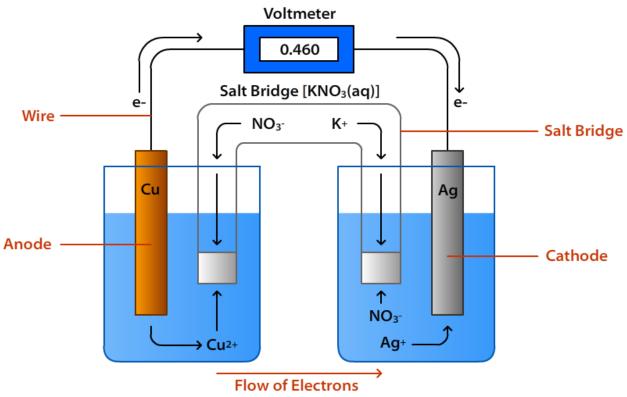
Chemistry of Voltaic Cells

An electrochemical cell consists of two parts, called **half-cells**, in which the separate oxidation and reduction reactions take place. Each half cell contains a metal electrode in an electrolyte solution. The electrolyte is typically a salt solution whose positive ion is the same element as the electrode.

In the diagram below, the beaker on the left consists of a copper electrode immersed in a copper nitrate electrolyte solution. This half-cell is where the oxidation part of the redox reaction takes place. The copper atoms on the electrode lose two electrons, forming Cu^{2+} ions that move into the electrolyte solution. The electrons that are released from the copper atoms travel through the conducting wire to the silver electrode.

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$$

The beaker on the right consists of a silver electrode immersed in a silver nitrate solution. This half-cell is where the reduction part of the reaction takes place. When the electrons from the copper electrode reach the silver electrode, they are attracted to Ag^+ ions in the electrolyte solution. The Ag^+ are combine with the electrons in a reduction reaction, to form silver atoms.



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

CH40S

The electrode where oxidation takes place is called the **anode** of the cell. The electrode where reduction takes place is called the **cathode** of the cell. In a voltaic cell, electrons flow from the anode to the cathode through the connecting wire.

As the oxidation and reduction reactions proceed, the copper electrode will slowly be "eaten away" as the copper atoms turn into copper ions. At the same time, the silver electrode will be slowly growing larger as silver ions are turned into silver atoms and deposited on the electrode.

The final part of the cell is the tube connecting the two half-cells. This tube, called a salt bridge, contains an electrolyte solution (potassium nitrate in this example). Cotton plugs at either end of the salt bridge allow ions to move from one half-cell to the other, but prevent the two solutions from mixing completely.

This movement of ions through the salt bridge helps keep the half-cells electrically neutral. Cations (positive ions) move towards the cathode to balance the removal of silver ions from the solution near the cathode. Anions (negative ions) move towards the anode to balance the addition of copper ions in the solution near the anode.

Without this flow of ions within the cell, charge will begin to accumulate in each half-cell. As a result, the flow of electrons between electrodes would cease almost immediately.

Cell Notation

A voltaic cell, like the one above, can be represented by the following shorthand notation:

$$Cu(s)|Cu^{2+}||Ag^+|Ag(s)$$

In this notation, a single line (|) indicates a phase boundary such as the interface of an electrode and an electrolyte in a half-cell. A double line (||) represents a physical boundary such as the salt bridge between half-cells.

For other voltaic cells, this notation is written using the following form:

 $\underbrace{anode \ (-) \ | \ electrolyte}_{oxidation} \parallel \underbrace{electrolyte \ | \ cathode \ (+)}_{reduction}$

Cell Potential

The **cell potential** (E_{cell}) is the maximum voltage of the cell operating under standard conditions. It represents the ability of a cell reaction to move electrons through a wire from one electrode to the other. Because cell potential is measured in volts (V), it is often referred to as **voltage**.

Each electrode of a voltaic cell makes a contribution to the cell potential. Thus, the cell potential can be considered to be the sum of the contribution from the oxidation reaction at the anode and the reduction reaction at the cathode.

$$E_{cell}^0 = E_{oxidation}^0 + E_{reduction}^0$$

These contributions are called **electrode potentials**. The electrode potential for a reduction halfreaction is commonly called a **reduction potential**. The electrode potential for an oxidation halfreaction is commonly called an **oxidation potential**.

The reduction potentials for a number of reduction half-reactions are listed on the table **Standard Reduction Potentials of Half-Cells** (included in your data booklet). For example, the reduction of silver ions to form silver atoms, shown below, has a reduction potential of +0.80 V.

$$Ag^+ + e^- \rightarrow Ag(s)$$
 $E_{red}^0 = +0.80 V$

Oxidation potentials for oxidation half-reactions can also be determined using the same table, since the oxidation half-reaction is the reverse of the reduction half-reaction. For example, the reduction of copper ions to form copper atoms is shown below.

$$Cu^{2+} + 2e^- \rightarrow Cu(s)$$
 $E_{red}^0 = +0.34 V$

The oxidation of copper atoms to form copper ions would be written as:

$$Cu(s) \rightarrow Cu^{2+} + 2e^{-}$$

and would have an oxidation potential that was equal in magnitude, but opposite in sign to the reduction potential. Thus, $E_{\alpha x}^0 = -0.34 V$.

The cell potential for a battery consisting of a copper anode and a silver cathode would then be

$$E_{cell}^{0} = E_{oxidation}^{0} + E_{reduction}^{0}$$

= (-0.34 V)+(+0.80 V)
$$E_{cell}^{0} = +0.46 V$$

Ease of Oxidation and Reduction

The more positive the reduction potential of a molecule or ion, the more easily that species is reduced. The more negative the reduction potential, the harder the species is to reduce.

When constructing a voltaic cell, one of the first things you must determine is which of your two metal electrodes is the cathode (where reduction occurs) and which is the anode (where oxidation occurs).

Since reduction occurs at the cathode, the electrode that is more easily reduced will be the cathode. The electrode that is less easily reduced will be the anode. In other words,

- the electrode whose reduction potential is more positive will be the cathode
- the electrode whose reduction potential is more negative will be the anode

Example 1

Calculate the voltage produced by a voltaic cell composed of a silver electrode in a Ag^+ solution in one half-cell and an aluminum electrode in an Al^{3+} solution in the other half-cell.

Example 2

A voltaic cell is constructed using electrodes based on the following half-reactions:

$$Sr^{2+} + 2e^- \rightarrow Sr(s)$$

 $Fe^{2+} + 2e^- \rightarrow Fe(s)$

What is the anode and what is the cathode in this cell? What is the cell potential?

Worksheet

1. Write and label two half-reaction equations to describe each of the following reactions:

a)
$$Co(s) + Cu(NO_3)_2(aq) \rightarrow Cu(s) + Co(NO_3)_2(aq)$$

b)
$$Cd(s) + Zn(NO_3)_2(aq) \rightarrow Zn(s) + Cd(NO_3)_2(aq)$$

c)
$$Br_2(l) + 2KI(aq) \rightarrow I_2(s) + 2KBr(aq)$$

2. What is the relative strength of oxidizing and reducing agents for strontium, cerium, nickel, hydrogen, platinum, and their aqueous ions? Use the following information to construct a redox table.

$$2Sr(s) + 2Ce^{3+}(aq) \rightarrow 3Sr^{2+}(aq) + 2Ce(s)$$

 $Ni(s) + 2H^+(aq) \rightarrow Ni^{2+}(aq) + H_2(g)$

 $2Ce^{3+}(aq)+3Ni(s) \rightarrow no \ reaction$

 $Pt(s) + 2H^+(aq) \rightarrow no \ reaction \ (assume \ Pt^{4+})$

3. A silver oxide cell is often used when a miniature cell or battery is required, as in watches, calculators, and cameras. The following half-reaction equations occur in the cell.

$$Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$$

 $Zn(s) + 2OH^{-}(aq) \rightarrow Zn(OH)_{2}(s) + 2e^{-}$

- a) In which direction does the electric current flow, silver to zinc or zinc to silver?
- b) Which is the anode and which is the cathode?
- c) Write the balanced redox equation for the silver oxide cell.
- 4. Indicate whether the following processes occur at the cathode or the anode of a voltaic cell.
 - a) reduction half-reaction
 - b) oxidation half-reaction

- 5. For each of the following cells, use the given cell notation to write chemical equations to represent the oxidation, reduction, and net redox reactions. Calculate the cell potential.
 - a) $Zn(s)|Zn^{2+}||Ag^{+}|Ag(s)$
 - b) $Zn(s)|Zn^{2+}||Cu^{2+}|Cu(s)$
 - c) $Sc(s)|Sc^{3+}||Cu^{2+}|Cu(s)$
 - d) $Cr(s)|Cr^{2+}||Sn^{2+}|Sn(s)|$
- 6. Using the following cell, refer to the reduction potential of gold in your Data Booklet, and calculate the reduction potential for the indium(III) ion.

$$In(s)|In^{3+}||Au^{3+}|Au(s)$$
 $E_{cell}^{0} = +1.84 V$

7. Use the following cell, and the table of reduction potentials in your Data Booklet, to determine the reduction potential and possible identity of the unknown $X^{2+}|X(s)$ redox pair.

$$2Ag^{+}(aq) + X(s) \rightarrow 2Ag(s) + X^{2+}(aq)$$
 $E_{cell}^{0} = +1.08 V$

8. For each of the following cells, draw a diagram of the cell, labeling the electrodes, electrolytes, direction of electron flow, and direction of ion movement.

a)
$$Zn(s)|Zn^{2+}||Cu^{2+}|Cu(s)|$$

b) $Sc(s)|Sc^{3+}||Cu^{2+}|Cu(s)$