If an element doesn’t occur naturally, where does a sample of it come from?

**The Model: A Battery Used as an “Electron Pump”**

If a battery is used to “pump” electrons from one electrode to a second electrode, it is possible to force a non-spontaneous reaction to occur. Let us at the moment consider an electrolytic cell that has inert electrodes. An inert electrode is made of some electrically-conducting substance, which is resistive to being oxidized or reduced. Graphite or an unreactive metal, like gold or platinum, may be used. In the cell to the right, the electrodes are submerged in an aqueous solution of some soluble salt, a strong electrolyte. (While the salt is represented generically as “MX”, nothing is implied about the charges of the cation and anion—their charges do not have to be 1:1.)

**Key Questions**

1. As the battery pumps electrons from the electrode on the left to the electrode on the right, what charge begins to accumulate on each electrode? (Circle your choices.)
   
   **Electrode on left:** positive or negative  
   **Electrode on right:** positive or negative

2. What species flows to the electrode on the left? to the electrode on the right? *Hints:* Do like charges attract or repel? Do opposite charges attract or repel? (Circle your choices.)
   
   **Electrode on left:** anions or cations  
   **Electrode on right:** anions or cations

3. In each of the following half-reactions, are electrons reactants or products?
   
   **Oxidation:** \( e^- \) is reactant or product  
   **Reduction:** \( e^- \) is reactant or product

4. In the electrolytic cell, which species are likely to be oxidized? to be reduced? (*Circle all choices that apply.*)
   
   **Species likely to collide with anode and be oxidized:** anions  
   **Species likely to collide with cathode and be reduced:** anions
5  a. Now consider the **electrolysis** of Na$_2$SO$_4$(aq) using inert electrodes exposed to the air. At the anode, either sulfate or water may oxidize:

\[
2 \text{SO}_4^{2-} (aq) \rightarrow \text{S}_2\text{O}_8^{2-} (aq) + 2 \text{e}^- \quad E_{ox}^o = -2.00 \text{ V}
\]

\[
2 \text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4 \text{H}^+(aq) + 4 \text{e}^- \quad E_{ox}^o = -1.23 \text{ V}
\]

Which species would you predict is the one that is oxidized at the anode? **Briefly explain why.**

H$_2$O will be oxidized (instead of SO$_4^{2-}$) because H$_2$O has the greater (least negative) oxidation potential.

b. When Na$_2$SO$_4$(aq) is electrolyzed, either sodium cations or water may be reduced:

\[
\text{Na}^+(aq) + \text{e}^- \rightarrow \text{Na}(s) \quad E_{red}^o = -2.71 \text{ V}
\]

\[
2 \text{H}_2\text{O}(l) + 2 \text{e}^- \rightarrow \text{H}_2(g) + 2 \text{OH}^-(aq) \quad E_{red}^o = -0.83 \text{ V}
\]

Which species would you predict is the one that is reduced at the cathode? **Briefly explain why.**

H$_2$O will be reduced (instead of Na$^+$) because H$_2$O has the least negative reduction potential.

c. Suppose Na$_2$SO$_4$(aq) is electrolyzed using inert electrodes which are exposed to the air. On the following schematic of the electrolytic cell…

i. draw what is being consumed and what is being produced at each of the electrodes.

ii. draw arrows indicating the flow of each reactant and product.

d. Why cannot pure water be electrolyzed? (**i.e.,** Why must sodium sulfate or some similar electrolyte be dissolved in the water? **Hint:** Consider the flow of ions in the aqueous solution between the electrodes.)

As water is oxidized, H$^+$ is generated at the anode. And as water is reduced, OH$^-$ is generated at the cathode. If this were pure water, then the residual solution would become positively-charged at the anode and negatively-charged at the cathode. But a solution MUST remain electrically neutral. Thus the need for the salt in the solution. As H$^+$ is generated at the anode, SO$_4^{2-}$ migrates to the anode to negate the build-up of positive charge. And as OH$^-$ is generated at the cathode, Na$^+$ migrates to the cathode to negate the build-up of negative charge.
6. Let us now consider the electrolysis of \( \text{CuSO}_4(aq) \) using inert electrodes exposed to the air. The possible processes at the electrodes are:

**at the anode**
- \( 2 \text{SO}_4^{2-}(aq) \rightarrow \text{S}_2\text{O}_8^{2-}(aq) + 2 e^- \quad E_{\text{ox}}^o = -2.00 \text{ V} \)
- \( 2 \text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4 \text{H}^+(aq) + 4 e^- \quad E_{\text{ox}}^o = -1.23 \text{ V} \)

**at the cathode**
- \( \text{Cu}^{2+}(aq) + 2 e^- \rightarrow \text{Cu(s)} \quad E_{\text{red}}^o = 0.34 \text{ V} \)
- \( 2 \text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{H}_2(g) + 2 \text{OH}^- (aq) \quad E_{\text{red}}^o = -0.83 \text{ V} \)

a. Circle the half-reaction that occurs at the anode and the reaction at the cathode.

b. Write the overall cell reaction and determine the absolute minimum voltage that the battery must have to force this nonspontaneous reaction to occur. (I’ve said “absolute minimum,” because ordinarily an additional voltage known as an overvoltage (a.k.a. over potential or junction potential) must be supplied to overcome the slow reaction kinetics due to the high activation energy required for gases to form at the electrode—overvoltages vary, but are about 0.4 to 0.6 V for \( \text{O}_2 \) and \( \text{H}_2 \).

- **Overall reaction**: \( 2 \text{Cu}^{2+} + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{Cu(s)} + \text{O}_2(g) + 4 \text{H}^+ \)
- **Minimum** \( E_{\text{cell}}^o = E_{\text{ox}}^o + E_{\text{red}}^o = -1.23 \text{ V} + 0.34 \text{ V} = -0.89 \text{ V} \) The negative sign means that the process is nonspontaneous, hence \( 0.89 \text{ V} \) must be used.

c. If overvoltage is considered, what’s the approximate \( E_{\text{cell}}^o \)? \( E_{\text{cell}}^o = 0.89 \text{ V} + (0.4 \text{ to } 0.6) = 1.29 \text{ to } 1.49 \text{ V} \)

The Model: Electrolysis of Molten Salt

If we want to avoid the possibility of more than one half-reaction taking place at each electrode, the best way to do that is to limit which species can interact with the anode and cathode. Suppose instead of an aqueous solution of a salt (again, generically represented as “MX”) we electrolyze the **molten salt** [i.e., “MX(l)”). Then it is possible that both the cations of the salt would be reduced to the elemental state at the cathode and the anions of the salt would be oxidized to the elemental state at the anode.

**Key Questions**

7. Why must a salt be in the liquid state if it is to be electrolyzed?

A solid is electrically nonconductive, because in order for a substance to conduct electricity it must have flowing charged particles. When a salt is melted, then its cations and anions are free to flow and they can complete the electrical circuit to conduct charge.

8 a. What is an advantage of electrolyzing a molten salt over electrolyzing an aqueous solution of that salt?

When a molten salt is electrolyzed, there is only one species that will be oxidized at the anode and only one species that will be reduced at the cathode. But if an aqueous solution of the salt is electrolyzed, water might be oxidized or reduced instead of the ions of the salt.

b. What is a procedural challenge to electrolyzing a molten salt?

Salts typically have very high melting points. So the electrolytic cell must be maintained at a high enough temperature to keep the salt molten.
9. Elemental magnesium does not occur freely in Nature, but Mg$^{2+}$ is the third most abundant ion in sea water. At a concentration of 0.056 $M$, there is a virtually inexhaustible supply of magnesium in our oceans! Once magnesium chloride salt is isolated from sea water, it can be electrolyzed to yield magnesium metal. The light-weight magnesium metal is moderately strong, so it is a useful metal for construction (e.g., of airplanes). The combustion of magnesium metal produces an intense light, so it is also used in pyrotechnics.

a. Write the oxidation and reduction half-reactions that occur at the anode and cathode, respectively, when MgCl$_2$(l) is electrolyzed using inert electrodes.

Half reaction at anode: \[2\text{Cl}^- \rightarrow \text{Cl}_2(g) + 2\ e^-\]

Half reaction at cathode: \[\text{Mg}^{2+} + 2\ e^- \rightarrow \text{Mg}(l)\]

b. Elemental magnesium metal, Mg, and chlorine gas, Cl$_2$, react explosively with each other! So when MgCl$_2$(l) is electrolyzed, the products must be prevented from recombining. Use the design of the electrolytic cell to the right and the following physical data to explain how these elements may be collected when molten magnesium chloride, MgCl$_2$(l), is electrolyzed using inert electrodes.

<table>
<thead>
<tr>
<th>$T_f$ (°C)</th>
<th>$d$ (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>649</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>714</td>
</tr>
</tbody>
</table>

Since the temperature must be above 714 °C in order to keep the MgCl$_2$ molten, the produced Mg will be liquid as well. The elemental magnesium is less dense than the molten salt, so liquid Mg floats to the top and can be collected on the right.

The chlorine will be a gas, hence Cl$_2$ may be collected on top at the left.

It is important to note that the reservoir with MgCl$_2$ needs to have a dividing wall that would prevent gaseous Cl$_2$ from recombining with molten Mg. If the elements are allowed to meet each other, they will simply reform MgCl$_2$ and then the electrolysis would have been for nothing!
The Model: Electroplating

Electroplating is the process of using electrical current to reduce cations of a desired material from a solution and coat a conductive object with a thin layer of the material (e.g. such as a metal). Electroplating is primarily used for depositing a layer of material to give it a desired property (e.g., abrasion and wear resistance, corrosion protection, aesthetic qualities, etc.) to a surface that otherwise lacks that property.

Another application uses electroplating to build up thickness on undersized parts as seen in the electrolytic cell to the right where an external power source is used to increase the thickness of the tin cathode.

Key Questions

10. The possible processes at the electrodes are:

**at the cathode**

\[
\text{Sn}^{2+}(aq) + 2e^- \rightarrow \text{Sn}(s) \quad E_{\text{red}}^\circ = -0.14 \text{ V}
\]

\[
2 \text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2 \text{OH}^-(aq) \quad E_{\text{red}}^\circ = -0.83 \text{ V}
\]

**at the anode**

\[
\text{Cu}(s) \rightarrow \text{Cu}^{2+}(aq) + 2e^- \quad E_{\text{ox}}^\circ = -0.34 \text{ V}
\]

\[
2 \text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4 \text{H}^+(aq) + 4e^- \quad E_{\text{ox}}^\circ = -1.23 \text{ V}
\]

a. Circle the half-reaction that occurs at the cathode and the half-reaction at the anode if the voltage is kept “low.” (Water will also react if the voltage is high enough.)

b. Write the overall cell reaction and determine minimum voltage that the battery must have to force this nonspontaneous reaction to occur. (Do not consider overvoltage since gases are not involved.)

Overall reaction: \[
\text{Sn}^{2+}(aq) + \text{Cu}(s) \rightarrow \text{Sn}(s) + \text{Cu}^{2+}(aq)
\]

Minimum \( E_{\text{cell}}^\circ = E_{\text{ox}}^\circ + E_{\text{red}}^\circ = -0.34 \text{ V} + (-0.14 \text{ V}) = -0.48 \text{ V} \) The negative sign means that the process is nonspontaneous, hence \(-0.48 \text{ V}\) must be used.

c. If water were to react at each electrode, what is the minimum voltage the battery must have for water to under go hydrolysis and produce hydrogen gas at the cathode and oxygen gas at the anode? (Since gases are involved remember to consider overvoltage) What is the net reaction involving water at each electrode?

Overall reaction: \[
2 \text{H}_2\text{O}(l) \rightarrow \text{H}_2(g) + \text{O}_2(g)
\]

Minimum \( E_{\text{cell}}^\circ \) for the hydrolysis of water = \( E_{\text{ox}}^\circ + E_{\text{red}}^\circ = -1.23 \text{ V} + (-0.83 \text{ V}) = -2.06 \text{ V} \) The negative sign means that the process is nonspontaneous, hence \(-2.06 \text{ V}\) must be used.

d. What is the minimum voltage (remember to consider overvoltage) the battery must have for both hydrogen gas to form (but no O\(_2\) at the anode) and tin to plate on the cathode?

\[
E_{\text{cell}}^\circ = E_{\text{ox}}^\circ + E_{\text{red}}^\circ = \left| -0.34 + (-0.83) \right| = 1.17 + (0.4 \text{ to } 0.6) = 1.57 \text{ to } 1.67 \text{ V}
\]
The Model: Calculating the Mass of Metal Electroplated

A common method of electroplating is achieved using the object to be electroplated as the cathode (e.g. the spoon in the figure below) and use as the anode the metal to be plated (e.g. silver) both submerged in an aqueous solution containing the ions to be plated (e.g. AgNO\(_3\)(aq)).

In the figure below, silver anode is oxidized (Ag\(_s\) → Ag\(^+\)(aq) + e\(^-\)) and at the cathode Ag\(^+\) is reduced (Ag\(^+\)(aq) + e\(^-\) → Ag\(_s\)). Thus there is no net reaction. The overall process consists of simply moving silver atoms from one electrode to the other. Since this is not a spontaneous process, an electrical current is needed to drive the process. The mass in grams of silver electroplated on the spoon is calculated using the following relationships:

<table>
<thead>
<tr>
<th>Mass (g) of substance oxidized or reduced</th>
<th>molar mass (g/mol)</th>
<th>mole of substance oxidized or reduced</th>
<th>Balanced half-reaction</th>
<th>mole of electrons transferred</th>
<th>Faraday Constant (C/mol e(^-))</th>
<th>Charge (C)</th>
<th>time (s)</th>
<th>Current (A)</th>
</tr>
</thead>
</table>

The approximate mass of silver electroplated can be calculated from the electrical current in amps and the amount of time the current ran:

**Current:** 7.50 amps at a minimum of 0.80 V

**Time:** 30.0 minutes

Useful Info. Needed to Calculate the Mass of Ag Electroplated:

- 1 ampere (A) = 1 Coulomb per sec: 1 A = 1 C / s
- Charge of 1 mol of electrons = 96,485 C = 1 Faraday
  \[ 1 \text{ F} = 96,485 \text{ C} / 1 \text{ mol e}^- \]
- Ag\(^+\)(aq) + e\(^-\) → Ag\(_s\)  \( E^\circ_{\text{red}} = 0.80 \text{ V} \)
  - Hence, 1 mol of electrons will plate 1 mol of Ag
- Molar Mass of Ag: 107.9 g/mol

**Key Question**

11. If the electrolytic cell above were run at 7.50 A for 30.0 minutes, use dimensional analysis to show that the maximum mass of silver that can be electroplated is 15.0 g.

\[
\frac{7.5 \text{ C}}{s} \times \frac{1800 \text{ s}}{1 \text{ mol e}^-} \times \frac{1 \text{ mol Ag}}{96,485 \text{ C}} \times \frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} = 15.1 \text{ g Ag}
\]

12. How long will it take (in hours) to electroplate 40.0 g of Chromium onto a small automotive accessory from an aqueous Cr(NO\(_3\))\(_3\) solution using a current of 12 amps?

Cr = 51.0 g/mol. Use dimensional analysis to show your work.

\[
(40.0 \text{ g Cr}) \times \frac{1 \text{ mol Cr}}{51 \text{ g Cr}} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Cr}} \times \frac{96,485 \text{ C}}{1 \text{ mole e}^-} \times \frac{1 \text{ s}}{12 \text{ C}} \times \frac{1 \text{ hr}}{3600 \text{ s}} = 5.26 \text{ hr}
\]
13. Zinc plating (galvanizing) is an important means of corrosion protection. Although the process is done customarily by dipping the object into molten zinc, the metal can also be electroplated from an aqueous Zn²⁺ solution. How many grams of zinc can be deposited on a steel tank from a ZnSO₄ solution when a 0.755 amp current flows for 2.00 days? Use dimensional analysis to show your work.

\[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \]

\[
\text{Mass Zn (g)} = \frac{0.755 \text{ C}}{1 \text{ s}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{24 \text{ h}}{1 \text{ day}} \times 2.00 \text{ day} \times \frac{1 \text{ mol } e^-}{9.65 \times 10^4 \text{ C}} \times \frac{65.39 \text{ g Zn}}{2 \text{ mol } e^-} = 44.2 \text{ g Zn}
\]

14. Electrolysis of molten NaCl is the major means of producing sodium metal. If 215 g of Na metal forms… Use dimensional analysis to show your work and circle your answers.

a. How many moles of electrons are required?

\[ \text{Na}^+ + e^- \rightarrow \text{Na} \quad \text{Hence, mole } e^- = \text{ mole Na} \]

\[
mole e^- = 215 \text{ g Na} \times \frac{1 \text{ mol Na}}{23.0 \text{ g Na}} \times \frac{1 \text{ mol } e^-}{1 \text{ mol Na}} = 9.3478 \text{ mol } e^- = 9.35 \text{ mol } e^-
\]

b. How many coulombs are required?

\[
\text{Charge (C)} = 9.3478 \text{ mol } e^- \times \frac{96,485 \text{ C}}{1 \text{ mol } e^-} = 9.01925 \times 10^5 \text{ C} = 9.02 \times 10^5 \text{ C}
\]

c. How many amps are required to produce this amount in 9.5 hr?

\[
\text{Current (A)} = \frac{\text{charge}}{\text{time}} = \frac{9.02 \times 10^5 \text{ C}}{9.50 \text{ hr}} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ A } \cdot \text{s}}{1 \text{ C}} = 26.4 \text{ A}
\]

15. In the electrolysis of a molten mixture of CsBr and SrCl₂, use your knowledge of periodic trends in ionization energy and electron affinity to identify the product that forms at the negative electrode (cathode) and at the positive electrode (anode). Explain your reasoning.

Substance formed at the cathode: Sr(l)  \text{Reasoning:}

\text{Reduction occurs at the cathode; therefore Sr should be more easily reduced than Cs since the valence shell of Sr is the 5th energy level, while that of Cs is the 6th. Hence, Sr should be more easily reduced than Cs since the electron gained by Sr is added to a an energy level closer to the nucleus—i.e. Sr should have a higher reduction potential than Cs.}

Substance formed at the anode: Br₂(g)  \text{Reasoning:}

\text{Oxidation occurs at the anode, hence the anion that most easily loses electrons will be oxidized, and that’s the bromide ion since it is larger (n = 4) than the chloride ion (valence shell is n = 3).}