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Chapter Electrochemistry

SECTION 3 ELECTROLYSIS

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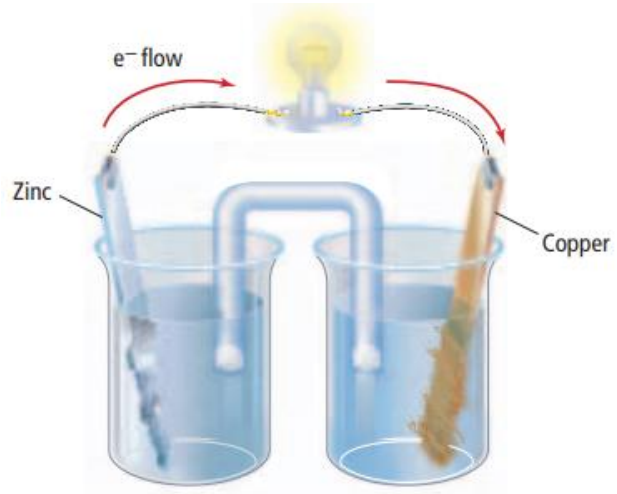
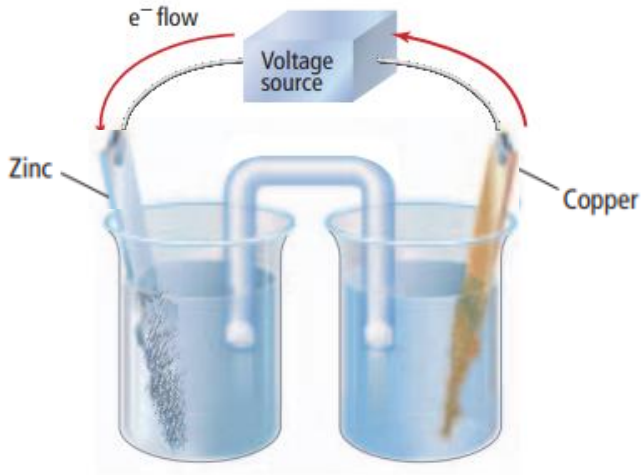
Reversing Redox Reactions:

- ✓ When a battery generates electric current, electrons given up at the anode flow through an external circuit to the cathode, where they are used in a reduction reaction.
- ✓ **A secondary battery** is one that can be recharged by passing a current through it in the opposite direction.

Comparison phase	Voltaic cell	Electrolytic cell
Anode charge	negative	positive
Cathode charge	positive	negative
Wire connected to	Light bulb	Voltage source
Energy transformation	Chemical to Electrical	Electrical to Chemical
Electron flow	From anode to cathode	From anode to cathode
Type of redox reaction	Spontaneous	Nonspontaneous



Voltaic cell



Electrolytic cell

- ✓ In this voltaic cell, the oxidation of zinc supplies the electrons to light the bulb and reduce copper ions.
- ✓ The spontaneous reaction continues until the zinc is used up.

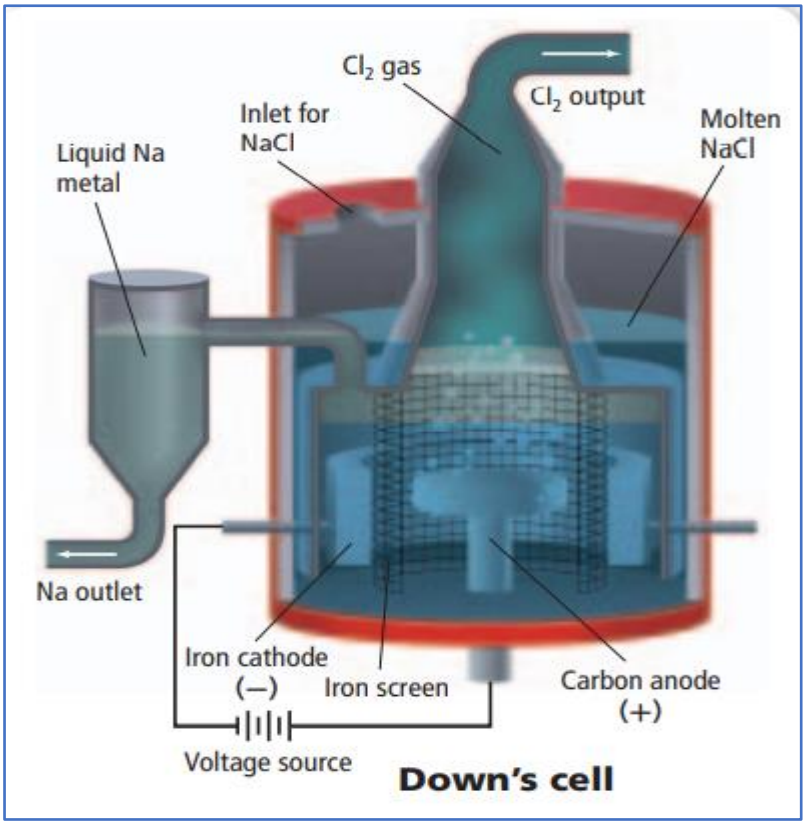
- ✓ When an outside voltage is applied, the flow of electrons is reversed and the nonspontaneous reaction occurs, which restores the conditions of the cell.

- ✓ the cell can be regenerated if current is applied in the reverse direction using an external voltage source.
- ✓ The voltage source is required because the reverse reaction is nonspontaneous.
- ✓ **Electrolysis** is the use of electrical energy to bring about a chemical reaction.
- ✓ **An electrolytic cell** is an electrochemical cell in which electrolysis occurs. For example, when a secondary battery is recharged, it is acting as an electrolytic cell.

Applications of Electrolysis:

Electrolysis of molten NaCl :

- ✓ Electrolysis can separate molten sodium chloride into sodium metal and chlorine gas.
- ✓ This process is carried out in a chamber called a Down's cell, as illustrated in Figure.
- ✓ The electrolyte in the cell is the molten sodium chloride itself.
- ✓ Ionic compounds can conduct electricity only when their ions are free to move, such as when they are dissolved in water or are in the molten state.
- ✓ At the anode, chloride ions are oxidized to chlorine (Cl_2) gas.
  $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
- ✓ At the cathode, sodium ions are reduced to sodium metal.
  $Na^+(l) + e^- \rightarrow Na(l)$
- ✓ The net cell reaction is the following.
  $2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$



Electrolysis of brine

- ✓ The decomposition of brine, an aqueous solution of sodium chloride, is also carried out by means of electrolysis.
- ✓ Two reactions are possible at the cathode: the reduction of sodium ions and the reduction of hydrogen in water molecules.

$$Na^+(aq) + e^- \rightarrow Na(s)$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

- ✓ However, the reduction of sodium (Na^+) does not occur because water is easier to reduce, and thus is reduced preferentially.
- ✓ Two reactions are also possible at the anode: the oxidation of chloride ions and the oxidation of oxygen in water molecules.

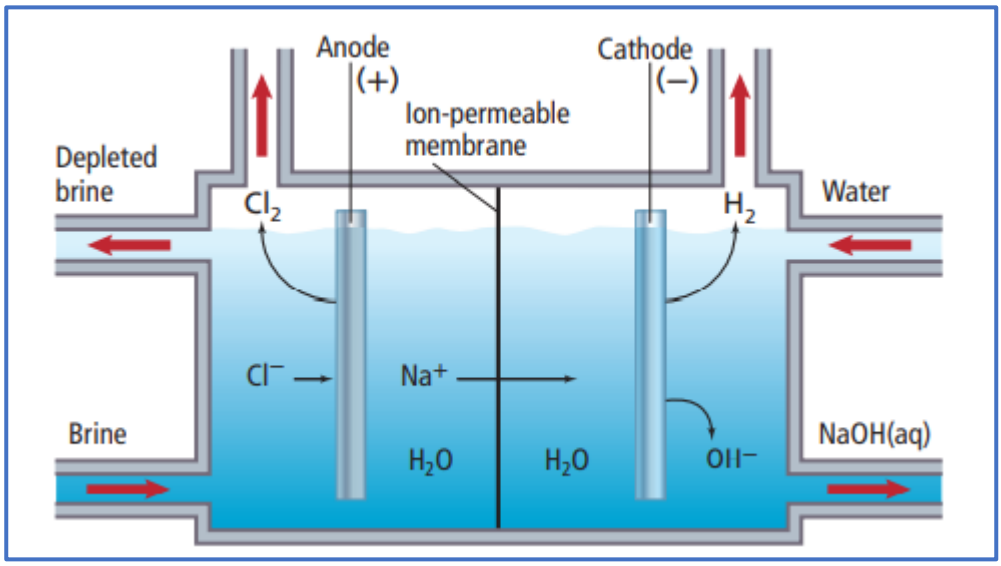
$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

- ✓ Because the desired product is chlorine (Cl_2), the concentration of chloride ions is kept high in order to favor this half-reaction.
- ✓ The overall cell reaction is as follows.

$$2H_2O(l) + 2NaCl(aq) \rightarrow H_2(g) + Cl_2(g) + 2NaOH(aq)$$

- ✓ All three products are commercially important substances.



Electroplating

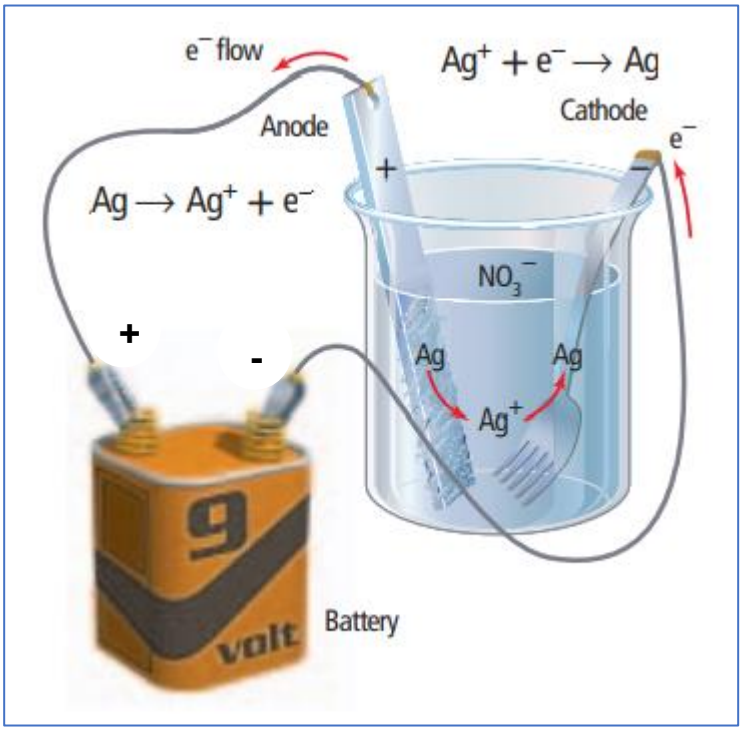
- ✓ Objects can be electroplated with a metal such as silver .
- ✓ The object to be silver-plated is the cathode of an electrolytic cell.
- ✓ The anode is a silver bar or sheet.
- ✓ At the anode, silver is oxidized to silver ions as electrons are removed by the power source.

$$Ag \rightarrow Ag^+ + e^-$$

- ✓ At the cathode, the silver ions are reduced to silver metal by electrons from the external power source.

$$Ag^+ + e^- \rightarrow Ag$$

- ✓ The silver forms a thin coating over the object being plated.
- ✓ Current passing through the cell must be carefully controlled in order to get a smooth, even metal coating.
- ✓ Other metals are also used for electroplating.
- ✓ You might have costume jewelry that is electroplated with gold.
- ✓ Or you might admire an automobile whose steel parts such as the bumper have been made more corrosion-resistant by being electroplated first with nickel and then with chromium.



Revision :

1- Define electrolysis and relate the definition to the spontaneity of redox reactions.

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2- Describe the anode and cathode of an electrolytic cell in which gold is to be plated on an object.

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3- Calculate the voltage of the Down's cell. Should the potential be positive or negative?

$2Cl^- \rightarrow Cl_2 + 2e^-$ $E^0 = +1.35827$ V

$Na^+ + e^- \rightarrow Na$ $E^0 = -2.71$ V

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4- How can the spontaneous redox reaction of a voltaic cell be reversed?

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5- Where does oxidation take place in an electrolytic cell?

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6- Down's Cell What reaction takes place at the cathode when molten sodium chloride is electrolyzed?

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7- Describe what happens at the anode and the cathode in the electrolysis of KI(aq).

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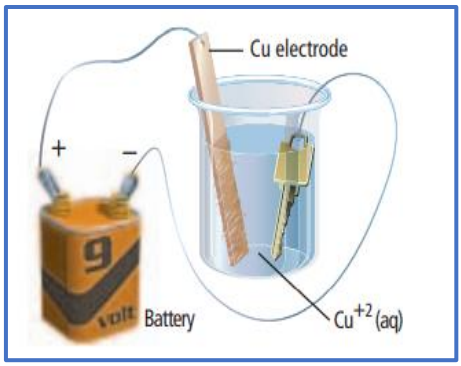
8- Electroplating Figure shows a key being electroplated with copper in an electrolytic cell. Where does oxidation occur? Explain your answer.



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9- Answer the following questions based on Figure

a. Which electrode grows? Write the reaction that occurs at this electrode.

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b. Which electrode disappears? Write the reaction that occurs at this electrode.

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c. Explain what happens to the copper ions in solution.

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