCl}_{2(\text{aq})} \rightarrow \text{Mg}(\text{OH})_{2(\text{s})} + \text{CaCl}_{2(\text{aq})}$



- (c) The ions present in the electrolysis cell are  $\text{Mg}_{(\text{l})}^{2+}$  and  $\text{Cl}_{(\text{l})}^{-}$ .



- (d) Dolomite has the advantage of being a more concentrated source of magnesium than seawater and may require fewer initial reactions before the electrolysis. A possible disadvantage is that it is more difficult and requires more energy to mine the solid than to pump the seawater. Another disadvantage is that the seas contain an almost limitless supply of magnesium salts, whereas dolomite is likely present in more limited and localized quantities.