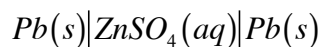


## Electrolysis

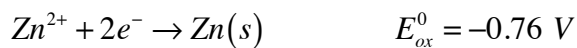
An electric cell contains reactants chosen to react spontaneously to convert their chemical energy into electrical energy. Such cells can be used to power a portable MP3 player, start a car, etc.

A voltaic cell produces electricity spontaneously because each half-cell contains both oxidized and reduced entities. The cell potential  $E_{cell}^0$  is always greater than zero. In a redox table, the stronger oxidizing agent present in the cell will always be above the stronger reducing agent present.

If a cell does not contain all oxidized and reduced species shown in the half-reaction equation, it is possible that the reactants (electrode and electrolyte) present will not react spontaneously. For example, if lead electrodes are placed in a solution of zinc sulfate and the electrodes are connected with a wire, there is no evidence of any reaction.



The strongest oxidizing agent present in this cell is  $Zn^{2+}$  and the strongest reducing agent present is  $Pb(s)$ . A quick check in the redox table shows that the oxidizing agent is below the position of the reducing agent. Also, the cell potential is negative.



$$\begin{aligned} E_{cell}^0 &= E_{ox}^0 + E_{red}^0 \\ &= (-0.76) + (-0.13) \\ &= -0.89 V \end{aligned}$$

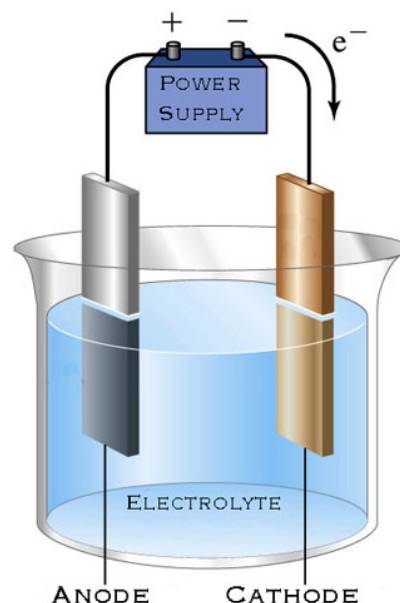
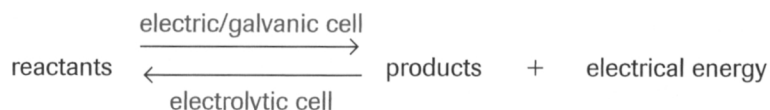
Since the cell potential is negative, we conclude that the lead will not be oxidized spontaneously in the zinc sulfate solution. This cell would not produce electricity because the reaction is not spontaneous.

At first glance, such a cell may not seem very useful. However, by supplying electrical energy to a non-spontaneous cell, we can force the reaction to occur. As we will see later, this is useful for producing a number of substance, particularly elements. For example, the zinc sulfate cell discussed above is similar to the cell used in the industrial production of zinc metal.

The term electrochemical cell is used to refer to either a cell with a spontaneous reaction, such as the voltaic cell, or a cell with a non-spontaneous reaction, which we will call an **electrolytic cell**.

An electrolytic cell, such as the one shown on the right, consists of two electrodes, an electrolyte, and an external battery or power source. **Electrolysis** is the process of supplying electrical energy to force a non-spontaneous redox reaction to occur.

In an electrolytic cell, the chemical reaction is the reverse of that of a spontaneous cell. However, most of the scientific principles we've already learned also apply to electrolytic cells (see table below).



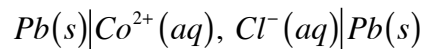
	<b>Voltaic cell</b>	<b>Electrolytic cell</b>
Spontaneous	yes	no
Cell potential	positive	negative
Cathode	<ul style="list-style-type: none"> <li>strongest oxidizing agent present undergoes a reduction</li> <li>positive electrode</li> </ul>	<ul style="list-style-type: none"> <li>strongest oxidizing agent present undergoes a reduction</li> <li>negative electrode</li> </ul>
Anode	<ul style="list-style-type: none"> <li>strongest reducing agent present undergoes an oxidation</li> <li>negative electrode</li> </ul>	<ul style="list-style-type: none"> <li>strongest reducing agent present undergoes an oxidation</li> <li>positive electrode</li> </ul>
Direction of electron movement	anode → cathode	anode → cathode
Direction of ion movement	anions → anode cations → cathode	anions → anode cations → cathode

A secondary cell is a rechargeable cell such as a nickel-cadmium (NiCad) cell. A secondary cell can be used to illustrate the difference between an electric cell and an electrolytic cell. As the cell discharges, electrical energy is spontaneously produced and the cell functions as an electric cell.

When the cell is recharged, the electrical energy forces the products to react and re-form the original reactants. During recharging, the secondary cell is functioning as an electrolytic cell.

**Example**

An electrolytic cell containing cobalt(II) chloride solution and lead electrodes is assembled.



- (a) Predict the reactions at the cathode and anode, and in the overall cell.
- (b) Draw and label a cell diagram for this electrolytic cell, including the power supply.
- (c) What minimum voltage must be applied to make this cell work?



## Worksheet

- Describe the type of agent reacting and the process occurring at the cathode and anode of an electrolytic cell.
- What is different about the cathode and anode of an electrolytic cell versus a voltaic cell?
- Describe the movement of electrons and ions within an electrolytic cell.
- Explain why a power supply is necessary for an electrolytic cell.
- Predict the cathode, anode, and net cell reactions for each of the following electrolytic cells. Calculate the minimum voltage that must be applied to force the cell reaction to occur.
  - $Pt(s)|Na^+(aq), OH^-(aq)|Pt(s)$
  - $Cu(s)|Cu^{2+}(aq), SO_4^{2-}(aq)|Cu(s)$
  - $Pt(s)|SnBr_2(aq)|Pt(s)$
- Two tin electrodes are placed in an aqueous solution containing potassium nitrate and magnesium iodide.
  - If a power supply is connected to force any reactions to occur, what would be the reactions at the cathode, anode, and in the overall cell?
  - Draw and label a cell diagram, including electrodes, electrolyte, power supply, and the direction of movement of electrons and ions.
  - Would a 1.5 V cell be suitable as a power supply? Justify your answer.
- Which of the following cells would produce a spontaneous reaction? Explain.
  - $Ag(s)|FeCl_3(aq)|Ag(s)$
  - $Cu(s)|Pb(NO_3)_2(aq)|Cu(s)$